Variability in coloured titanium surfaces for jewellery

Lynne Bartlett

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Abstract

Titanium was recognised as an important new metal for jewellery design in the late 1960s, principally because of the thin film interference colour that could be created on its surface by thermal or electrochemical oxidation.

The control of this surface colouring in the jewellery workshop can be problematic. Therefore this study seeks to identify the causes of colour variability, thereby providing a basis for greater control within jewellery practice.

An historical survey of titanium jewellery in the UK identifies the key practitioners in the field and an overview of their techniques clarifies the nature of workshop practice, highlighting the problems of colour variability.

The characterisation of colour variability is facilitated by the experimental verification of a colour definition system, which permits precise colour description of, and hence comparison between oxidised titanium surfaces.

The core of the study is the experimental examination of samples of coloured titanium, prepared by two methods of oxidation selected from the field survey. The techniques of X-Ray Diffraction, Scanning Electron Microscopy, White Light Interferometry, Focused Ion Beam Imaging and Transmission Electron Microscopy are used to evaluate the contribution to colour variability made by each of the component parts of the oxidised surface. Investigations encompass titanium sheet with different surface finishes and the detailed nature of the oxide layer formed thereon, in terms of composition, crystallinity, homogeneity and thickness.

The results confirm the presence of two different crystalline forms of titanium dioxide, anatase and rutile, within the oxide film but establish that these differences cannot account for the degree of colour variation experienced.

The major outcomes of the study are the comparison of the different oxide structures created by the two methods of oxidation and the direct measurement of the layer thicknesses. The thermally created oxide film is shown to be completely crystalline but of variable thickness, which, since surface colour depends on layer thickness would produce colour variation. Electrochemical oxidation, recognised as a more controlled colouring method, is shown to produce an oxide film of more regular thickness but with a more complex structure; consisting of layers of amorphous oxide 'sandwiching' a central crystalline region, which contains irregular, random voids. These voids and their random distribution are identified as a significant cause of colour variability in anodised titanium surfaces and indicate how control might be achieved.

Acknowledgements

My thanks go to the members of staff in the Materials Department at Imperial College, University of London, who provided the major part of the scientiifc analytical measurements. The work was initially sponsored informally by the late Professor Harvey Flower and subsequently by Dr Mary Ryan and Dr Barbara Shollock, who facilitated access to the equipment in the department: Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Focused Ion Beam (FIB), White Light Interferometry (WLI) and Transmission Electron Microscopy (TEM).

The first SEM measurements were made by Professor Harvey Flower, whose early encouragement provided the necessary impetus for the project. The Focused Ion Beam (FIB) and White Light Interferometry (WLI) were performed by Richard Chater, senior technician in the Materials Department, who also used the FIB to cut the foils that were subsequently examined by Transmission Electron Microscopy (TEM).

I am also grateful to my colleagues in the Department of Digital Imaging at the London College of Communication (LCC), led by Professor Lindsay MacDonald, for advice on colour measurement and additional SEM analysis, which was carried out there by Anna Fricker. The initial colour measuring trials were performed by Dr Sophie Triantaphillidou at the University of Westminster and Professor Tony Johnson at LCC. Professor Johnson also advised on the use of the instruments for the subsequent programme of colour measurements at LCC.

The samples of coloured titanium and background information generously supplied by Peter Hayfield, formerly of IMI, are gratefully acknowledged as are the titanium samples provided by Andrew Wilson and Matthew Thomas from the Research Department of Timet UK Ltd.

Thanks also go to the individual jewellers and organisations who kindly supplied images for use within the research or permitted photographs to be taken. The sources are indicated with the images.

Finally thanks are due to my supervisory team; Director of Studies, Ian Padgett, Dr Richard Hughes and Simon Fraser, who have patiently guided me through the lengthy process of a part-time research project.

Glossary

Allotrope	Term used to describe the different crystal forms of a metal
Billet	Term used for metal ingot within the metals industry
Chroma	Saturation of a colour or colourfulness
CIE	Commission Internationale de l'Éclairage, international body established in1931 to coordinate colour measuring systems
Destructive Interference	Interaction of refracted and reflected light waves which occurs in thin film interference when the waves are completely out of phase thus eliminating a wavelength from white light with the result that colour is observed
Dislocation	Imperfections in a crystal lattice caused by missing atoms
Descaling	Industrial process for removing the surface corrosion or scale formed during the manufacturing process
Electrolyte	Solution, usually aqueous, used to carry the current
Ellipsometry	Ellipsometry is a common optical technique for measuring thin films. It relies on the polarization changes caused by reflection or transmission from a material structure to deduce the material's properties, like thickness and optical constants.[1]
Etchant	Corrosive substance or mixture used to chemically clean a metal surface, e.g. Hydrofluoric acid (HF)
First Order Tints	Newton's description of the sequence of interference colour hues, (see also Second and Third Order Tints).
Grain enhancement	May be used to describe the etching of a metal surface to reveal the grain structure under magnification or the process used to increase the size of metallic crystals so that they are visible to the naked eye
Grains	Metallurgical terms for crystals, especially those at the surface of the metal
High Colours	Customarily used to describe interference colours produced by anodising at high voltages
Hue	Colour attribute which refers to perceived spectral colour
Lattice	The three-dimensional, symmetrical arrangement of atoms or molecules to form a crystal structure
Low Colours	Customarily used to describe interference colours produced by anodising at low voltages
Micron	Unit for measuring small distances, 1000 nm
Nanometre	Unit for measuring small distances. 10^{-9}metre
Nucleation	Process which initiates crystal growth
Optical density	A measure of the speed at which light travels through a substance
Oxide Species	The possible crystal forms adopted by titanium dioxide
Polymorph	Different crystal forms exhibited by the same chemical compound
Potentio-dynamic	Mode of anodising in which voltage is steadily increased
Potentiostatic	Mode of anodising in which voltage is kept at a constant value
Reflectance	Light emitted from a surface compared with the light incident on the surface

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[1] www.jawoollam.com, Ellipsometry tutorial, 2009.

Refraction	The change in direction of light rays when they move between substances of differing optical density
Refractive index	Ratio that compares the optical density of a substance with that of a vacuum
Refractory metals	Metals with high melting points, usually encompasses titanium, zirconium, niobium and tantalum
Relative Reflectance	Light emitted from an illuminated surface compared to a standard white surface, the basis of spectrophotometer measurements
RT blanking	Technique for cutting shapes from metal sheet using a steel template
Scale	Surface corrosion products formed on metals as a result of the manufacturing processes
Second order tints	See First order tints
Sintering	Process used to create a solid shape by compression of metal powder below its melting point
Spectrophotometer	Instrument for measuring the ratio of incident to reflected light across the visible spectrum
Third order tints	See first order tints
Titanium sponge	Form in which titanium is first manufactured

Chapter 1

1.1. Introduction

This chapter introduces titanium in the context of its discovery and industrial uses and establishes the early history of its adoption as a metal for designed jewellery. The historic survey of the use of titanium for jewellery in the United Kingdom (UK), where its use was pioneered, provides the contextual background from which it is possible to select key practitioners who were involved in the establishment of titanium as a jewellery metal. The selected jewellers were those who had made significant contributions to the techniques used for its manipulation and colouring.

Titanium has gained a reputation as a difficult material, alongside platinum, for smaller workshop jewellers as it can be harder to manipulate than the traditional jewellery metals such as silver or gold and also unpredictable in colouring behaviour. This latter problem area is particularly significant because it is the colour potential of titanium, as will be documented subsequently, that is the most alluring feature for the jewellery designer and consumer. As little has been written about the use of titanium in the jewellery workshop since the late 1970s[1], the information spread by word of mouth has resulted in misinterpretation and misunderstanding of its properties and use. By documenting, in the following chapter, the processes used by jewellers since its first introduction as a metal for jewellery design at the School of Jewellery in Birmingham in 1965,[2] this research sets out, *inter alia*, to eliminate misconceptions about titanium, which have arisen in the field of workshop jewellery,

Titanium, as set out in greater detail below, was seen as the exciting new metal of the twentieth century but whether it would have been used as a material for jewellery fabrication is doubtful without the express encouragement of the titanium manufacturers in their open-minded search for new outlets. The initiative was taken by a senior researcher at ICI's R&D laboratory, which turned a casual interest from designers, intrigued by the colour potential of titanium, into an opportunity for the creative exploration of the new metal. The details of the introduction of titanium to design students and the history of its use are documented in greater detail later in the chapter.

With guidance and support from industry, the early users of titanium for jewellery set out to explore the scope of the new material. Fabrication techniques, suitable for gold and silver, had to be adapted and the sequence of production steps had to be amended

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[1] Ward, James Brent, *The Colouring and Working of Refractory Metals,* Worshipful Company of Goldsmiths' Project Report No. 34/1, London September 1978

[2] See **1.5.** The History of Titanium in Jewellery, p13.

so that all the forming of a piece was completed before colouring took place. Those with a problem-solving approach to the new material were most successful in their design applications but they failed to address the fundamental principles of the process and this ultimately set limits to their art. The lack of understanding of the basis of colour formation meant that when problems were experienced in colouration which could not be resolved empirically the enthusiasm for the use of titanium declined.

This research discusses the problem area of colour variability and proposes a new approach to its investigation. This new approach considers the basis of colour on titanium, thin film interference, and how the physics and chemistry of the oxidation processes and the resulting oxide layers, which produce the appearance of colour on titanium, may be analysed to identify the major contributing factors in colour variation. Such an analysis will provide a platform of consolidated knowledge for further research into process modification to resolve the problems of colour variation.

Before discussing the jewellery use of titanium, the next part of the chapter presents a brief outline of the impact of the introduction of titanium on industry in general. An historical overview of the history of titanium discovery and exploitation is presented in more detail later in the chapter and details of its metallurgy are considered in Chapter 4.

1.2. Titanium – the New Metal

Although known in theory since the late eighteenth century[3] it was only in the second half of the twentieth century that titanium was produced as fabricated metal, introducing new concepts in engineering design. The excitement created in the scientific industry by the introduction of a metal with the toughness of steel and the light weight of aluminium is exemplified by the numerous articles about titanium published in the house journal of its UK manufacturers, ICI. '*Until a few years ago few people had even seen it; it is not yet a common metallurgical commodity, and few metallurgists have experience of it or know much about it. This, therefore, is the justification for referring to it as a new metal, which it is, inasmuch as we are just now witnessing its industrial birth.*'[4]

The huge technical and financial resources needed to produce significant volumes of the new metal were made available by the potential foreseen for its application in the highly technically demanding and expanding aerospace industry. Such concentrated, focused effort meant that production of titanium was scaled up from laboratory sample to commercial production, at a rate of ca 1000 tons/annum, in less than 10 years[5]. This

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[3] See: **The History of Titanium, discovery, occurrence and use**, p. 10 for details.
[4] Cook, Maurice, *Titanium The New Metal with Big Possibilities,* The ICI Magazine, <u>32,</u> 207, January 1954, p2.
[5] Clapham, Michael, *Who Uses Titanium?* The ICI Magazine, March 1957, p 84.

compares with the new metal of the nineteenth century, aluminium, which took 50 years to reach the same level of development, and iron and steel, which have been in continuous development for centuries.

The first reverse in the fortune of titanium, after ten years of continuing expansion, came with the cancellation of the US aerospace programmes but this proved to be an opportunity for the exploitation of its other outstanding property, corrosion resistance. As volumes of titanium became available for new markets, the chemical and other process industries were able to capitalise on the corrosion resistant behaviour of the metal that had been noted in the laboratory. This led to intensive investigation of the surface oxides on titanium which protect the metal from further attack, and it is the extensive literature in this field that provides the scientific theoretical background to this research enquiry. Surface oxides on titanium exhibit a wide range of colours and, as colour has always fascinated the artist, undoubtedly the colour exhibited by oxidised titanium was attractive to jewellers. Figure 1.1 illustrates this in the setting of a piece of titanium 'sponge', the form in which the metal is first made, as a 'gemstone' in a silver pendant in 1963 by Malcolm Green.

Figure 1.1: Titanium sponge set in silver pendant, 1963, Malcolm Green, Collection of Worshipful Company of Goldsmiths.

However no attempt was made to exploit this property of the metal until the 1960s when an initiative from industry in the UK was directed towards the design community[6].

While it is probable that industry hoped for high-value, volume outlets it was in the sphere of studio jewellery by designer/makers that titanium made its initial impact. Studio jewellers, working from independent workshops, producing unique pieces or limited editions, are one of the categories of jewellery manufacture in the UK described by Janice

[6] See **The History of Titanium in Jewellery, introduction and use in the UK,** p13. for details

West; *'There are four general categories of jewellery. The most precious, often commissioned is referred to as fine jewellery; studio or contemporary jewellery has been the area of avant-garde developments and experimentation; high-street jewellery, which at best tends to consist of watered-down versions of fine jewellery, usually silver or low-carat gold; the fourth category might be described as unwearable wearables and is perhaps more an idea about jewellery than jewellery as such. These works rarely exist outside galleries and museums.'[7]*

Whether, as suggested by Ralph Turner[8], the studio jewellery movement was a product of 1930s and 1940s USA, or a development of the Arts and Crafts Movement which flourished in the UK in the 1890s, the sector grew rapidly in the UK in the 1960s stimulated by two significant events.

The publication of the First Report of the National Advisory Council on Art Education under the chairmanship of Sir William Coldstream, known as the Coldstream Report[9] in I960, recommended, among other proposals, the establishment of degree-level courses in design. The subsequent development of courses, such as that at the Central School, were, '*created to develop the designer-jeweller'* capable of *'creating their own designs and'* with '*the varied technical expertise to be able to make exactly what their imaginations dictated.'[10]*

The second event was the International Exhibition of Modern Jewellery curated by Graham Hughes at Goldsmiths' Hall in 1961. As Clare Phillips, one of the many authors to cite this exhibition as a seminal influence on contemporary UK jewellery, writes; *'The aim of the exhibition was to demonstrate jewellery's artistic potential and to reverse the depressed state of the British jewellery trade, which had suffered greatly both during and after the Second World War due to austerity measures and prohibitive purchase taxes. … as the exhibition catalogue stated, "proved, if proof be needed, that cheap materials need not mean artistic insignificance, and that creative imagination shown with one visual art can very often be diverted to another" These were important lessons, recognizing alternative priorities within jewellery, and helped to consolidate the position of the emerging artist-jewellery movement.'[11]*

By the mid-1960s design-focused courses were widely established and provided a body of students receptive to the use and exploration of new materials such as titanium. This was also a period when the idea of the UK being at the forefront of developments in science and technology was introduced to the wider public in a speech made by Harold Wilson, as Leader of the Opposition, at the Labour Party Conference in 1963[12], *"the Britain*

[7] West, Janice, *Made to Wear, Creativity in Contemporary Jewellery*, Lund Humphries Publishers, London 1998, p10.
[8] Turner, Ralph, *Jewelry in Europe and America,* Thames and Hudson, London 1996, p9.
[9] Coldstream, W et al, *Report of the National Advisory Council on Art Education,* HMSO, London 1960.
[10] West, Janice, *Made to Wear, Creativity in Contemporary Jewellery*, Lund Humphries Publishers, London 1998, p16.
[11] Phillips, Clare, *Jewels and Jewellery,* V&A Publications, London 2000, p118.
[12] http://en.wikipedia.org/wiki/Harold_Wilson

that is going to be forged in the white heat of this revolution will be no place for restrictive practices or for outdated measures on either side of industry". The establishment of a Ministry of Technology by the in-coming Labour Government in 1964 further stressed the role of technology and promotion of the use of titanium for jewellery, a technical development pioneered in the UK, could be seen in context of the climate of encouragement for technological development.

1.3. Titanium – a Jewellery Metal

The jeweller's art has largely been associated with the manipulation of precious metals using techniques that have been developed and refined over centuries. A practised jeweller knows the traditional jewellery metals by how they perform under specific conditions and attains an expertise in controlling these materials in order to achieve the desired design outcomes. The skills most valued by the craft metalworker are literally 'hands on' and have been disseminated by practical experience from master to apprentice. Although well understood and researched by the guilds, it has rarely been deemed necessary for the practising jeweller to know or understand the physics and chemistry of a metal and why it performs in a particular way.

The contrasting properties between the noble metals; gold, silver and platinum, traditionally used for jewellery, and the new metal, titanium, explain the need for different skills for its successful manipulation. Gold and silver are wonderfully malleable metals and, with judicious annealing, they can be extensively reworked. Lower melting alloys can be used to join parts together by soldering and, if fabrication disasters occur, the whole item can be melted down to provide raw material for another creation. Titanium by contrast is a hard, unresponsive metal that is difficult to shape and slow to work. It cannot be soldered in the workshop or annealed or reworked.

However the colour palette of the precious metals is limited to white, yellow and red. Designs for polychrome jewellery had to incorporate other materials, commonly vitreous enamels and gemstones. The introduction of titanium into this arena had an impact as dramatic as the change from black and white printing to full colour or from black and white film to Technicolor.

For the majority of jewellers it was the colour potential of the new metal that was most alluring and limitations on workability were accepted initially in order to explore the exciting new design possibilities that could only be achieved by using titanium. It was recognised that successful design outcomes would only be possible by the development and use of new process techniques.

Industry had discovered that colour on titanium could be produced by heat oxidation in air or electrochemically, by anodising in an aqueous solution. Jewellers therefore had to grapple with the oxidation procedures and devise their own pragmatic solutions to the application of these processes. Hitherto the limited range of coloured metals, produced by alloying, had been purchased from specialist suppliers but with titanium, jewellers needed to devise their own methods for colouration to produce specific designs. Electrical processes, such as the plating of a silver or base metal artefact with gold, although familiar to jewellers are usually carried out by specialist craftsmen but anodising titanium to produce surface oxides, and hence colour, is such a crucial part of the design process that jewellers had to engage fully with the procedure and familiarise themselves with the electrical equipment and the inorganic solutions used as electrolytes. The use of heat to generate an oxide layer on titanium was a more familiar process for the jeweller but came at a radically different stage in the procedure, being the final or penultimate step in the creation of a jewellery item rather than part of the initial production as is the case in the working of precious metals.

The detailed analysis of workshop techniques and procedures synthesised from the researcher's own practice and a survey of key jewellers responsible for the development of the use of titanium as a jewellery metal is presented in Chapter 2.

The following parts of the chapter present in greater detail the history of titanium and its use for jewellery, beginning with a brief history of its discovery and initial exploitation.

1.4. The History of Titanium, discovery, occurrence and use

Titanium is truly a 20th Century metal for, although the existence of the new element was established in the late 18th century, it was not isolated as a pure metal until the early 1900s. Titanium was discovered in 1790 by William Gregor, a Cornish cleric and amateur mineralogist. In 1791 he published his discovery of the presence of the oxide of an unknown metal, which he called menaccanite, during his experiments on the black beach sands of Cornwall (ilmenite). In 1795 Martin Heinrich Klaproth, a German chemist, isolated a similar oxide from 'red schorl' (rutile) from Hungary. He acknowledged Gregor's prior discovery but named the new metal element, present in the oxide, titanium[13].

'Wherefore no name can be found for a new fossil [element] which indicates its peculiar and characteristic properties, in which position I find myself at present, I think it is best to choose such a denomination as means nothing of itself and this can give no rise to any erroneous ideas. In consequence of this, as I did in the case of uranium, I shall borrow the name for this

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[13] Barksdale, Jelks, *Titanium, Its Occurrence, Chemistry and Technology,* 2nd Edition, Ronald Press Co., New York 1966.

metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this metallic genus, titanium.'

Over 100 years later, in 1910, MA Hunter, working for General Electric in the USA, isolated the pure metal[14] in the course of investigations into new materials for lamp filaments. Titanium was not found to be a suitable metal for this purpose and it was decades after, in 1932 in Austria, that Dr Wilhelm Kroll developed a potential industrial process for its production. Titanium may have remained an interesting curiosity for metallurgists had not the metal's unique combination of properties, light weight and high strength been needed by the USA aerospace programme in the 1950s. Titanium can therefore be described as a 'space age' metal and a quote from a speaker at the First International Titanium Conference held in London in 1968 emphasises just how new the metal was[15]: *'In 1941 virtually no metallurgist in the USA had seen a piece of ductile titanium, by 1948 a number had dealt with the mysteries of the metal.'*

The late isolation and exploitation of titanium could be taken as an indication that it is a rare element but this is not so. Titanium is relatively abundant at 0.6 % of the earth's crust and it is also present in the atmosphere of the sun and in interstellar space. It is the ninth most common element and the fourth commonest structural metal after aluminium, iron and magnesium. However it is very reactive and unlike gold, silver, copper and iron, it is never found as a pure metal. This very reactivity is why it is so difficult to isolate and process as a pure metal. Even today a batch method is used which makes production relatively slow and expensive.

Titanium is a silver-grey light-weight metal with a specific gravity of 4.5, half that of copper at 9, and comparable with that of the other common light weight metal, aluminium, which has a specific gravity of 2.7 but its melting point is 1668°C compared to aluminium at 660°C and copper at 1083°C. As can be seen in Table 1.1[16], titanium fills a space between aluminium and iron in terms of weight but has a higher melting point. In addition to its light weight and high melting point titanium is as strong as steel. This is illustrated in a paper by Serge Salat,[17] discussing the architectural use of titanium. The value for tensile strength of titanium quoted at 483 Rm(Mpa) is equivalent to that of stainless steel grades which are in the range 350-510 Rm(Mpa).

The commercial production of titanium started in the 1950s, based on the Kroll process, and developed rapidly as a material restricted to aerospace applications for both

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[14] McQuillan, A D, McQuillan, M K, *Metallurgy of the Rarer Metals, No. 4, Titanium,* Butterworths, London 1956.

[15] Lippert, T W, *1st International Conference on Titanium 1968,* Jaffee, RI and Promisel, NE,(ed), Pergamon Press, London, p.6, 1970.

[16] Information from McQuillan, A D, McQuillan, M K, *Metallurgy of the Rarer Metals, No. 4, Titanium,* Butterworths, London 1956.

[17] Salat, Serge, *Three case studies for the architectural and structural use of titanium,* Ti-2007 Science and Technology, edited by Ninomi, M. et al, The Japan Institute of Metals, 2007.

Metal	Specific gravity	Melting point (deg.C)	Atomic number
Aluminium (Al)	2.7	660	13
Titanium(Ti)	4.5	1668	22
Iron (Fe)	8	1535	26
Copper (Cu)	9	1083	29
Silver (Ag)	10.5	960	47
Gold (Au)	19.3	1062	79

Table 1.1: *Comparison of properties of titanium with other metals.*

strategic and cost reasons. Production of titanium grew from 75 tons in 1951 to 6000 tons in 1957 when USA government policy changed significantly. The USA space programme had provided the impetus for the growth of titanium production, and therefore the radical change in policy and consequent drop in demand caused a crisis, and, in 1958, the price of the metal dropped substantially[18]. This released a significant volume of metal to other industries and the consequent price fall put titanium within reach of other applications such as the chemical process industries where its property of corrosion resistance proved particularly useful. These applications were so successful that by 1977 about half the titanium produced was used in non-aerospace applications. The metal went from curiosity to commodity in 10 years and has suffered a cyclical demand pattern throughout the last five decades. Shipments in 2006 showed high demand at 75kt.
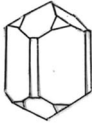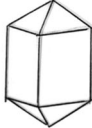
The seeming paradox of a reactive metal being used as a corrosion-resistant element is explained by the fact that a thin, tough, protective oxide layer forms on the surface of the metal within minutes of its production, unless it is in an inert atmosphere. This layer of titanium dioxide, only a few nanometers thick, protects the metal from further attack.

Titanium dioxide occurs naturally in three crystal forms: rutile and anatase which are both tetragonal and brookite which is rhombohedral. Which form develops when the metal is oxidised depends on the conditions under which the oxide is formed. Low temperatures favour anatase and high temperatures rutile. Brookite is formed at intermediate temperatures. Anatase is transformed slowly to rutile at temperatures below 610°C but rapidly above 730°C. Table 1.2[19] illustrates the common crystal habits of the

[18] Lippert, T W, *1st International Conference on Titanium 1968,* Jaffee, RI and Promisel, NE,(ed), Pergamon Press, London, p.6, 1970.
[19] Copied from Deer, W A, Howie, R A, Zussman, J, Rock Forming Minerals*,* Longmans,1962.

Crystal Forms of Titanium Dioxide

Name	Diagram	Crystal system	Hardness	Refractive index (range)	Specific gravity	Formation temperature (deg.C)
Rutile		tetragonal	6/6.5	2.62/2.9	4	High
Anatase		tetragonal	5.5/6	2.493/2.554	4	Low
Brookite		orthorhombic	5.5/6	2.583/2.705	4	Medium

Table 1.2: Crystal habits and properties of the polymorphs of titanium dioxide.

three polymorphs.

As it is the oxidation of titanium that produces the coloured surfaces, so attractive to jewellers, the different refractive indices of the various polymorphs have implications for colour development. These aspects are discussed in subsequent chapters in the context of thin film interference, Chapter 3 and oxide layer investigation, Chapter 5.

The next part of this chapter presents in more detail the history of titanium for jewellery use, highlighting the significant practitioners in the field.

1.5. The History of Titanium in Jewellery, introduction and use in the UK[20]

To understand the impact made by the arrival of a new metal in a largely traditional craft area it is important to appreciate the conditions of the jewellery industry in the UK at the time. Most of the jewellery manufacturing facilities in the UK had been adapted for the production of strategic engineering parts during the Second World War and thus there was a hiatus in jewellery making for several years.

After the war the extremely high purchase tax on luxury goods such as jewellery made it very difficult for new designs to enter the market. It was also not particularly easy to obtain precious metals and a licence to purchase gold was still necessary until the early

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[20] This text is taken from papers presented to the Society of Jewellery Historians in London in October 2005 and the 11th International Conference on Titanium in Kyoto in June 2007 and also forms part of an on-line exhibition of titanium jewellery curated by the researcher at www.reflectionandrefraction.co.uk.

1970s. At the same time the lack of tax on antique and second-hand jewellery encouraged a trend, reported anecdotally, for new 'antique' pieces.

The situation had a stifling effect on jewellery design and manufacture in the UK throughout the 1950s, where designs were often copied from the nineteenth and early twentieth centuries and the training of the jeweller at the bench continued to follow a traditional apprenticeship system with emphasis on special skills and technical excellence and expertise. However the next decade saw an amazing growth in the sector and in the early 1960s two major events resulted in radical changes in design and making.

In 1961 Graham Hughes organised the International Exhibition of Modern Jewellery at Goldsmiths' Hall[21]. The work, featuring innovative design, displayed in distinctive showcases that were designed for the exhibition, had an enormous impact on the jewellery world in the UK.

The other notable event of the early 1960s was the publication of the Government's Coldstream Report[22], as mentioned previously in the chapter, which resulted in major changes in education in the art and design fields with the introduction of degree-level course in areas such as jewellery. New colleges and courses set a framework for the rapid adoption and exploitation of new materials especially in the growing sector of studio jewellery made by individual designer/makers.

Examples of the new educational regime were the transfer of the, often part-time, courses in jewellery and silversmithing techniques from the Central School of Arts and Crafts to Sir John Cass College and the establishment, at the soon to be rechristened Central School of Art and Design, of a full-time degree course in Jewellery Design.

The school at Birmingham was part of the expansion across the UK of courses where students were encouraged to think about and experiment with materials other than precious metals and gemstones[23]. Many colleges used tutors from other creative disciplines to encourage a cross-fertilisation of ideas. In 1965 the new metal, titanium, was introduced into this highly energised and creative environment.

The initiative for the use of titanium as a medium for jewellery manufacture came from industry where in the early 1960s a period of low demand in the aerospace industry and increasing production capacity of the metal created a need for the development of new areas of application. Investigations into the use of titanium for decorative purposes had been carried out in the research laboratories of the major UK manufacturer of this new metal, Imperial Metal Industries (IMI). At the time IMI was the metals division of Imperial Chemical Industries (ICI), but was soon to become an independent company. A senior researcher in the IMI laboratories at Witton was J B Cotton who had a particular interest in

[21] Turner, Ralph, *Jewelry in Europe and America,* Thames and Hudson, London 1996.
[22] West, Janice, *Made to Wear, Creativity in Contemporary Jewellery*, Lund Humphries Publishers, London 1998.
[23] Hunt, Terry (ed), *Finely Taught Finely Wrought,* Birmingham School of Jewellery, Birmingham 1990.

the colouring potential of titanium and had published papers on the subject[24].

In 1964 Cotton approached one of the tutors at the nearby School of Jewellery in Birmingham, Gerald Whiles, with the idea that titanium could be exploited and promoted for the production of consumer products and would be a worthwhile new material for the students to explore. Initially it was the silversmithing students at Birmingham who were involved in the project and a group of them visited IMI and were given samples of different forms of titanium including sheet, wire and tube to experiment with and advice on process

Figure 1.2: JB Cotton (front centre) and his team at IMI Research ca 1971, image courtesy of Peter Hayfield

techniques, including colouring by anodising, from the technical staff at IMI, including Peter Hayfield. Figure 1.2 shows J B Cotton and his team at IMI.
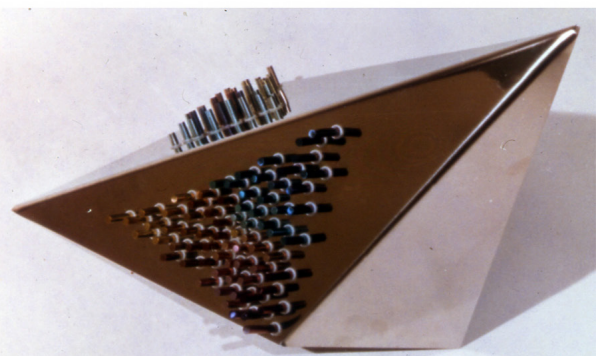
Figure 1.3: Two sculptures made by silversmithing students at Birmingham 1964/5 using titanium sheet and rod, property of Peter Hayfield.

[24] Cotton, J B, *Chemistry and Industry,* 1958 No. 3, 68, 1958.

All the metal forming techniques were tried including some, such as forging, that the technicians at IMI thought would be difficult or dangerous. Titanium at high temperatures can self-ignite and titanium dust can be explosive. Images and, in some cases, actual pieces of work survive from this time as shown in Figure 1.3 but the makers have yet to be identified.

Observing the exciting developments with the use of the new metal in the Silversmithing School, the jewellers asked to be included in the project and this is when titanium was first used for designed jewellery. One of the pioneer jewellers who first used
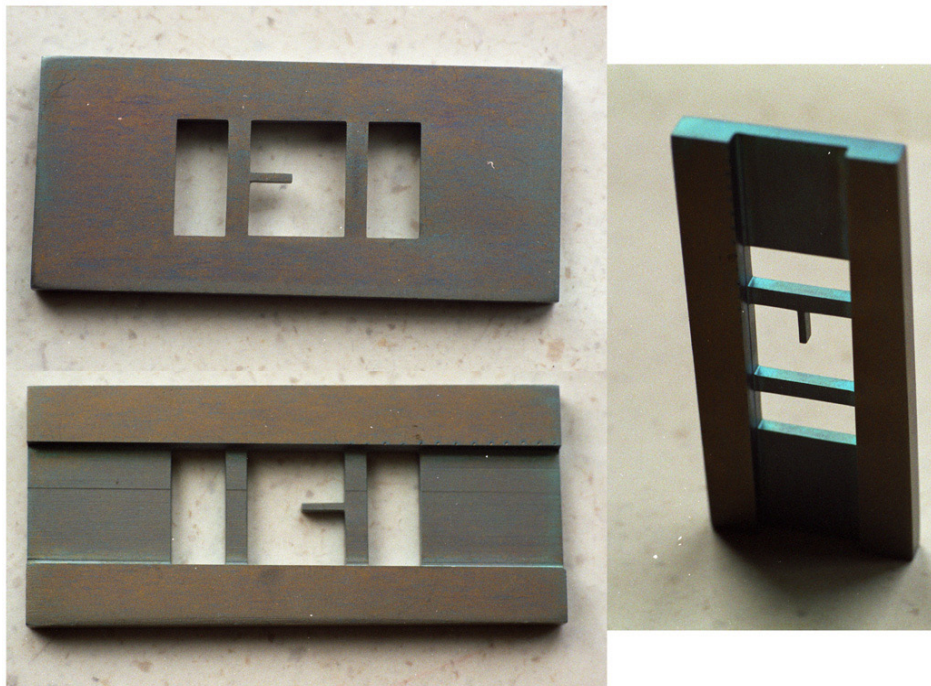
Figure 1.4: *Belt buckle machined from a thick sheet of titanium and coloured by anodising (three views), Ann Marie Shillito 1967.*

titanium at Birmingham (1965-1968) was Ann Marie Shillito and the belt buckle, illustrated in Figure 1.4, is the first identifiable piece of titanium jewellery. The buckle was machined from thick sheet and coloured by anodising. The buckle is discussed further in Chapter 2.

Another practitioner of note in the early decorative use of titanium was Pietro Pedeferri. Although a University researcher in the field of electrochemistry in Milan, he was inspired by the colour possibilities of the metal to produce compositions on titanium as shown in Figure 1.5. The pieces range in size from 6x4 cm to 20x30 cm. His artistic experiments started in 1968 and he has published several books on the subject of titanium art[25,26] as well as many scientific papers.

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[25] Pedeferri, Pietro, *Drawings on Titanium,* clup, Milan 1981
[26] Pedeferri, Pietro, *Colours on Titanium,* clup, Milan 1982.

Figure 1.5: Titanium painting by Pietro Pedeferri, 2005 (ca 30 cmx30 cm)

In its drive to develop new markets for titanium, IMI produced decorative finishes with faceted effects, which on subsequent anodising produced multicoloured surfaces, as shown by the example in Figure 1.6.

Various students at Birmingham experimented with the use of this material including Margaret Fleming, as featured in the local press, Figure 1.7, but the majority of the students found the highly patterned, grain-enhanced materials unusable in their work.

Some mass-market jewellery manufacturers, such as Stratton, used this material for cufflinks etc. but quality control was a problem as it proved impossible to produce repeat sheets of patterned metal. (I am indebted to Peter Hayfield for samples of this material).

Figure 1.6: Example of anodised grain-enhanced titanium sheet from IMI.

At the same time salesmen from IMI were looking for other decorative applications. They approached a company in the Birmingham area, active in metal etching, Lewis and Clayton. The company used titanium to create 'pictures', such as that shown in Figure 1.8, which were 'painted' by using a brush anodising technique. This technique is described in

Titanium, the metal used in spacecraft, has another application at the Birmingham School of Jewellery and Silversmithing this academic year. Imperial Metal Industries has produced a decorative titanium in a spectrum of colours and three different finishes, which is anodised and treated to reflect light. Maggie Fleming, aged 20, an Edinburgh student at the school, fits a headband which incorporates the new metal on the head of fellow-student Susan Aldcroft.

Figure 1.7: Clip from local newspaper, courtesy of Hamish Bowie, showing use of grain enhanced material.

more detail in Chapter 2.

Word of mouth spread of the use of titanium from Birmingham through the 'close-knit' jewellery school network in the late 1960s as tutors and students saw pieces incorporating the new metal in degree shows. Eric Spiller recalls using it at Central in 1968 but he had been aware of the material in its industrial context. A chance discussion during a student visit to the London Metal Exchange rekindled his interest and enabled him to obtain supplies of the metal. David Poston first used titanium at Hornsey in 1969 but did not work with it seriously until much later. Alan Wright notes that samples of titanium from IMI were brought into class at Central

Figure 1.8: Example of Lewis and Clayton titanium picture, created using a brush anodising technique, collection of Peter Hayfield.

in 1969 and a necklace that he produced, Figure 1.9, was one of the first pieces of titanium jewellery to be featured in a mainstream magazine. It was illustrated in Vogue in 1970, Figure 1.10, but ironically only in black and white and the text states only *'Titanium collar by Alan Wright'*.

By the early 1970s titanium had become a regular product used

Figure 1.9: *Titanium collar by Alan Wright, 1970, image courtesy of Alan Wright.*

in Jewellery courses. Several of the jewellers who had experimented with titanium on

Figure 1.10: *Copy of page from Vogue, 1970, showing model wearing titanium collar, text reads:' Titanium collar by Alan Wright'.*

undergraduate courses continued their studies at the Royal College of Art (RCA) and developed their work there. Others were first introduced to titanium at the RCA but did not develop work incorporating it until setting up their own workshops.

Many museum collections include the cloudscape brooches of Ed de Large, such as the one illustrated in Figure 1.11 from the
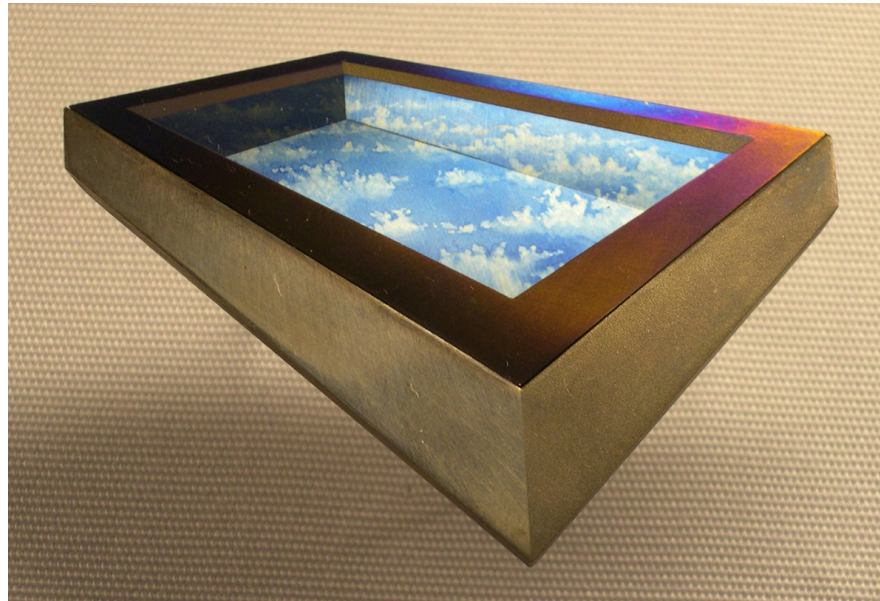
Figure 1.11: *Titanium brooch in a silver frame by Ed de Large, late 1970s, photograph courtesy of Ann Allnutt.*

Pforzheim Museum. He developed his own painstaking heat and anodising techniques, using precise masking and brush anodising with the finest of brushes.
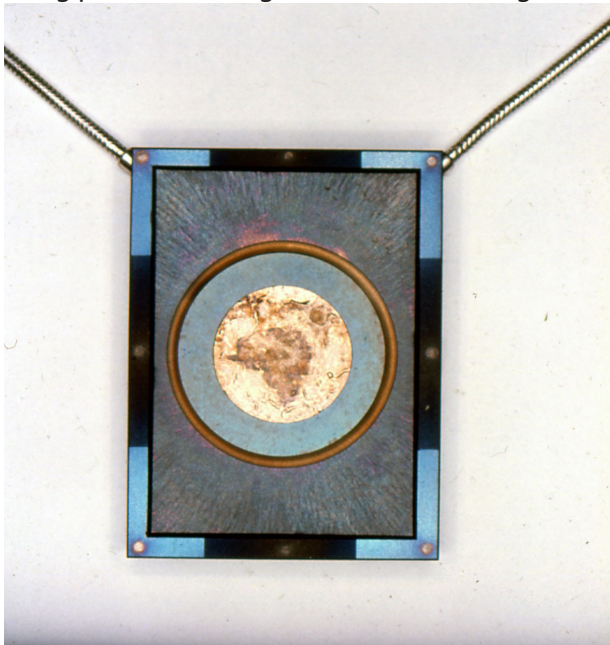
Figure 1.12: *James Brent Ward pendant from late 1970s, titanium frame and insert with gold amalgum centre and gold rivets, image courtesy of JB Ward.*

His contemporaries at the RCA were Kevin Coates and James Brent Ward who both used titanium but in very different ways. The latter made scenic pieces, Figure 1.12, with a freer approach and was interested in the technical aspects of the metal and its processing. It was while he was a student at the RCA that James Brent Ward, with sponsorship from the Goldsmiths' Company, published a report in 1978 that became the standard guide for jewellers on working with refractory metals[27].

Kevin Coates had yet a

[27] Ward, James Brent, *The Colouring and Working of Refractory Metals,* Worshipful Company of Goldsmiths' Project Report No. 34/1, London September 1978.

different response to the metal and titanium was just one of many materials, chosen for their visual impact, that he used when creating his jewels inspired by myth and music, see Figure 1.13. The three had a joint exhibition at the Electrum Gallery in October 1976, one of the first to be devoted to the new metal.

Figure 1.13: Brooch by Kevin Coates, titanium, gold and silver, ca 1979, V&A Jewellery Gallery.

The previous year the first Loot exhibition organised at Goldsmiths' Hall included titanium pieces by five jewellers. In the second year of the Loot exhibitions in 1976, eleven of the three hundred and thirty exhibitors showed work incorporating titanium. In the catalogue, Graham Hughes, the Art Director at Goldsmiths' Hall, noted the use of '*a new metal and new colour'* in the pieces exhibited. Among the exhibitors were Graham Crimmins and Scilla Speet who had started working with titanium as students at Birmingham in 1968. Speet went on to the RCA (1970-73) and produced pieces that involved setting titanium rod into silver as seen in Figure 1.14

Figure 1.14: Two silver bangles with titanium rod inserts (one coloured by paintbrush technique) by Scilla Speet, 1972.

While a second year student at the RCA in 1974, Lexi Dick used titanium in combination with stainless steel to produce the chain-mail neckpiece illustrated in Figure 1.15, but this was to be her only use of the metal.

It was Mike Pinder, as a tutor at Manchester with the encouragement of his fellow staff member, Ann Marie Shillito, who explored and developed the use of titanium wire for chain mail. The silver and titanium chain-mail necklace with lapis lazuli from 1982,

Figure 1.15: Steel and titanium chain-mail neckpiece by Lexi Dick, 1974, image courtesy of RCA.

illustrated Figure 1.16, demonstrates his use of the technique incorporating two distinct colours of anodised titanium.

The LOOT exhibition in Minneapolis in 1978 featured a significant number of titanium pieces and subsequent workshops given in the USA by UK jewellers, such as Ed de Large, carried the use of titanium across the Atlantic.

One of the students who came to the RCA

Figure 1.16: Silver and anodised titanium chain-mail necklace with lapis lazuli, Mike Pinder 1982, image courtesy of M Pinder.

from Hornsey in the late 1970s and also exhibited in the Loot exhibitions from 1979 was Clarissa Mitchell. As well as using titanium for frames, Figure 1.17, she also researched the use of titanium sputtering on other materials[28].

In the late 1970s Ann Marie Shillito became aware of the use of titanium for surgical implants and devised integral earwires, hand cut, for titanium earrings. Experiments in the late 1980s with laser cutting, in collaboration with Heriot-Watt University, produced brooches with integral pins. Both these innovations are discussed in more detail in Chapter 2.

Figure 1.17: *Titanium sunglasses by Clarissa Mitchell, 1981, image courtesy of RCA.*

Another Birmingham student from 1973-77, Brian Podschies became interested in the challenging metal and, after using the standard colouring techniques, developed a hot-forging technique as illustrated in Figure 1.18.

His forging technique produced quite different results from those developed by David Poston in 1983 when he began hot forging the metal to produce finished grey/ black pieces, Figure 1.19.

For the first decade of its use, up to the mid 1970s, titanium was regarded as a special material used principally by designer/makers to produce one-off or

Figure 1.18: *Titanium forged bracelet with bronze hinge by Brian Podschies, 1985*.

limited edition pieces. The second half of the 1970s and the early 1980s saw production move to a more industrial scale. A substantial volume of simple, inexpensive pieces began

[28] Mitchell, Clarissa and Lee, Mike, *Titanium sputtering* ,RCA Papers No 11, RCA London 1981.

Figure 1.19: Titanium four part hot-forged bracelet by David Poston, 1984.

to appear in the windows of the High Street Jewellers. Companies such as Simbol, Prism and Dust concentrated on producing simple multi-coloured jewellery, as illustrated in Figure 1.20, for the mass-market and the perception of titanium changed.

Barry and Sally Milburn, who both studied at Central in the late 1970s, were inspired by the work of Ed de Large but saw titanium

Figure 1.20: Titanium and silver pendants by Dust ca 1980, image courtesy of P Gainsbury.

jewellery as a way to achieve their ambitions for a volume jewellery manufacturing business, a selection of which is shown in Figure 1.21.

Artist/craftsmen found it difficult to sell their individual designs as customers became accustomed to the inexpensive products available. Those jewellers who found the problems of using titanium too frustrating, both technically and commercially, but liked the colour possibilities moved on to niobium and tantalum, other refractory metals (so-called because of their high melting temperatures). Both were introduced to jewellers in

Figure 1.21: Titanium earrings (acid etched and anodised) by Prism 1980s, image courtesy of Prism.

the UK by Peter Gainsbury, Technical Director with the Goldsmiths' Company.

Students in the early 1980s were often inspired by the intricate images created by Ed de Large. One of these was Debby Moxon who went on to develop her own particular method of heat-colouring titanium. Using precise geometric scoring and a fine flame she created a deceptively simple style, illustrated in Figure 1.22, whose complexity only becomes apparent with knowledge of the behaviour of the metal. The details of this technique are discussed

Figure 1.22: Brooch by Debby Moxon from 1982/3, illustrating her sophisticated use of heat-colouring.

in Chapter 2.

Inevitably during the late 1980s the use of titanium in standard high-street pieces reduced its special appeal for the more design-led jewellers and only the most committed makers continued to use it. A notable example is Brian Eburah who studied at Central 1973-6 and still features titanium in his work today, see Figure 1.23 below.

Figure 1.23: Titanium, gold and silver brooch with topaz by Brian Eburah, 2005.

The light weight of titanium, so important in industry, has been seen as a disadvantage in a jewellery market where, for historic reasons, related to the use of precious metals, value

Figure 1.24: Open University mace made completely of titanium, 1972.

has been connected with weight. Writing in the Financial Times in 2002, Vivienne Becker disparages *'tinny titanium'*. The possibilities offered for larger scale wearable pieces, which have to some extent been realised with aluminium have not been exploited for titanium. The benefit of the lightness of titanium has been successfully used in maces, notably that for the Open University, which was designed by Eric Clements and made at Birmingham by Hamish Bowie, shown in Figure 1.24, and, appropriately, for the Birmingham Polytechnic mace, Figure 1.25, designed and made by Terry Hunt in 1988.
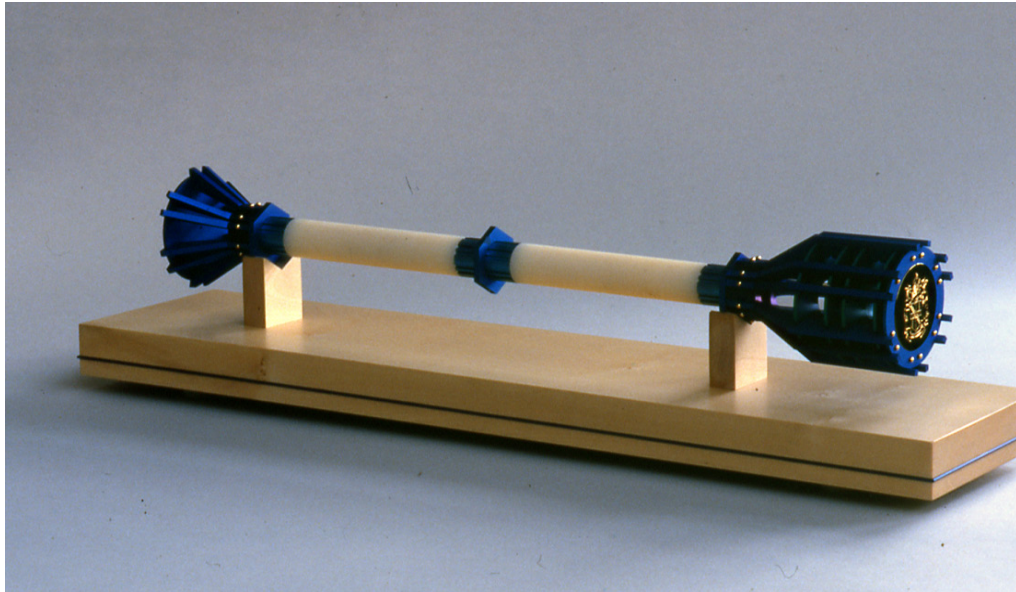
Figure 1.25: Birmingham Polytechnic mace, nylon shaft with titanium fittings, Terry Hunt, 1988, image courtesy of T Hunt.

Apart from a few enthusiastic designer/makers, who continued to explore the potential of titanium, and curious students, who wanted to try working with an unusual metal, very little exciting and innovative work was produced after the early 1990s.

There are examples of well-known jewellers using titanium to create examples of their established design style, e.g. Wendy Ramshaw and David Watkins. Figure 1.26 shows a ring set by Ramshaw and a bracelet by Watkins from the late 1990s which are on display in the Science Museum in London.

In recent years the public have become more familiar with the pale grey of uncoloured titanium and have appreciated the strength and lightness of the material, particularly in sports equipment and spectacle frames. A very visible usage in the early 21st century has been the iconic Apple-Mac Titanium Power Book. The popularity of body piercing and the biocompatibility of titanium have been combined to produce a wide range of titanium body jewellery both natural and anodised. This is mass-produced, as are the increasingly popular titanium rings. A wide range of titanium rings, often inlaid or combined with precious metals and diamonds, are now offered and the 'industrial' image of the metal is
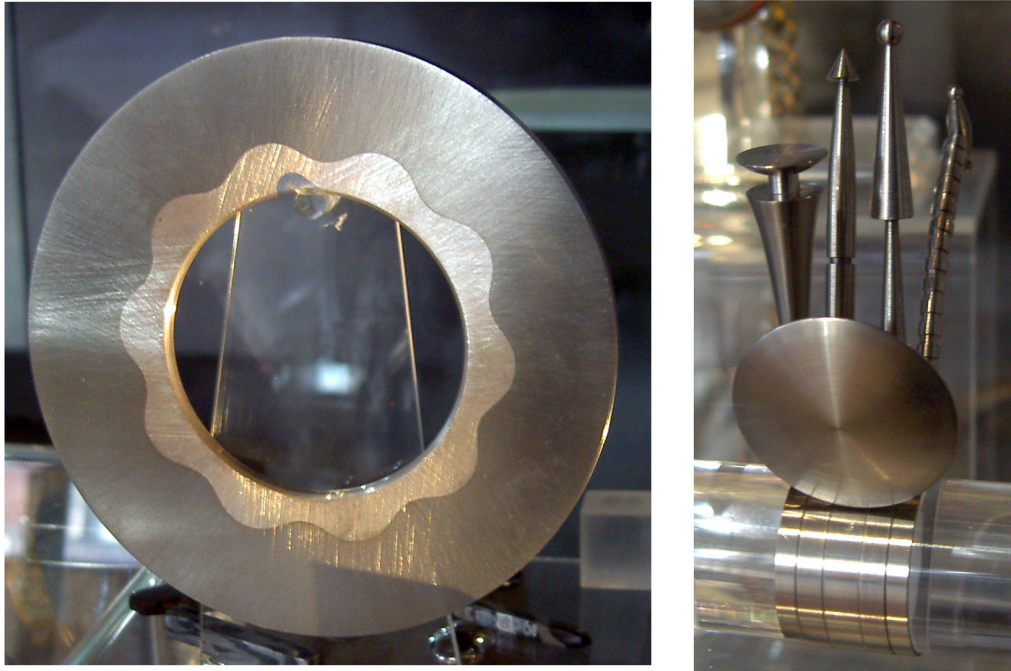
Figure 1.26: *Titanium bracelet with silver insert by David Watkins, 1997 and titanium ring set by Wendy Ramshaw, 1995.*

being successfully marketed to men.

There are however a few early signs of a renewed interest in the colouring of titanium. Recently, Joel Degen, who appreciated uncoloured titanium as it was *'in tune with the machine aesthetic'* of his work, has started to reintroduce colour, as shown in Figure 1.27.

Figure 1.27: *Selection of titanium, gold and stainless steel brooches by Joel Degen, 2005, image courtesy of Joel Degen.*

The production ranges of titanium jewellery are starting to feature engraved areas

that are subsequently anodised.

At least two jewellers have researched the decorative potential of the use of lasers to create coloured pattern on titanium. Dr Sarah O'Hana, a jeweller who worked within the school of Mechanical Aerospace and Civil Engineering at the University of Manchester combined computer graphics and lasers to produce patterned titanium pieces as illustrated in Figure 1.28. Dr Ann-Marie Carey, who produced laser-patterned niobium bowls as part
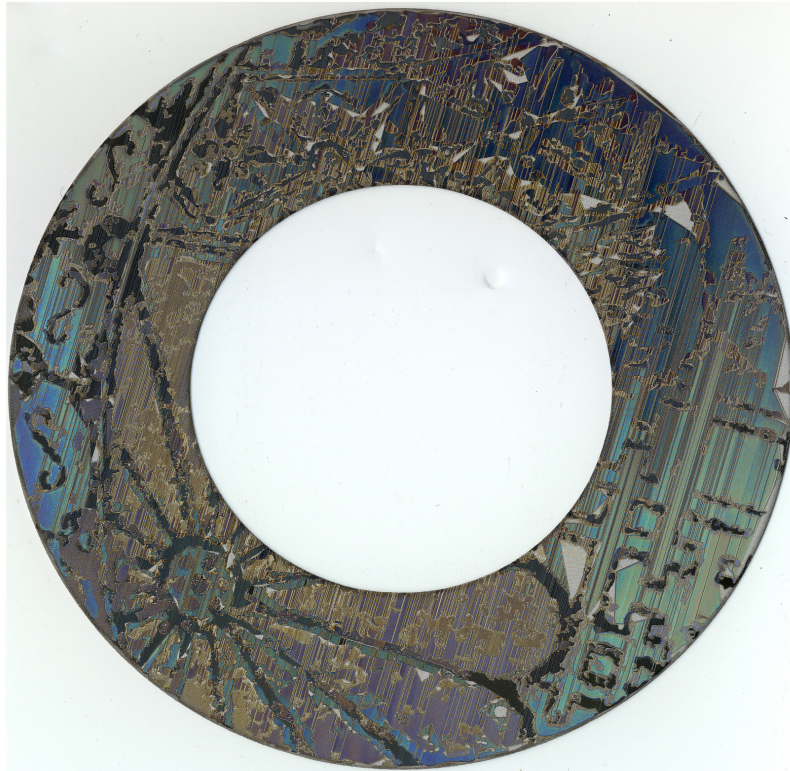
Figure 1.28: Laser pattern titanium bangle, Sarah Ohana, 2007, image courtesy of Sarah O'Hana.

of an MPhil project at the RCA developed her work on laser marking of titanium at the Innovation Centre, part of the School of Jewellery in Birmingham where it all began forty years ago.

A more recent fabrication method was explored by Jo Hayes-Ward, a student at the RCA. The method uses a combination of computer-aided design and the sintering process to produce the piece in Figure 1.29. Sintering is a form of processing akin to casting in which titanium powder is compressed below its melting point, However this material, when anodised, as seen in brooches by David Watkins at Creation II[29], takes only a faint tint when anodised.

Other recent developments have seen titanium used as a mount for gem-set jewellery.

[29] Creation II, exhibition at Goldsmiths' Hall, 2009.
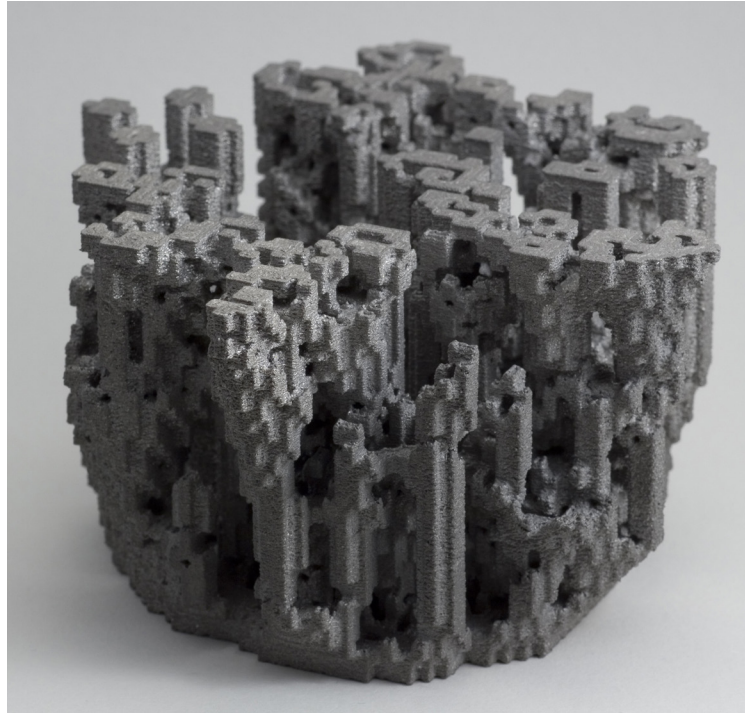
Figure 1.29: *Sintered titanium, Jo Hayes-Ward, 2006 Image courtesy of Jo Hayes-Ward.*

1.6. Conclusions

The brief outline of the properties of titanium and its industrial history, presented in this chapter, emphasised the impact that this unusual metal had, both industrially and artistically, in the second half of the twentieth century.

The history of the early decades of the use of titanium in jewellery has been presented for the first time. This historic survey confirms that it was an initiative from industry, in the search for new outlets for an expanding level of production of the metal, which prompted the use of titanium as a jewellery material.

The study also shows that the industry initiative coincided with changes in the education of jewellery designers, which had produced an expanded cohort of students eager to experiment with and exploit new materials. It was from among these jewellers that the historic survey identified the key practitioners in the field responsible for refining and developing the workshop procedures for processing and colouring the metal and, via a structured programme of workshops, spread its use across the USA.

Chapter 2 presents the programme of discussions with these key practitioners, designed to identify both the range of techniques that were developed and the problems experienced in the colouring of titanium.

Chapter 2

2.1. Introduction

Chapter 1 established that the use of titanium for designed jewellery was a technical innovation, pioneered in the UK and instigated by the titanium metal producers. The research that traced the development of titanium jewellery in the UK identified key practitioners in the field. This chapter, which is presented as three main parts, synthesises an overview of the workshop techniques developed by these jewellers and assesses the experiences of individual designer/makers in the use of titanium. The resultant technical review provides essential information for the conduct of the research project as it enables the uncertainties in the existing titanium colouring processes to be clarified. Such clarification leads to a definition of the variability of colour outcomes experienced by the studio jeweller, as exemplified in the researcher's own practice, which provided the impetus for this research project.

As explained in Chapter 1, jewellers relished the new design possibilities that the use of the new metal, titanium, made accessible by virtue of the coloured metal surfaces that could be obtained without the use of paints or dyes. The coloured surface of titanium is achieved by the oxidation process, which creates a thin, colourless, transparent oxide film adhering to the reflective surface of the metal thereby producing the conditions required for the optical effect known as thin film interference. This phenomenon, as is discussed in detail in Chapter 3, depends on the geometry of the oxide layer, in particular its thickness, and therefore the control of the oxide layer growth is a key factor in the process. Although the colouring processes recommended by the metals industry were adjudged by the practitioners to be superficially straightforward and simple, in practice jewellers found that exact reproduction and repetition of a specific hue could be difficult and unpredictable.

The colour development on titanium is a continuous dynamic process that depends on the growth of the oxide layer on the metal surface fuelled by the input of energy in the form of heat or electricity (anodising). Oxygen is supplied either from the surrounding air in the case of heat or from the water in the electrolyte solution in anodising. In order to obtain the desired design outcome the individual jeweller had to control the energy input until the required colour was obtained. Jewellers therefore had to devise their own methods for working with titanium and in particular their own techniques for colouring it. However little was published on the subject so that information about the techniques pioneered by the early users of the new metal as a medium for their own creativity was in danger of being lost.

The first part of this chapter presents a review of the technical practices for the fabrication and colouring of titanium that have been developed over the forty years of its use as a jewellery metal. Although the primary focus of the research is the colouration of the metal, details of any novel fabrication methods are included, as the combination of form and colour produces the design outcome that jewellers strive to achieve in a finished piece.

Information about the techniques developed by key practitioners, whose experimental approach to the new metal were responsible for the rapid success of titanium as a jewellery material, was collected in a series of informal interviews. The methodology used for the identification of these jewellers and the collection and collation of the information about their practice is briefly described together with an analysis of the collated results of these investigations. The information obtained from these practitioners is incorporated into a review, which details the workshop procedures for forming and colouring titanium and explores any misconceptions that have built up over the years about working with titanium.

The second part of the chapter considers the issues relating to colour variability experienced by jewellers when oxidising titanium. These issues, identified during the review of technical practice, describe the range and type of unexpected/unwanted variation in colour which may occur when anodising or heating titanium. An example from the researcher's own practice is used to demonstrate in detail the types of variability which are described more generally by other practitioners. Following from the outline of the types of variability that can occur during the workshop colouring of titanium, this part of the chapter then considers the possible sources of this variability, thus defining the research questions for the project. The discussion of colour variability within this part of the chapter highlights the need for precise colour definition as an aid to clear communication of colour.

The investigation of the variability issues thus defined requires experimental samples specifically created for the project. The third and final part of the chapter presents a schedule of experimental samples, including preparation and colouring procedures. These procedures are selected from the workshop colouring techniques described in the first part of the chapter.

2.2. Review of Jewellery Workshop Practice

This part of the chapter describes the techniques and procedures most commonly used to colour titanium in a jewellery workshop and discusses the results obtained. The methods are based on the author's own practice, which was developed from a college workshop project, supplemented with information from other sources. These include the

limited number of publications[1,2] on the subject and information from other titanium jewellery practitioners obtained in the course of a series of informal interviews conducted for the research project.

2.2.1. Sources of Information and Methodology

The information gathered in the course of the construction of the history of the development of titanium use for jewellery, presented in Chapter 1, identified the early users of the material. The objective of the project was to obtain information from a representative number of jewellers, with varying degrees of involvement with the novel metal in the early decades of its use, rather than to survey all the users of titanium in jewellery. Therefore the methods chosen for information gathering were a questionnaire followed by informal interviews with selected respondents as detailed below.

Jewellers in the UK who had worked with titanium in the 1960s, 1970s and early 1980s were identified from exhibition catalogues, such as those of the Loot exhibitions at the Goldsmiths' Hall[3], particularly in 1976 where, as quoted in Chapter 1, eleven makers using titanium were featured. The archives of the Royal College of Art (RCA), the Crafts Council and Goldsmiths' Hall produced an additional list of twenty-eight students or designer/makers who had used titanium in the period. The timeframe was chosen in order to gather data from the early users of the material when its properties were being explored and the time-line of jewellers using titanium at the major colleges in the UK, 1963-1983, (Table 2.1A p 221 in Appendix) shows the periods of graduate and postgraduate studies for a number key practitioners in the early years of their use of the new metal.

The initial approach was made to the identified group of jewellers in the form of a simple, two page questionnaire with a covering letter as an introduction. The questionnaire was devised in order to introduce the project to the selected jewellers and gather preliminary information from them about their use of titanium. No specific theoretical model was used for the design of the questionnaire. The aim was to ask questions in an unambiguous manner and to limit the questionnaire to two typed pages. A draft version was tested with one jeweller and minor amendments made before the final document was sent out. The covering letter explained the background to the request and outlined how the material would be used. Copies of both letter and questionnaire are included in the Appendix (p 218).

Of the identified group of thirty-nine jewellers in the UK who had exhibited pieces

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[1] Ward, James Brent, *The Colouring and Working of Refractory Metals,* Worshipful Company of Goldsmiths' Project Report No. 34/1, London September 1978.
[2] Untracht, Oppi, *Jewelry Concepts and Technology,* Robert Hale, London 1982.
[3] Hughes, Graham, *Introduction to Loot Exhibition Catalogue,* Goldsmiths' Hall, London 1976.

featuring refractory metals, thirty-three were traced and sent copies of the questionnaire. Repeated requests failed to elicit responses from six jewellers and one specific refusal to participate. Of the remaining twenty-six respondents two had used only tantalum and niobium. The replies from the twenty-four positive respondents were tabulated in a spreadsheet, Table 2.2A in the Appendix (p.227), together with information from two documented early users in the USA who had been influenced by jewellers from the UK to experiment with titanium. These results provide information from a range of jewellers about their awareness and use of titanium together with their comments about the good and bad points of the material in a jewellery context.

Questionnaire Results

The recorded comments and opinions of the respondents to the questionnaire, as summarised in the spreadsheet, identify both the common themes among the practitioners and the individual factors, which characterised and defined their use of titanium. The target group of jewellers produced a wide range of responses to the new metal. The responses ranged from those who having satisfied their curiosity about the new material chose to move forward with more traditional jewellery metals, to those for whom titanium became a lifelong obsession. Although a few jewellers pioneered the use of titanium while at college in the late 1960s, the majority of the respondents became aware of the new metal during the 1970s and started to use it soon afterwards. It was only as the metal became more widely used in the second half of the 1970s that public exhibitions and the work of such artists as Ed de Large were cited as inspirations to work with titanium.

For all the respondents to the questionnaire it was the design potential offered by the colourability of titanium that was quoted as the principle attraction of the new metal. The context varied with the jeweller from a desire to match other coloured materials, such as Chinese silks in the case of Judy Keeling, to a need for colour in a particular feature, such as a watch face quoted by Eric Spiller. Many expressed an overall appreciation of the innovation potential of the range of colours achievable with titanium and the opportunity to work with a completely new material with new potential.

Analysis of the questionnaire responses showed that titanium was used to make all forms of jewellery; brooches, necklaces, rings, earrings, pendants and bracelets. Initially both methods of colouring, i.e. heat and anodising, were widely used but following the publication of the Goldsmiths' Report in 1978[4], which included a design for an anodising unit, anodising became the preferred method of colouring for the majority of users.

Although six of the jewellers in the group mentioned the lightness in weight of the metal as an attractive feature only one, Joel Degen, suggested that this allowed larger pieces

[4] Op Cit.

to be made. Conversely another jeweller, Mike Pinder, cited the light weight of the metal as a negative attribute. Almost all respondents remarked on the problems of working with titanium in terms of its hardness and difficulty of processing, especially when compared to the more commonly used jewellery metals, gold and silver.

A variety of suppliers were mentioned as sources of titanium, principally Titanium International, but many sourced their requirements as scrap metal from aircraft manufacturers. Apart from occasional batches of titanium that were especially hard, few problems were quoted with availability of metal or cost.

In summary, while some jewellers found titanium an interesting challenge and worth the effort required in manipulating the metal in order to exploit the creative possibilities given by the colouring of the surface, others approached it in a similar way to gemstones or enamelled plaques and set pieces of coloured titanium within a silver frame or mount.

Jewellers, such as Jacqueline Mina, Figure 2.1, Lexi Dick and Vicki Ambery-Smith, satisfied their curiosity about the new metal with initial experiments before developing their own practice using more traditional materials.

Another group of early titanium users, frustrated by the 'unresponsiveness' of titanium in comparison with silver found that an alternative refractory metal, niobium, had a similar colour potential as it could also be anodised to produce interference colours but could be chased using conventional silversmithing techniques and tools to form three-dimensional pieces. In particular three jewellers, Pauline Gainsbury, Jane Townsend and Jeanne

Figure 2.1: *Titanium and gold pendant by Jackie Mina.*

Werge-Hartley, moved from using titanium to the denser and more malleable niobium.

However a few jewellers relished the stimulus to their creativity that working within the constraints imposed by the properties of a metal such as titanium and the satisfaction of overcoming the difficulties of forming, joining and colouring it.

This latter group were considered to be key practitioners in the field of titanium jewellery, either for reason of their early involvement with the metal and/or because they developed novel techniques for forming or colouring the material. Illustrations of their work have been used to exemplify the technical innovations in their use of titanium in jewellery and specific techniques have been included in the Synthesis of Jewellery Workshop Practices which follows the reports of the individual interviews.

The following jewellers were interviewed and the highlights of their practical innovations, developed by empirical research, are discussed below. The first 'wave' of users comprises Ann Marie Shillito, James Brent Ward, Edward De Large and Kevin Coates and their work shows how the practice of workshop use of titanium developed from the initial advice given by industry. The second 'wave' of titanium jewellers, Reema Pachachi, David Poston, Brian Podschies and Debby Moxon, encountered titanium as an established specialist material and sought to redefine the aesthetic of the practice either in colour or form. Finally the founders and owners of Prism, Barry and Sally Milburn are included as an example of small-scale industrial use of titanium for jewellery.

2.2.2. Interviews

Ann Marie Shillito

Ann Marie Shillito is included as a key jeweller in the development of the use of titanium in jewellery because she was in the first cohort of jewellery students to use the new metal while an undergraduate at Birmingham. She developed or improved techniques for forming and patterning titanium through continued experimentation over many years and thus the evolution of her practice merits detailed consideration. The following overview summarises the information obtained in a series of interviews, concentrating particularly on the experimental phases of her technical innovations.

A belt buckle that she made in 1967 is the earliest identified designed piece of titanium jewellery (see Figure 1.4 in Chapter 1). The buckle was milled and pierced from a thick sheet of metal and coloured by anodising. The differing colour on the face of the buckle and on the edges can be a feature of anodised titanium and it is evident that the surface shows a grained colour.

Shillito continued her experimentation with titanium at the RCA from 1968 and it is possible that her arrival there may have encouraged other students to experiment with

the new metal. In 1969 Professor Robert Goodden, Head of the School of Silversmithing and Jewellery at the RCA noted that, '*Some students experimented in the use of titanium as a jewellery material. The metal has several properties to recommend it for the purpose; it has the strength of steel but only half the weight; its air-formed surface film of oxide can be dissolved and re-crystallised by thermal etching to give a faceted, granular appearance; and the transparent film of oxide can be increased by electrical anodizing in a variety of acids to a range of thicknesses which give rise to colour by interference without the use of colouring agents. The*
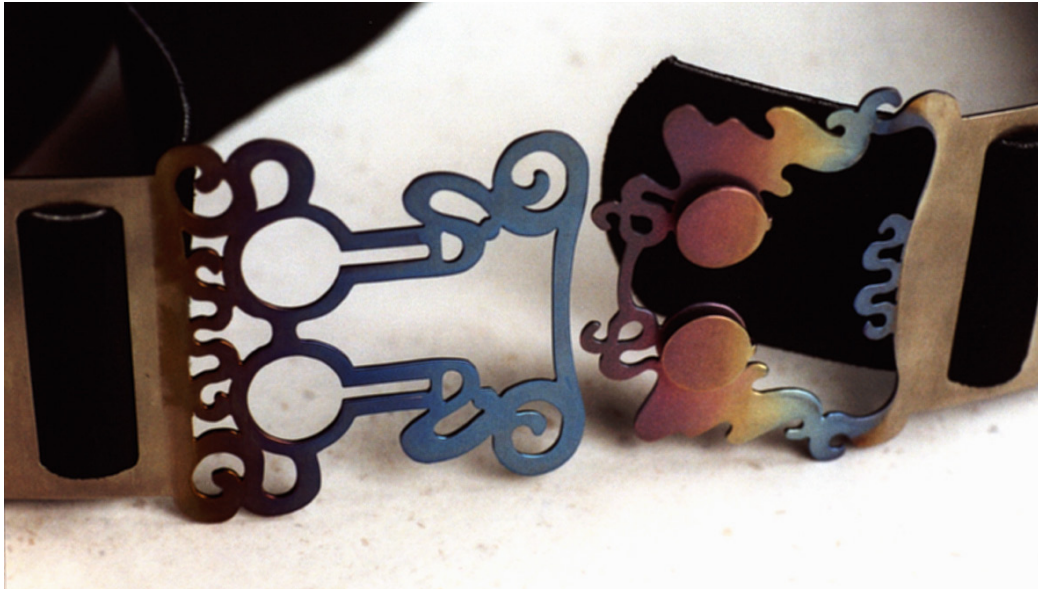
Figure 2.2: *Belt buckle sawn from titanium sheet and coloured by dip anodising, Ann Marie Shillito, 1970.*

colours are soft and beautiful – much 'greyer' than those of soap bubbles for instance.[5]

The dip-anodised belt buckle, illustrated in Figure 2.2, was produced for a

Figure 2.3: *Elements designed for a belt buckle by Ann Marie Shillito and 'painted' by Lewis and Clayton.*

[5] Goodden, Robert, *Court/Rector's Report 1968-1969,* RCA, 17th December 1969, p 10.

competition in 1970 while Shillito was at the RCA. This piece demonstrates an early use of this technique, which involves gradually removing a piece from the electrolyte bath as the voltage is increased in order to get colour variation. The dip-anodising technique is described in detail in the Synthesis of Practice, presented below.

After graduation in 1971 Shillito developed her studio jewellery practice featuring titanium, employing Lewis and Clayton to brush anodise the metal to her designs, Figure 2.3.

Lewis and Clayton's involvement with brush anodising is detailed in Chapter 1 and the technique is discussed later in the chapter. Shillito also continued to experiment with other techniques including the casting of silver around titanium, which would be simultaneously coloured by the heat of the casting process. As can be seen from the illustrated experimental pendant, Figure 2.4, the colour is patchy, probably a result of the inherent lack of control of the heating.

Later experiments with lower temperature casting and smaller pieces of titanium, as exemplified by the ring from 1995, Figure 2.5, achieved using a more sophisticated casting with a rubber mould, show a more controlled outcome but the colour is restricted to blue.

However in the early 1970s the use of titanium with precious metals was problematic because of the hallmarking regulations in force at the time. It was illegal to sell precious

Figure 2.4: *Experimental cast silver and titanium pendant, showing patchy colour, Ann Marie Shillito, 1974.*

Figure 2.5: *Cast silver ring with titanium inserts, Ann Marie Shillito, 1995.*

metal items above a certain weight without a hallmark but the hallmarking of mixed metals was not permitted. Effectively this meant that titanium had to be used on its own and Shillito found that this restriction acted as a spur to her creativity and ingenuity as exemplified in the anodised belt buckle and much of her subsequent experimentation sought to devise designs where the titanium was its own fixing. An amendment to the regulations in 1974 permitted the use of mixed metals but the silver or gold component could not be hallmarked and had to be described as precious white or yellow metal.

The acquisition of anodiser in 1979 instigated a period of experimentation with colouring and resists and the use of niobium inlay to achieve colour contrast. Having learned of the use of titanium for surgical implants, Shillito devised earrings with integral earwires, illustrated in Figure 2.6, suitable for wearers with sensitivity to even silver posts.
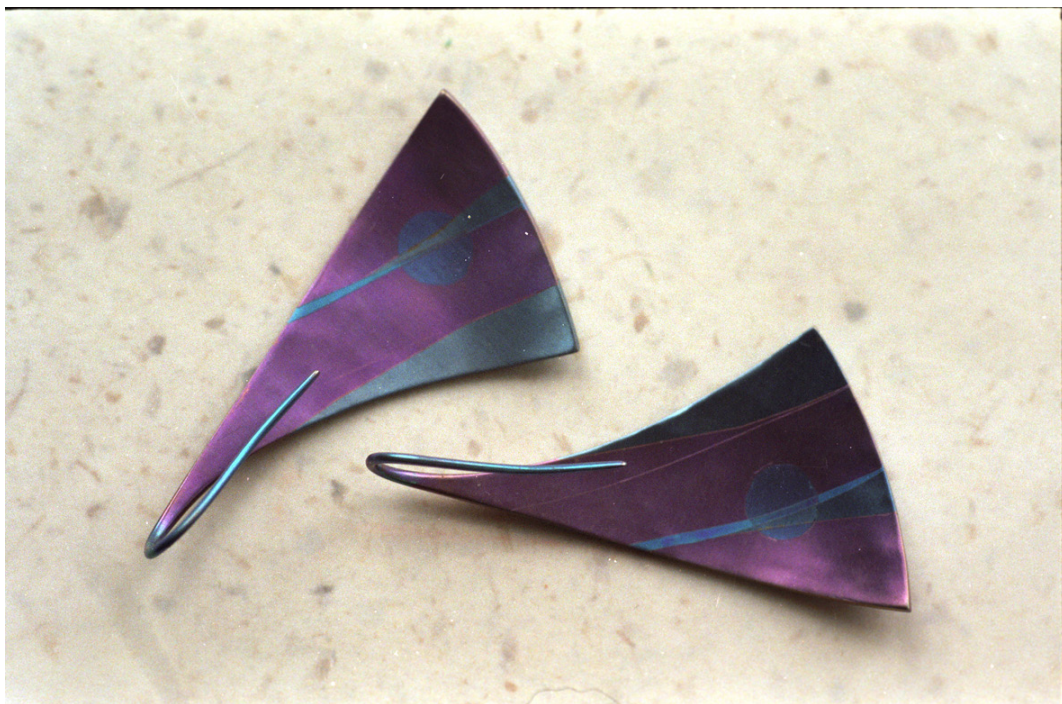
Figure 2.6: *Titanium earrings, with niobium inserts for colour contrast, featuring hand cut integral wires, Ann Marie Shillito, 1978.*

Initially these were hand cut as were brooches with integral pins, cut from the same sheet of metal but subsequently she used RT blanking and photoresists and then laser cutting in collaboration with Heriot-Watt University, see brooches in Figure 2.7. Laser cutting was also used to form three-dimensional shapes from flat sheet and limited experiments were conducted with forging titanium.

During the course of the interviews, Shillito noted that, in her experience, an etched surface gives stronger colours when anodised than a polished one and that vacuum etching results in particularly vivid hues. She also mentioned that from a production point of view, the colouring of niobium by anodising is more reproducible than the similar

Figure 2.7: *Laser cut titanium brooches with integral pins, Ann Marie Shillito, 1991.*

method of colouring titanium. In particular when niobium is partly covered with a resist and then anodised to a 'high' colour i.e. using a high voltage, removal of the resist and further anodising to a 'low' colour i.e. low voltage, leaves the previous colour unaltered. If the same procedure is followed for titanium, the oxide layer continues to build over the whole surface and the original 'high' colour may be altered.

In summary Shillito used and developed a variety of colouring and forming techniques which have become standard procedures in the fabrication of titanium jewellery. However the multi-coloured nature of her designs encompasses possible variations of colour outcome.

James Brent Ward

James Brent Ward is selected as a key figure in the development of titanium jewellery because he researched and wrote one of the few contemporary publication about the decorative use of titanium. He first used titanium while a student at the Central College of Art and Design (CCAD) in London in early 1970s where both Alan Wright and Eric Spiller had noted the introduction of titanium to the jewellery workshop ca 1969. Brent Ward's graduate show in 1973 included titanium pieces as reported in Design[6]; '*Some materials are easier to work, others more of a challenge. James Brent Ward found the latter was true of titanium. Unlike silver, it can[not] be soldered except in a vacuum, and it takes up to three days*

[6] Hughes Stanton, Corin (ed), *Diploma Season: Central Jewellery Nine,* Design Journal London 1973, p 61-68

to polish satisfactorily. It is coloured by being dipped into an electrolytic solution and having a current passed through it, the different colours being dependent on different voltages. James used both polished and unpolished titanium, but feels he is still at the experimental stage.'

This contemporary quotation highlights the experimental approach to titanium
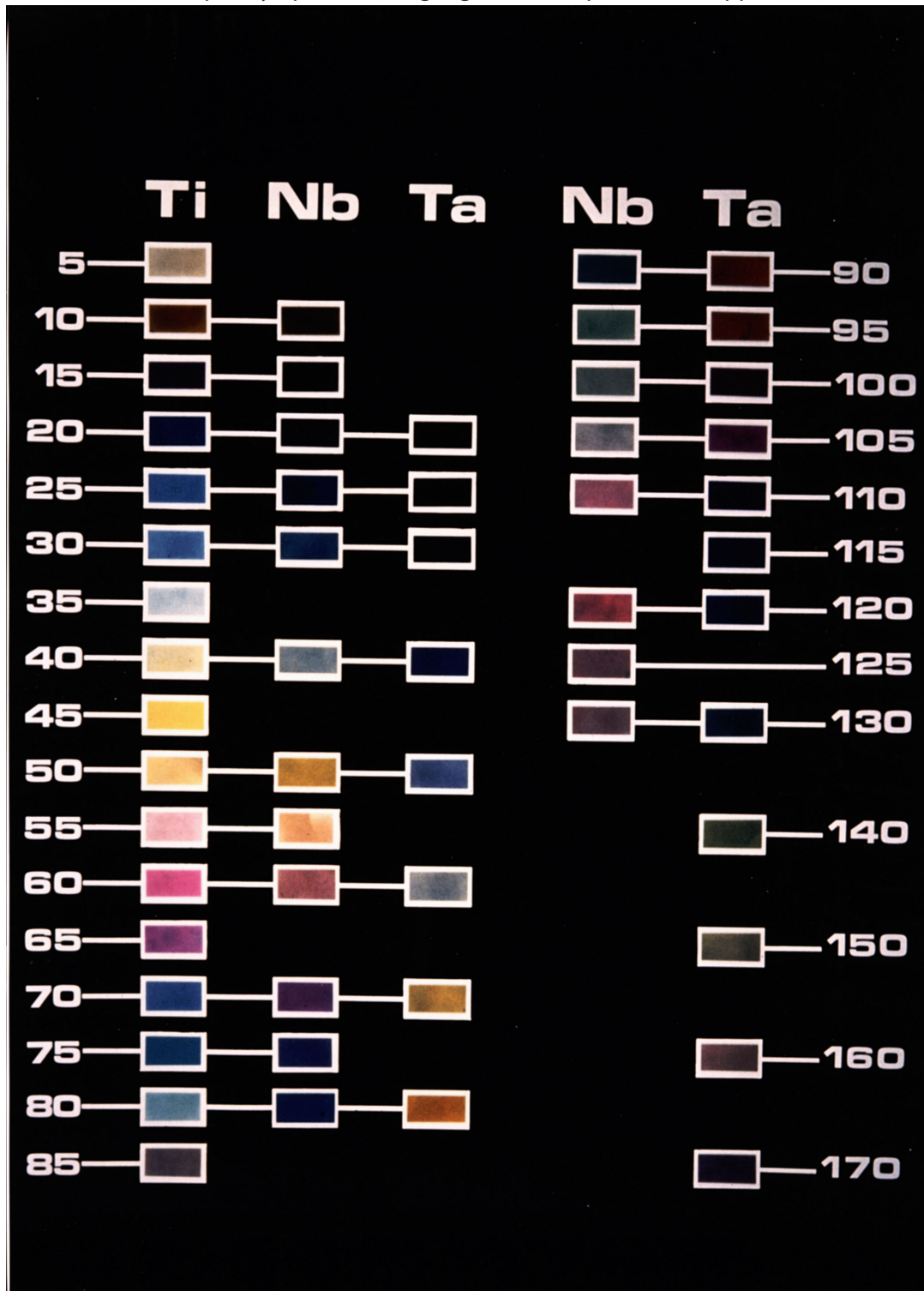
Figure 2.8: *Colour chart produced as part of the Goldsmiths' Bulletin, showing colours produced at specific voltages for titanium, niobium and tantalum.*

that was still current in the field of titanium jewellery in the early 1970s. Encouraged by Peter Gainsbury, Technical Director at the Goldsmiths' Company, Brent Ward undertook a structured programme of research into the use of titanium while at the RCA between 1974 and 1977. The resulting paper, based on this research, was published by the Worshipful Company of Goldsmiths as a technical bulletin entitled 'The Colouring and Working of Refractory Metals' in 1978 (reissued in 1982).

This seminal paper was essentially a workshop manual, which described procedures that could be used by jewellers to form, finish and colour the refractory metals, titanium, niobium and tantalum. The only theoretical aspects of the oxidation process were covered in a short appendix by Peter Gainsbury, which outlined the optics of interference showing how the colour is derived from the geometry of the thin oxide layer grown on the surface of the metal. A further appendix by Robert Hunt from the City of London Polytechnic describes the anodising power supply unit that was constructed for use at the RCA. This appendix also includes circuit diagrams, which give guidance for the construction of similar units and was used as a blueprint by other practitioners.

The bulletin included a printed colour chart, Figure 2.8, which has subsequently been used as the standard colour reference for titanium. The colour patches printed in the bulletin show the sequence of colours derived by anodising experimental samples of titanium at increasing voltages. The colour of other examples of oxidised titanium is assessed by visual

Figure 2.9: Titanium bowl, pressed, hammered, polished and anodised, James Brent Ward ca 1978, image courtesy of JB Ward.

comparison with the colours recorded for these experimental samples.

In particular the chart has been used as a guide to determine the voltage required to produce a specific colour, although in practice this is not an exact correlation for all titanium sheet. However a consequence of the use of this colour chart has been a tendency to refer to colours in general terms in relation to the level of voltage required to produce them. Thus colours produced by voltages between 5-30V are called 'low' colours, browns, dark purples and blues, and those produced by voltages above 60V are called 'high' colours, pinks, turquoises and greens. These terms are used whether the colour on the titanium has been generated by heat or by anodising.

In addition to the publication of the bulletin Brent Ward presented papers about his research at conferences, notably in the USA[7]. He continued working with titanium and other refractory metals, developing larger three-dimensional bowls, such as Figure 2.9, anodised by using the bowl as the electrolyte bath. He currently acts as a consultant on the use of refractory metals to many jewellery companies.

Edward de Large (Ed de Large)

Ed de Large is included here as one of the most distinctive and influential jewellers who used titanium. He was a contemporary of both James Brent Ward and Kevin Coates at the RCA and would have been aware of the work that they were doing with titanium. Latterly he travelled extensively in the USA giving workshops on the use of titanium and is cited by many American jewellers as a source of inspiration in the use of the exciting new metal.

De Large first used the new metal while at the RCA, when titanium provided a design solution to the problem of a suitable material for the base of a commissioned gold goblet. The stem of the goblet, Figure 2.10, was turned and milled to a cylinder about 5 cm diameter and 5 cm depth. The technical staff at the Royal School of Mines were consulted for advice about the anodising conditions and procedures and the actual colour of the titanium was decided as the piece was being anodised. De Large also used the metal for the construction of a chessboard, which won him a travel scholarship to Japan for three

Figure 2.10: Gold bowl with titanium base, Ed de Large, 1974, image courtesy of RCA.

[7] Winkler, Nathan B, *Jewelers' Circular-Keystone,* USA, January 1980, p.152.

months in 1975 to study Japanese metalworking techniques.

As de Large explained during the interview, the trip inspired him to work on surface effects and he became increasingly intrigued by the challenge and potential of titanium. Writing in Crafts he described that he saw titanium as a medium that would allow him to explore his fascination with optical illusions as he developed his studio business. '*Titanium is hardly malleable, it is impossible to solder, and it is extremely difficult to form using normal silversmithing methods. This last limitation was perhaps fortuitous, in that it encouraged me to suggest a third dimension in my pieces where none existed (they are all flat). I don't draw or engrave lines on titanium, rather, I use stencils to define areas in the composition, creating the illusion of different planes by juxtaposing highly iridescent satin planes with matt and velvety sandblasted ones, achieved with wet and dry emery papers, glass-fibre brushes and small grinding wheels. The varied surface textures dramatically affect the appearance of the colours, which gives the actually simple, organised composition a complex appearance, with the play of light altering the atmosphere of a piece from, say, bright and cheerful, to menacing.*'[8]

By continuous experimentation he developed his own methods for creating complex images such as that illustrated in Figure 2.11, implying three-dimensional structures on flat

Figure 2.11: *Brooch titanium set in silver frame, cloudscape with optical illusion, Ed de Large, 1978, image courtesy of Ed de Large.*

[8] De Large, Edward, *On Titanium,* Crafts, September/October 1979, p22.

surfaces.

As he explained, each piece was meticulously designed with a line drawing before any fabrication. Colouring was achieved by anodising, or more rarely heating, with special effects obtained by masking, usually with opaque scotch tape cut with a scalpel but sometimes with nail polish. The carefully prepared tape shapes were burnished onto the metal to avoid seepage during anodising but the process had to be done at speed to minimise the danger of such seepage blurring the edges of the shapes. Some pieces were dip anodised to get a graduated colour but for others where a specific colour was required, the piece would be placed in the bath and the current switched on at the relevant voltage. The anodising equipment had to be robust and a large transformer was used. The fine detail of some pieces was achieved by brush anodising using a very fine paint brush which could be as small as a couple of hairs. For the majority of his brooches, the construction was limited to a flat sheet of titanium set in a solid silver frame and all the detail was expressed within the decoration of the surface of the sheet.

As de Large explained, the key to his successful colouring of titanium was the prior surface preparation, particularly the avoidance of grease and dust contamination. However he mentioned that overheating can deaden colours and colouring results can be unpredictable in much the same way as glazes on ceramics, the subject of his undergraduate studies.

Kevin Coates

Kevin Coates was a contemporary of James Brent Ward at CCAD in the early 1970s (their graduation show was reviewed in Design magazine in 1973 –see above) and later together with James Brent Ward and Edward de Large at the RCA, 1973-6. His distinctive pieces use a wide range of materials and while at the RCA he incorporated titanium in his work together with gold, silver; both organic and inorganic gem materials and resin. He is cited here for his work with titanium and gold, Figure 2.12, which was considered noteworthy by the Head of School, Philip Popham: '*Kevin Coates, a second year student, is designing very exciting jewellery combining 18K gold*

Figure 2.12: Titanium and 18ct gold 'Magpie' brooch, Kevin Coates, 1974, image courtesy of RCA.

and coloured titanium. He has perfected by genuine research, a difficult and ingenious process developed to suit his own requirements. Suitably shaped pieces of titanium (which cannot be soldered) are secured by modelled wax and then embedded in plaster for lost wax casting. The plaster holds the titanium in place while the wax is burnt away and molten gold poured into the recesses so left which, on cooling, permanently unites both metals.'[9]

The process, essentially one of casting the precious metal around the pre-formed titanium shapes, appears to be similar to that used by Ann Marie Shillito, as discussed above, which used silver and titanium. Both techniques were developed at about the same time but neither jeweller published any procedural details so the only evidence is from images of the pieces created.

Reema Pachachi

Reema Pachachi can be regarded as one of the second wave of jewellers to use titanium and, being an undergraduate at CCAD in1973/4 while James Brent Ward was working there as a technician, would have been aware of the work being done with the new metal. However she did not experiment with titanium until at the RCA in 1976 and did not develop her own practice using titanium until after graduation in 1980.

Her work epitomises her stated dislike of the '*rainbow'* image and *'muddy'* colours then seen as typical for titanium. As she explained in the interview, it arose out of a deliberate reaction against the multi-hued, patterned pieces that had been produced by the early users of titanium in jewellery. Her stated aim was to emulate the way a painter would use colour by juxtaposing blocks of complementary colours such as purple/blue with cinnamon.

The texture of the surface was also a major influence in her work and she always used an etch finish to create a matt surface. Not only did Pachachi react against the colour and patterning used by the earlier exponents of titanium in jewellery but she also eschewed the use of silver frames for titanium panels by setting brooches on wires, stating that if she used traditional silver fittings she *'might just as well use enamel'* rather than titanium.

In order to realise her designs, incorporating uniform areas of solid subtle colour, she used an etchant mixture of hydrofluoric acid (HF) prior to anodising with masking to delineate the surface shapes. Figure 2.13 shows a pair of titanium earrings in the collection of the V&A.

Pachachi's business developed rapidly in the early 1980s but she stressed that the production of a pair of pieces with exactly the same colour, especially required for earrings, was particularly difficult, commenting that *'titanium jewellery is hellish to produce in volume'*. Even the use of HF mixtures to prepare the titanium surface prior to anodising,

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[9] Popham, Philip, *RCA Seventh Meeting of the Court,* 9th December 1974, p 16.

considered essential to get intense colour, did not make the process completely predictable. She explained that in her experience the highly corrosive acid etch mixture had a limited shelf life, losing its efficiency unpredictably over time, a process known as depletion. However depletion of the mixture is only apparent after the piece
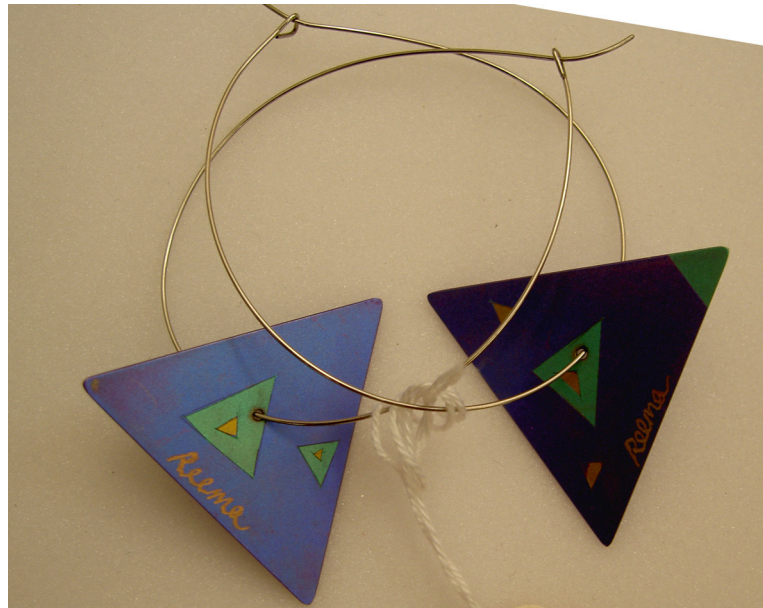
Figure 2.13: *Triangular titanium earrings on steel wires, Reema Pachachi 1980s.*

has been anodised and is often manifest as an uneven streaking of the colour. This meant that many attempts were often required to achieve a suitable match, making it a time-consuming and hence costly process. The health and safety issues with handling the highly corrosive etchant mixture (a fume cupboard is essential) meant that when she moved her workshop it resulted in a change of direction and she stopped using titanium in the mid 1980s.

From Pachachi's comments it is clear that the uncertainty of colour outcome was a major problem by no means always overcome by the use of HF etching. In contrast to previously cited practitioners, her desire for larger uniform areas of colour highlighted this difficulty with anodised colour on titanium.

David Poston

David Poston is included as a key practitioner in the use of titanium for jewellery because as he described in the interview, his own practice '*being much more interested in 3D form than decoration*' aimed to take titanium jewellery in a different aesthetic direction from what he described as '*'The initial explosion of coloured flat titanium*'. A lifelong exponent of the importance of form in jewellery his typically forthright comment on much titanium jewellery was delivered in an e-mail in early 2006[10] '*As 60's students we learned that titanium could be coloured by heating, exploited by a few. Then James Ward and friends started their clever electrolytic work at the Royal College, culminating in Ed de Large's extraordinary visual work. This was followed by an offensive blizzard of flat metal butterflies infesting every craft*

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[10] Poston, David, *TitaniumworkspielsNo.144010.doc,* 30/03/06.

gallery in the land, an unnerving example of what happens when lesser imaginations are presented with a painting-by-numbers Craft opportunity.'

Poston first saw and worked with titanium at Hornsey in the early 1970s but his reaction against the two-dimensional nature of much jewellery, particularly that made from titanium, as quoted above, led him to try, unsuccessfully, the cold-forging techniques that he used for stainless steel to create three-dimensional shapes in titanium. As he explained, his interest was rekindled in 1983 following a demonstration by Bill Seeley of three-dimensional work at the SNAG Monterey conference in the USA. Seeley had himself become interested in titanium following presentations at a previous conference of a paper by James Brent Ward. Poston developed his own hot forging techniques, which produced a subtle and sensuous dark brown/grey surface, Figure 2.14.

Figure 2.14: *Hot-forged two-part titanium neckpiece with18ct gold detail, David Poston, 1984.*

Returning to jewellery after a gap of twenty years, Poston has, to quote him directly; '*deliberately turned to different design approaches, materials and technologies'*. The experimental bangle, illustrated in Figure 2.15, which is typical of his new work, has been constructed by laser welding thin titanium sheet over a wooden core.

The hot-forging technique developed by Poston produces a soft dark brownish-grey coloured surface on titanium, which is unlike any other heat-coloured surface. The structure of this surface would be worth more detailed study in a future project.

Figure 2.15: *Experimental laser welded titanium bangle, David Poston, 2006.*

Brian Podschies

As Brian Podschies described it in the course of the interview, he 'dabbled' with titanium while a student at Birmingham from 1973-77. Later he developed a tool to corrugate titanium sheet using a fly-press but it is for his innovative use of hot forging that he is included among the key jewellers who used titanium.

Podschies interest in titanium was sustained because, as he explained, the use of such a challenging metal inevitably meant being confronted by problems, the solving of which provided a stimulus to creativity. Having used the standard colouring techniques, to quote his own

Figure 2.16: *Titanium forged brooch with silver bar and gold wire by Brian Podschies, 1985.*

words, he became 'bored with just colour' and he began to experiment with hot forging as a way to achieve what he described as more visually 'organic' surfaces. In contrast to David Poston who used the forging process to develop a finished surface, Podschies further manipulated the forged metal surface by part etching and anodising producing unique multi-coloured pieces.

The titanium was heated with a torch in a muffle on the hearth up to 1000°C and then forged on formers while hot with more than one heating used for larger pieces such as vases. This technique produced thick white oxide layers which, if left to cool slowly after heating, resulted in bland surfaces, so a brief cooling period was followed by quenching in cold water to *'shatter'* the oxide surface. Layers of colour were then developed by masking followed by sandblasting and/or chemical etching to remove part of the thick oxide layer, and finally anodising. His techniques produced random combinations of thick oxide encrustation and areas exhibiting interference colour as can be seen in Figure 2.16.

Debby Moxon

Debby Moxon is included here because of her innovative use of heat colouring of titanium. As for many users of titanium, her first encounter with the metal was as a means to solve a design problem. In her case it was the production of coloured hands for a clock, while she was at Sheffield In the early 1980s. Subsequently the intricate images created by Ed de Large inspired her to experiment with titanium while establishing her own workshop.

Although the clock-hands had been anodised, Moxon started to explore alternative
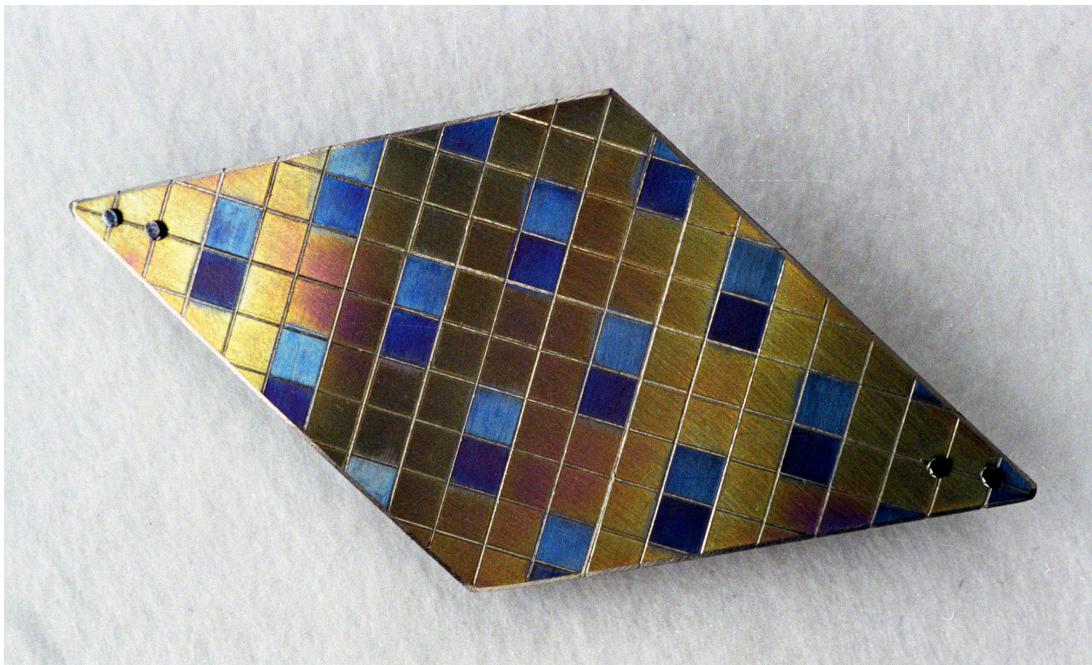
Figure 2.17: *Heat-coloured titanium brooch with silver riveted pin, Debby Moxon, 1982/3.*

colouring methods and researched the possibilities of more controlled heat colouring of the metal. As she explained during the course of the interview, Moxon developed her own heat-colouring method for titanium using precise geometric scoring, masking with flux and heating with a fine flame to produce intricate surface patterns that juxtaposed 'high' and 'low' colours, see Figure 2.17. The variability of colour of the heat-generated coloured surfaces was not visually apparent on the finished piece, except under magnification, because the individual cells of colour created by the process were very small (2-3mm). This method gives clear bright colours without a chemical pre-etch but, as Moxon stressed, preparation of the surface of the thin titanium sheet prior to heating is a critical step achieved by careful abrading with emery paper.

A more recent technique involves the use of a marking pen to create a pattern on the surface of the abraded titanium which, on heating, produces a parti-coloured effect, with spots of completely

Figure 2.18: *Multi layered, heat-coloured, riveted titanium brooch, patterned with ink spots, Debby Moxon, 2003.*

different hue where the ink from the pen had been, Figure 2.18, Moxon continues to use titanium and develop different techniques for heat colouring the metal based on experiment.

The colouring techniques developed by Moxon over more than twenty years of experimentation demonstrate that bright colours may be achieved without the use of HF etching solutions. However, despite the continuous experience, experiment and meticulous attention to detail, Moxon reported that unexpected colouring results sometimes occur.

Prism - Barry and Sally Milburn

As the use of titanium by designer/makers expanded during the late 1970s more general interest in the material was created. A few small manufacturing companies sought to exploit this interest by producing titanium jewellery on an industrial scale for supply to the High Street retailers. For the study only one of these companies, Prism, was selected

and the founders of the company in 1980, Barry and Sally Milburn, were interviewed.

While the Milburns were students at CCAD from 1976, both Ed de Large and James Brent Ward lectured there on the use of titanium and, as they explained during the interview, the Milburns saw this new metal as a way to achieve their ambitions to develop a small manufacturing business supplying jewellery to a range of retail outlets.

They also stated that they found titanium an easier material to process than they had been led to believe particularly as they learned to work with the metal rather than against it. This meant experimenting in order to develop methods suited to the material rather than applying those used for the more traditional jewellery metals such as silver. The production of earrings was a major part of the business and these were shaped by turning welding rods of CP titanium, making spirals of wire and shaping sheet: designs being adapted to the form in which the raw material was available. Because they wanted to achieve bright colours, after forming, the titanium pieces had to be prepared with a hydrofluoric acid (HF) etch prior to anodising in ammonium sulphate solution at voltages in the region of 120 volts.

To obtain a bright finish, lactic acid was added to the HF etchant mixture and Barry Milburn noted that it was important to have a fresh etching solution for good colour results. Special jigs were devised for dip anodising to achieve graduated colour and many pieces were anodised at the same time. The voltage was pre-set and the loaded jigs were dipped in and out of the electrolyte bath with creep of the solution prevented by running a hairdryer across the liquid surface as the pieces were dipped. The sensitivity of the colouring process meant that better results were achieved if one person carried out the etching and anodising in batches, using freshly prepared etchant solution.

The colouring of titanium was discontinued in 2000 when the investment costs for remodelling their premises to include up-dated fume cupboards proved too expensive but titanium jewellery continued to be made and the natural grey colour of the metal has proved to be popular in jewellery designed to be worn by men.

2.2.3. Synthesis of Jewellery Workshop Practices

As previously stated the information obtained from the questionnaire responses, the interviews with individual practitioners, reported above, and published literature have been synthesised with the researcher's own practice to construct the following summary of workshop practice for the production of titanium jewellery.

Fabrication

The colouring is the final or penultimate step in the process of making a piece of

titanium jewellery. Fabrication and forming of the metal must be done first. Although the oxide layer is permanent and tough, the steel tools used in jewellery making may damage it. Therefore only a final mechanical fixing such as setting or riveting should be undertaken after the titanium surface is coloured.

Industrially titanium is prepared for anodising by acid etching with a hydrofluoric acid mixture. This used to be a technique used by jewellers, especially when anodising to high voltages, but health and safety requirements have restricted the availability and use of such materials. Even when using an acid etch, jewellers have reported that a uniform surface, prepared mechanically, is needed before etching, e.g. James Brent Ward. Others have commented on the limited 'shelf-life' of the acid mixtures used and that exhaustion of the mixture only becomes apparent when patchy results are observed after anodising the treated titanium, e.g. Reema Pachachi.

The mechanical finishing procedures, used to prepare the surface of a titanium jewel, are common to both methods of colouring and only the patterning techniques vary with the mode of colouring.

Surface Preparation

Once the piece or its components parts have been shaped as required, the surfaces are filed to remove any tool marks and then finished with mechanical abrasion. The degree of abrasion or polish depends on the design of the piece and can be varied in different component parts or areas. Emery papers of different grit and polishing compounds on the wheel of a standard polishing motor may be used. After polishing, and prior to either colouring process, the metal surface is thoroughly washed, degreased and dried. It is important to keep the cleaned surface protected before colouring, as the freshly prepared titanium surface is very reactive and therefore is particularly susceptible to contamination, especially from the natural oils in finger marks.

Colouring

The majority of the colouring techniques described in the following paragraphs were based on the recommendations given by IMI in the 1960s. Although they have been adapted by practitioners to suit their own specific requirements, the methods have not been radically altered except for patterning procedures. Variations to these techniques, which have not become widely used in the workshop, are outlined in the relevant paragraphs in this chapter but the programme of experiments, designed to explore the procedures, is reported in Chapter 6.

Heating

The simplest and most immediate colouring method is heating. This may be either with a gas flame or in a temperature controlled kiln.

Heating with a Flame

Colour development on the surface of titanium may be directly observed when it is heated with a flame. With practice the jeweller can control the effect within certain limits to produce the desired colour. A fine flame produces a localised spot of colour and a soft broad flame can give a more even colour across the surface. However titanium is a poor conductor of heat, having a thermal conductivity generally quoted below 20 Watts/metre Kelvin, W/(m-K) compared to iron in the range 55 to 80 W/(m-K), depending on the purity, aluminium at approximately 200 and silver, a highly conducting metal, at over 400. This means that one part of a sheet or rod of titanium can be heated strongly while the rest of the surface is almost unaffected and therefore large surface areas cannot be coloured uniformly by this means.

Surface Pattern

Pattern may be introduced by masking areas of the surface with materials, which will withstand the high temperatures, such as 'Tippex' or by selective heating of the surface area with the flame. The masked titanium is first heated to the 'highest' desired colour, i.e. that of greatest oxide thickness. Some or all of the masked areas are then uncovered and the piece is re-heated. A good example of heat control is that used by Debbie Moxon (see above and Chapter 1) who produced areas of differently coloured squares using a fine flame and repeated masking and heating. The poor thermal conductivity of titanium, quoted above, means that there is no change in the previously coloured areas when the piece is reheated, provided the flame is carefully positioned.

Random patterning can be achieved by filing through the oxide layer to the bare metal and re-heating the piece, Figure 2.19. The re-heating thickens the existing oxide and produces a new

Figure 2.19: *Heat-coloured titanium annular brooch with titanium pin, patterned by filing and re-heating, Lynne Bartlett, 2002.*

thinner oxide layer on the filed areas. This process may be repeated several times to create a multicoloured surface.

Drawing on the surface with some marker pens and subsequent heating can produce pattern. The mechanism is not completely understood but, as the ink burns off the surface, it seems to provide a 'hot spot' and thus a different oxide thickness and colour. This technique. is explored further in Chapter 6 to confirm the procedures necessary for its successful application.

Heating in a Kiln

A thermostatically controlled kiln, such as one used for vitreous enamelling, gives more temperature control than a flame but the temperature variation within a kiln chamber is significant. Early experiments by the researcher established that a kiln, temperature controlled at 700^0C, gives the most satisfactory results in terms of speed of oxidation. At this temperature the oxide develops in a matter of minutes but does not grow rapidly to the thickness beyond which the interference colour is no longer observable, estimated to be above 300 nm.

The piece to be coloured is supported on a pre-heated refractory block and placed in the centre of the kiln. It is not possible to see the development of the colour in situ in the majority of kilns and therefore the piece must be withdrawn for observation. The production of specific colours is difficult and requires prior experimentation and/or continual removal of the piece to monitor progress. As with flame-colouring the poor heat conduction of the titanium means that a piece will show colour gradation in line with the temperature gradient in the kiln. This may be offset to some extent by reversing the piece when it is withdrawn for observation or by using a more sophisticated kiln equipped with a rotating stage.

Anodising

Anodising is a more controllable method for oxidising, and therefore colouring, a titanium surface. It is an electrochemical process in which the titanium to be coloured is connected to the positive pole of a direct current (dc) generator. The circuit is completed by an electrolyte, which may be almost any aqueous acidic medium but is most commonly a 10% ammonium sulphate solution in water, and a metallic counter electrode, usually stainless steel or titanium.

The use of an ammonium sulphate solution was suggested by Imperial Metal Industries (IMI) in their advice to students in the 1960s and was recommended in the paper by James Brent Ward. Some early practitioners, such as Eric Spiller, reported that 'Coca-Cola' could be used as an electrolyte but that it was messy and the results were unpredictable. Other commonly used electrolytes for anodising titanium for colouring have been dilute

sulphuric or orthophosphoric acids. Investigations of the corrosion behaviour of titanium in diverse industrial environments have involved the study of the anodising of the metal using a wide range of chemicals as electrolytes but these are not applicable for workshop practice.

Similarly, corrosion studies have used temperature-controlled equipment and examined the anodising of titanium at elevated temperatures. In the anodising of titanium for colouring purposes the heating of the electrolyte is unnecessary. It is carried out at ambient temperature, which may vary, typically between 15^{0}C and 30^{0}C.

Any equipment that generates a direct current may be used to anodise titanium and early practitioners used dry batteries. However these had a limited voltage range and therefore limited the colour range that could be achieved.

Custom-built anodising units were designed specifically for anodising titanium and constructed, using transformers to convert ac to dc current with voltage ranges up to 150 volts. A control system allows variation of the voltage in small increments so that a precise oxide layer thickness may be achieved, depending on the precision of the anodising equipment used.

Anodising can take place with the article immersed in a bath of electrolyte or by using a brush as described below.

Immersion Anodising

The prepared titanium is immersed in a bath of electrolyte by use of a suitable conducting jig. This may be a simple titanium wire hook or a more complex construction depending on the form of the piece to be anodised. Ideally the work should be fully immersed and placed as far from the counter electrode as possible. (in order to even out the electric field?) The anodising bath, typically an inert plastic container, may be varied in size depending on the size of work to be coloured. Some anodising systems are designed to be used with different baths while others have the bath, suspension system and counter electrode as fixed components of the equipment.

The procedure, described as potentio-dynamic, is to place the titanium being anodised in the bath, switch on the anodising unit and slowly increase the voltage, typically at a rate of 0.5-1 volt/second, to the required level. It is possible to observe the colour change as the voltage increases but the film of electrolyte adhering to the oxidised surface masks the precise hue. An alternative method is to increase the voltage rapidly to the desired level and then hold it steady for a minute. The current is then switched off and the coloured titanium is removed from the bath, rinsed and dried with a clean cloth or paper towel. Although research papers on corrosion quote extended periods for anodising, this has not been traditionally used in the workshop. A small programme of experiments,

carried out to assess the effect of longer anodising periods on the colour development, is reported in Chapter 6.

When producing volumes of items and colouring them at high voltage, some practitioners, such as James Brent Ward, stress the need for speed in removing them from the electrolyte. With some anodising equipment it is possible to pre-set the voltage before introducing the titanium into the bath.

In most cases the titanium piece being anodised is fully immersed in the electrolyte until the desired colour is reached but colour gradation can be achieved by dip anodising, Figure 2.20. This is a procedure in which the titanium is firstly immersed in the bath and the current switched on as for standard anodising but then the piece is slowly removed from the bath while increasing the voltage at a steady rate. The

Figure 2.20: Dip anodised titanium pin with cultured pearls set in silver, Lynne Bartlett, 1999.

titanium is still a part of the electrical circuit but no more oxide is produced on the area removed from the electrolyte. This factor forms the basis of the brush anodising technique.

Brush Anodising

Brush anodising was used from early times and employed commercially by Lewis and Clayton to create images on a titanium sheet in the manner of 'Painting by Numbers'. The cathode of the anodising unit is connected to the metal ferrule of a standard artists' paintbrush, as demonstrated in Figure 2.21.

The titanium to be coloured is connected to the anode of the anodising unit and placed on an insulated surface. The voltage is preset to the desired value and the brush is dipped into the electrolyte and applied to the area to be coloured. With practice this can be a versatile and effective technique, especially for an overall, painterly design or for small areas of colour.
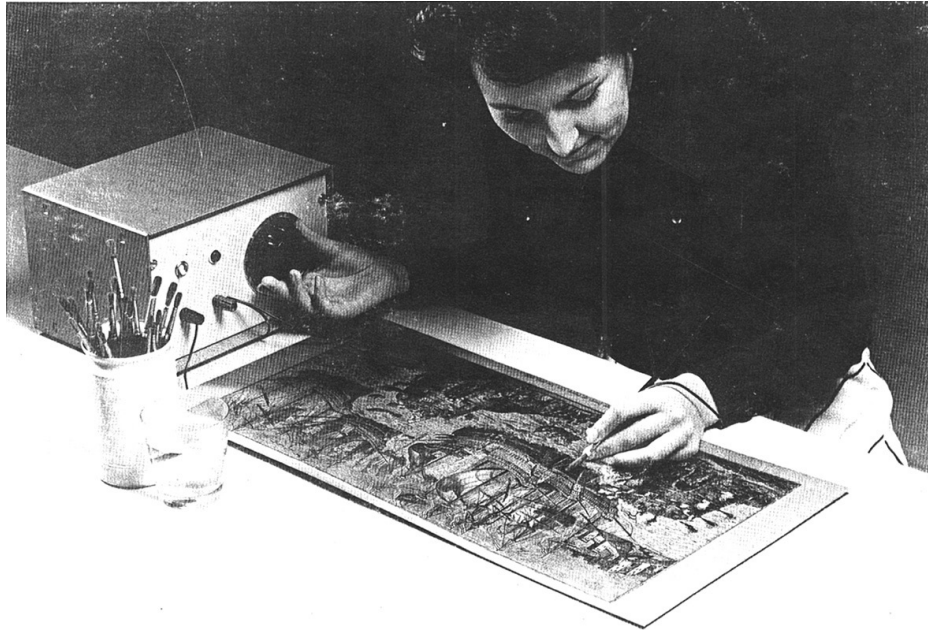
Titanium colour artist Estelle Parish working on the picture titled "The Departure of Henry VIII"

Figure 2.21: *Image from Lewis and Clayton catalogue showing brush anodising of titanium.*

Surface Pattern

As for patterning with heat, the most common method used to create patterns when immersion anodising is to mask areas of the titanium so that the electrolyte solution, specifically the water, is prevented from reaching the metal surface. A wider variety of materials can be used for this purpose when colouring by anodising than when heating. Many proprietary lacquers and similar preparations have been used and also insulating tapes. Fine detail may be achieved by burnishing precisely cut pieces of invisible tape onto the surface of the titanium, as in the work of Ed de Large shown above, anodising the piece, removing the masks and re-anodising.

However a major misconception has arisen in practice when carrying out multiple anodising steps with masking. In the recommended technique the highest voltage colours are produced first as subsequent anodising conducted at lower voltages was thought to leave the higher voltage colours unaffected. While this is true for niobium for titanium in practice there is some thickening of the oxide layer across all of the exposed, immersed surface and this may alter the colours created initially. This needs to be taken into account by careful planning and prior experimentation in order to achieve a particular result.

Finished Surfaces

The exact colour of the titanium surface can only be assessed when the piece has

been washed and dried. The oxidised surface gives a permanent colour which is robust under most normal wear conditions. The robustness of the oxidised titanium surface can be manifest in two ways; resistance to abrasion in wear and stability in terms of adherence to the metal surface. An issue of particular concern to the jewellery buyer/wearer and therefore to the jeweller, is durability in wear, so that the designed colour appearance, critical to the aesthetic of a piece of jewellery, is maintained over time.

All jewellery needs regular cleaning to remove the inevitable build up of dirt and grease and in this regard oxidised titanium maintains its colour well in comparison with silver, which is easily tarnished. Metal surfaces are also subject to abrasion in daily wear. Scratches on a silver surface dull the surface sheen but the appearance can be restored by polishing. Abrasion of the coloured titanium surface may destroy the thin oxide layer and hence remove the colour completely. For this reason it has become a traditional practice within the jewellery industry not to use oxidised titanium for items that are subject to continual abrasion and knocks such as rings and bracelets. Whether such a precaution is equally applicable for both forms of titanium colouring is unclear but there is evidence to suggest that heat-coloured surfaces are more durable than those that are anodised. The links of a titanium wire chain that were heat-coloured show little abrasion compared to those of a similar chain, made from wire from the same source, which were anodised. The wear characteristics and oxide-layer adhesion to the titanium surface are discussed further in Chapter 6.

2.2.4. Difficulties within Workshop Colouring Practices

The conclusion from the survey of practice is that only anodising has the potential to produce consistently coloured areas on titanium jewellery; heating except in small areas, is less controllable under workshop conditions. In practice, although anodising gives the jeweller more control of the energy input, the outcomes in terms of colour are by no means always predictable. Indications from the interviewed jewellers reveal similar common problems and frustrations when working with titanium; colour is described as streaky or patchy, there is poor repeatability of colour and hence difficulty in the production of matched pairs of items, as required for earrings. These were quoted as major difficulties experienced in the colouring of titanium, which, together with the time-consuming reprocessing of mismatched items, contributed to the concept of titanium as a 'difficult' material.

The unpredictable outcomes could be roughly categorised in two ways. The first was a lack of homogeneity in colour across the surface and the second was difficulty in exactly reproducing the colour obtained after following the same sequence of steps and

procedures. Although poor preparative techniques and lack of care with anodising can lead to both types of variability being observed, it was reported that even with meticulous attention to surface cleaning and degreasing prior to oxidation, carefully timed anodising and good control of anodising voltage, both forms of variability can occur randomly, either singly or together.

Some practitioners effectively avoided possible problems of colour variability by designing multi-coloured titanium jewellery, incorporating colour variation as a design feature, but where design development required particular colours and specific areas of colour there were problematic outcomes.

2.3. Colour Variability

As described above, heat colouring of titanium produces the more robust surface but is inherently variable and only small areas can be reliably coloured to a consistent hue. Therefore the only feasible method that could produce large areas of one colour is immersion anodising but this often produces variability in the coloured surface. This part of the chapter examines the unpredictable and variable outcomes which may occur when colouring titanium by anodising. The examination of the types of colour variability experienced by jewellery practitioners is followed by the consideration of the possible sources of the variability and how these may be evaluated.

The key research question arising from these considerations therefore becomes: what factors lead to the occurrence of variability when titanium is coloured in the workshop?

2.3.1. Types of Variability

The variability of colour of an anodised titanium surface, as described by jewellers in the previous part of the chapter, can be manifest in two ways although both may be present at the same time:

- Lack of uniformity across the surface area with patches, stripes or areas of the surface having a different hue.
- Non-reproducibility of a surface colour where pieces cut from the same sheet of material and prepared and anodised in the same way are different in hue.

The variation in colour across the surface of the oxidised titanium, the first type of variability, may produce random patches and shading of slightly different colour but with no observable repetition in terms of location of the patches, e.g. no edge effects or fading in the centre.

The lack of repeatability of a specific colour, in the second form of variability, can

occur even though great care had been taken to prepare the samples in the same way; using the same materials and anodising to the same voltage with the same equipment at the same rate of ramp of the voltage, and placed at the same position in the anodising bath of the same electrolyte solution.

The close examination of coloured titanium surfaces and the description of variation in hue resulting from either or both types of variability indicated the need for precise colour definition. In order to compare the colours produced by oxidising titanium, unambiguous terms for colour description were required for clarity of communication. This was particularly the case when describing the colour in terms of hue (type of colour, e.g. red, blue) and saturation (depth of colour). The subjective terms such as bright bluish/green and pale orangey/pink proved inadequate. The only existing colour reference for the workshop jeweller was the colour chart published as part of the Goldsmiths' Technical Bulletin, see above. This chart is discussed in greater detail in Chapter 3 and while it is acknowledged that such visual comparative systems have general utility, the comparisons are imprecise. Therefore an objective measurement of colour was required for the accurate reporting of colour and colour variation. The proposed system is presented and considered in detail, including verification, in the next chapter (Chapter 3).

However one of the sets of samples prepared for colour measuring can be used to illustrate the first way in which variability of anodised colour on titanium may be manifest. The examination of this sample set is presented below.

2.3.2. Examples of Variability

A set of anodised samples of commercial purity (CP) titanium sheet, prepared to confirm the utility of the colour appearance measuring technique for titanium, presented in Chapter 3, provides examples for the examination of one type of variability of colour that may occur during the anodising process. The samples were prepared from 0.71mm thick sheet cut into 5 cm by 5 cm squares by the supplier, as requested. The samples were then prepared for anodising by smoothing the rough edges and sharp corners with a file. Care was taken not to file across the surface of the sheet but as the material was from a scrap source, some of it was scratched when received. The sample squares were then repeatedly washed and degreased, following the standard procedure adopted for the project, which is detailed in the following part of the chapter. Two sets of samples were produced, each anodised at 5V intervals so that the colour quality of a wide range of different coloured surfaces could be assessed across the interference spectrum.

The first 19 samples from one of the sample sets, designated **TA1,** namely those anodised from 10V up to 100V at 5V intervals, were examined for variability in this part of

the study and the observations are summarised in Table 2.1.

When examining the sample coupons, evidence was sought for repeated occurrences of variation in colour in terms of the size, shape and location of the colour variations. The degree of variation in terms of hue and differences between the front and back of each sample coupon was compared so that any consistency or repeatability, indicating a pattern to the variation. could be assessed. However no pattern to the occurrence, degree or frequency of the variability was discernible.

Examination of coloured sample set TA1

Sample / voltage	Wavelength of Maximum Absoption (nm)	Maximum absorption outside visible	CIELab L*	a*	b*	Colour	Appearance	Comments
TA1-10v	380	x	60.5	4.29	29.3	ochre	bright, uniform surface(even where scratched	very easily marked with fingerprints
TA1-15v	520		40	11.3	-8	puce	uneven patchy dull reddish purple colour/edges gold	very easily marked
TA1-20v	540		38.9	11.6	-13	blue/violet	random patches on one side and uneven stripes of brown, purple and blue on the other with sheet marking visible	very easily marked
TA1-25v	540		40.4	9.92	-13	blue/violet	similar to 20v sample, small bright blue spot, dark blue and purple patches on reverse	very easily marked
TA1-30v	640		45.5	-3.9	-27	blue	some just perceptible darker streaks	easily marked
TA1-35v	670		51.1	-7.6	-26	mid-blue	even colour on one side except at one edge, scratches same colour, reverse streaked with lighter blue	easily marked
TA1-40v	700	x	61.1	-11	-15	pale turquoise	yellowish patches on both sides	not easily marked
TA1-45v	700	x	66.5	-10	-5.6	v.pale turquoise	even colour on one side streaks of shades of yellow and pale blue on reverse	not easily marked
TA1-50v	380	x	72.2	-8.4	1.55	greenish silver	even on one side sheet markings just perceptible on other side	not easily marked
TA1-55v	380	x	76.6	-7.6	5.81	yellowish silver	clear markings in pale orange on v. pale yellow on reverse	not easily marked
TA1-60v	390		74.8	-4.7	18.1	v.pale yellow	pale orangy streaks on reverse	not easily marked
TA1-65v	400		77.7	-5.1	23.4	pale yellow	pale yellow with pinkish overtones	not easily marked
TA1-70v	420		74.5	-1.2	33.8	yellow	reverse streaked with pink and bright pink sheet markings revealed	not easily marked
TA1-75v	440		72.7	2.01	43.5	orange yellow	pinkish streaks on one side	not easily marked
TA1-80v	470		65	14.1	27	pinkish orange	mottled pink/yellow surface more streaky on reverse pink line where hook attached	not easily marked
TA1-85v	500		57.3	25.3	4.9	orangish pink	colour shifts with angle of view	not easily marked
TA1-90v	530		52.7	23.7	-11	pink	purplish streaks just visible on one side	not easily marked
TA1-95v	550		49.4	16	-20	purple	bluish edge streaky on reverse	not easily marked
TA1-100v	580		50.1	-0.6	-18	dull greenish blue	green lettering and bright pink line where jig attached	not easily marked

Table 2.1: *Tabulation of the variations in colour for sample set TA1, prepared for colour measurement (see Chapter 3).*

As can be seen from the table, the colour measurement co-ordinates were recorded together with the wavelength of maximum absorption, a simple visual colour assessment and a description of colour variability and surface quality for each sample coupon. The notes to the table outline the observed types of variability. The pre-existing scratches on some of the sample surfaces have the same colour appearance as the surrounding surface

but most samples show evidence of random colour variation.

A particularly noticeable feature of the anodised surfaces is the ease with which some surfaces can be marked by fingerprints. This is manifest in the first six samples anodised from 10V to 35V respectively, which have a matt surface appearance. In contrast the next sample in the set, which was anodised to 40V is not so easily marked. The theoretical thickness of this oxide layer, assuming it to be anatase (for details see Chapter 3), is 70 nm and the implication of the observed difference is that when the oxide layer reaches this thickness a change in the surface structure occurs. Having identified the apparent change in the nature of the oxide layer when this titanium sheet is anodised between 35-40V, it is essential that experimental studies include examples of material anodised above and below this voltage in order that the nature of this change may be clarified.

Evidence of the other type of colour variability, i.e. repeatability of colour was provided by a stock of titanium earrings held by a retail jeweller from the 1980s. The bulk of the stock consisted of pairs of earrings in five different designs, however the individual earrings from each design had become mixed together and it was very difficult to sort out exactly matching pairs of each design, presumably one reason why the stock remained unsold. Figure 2.22 records the comparison for one design.

Figure 2.22: Titanium earrings from 1980s showing colour variation.

Part of the problem was that the comparison made by juxtaposing the individual earrings highlighted the colour differences, which would have been imperceptible in normal wear. (It was also apparent that where code or pricing labels had been stuck on the anodised surface, the removal of these had lifted off the oxide layer completely exposing areas of uncoloured titanium. This ease of removal of the oxide layer will be examined further in Chapter 6.).

The processing of the **TA** material provided an unexpected further manifestation of variability in colour development. The apparently thorough cleaning of the titanium sheet
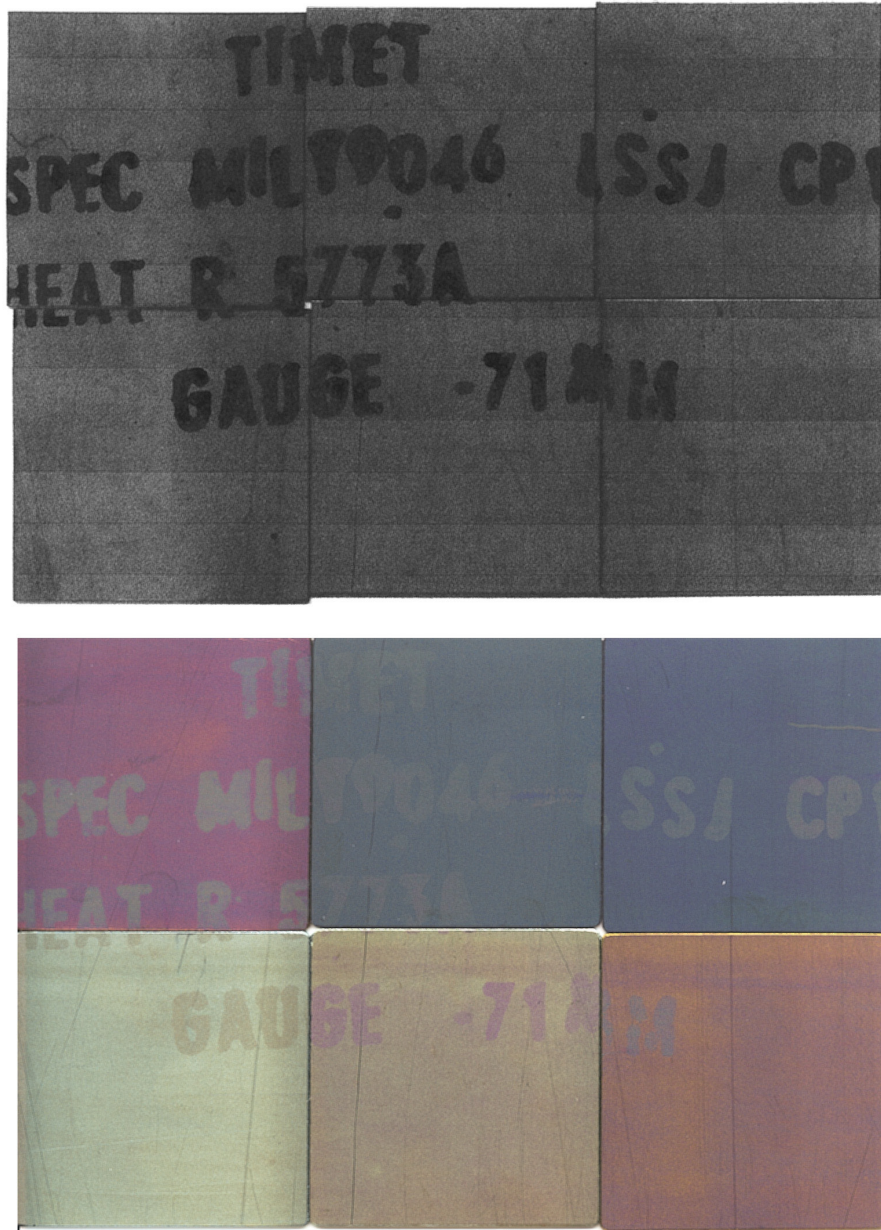
*Figure 2.23: Scan of markings on **TA** sheet of titanium from which samples were cut and anodised samples showing how markings reappear.*

had not removed all traces of the surface contamination, attributable to the inked grade markings routinely used by the supplier, as these marking re-appeared after anodising.

The identity marks on the sheet from which the samples were cut, giving details of the supplier, quality specification and thickness of the sheet were recorded by scanning the titanium sample squares before any further work was carried out. No traces of any of the sheet markings were visible after the cleaning process and the cleaned samples were divided randomly into two sets of 24 samples each, which were then anodised. Although the identification marks inked onto the titanium sheet by the manufacturer were apparently removed in the cleaning process, they reappeared as differently coloured areas, at 'higher' colours compared to the surrounding area after anodising, as shown in Figure 2.23.

The most likely probability is that some of the chemical constituents of the ink were not completely removed by the cleaning process and remained adhering to the titanium surface, producing a differential rate of oxidation. Contacts with the ink supplier have unfortunately not revealed the exact components of the ink, so that it is not possible to identify or confirm which of its constituents is responsible for the observed differences. The only information given is that the proprietary ink was composed of a resin and dye in a solvent, diacetone alcohol. The phenomenon emphasises how important the cleaning process is and the investigation of possible alternative procedures is reported in Chapter 6.

The examples of colour variability, described above show the problematic issues that may be encountered by both individual designer/makers and larger scale manufacturers of titanium jewellery. Before the problem of colour variability can be resolved it is important to identify the possible sources of such variation. The next section seeks to do this by consideration of the nature, including geometry, of the oxide layer created on the titanium surface in the jewellery workshop.

2.3.3. Sources of Variability

The search for the sources of colour variability, described above, raises questions about both the physically created system and the tolerances within the workshop practice used to create the oxidised metal. Although jewellery practitioners attempted to overcome colour variation problems empirically by extensive exploration of process parameters within workshop practice, there is no evidence that they investigated the physics and chemistry of the system.

Therefore this thesis argues that a new approach to the issue of variability of colour outcome is required. This new approach seeks to identify the sources of colour variability by establishing the relative significance of the roles played in its creation by the individual elements of the physical system that is an oxidised titanium surface. The research question

becomes one of the identification of the nature of the titanium metal surface and the oxide layer that is created thereon by oxidation, using jewellery workshop techniques.

In order to clarify the nature of the elements that need to be examined as possible sources of colour variability, the details of the system that is an oxidised titanium surface are presented as a schematic diagram in Figure 2.24.

The system can be described as consisting of five major areas each likely to have an
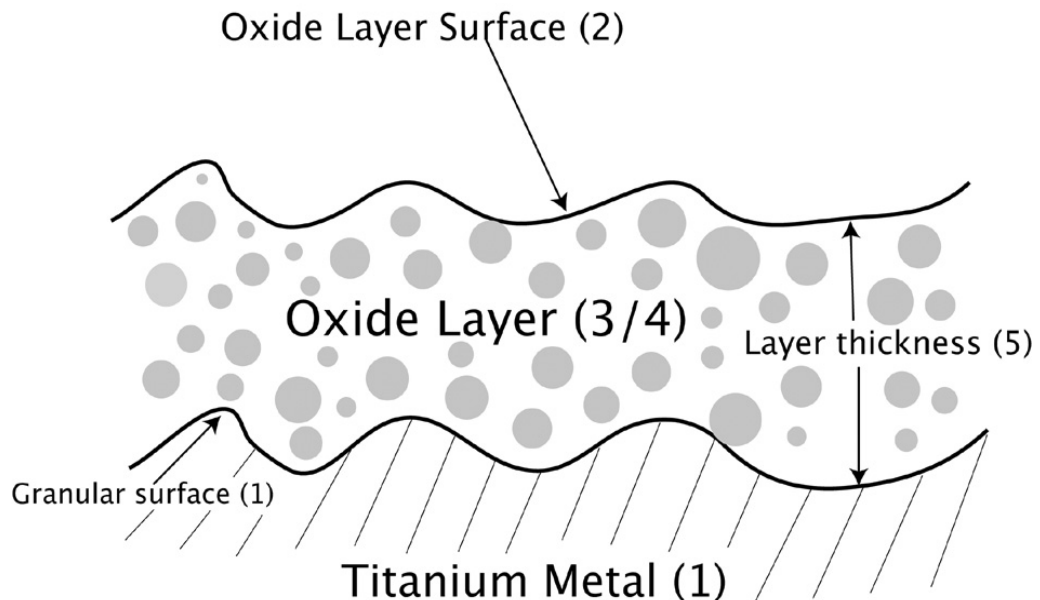
Figure 2.24: *Schematic diagram showing the elements contributing to the colour observed on oxidised titanium.*

impact on the colour development:

1.   the metal surface on which the oxide grows,

2.   the oxide layer surface which is the surface observed,

3.   the composition of the oxide layer,

4.   the homogeneity of oxide layer,

5.   the thickness of oxide layer and any variation in thickness of across the surface.

The experimental programme of the research is concerned with the examination of these five areas and the investigations of the individual components of the system are reported in detail in separate chapters; Chapter 4 discusses and compares both the metal and oxide surfaces and Chapter 5 examines the structure and thickness of the oxide layer. The results from the experiments will provide an assessment of the relative contribution that each of the areas makes to the colour development on titanium and hence possibly to colour variability.

The techniques and findings of metallurgical research are used to examine samples of oxidised titanium prepared for the purpose by the workshop methods described above

in the Synthesis of Jewellery Workshop Practices. Details of the material selection and sample preparation steps for all the sample sets used throughout the project are set out in the following part of this chapter.

2.4. Sample selection and preparation

This part of the chapter outlines the criteria applied, in terms of the metal selection, number of samples, individual sample size, pre-colouration procedures and colouring techniques, used for the preparation of the titanium samples required for the programme of experimental investigation. In order to examine and compare all aspects of the surface oxide layer produced by different methods of oxidation of titanium, both heated and anodised samples are required.

As discussed below, the primary experimental programme considered four different surface finishes and two basic colours, blue and gold. The rationale for the choice of these two colours is presented below. Additional coloured samples were prepared as required for specific test procedures and details of these are reported in the appropriate chapters but the following methods of cleaning and colouring were used for all samples.

2.4.1. Titanium form and purity

In order to establish a programme of experiments achievable within the scope of the project the metal used has been limited to commercial purity (CP) titanium and to thin flat sheet. The questionnaire results reported that, where known, the grade of titanium most likely to be available and used by jewellers was CP. Although the literature reported that some titanium alloys colour more readily than others, the use of alloyed material would have increased the complexity of the project by the addition of further variables. Therefore the investigation of alloyed material and profiled metal are subjects for future projects.

The production of titanium sheet is discussed in the context of its metallurgy in more detail in Chapter 4, but in summary it is produced industrially by rolling. Subsequently annealing and light pickling give the sheet a matt finish and further rolling produces a mirror finish.

The comparison of different metal surfaces and their oxidation behaviour is a significant part of the experimental programme. Therefore examples of titanium sheet with appreciably different surface finishes were selected for sample preparation. Three materials, all CP grade, designated **1**, **2** and **3**, from three sources were purchased for the programme, and a fourth surface finish was prepared by abrading samples of the two thicker materials using 1000 grade wet and dry paper.

Metal **1** - scrap sheet 0.5mm thick with a semi-matt finish,

Metal **2 -** sheet 0.406mm thick with a matt surface (USA),

Metal **3** - polished foil 0.125mm thick (UK),

These three examples of titanium sheet, together with the abraded material provided four distinctly different surfaces, representing a range of surface finishes that had been observed from jewellery practice.

2.4.2. Cleaning

The cleaning procedure for all the samples throughout the project was typically considered sufficient for general workshop use to remove the expected surface dirt and grease, namely a thorough wash with a mixture of ammonia and washing-up liquid followed by rinsing in running water, drying with paper towels and swabbing with acetone. This procedure was repeated to ensure the removal of any surface grease before any oxidation was carried out and was also used both before and after any mechanical polishing.

2.4.3. Sample Size

When comparing samples of all three materials for the initial investigation, coupons of different sizes were prepared so that there could be no confusion between the materials.

- Metal **1 –** sample size 3cm x 1cm x 0.5mm
- Metal **2** – sample size 2.3cm x 1cm x 0.406mm
- Metal **3 –** sample size 2.3cm x 0.6cm x 0.125mm (later revised to 2.3cm x1.0cm in area).

For the fourth surface finish, each coupon of the first two samples was scored across the middle and one half was abraded with 1000 grade wet and dry paper and the other half was left untouched. During this procedure, the unpolished half of each coupon was protected by wrapping it with Scotch tape. This meant that two different surface finishes were present on a single sample and that the oxidation behaviour of these surfaces could be observed and compared under the same colouring conditions.

For later investigations, the sample sizes were varied according to the requirements of the instruments used and these are described in the relevant section.

2.4.4. Colouring

Two colours were initially chosen for comparative examination, namely royal blue and gold. There are four reasons for the choice of these colours; they are easily visually distinguishable; both are readily obtained by both methods of oxidation; they fall either

side of the 'change' area, described in Section 2.3.2 above, at 35-40V for anodised material; and finally as a rough estimate, based on calculations discussed in Chapter 3, the gold colour is produced by an oxide layer approximately twice the thickness of that needed to produce the blue colour.

The colouring procedures for these samples are presented here as representative of the two principal colouring methods used throughout the project.

Heating

Of the various heating techniques, discussed above in the first part of the chapter, that which produced the most even colour, namely heating in a thermostatically controlled kiln, was

Figure 2.25: *Temperature-controlled Carbolite kiln, used for enamelling at CSM.*

selected for the preparation of sample coupons for further analysis. Heat oxidation was achieved by placing the specimens for timed intervals in a Carbolite kiln with a Eurotherm temperature control, Figure 2.25, set at 700°C.

Anodising

Of the possible procedures for anodising titanium, which were presented above in the first part of the chapter, the immersion anodising method was selected for the

Figure 2.26: *Titanium Art MK5 Anodiser and anodising bath at CSM.*

project. Each sample was suspended from a titanium wire jig in a ten percent aqueous ammonium sulphate solution using the anodising equipment shown in Figure 2.26, which was constructed in the 1980s and permitted the use of voltages up to 150V. The unit produces an output

of 0-150V at 4A, with the power supply protected by a fuse set at 5A. A dial controls the rate of voltage increase and the voltage output is shown digitally in an illuminated display. An ammeter indicates the current output value, which must be monitored, especially at higher voltages, to avoid blowing the protective fuse.

A potentio-dynamic anodising method was used where the voltage was ramped up at a rate of 0.5-1volt/sec to the desired level when the current was switched off and the sample removed from the electrolyte, rinsed in running water and dried with a clean paper towel. Any variations to this procedure are discussed in the section where relevant and specific variations of anodising techniques are reported in Chapter 6. The equipment did not allow a potentiostatic anodising technique to be employed. In this method the voltage is pre-set to the desired level before the piece to be anodised is placed in the circuit. This method avoids the risk of overshooting the planned voltage value inherent in the gradual increase in voltage.

2.4.5. Sample Identification

All the samples were given a unique identity notation comprising three elements; the code number for the metal, an alphabetical sequence number and either the anodising voltage or heating time, depending on the method of oxidation. A full list of all samples is included Table 2.3A p 222 in the Appendix together with the tests and/or procedures for which they were used.

2.5. Conclusions

In the first part of this chapter the issues of colour variability have been explored with reference to the workshop practices established by key practitioners in the development of titanium jewellery. The second part of the chapter confirmed and clarified the types of variability, identifying and illustrating two major types, which have been shown to be completely random in nature and occurrence. Also within the second part of the chapter the key research questions have been formulated:

- What conditions or factors produce variability in the colouring of titanium in the workshop?
- What is the nature of the oxide layer created by the workshop oxidation of titanium?
- How may the contributions of identified factors within the system and the structure of the oxide layer be evaluated?

In order to investigate these questions the interrelated factors contributing to the possible causes of colour variability, particularly for anodised titanium, have been identified for further examination. The techniques suitable for the evaluations are identified from the scientific literature discussed in Chapter 4 and 5. The scientific examination of oxidised titanium surfaces requires experimental samples and the methodology for their preparation, using the workshop techniques described, has been outlined.

The discussion of colour and its variability identified the need for an unambiguous colour appearance measuring system for use with coloured titanium and this is considered in the following chapter, Chapter 3, before proceeding with the experimental investigations of the oxide layer.

Chapter 3

3.1. Introduction

Coloured titanium surfaces are created without the use of paint or dye by controlled oxidation of the metal, producing an optical effect known as thin film interference. This phenomenon, responsible for the rainbow colours of soap bubbles, has been observed since the earliest investigations into the scientific basis of colour. This chapter therefore begins by presenting an outline of the theory of thin film interference, which is discussed with particular reference to titanium.

Discussion of the problems of colour variability in Chapter 2 highlighted the need for clear colour definition and communication within the project, when it became obvious that subjective terms such as bright bluish/green were not sufficiently precise. A system for the measurement of colour appearance of oxidised titanium, the viability of which is tested by experiment, is presented in the second part of this chapter and an easily transmitted method for the dissemination of the measured colour is demonstrated. The system has been used to characterise the colour appearance of the majority of samples prepared for use within the project.

The appearance of colour created by thin film interference, as will be explained below, depends on the geometry of the system and therefore the major factors impacting on the colour are the elements contributing to the architecture of the oxide layer and the metal substrate as shown in outline in Chapter 2. The final part of this chapter considers the use of the colour measurement data to compare different samples of oxidised titanium and to identify the parameters of the oxide layer thickness for each colour from theoretical colour/thickness calculations.

3.2. Colour and Thin Film Interference

3.2.1. Light and Colour

Colour does not exist without an observer. Substances absorb and reflect radiant electromagnetic energy at variable wavelengths but it is only in the presence of an organism with a suitably adapted visual system that colour is observed. Visible light is a small part of the electromagnetic spectrum which encompasses many forms of radiant energy. The usual unit for measuring wavelength is the nanometre (nm), which is 10^{-9} metres.

The electromagnetic spectrum ranges from cosmic rays with very short wavelengths (10^{-8} nm), to radio waves, with wavelengths measured in kilometres (10^{12} nm). In the

middle of this spectrum, between the ultra-violet and the infrared, is the visible region encompassing wavelengths in the range from 400 nm (violet) to 700 nm (red), as illustrated in Figure 3.1. The term white light is used to indicate radiation composed of all wavelengths in this range. When objects are illuminated by white light and specific wavelengths in the visible spectrum are removed, by whatever mechanism, the remaining wavelengths combine to produce the colour that is observed. The most common source of white light is the sun and the solar spectrum has maximum intensity in the green region of the visible spectrum. The image below has been adapted from Winter[1].
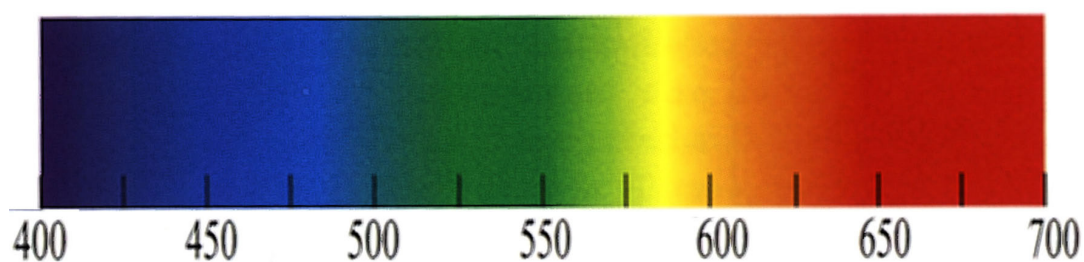
Figure 3.1: *Visible spectrum (adapted from Winter)*

The reduction or elimination of specific wavelengths of white light to produce observable colour may be achieved in several ways, e.g. dyes and pigments absorb the wavelength energy within their molecular or atomic structures. The phenomenon responsible for the appearance of colour on the surface of titanium is thin film interference and is a manifestation of Geometric Optics[2].

3.2.2. Thin Film Interference

Thin film interference was first described by Robert Hooke in 1665 in his publication Micrographia. As quoted by Wood and Oldham[3], he advanced a theory to explain the '*fantastical colours*' seen on soap bubbles, oxides on heated metal and air films between glass plates. Isaac Newton investigated the phenomenon further and, in 1704, published his observations and experiments with light including '*Observations concerning the Reflexions, Refractions and Colours of thin transparent Bodies*'[4]. He noted that bands of colour, which he called '*chromatic scales*', appeared in repeating sequences, which he called first, second and third order tints, as the film thickened. This phenomenon known as Newton's Rings is demonstrated in Figure 3.2.

[1] Winter, C H, *A Student's Guide to Spectroscopy*, OPL Press, Surrey, 2003, p12.

[2] Nassau, K, *Scientific American,* 243, 4, 124, 1980.

[3] Wood, A and Oldham, F, *Thomas Young, Natural Philosopher 1773-1829,* Cambridge University Press, 1954, p.143.

[4] Newton, Isaac, *Opticks,* Reprinted from the fourth edition (1730), G Bell & Sons, London, 1931

However while Newton's particulate (Corpuscular) theory of light could not satisfactorily explain thin film interference, his description of the colour bands as first, second and third order tints or colours continues to be used.

It was Thomas Young, a hundred years later, who used interference to confirm the wave theory of light. In his paper to the Royal

Figure 3.2: Apparatus, formerly on display in the Science Museum, showing Newton's Rings, a thin film of air between two compressed curved surfaces.

Society in 1801 he states: *'A further consideration of the colours of thin plates as they are described in the second book of Newton's Optics, has converted that prepossession which I before entertained for the undulating system of light, into a very strong conviction of its truth and sufficiency;'*[5]. After a period of a further hundred years, in 1905, Newton's corpuscular ideas of light were resuscitated by Albert Einstein and now modern theory states that light can show both particle and wave properties. However when examining thin film interference it is only the wave theory that needs to be considered.

Figure 3.3: Petroleum on wet tarmac showing range of interference colours, 2008.

Interference is observed when reflected light waves are out of phase such as when light is reflected and refracted by a thin transparent film. In many cases the film is attached to a reflecting surface but this is not essential. A common manifestation of this phenomenon is the range of colours produced by a thin film of petroleum on a wet road

[5] Peacock, George, ed. *Miscellaneous Works of the late Thomas Young,* John Murray, London, 1855, p.141.

surface, Figure 3.3.

Figure 3.4 is an idealised representation of thin film interference and explains how the geometry of the system creates the appearance of colour.

Interference Colour
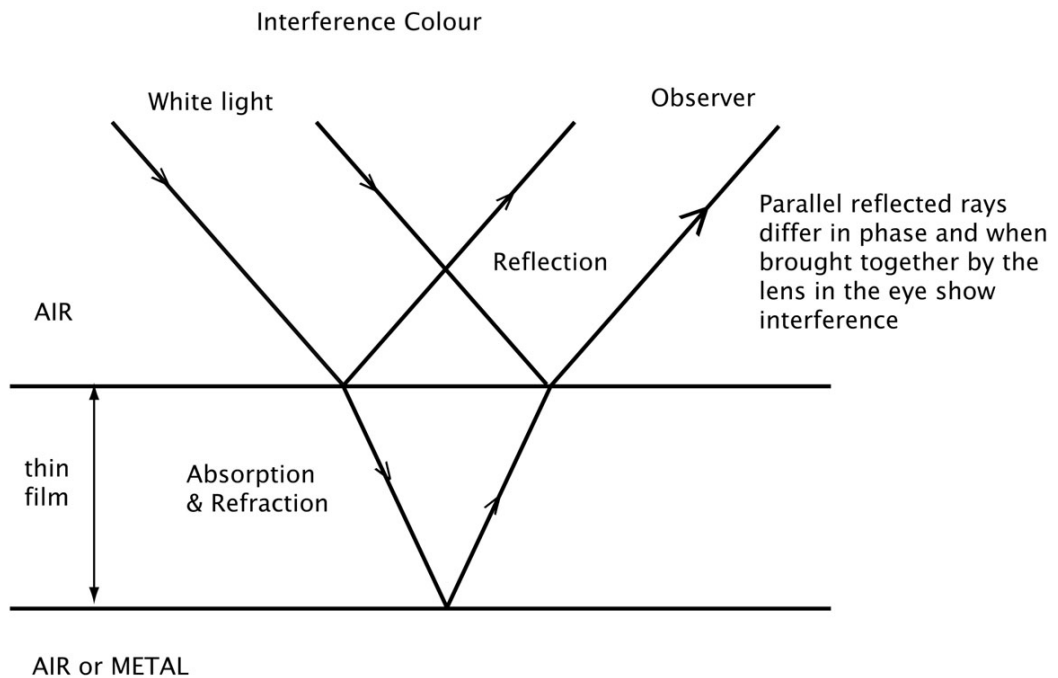
Figure 3.4: Simplified diagram of interference colour.

When a ray of the incident white light reaches the surface of the thin film, part of the light is reflected and part enters the film. The film, acting as a refracting layer, slows the incident light so that the light waves reflected from the upper and lower surfaces of the thin film are out of phase and interfere to reinforce some wavelengths and cancel others.

When a wavelength is cancelled destructive interference occurs and colour is observed. A wavelength is cancelled when the reflected and refracted rays are completely out of phase. The wavelength that is cancelled or absorbed varies as the film thickens and different colours are observed. The following diagram, Figure 3.5, adapted from the table by Evans[6] explains the sequence of colours or tints that are observed as the thickness of the thin film increases.

The diagram illustrates how the absorption bands, or more specifically the centre of each band, of the first, second and third order tints travel across the spectrum as the film thickens causing changes of the interference colour. In case **A** the absorption band is centred in the blue and thus the observed light appears yellow. In cases **B** and **C** the band travels through the green and yellow, giving purple and blue colours respectively. As the first order band leaves the visible spectrum and the second order band is still within the ultraviolet,

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[6] Evans, U R, *The Corrosion and Oxidation of Metals-Second Supplementary Volume*, Arnold, London, 1976, p.378.

case **D**, all the light is reflected and no colour is observed. Cases **E**, **F**, and **G** show the second order band moving across the spectrum producing repeats of the yellow, purple and blue tints. However the third order band follows more closely after the second order band and in case **H** the second order band absorbs in the red while the third order band has entered the blue. This produces an observable green colour.

The extra distance that the refracted ray travels compared to the reflected ray is
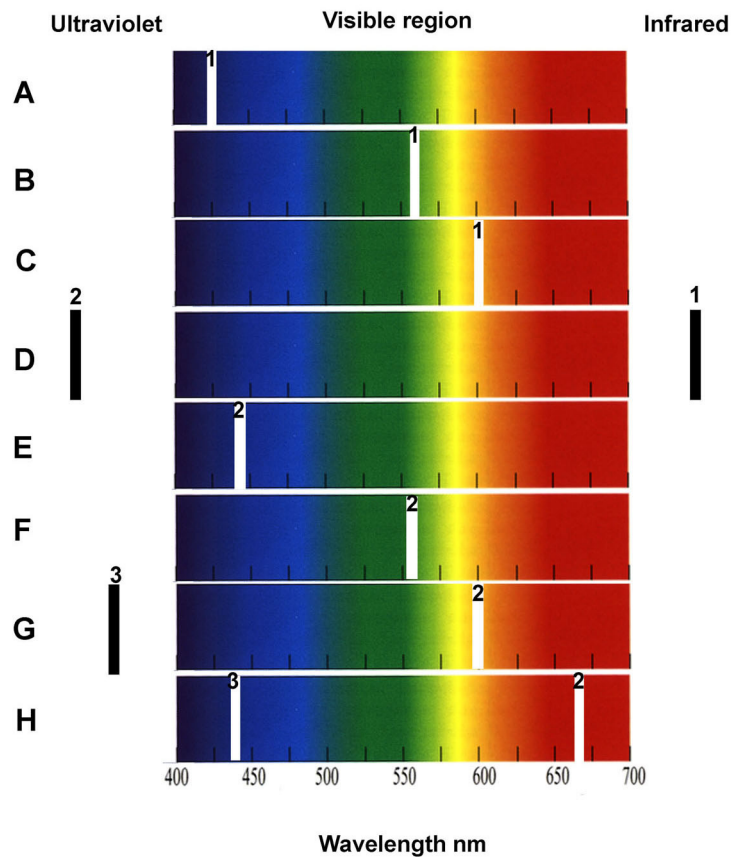
Figure 3.5: *Diagram based on Evans showing colour sequencing of interference bands.*

called the optical path difference. This can be related to both the wavelength of light that is cancelled, or eliminated from the visible spectrum, and hence the colour observed and also to the thickness of the layer needed to produce the colour.

As described above for destructive interference to occur and colour to be observed the waves must be completely out of phase. When this happens the optical path difference, **D** and the wavelength, **Y,** that is eliminated, can be related by the following simple equation, where m, is the order of tint.

D = Y (m – 1/2)   **m** is an integer 1, 2, 3, etc.

For example, in order to eliminate a wavelength in the yellow part of the spectrum at 580 nm, an optical path difference, or retardation, of 290 nm is needed for a first order tint (m =1), which produces an observable blue colour. For the system to produce a blue second order tint (m =2), the same wavelength, 580 nm, has to be eliminated but the optical path difference is increased to 870 nm. Tables of optical path differences and the resulting

interference colours have been calculated and published by Bruhat[7].

The relationship between the optical path difference and the colour appearance applies for all materials that exhibit thin film interference colours. The physical thickness of the layer and the optical density of the material of which the layer is composed both contribute to the optical path difference and will vary with different substances. In all cases the layer must be sufficiently transparent so that the incident light energy is not totally absorbed.

The optical path difference is a combination of the distance that the refracted ray travels within the thin layer and its retardation due to the refractive index (n) of the material of which this layer is composed. The refractive index of a material is a measure of its optical density and is a ratio that compares the speed of light within the material to the speed of light in a vacuum. The ratio is quoted by comparing the sine of the incident angle of the light ray travelling from the less dense medium with the sine of the angle of the refracted ray in the denser medium (Snell's Law). The optical path difference[8] may be calculated in terms of the thickness of the refracting layer and its refractive index as shown in Figure 3.6.

Thin Film Interference

i = angle of incidence, r = angle of refraction
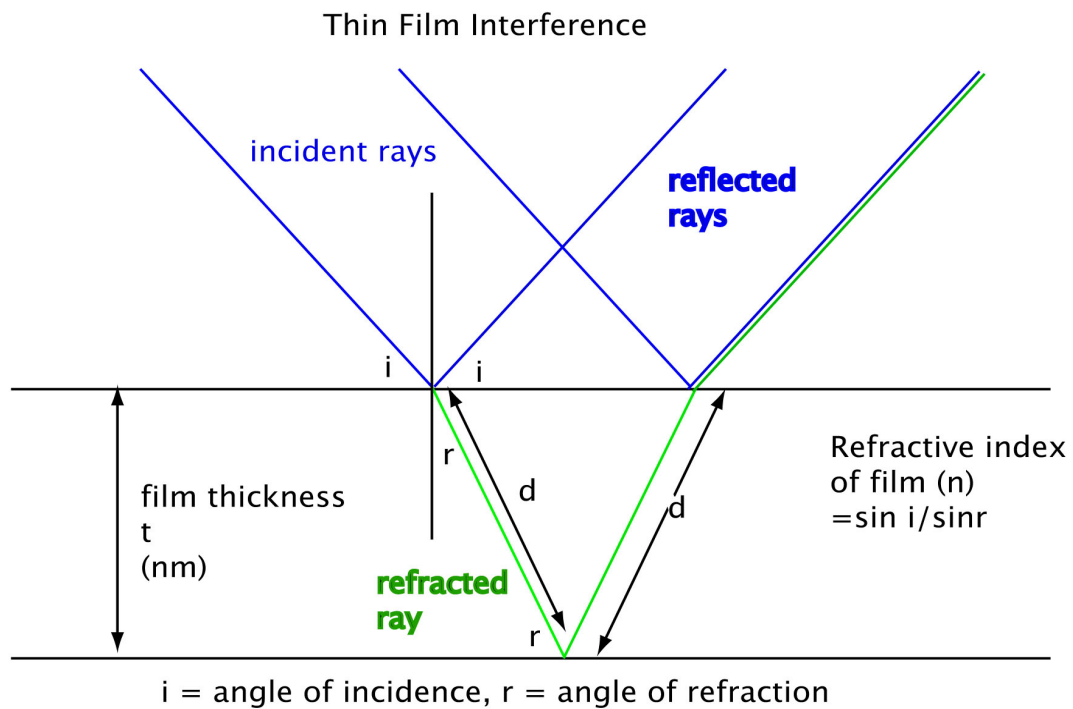
Optical path difference D =2d = 2nt/cosr x (1–sinrxsinr) = 2ntcosr

Optical path difference D = wavelength cancelled x (m–1/2)
where m is an integer 1,2,etc. representing the order of tint

Figure 3.6: *Diagram of interference calculation showing relationship between film thickness and optical path difference.*

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[7] Bruhat, G, *Optique,* 5th Edition, Masson et Cie. 1959, p.128.
[8] Dubal, L, Unpublished manuscript, Berne 1986.

For some thin films the angle of incidence of the light has to be taken into account, but for films with a high refractive index, interference colour is observed at normal incidence. Therefore for comparative purposes **cosr** becomes **1** and the optical path difference can be taken as **2nt**.

For all these calculations the interference phenomenon is greatly simplified but they may be used to illustrate features of particular systems. The combination of the two equations for calculation of the optical path difference produces a formula which relates the layer thickness (**t**) to the wavelength absorbed (**Y**), the order of tint (**m**) and the refractive index of the layer material (**n**):

t = Y(m-1/2)/2n

Therefore if the refractive index of the thin layer is known and the wavelength that is eliminated is deduced from the observed colour, then the approximate thickness of the film may be calculated.

Having reviewed the phenomenon of interference as applicable to all systems, the particular case of oxidised titanium is presented below.

3.2.3. Titanium Interference Colour

Titanium exhibits interference colour when the oxide layer on the surface of the metal is within certain thickness limits. A thin layer of oxide forms on the surface of titanium metal within minutes of its exposure to air. This layer is usually in the range 0.5 – 7 nm thick and too thin to show interference colour. However the air-formed oxide layer can be thickened by reaction with oxygen under the application of energy in the form of heat or electricity, i.e. anodising. The thickened films, which produce interference colours, are in the range 20 - 300 nm thick. As the oxide layer on titanium grows beyond this thickness the incident light is absorbed and interference colours are no longer observable.

The mechanics of interference colour on the surface of titanium are similar to those for any system that exhibits this form of colour, as described above. The metal provides the base reflecting surface and the oxide layer, formed by heat or anodising, is the thin refracting film. The colours observed encompass at least the first and second order tints, ranging from a dull reddish yellow through purple to blue for the first order and then through yellow, orange, pink, mauve and blue to green for the second order.

As shown in the previous section, the refractive index of the thin layer material is an important factor in determining the optical path difference and therefore colour. The detailed structure and composition of the thin layer formed on the surface of titanium

when it is oxidised will be considered in Chapter 5 but it is sufficient at this point to note that the effective refractive index of the thin layer influences the interference colour observed. The effective refractive index of the oxide layer is a combination of the composition and homogeneity of the material of which the layer is formed.

3.2.4. Summary

The brief outline of the theory of thin film interference has demonstrated the optical mechanism by which the appearance of colour is produced on an oxidised titanium surface. The theory of thin film interference emphasises the importance of two critical features of the geometry of the system that contribute to the colour observed; the thickness of the oxide layer and its refractive index. The interaction of both these features is crucial in determining the colour. The absorbed wavelengths that give rise to each colour can be used to derive theoretical values for oxide layer thickness which allows consideration of the likely differences in colour attributable to variations in the oxide layer composition. The utility of such information reinforces the need for a system of colour appearance measurement for titanium, as previously identified in Chapter 2 when analysing the causes of colour variability.

Considerable advances in colour measuring and colour matching systems have been made since the colour chart (p 41), still used by jewellers today, was first published in 1978 by JB Ward, as part of a paper sponsored by the Goldsmiths' Company[9]. A project was therefore undertaken to measure the colours directly.

The colour appearance measuring systems and the instruments that may be used to measure the reflectance data, on which they are based, are introduced in the following part of the chapter. The selection of a suitable method for measuring the colour appearance of oxidised titanium is verified by experiment and exemplified in use and a method for easy transmission of measured colour data is demonstrated.

3.3. Colour measuring

3.3.1. Measurement of Colour Appearance

Much effort has been expended in devising colour measurement systems for industries where the unambiguous communication of the data is a crucial issue, notably paint and textiles. Early systems such as that of the artist AH Munsell (1905) utilised a visual comparison between a test sample and an array of swatches depicting the essential components of a colour, namely the hue, saturation and lightness. The hue of a colour

[9] Ward, James Brent, *The Colouring and Working of Refractory Metals,* Worshipful Company of Goldsmiths' Project Report No. 34/1, London September 1978.

describes where it fits in the visible spectrum between red and violet; saturation describes the colourfulness, often called chroma; and lightness, the luminance or brightness on a scale from white to black. The system was devised empirically and aimed to achieve equal perceptual differences between adjacent samples. Hunt gives a fuller description of the Munsell system and its subsequent development.[10] A variant of this system in the form of the Munsell Colour Book is still in use.

Many systems were devised and used in different countries and for different industries. The establishment of the Commission Internationale de l'Eclairage (CIE), whose history is given by Malacara[11], aimed to produce agreed international standards for the communication of information on colour. The first CIE colour system was published in 1931. The purpose of a colour measuring system is to define a system of identifiers which at least approximately correlate with perceptual attributes of colour, so that measurement values indicate visual appearance.

Colour perception is a psychophysical phenomenon which depends on three factors: the nature of the incident light, the angle of view and the observer. CIE specifies the methodology of the measurement and the concept of a 'standard observer' derived from the perception of the average population with normal colour vision. These factors are incorporated in the design and construction of instruments which are used to measure colour.

Spectrophotometers measure the relative spectral reflectance of a surface at each wavelength throughout the visible region of the electromagnetic spectrum, 400-700 nm. In practice values are recorded at 5 or 10 nm bandwidths. Mathematical transformations[12] are used on the measured spectral data to produce uniform colour spaces CIELUV and CIELAB (1976) which more closely resemble human colour perception and enable comparisons to be made. The purpose of the CIELAB 1976 Uniform Colour Space is to provide a three-dimensional colour space with axes which correlate with perceptual attributes of colour in a way that is approximately perceptually uniform.

A detailed exposition of the CIELAB Colour Space is given by Fairchild[13] but in brief: L* represents the lightness on a scale from black to white, a* and b* are red-green and yellow-blue axes respectively. This is usually represented graphically with the x-axis depicting values of a*, with positive values as levels of redness and negative values levels of greenness. Similarly the y-axis depicts values of b*, with positive values for yellowness and negative values for blueness. In each case completely red or yellow is +100 and completely green

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[10] Hunt, RWG, *Measuring Colour,* 3rd Edition, Fountain Press, England 1998, p134.

[11] Malacara, Daniel, *Color Vision and Colorimetry,* Spie Press, Washington, USA 2002, p 32.

[12] The spectral reflectance values are used to compute XYZ tristimulus values which are then used to compute the CIELAB values.

[13] Fairchild, Mark D, *Color Appearance Models,* Addison Wesley Longman, Inc. Reading, Mass 1998, p219

or blue –100. The values quoted for the colour appearance being described represent its relative position within a notionally uniform colour space and do not have units. Thus the three values describe a three dimensional, almost cylindrical space.

The zero point for each value of L* is the mid point between the red-green and the yellow-blue axes and saturation increases from the mid-point to the circumference of the circle. Figure 3.7 illustrates a CIELAB space[14]. *CIELAB hue is measured in degrees starting with h_{ab} = 0 in the +a* (redness) direction and increasing counterclockwise. CIELAB chroma, C*, is measured as the length of the line from the neutral point (a* = b* = 0) to the sample point.*[15]
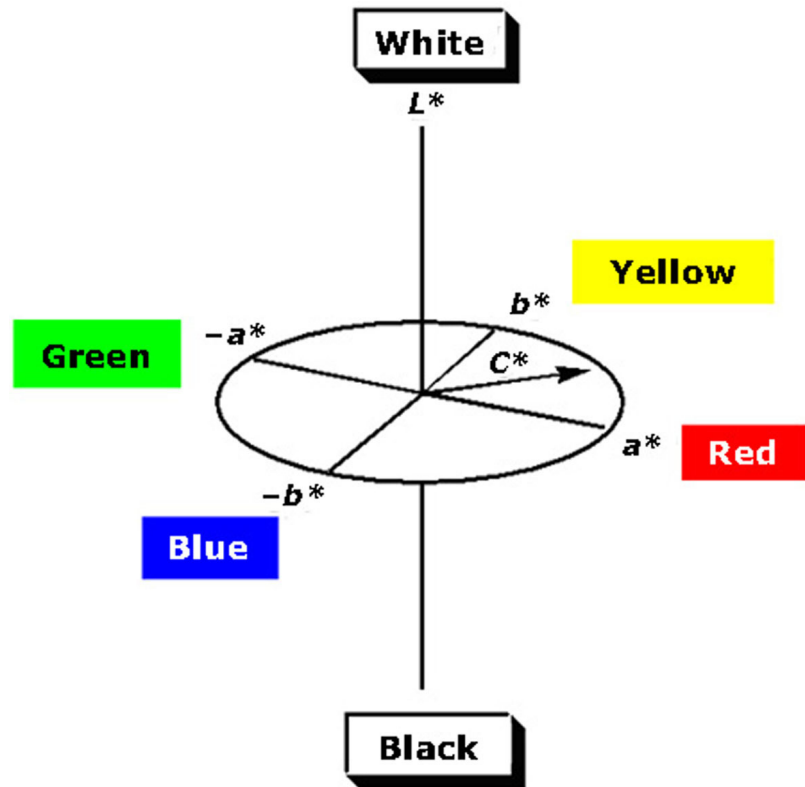
Figure 3.7: *CIELAB Colour Space showing projections of a* , b* , L* and C*.*

The coloured surface of oxidised titanium is not self luminous and is opaque and, for the purposes of colour measurement, not unlike a paint surface in appearance. The CIELAB system, used extensively for reflective media, was therefore deemed the most appropriate one to use for the measurement of the interference colour on titanium.

For the majority of the coloured surfaces for which the CIELAB system has been used, such as print or textiles, the colour is due to an applied pigment in the form of a paint or dye. As no pigment is present on a coloured titanium surface, the feasibility of the system for measuring its colour appearance had first to be confirmed.

In order to confirm that the coloured surface of oxidised titanium could indeed be measured using spectrophotometers and that the results could be meaningfully expressed in terms of the CIELAB colour space a series of experiments were performed.

[14] www.colour-journal.org/2007/1/5/07105article.htm.
[15] Berns, Roy S, *Billmeyer and Saltzman's Principles of Color Technology,* 3rd Edition, John Wiley & Sons, Inc. New York, 2000, p70.

3.3.2. Colour Measuring Experiments

The colour measuring experiments encompassed two main areas of investigation; the initial trials to prove the applicability of the proposed system and the use of the system to explore the colour development on different titanium surfaces. All the experimental samples of titanium were coloured by anodising, in order to produce the most even surface colour, as explained in Chapter 2, which is important for colour measuring. The programme of experiments, as detailed below, started with feasibility trials to confirm that the colour on titanium could be measured using the proposed procedure. These were followed by the application of the method to measure the colour of one type of oxidised titanium surface; testing the consistency of data over two sets of samples.

The subsequent experimental programme explored the use of the system for the comparison of the colour produced by anodising different types of titanium surface.

Feasibility

Although other researchers[16] had used an earlier variant of the CIE system to characterise the colour of anodised titanium, in order to test the feasibility of the proposed CIELAB measuring method, trials were conducted to establish the parameters in terms of instrumentation and illuminant for the measurements. Test measurements were carried out by two colour scientists working at different colleges with departments specialising in colour measurement, each using one of the two sets of samples which were prepared for the purpose.

For this phase of the experimental programme, small samples of material **2** (1.5 cm square) were used and the two sets were designated **2J** and **2K**. Both samples sets were prepared and anodised according to the preparation procedures given above in Chapter 2. Sample set **2J** consisted of nineteen samples anodised at 5V intervals from 25-115V. The smaller sample set, **2K,** comprised ten samples anodised at 10V intervals from 20-110V.

One researcher examined set **2J** using two types of spectrophotometer; a 0/45 instrument and an integrating sphere spectrophotometer. The other researcher used only an integrating sphere spectrophotometer to measure set **2K**. Malacara gives an outline of the two types of instrument[17] and the principles on which they are based. In general terms a 0/45 spectrophotometer is a simpler instrument, which is quick and easy to use. The integrating sphere instruments are more complex but allow greater differentiation between colour samples. They also have the additional option of two operating modes, which allow specular light to be included or excluded in the measurements. Figure 3.8, copied from Mc

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[16] Delplancke, J-L, Degrez, M,Fontana, A, and Winand, R. *Surface Technology,* 16, 153-162, 1982.
[17] Malacara, Daniel, *Op. cit*, p120.

Donald[18], illustrates the optical geometry of these two types of spectrophotometer.

Light source — Detector — 0/45

Light source — Detector — 0/D
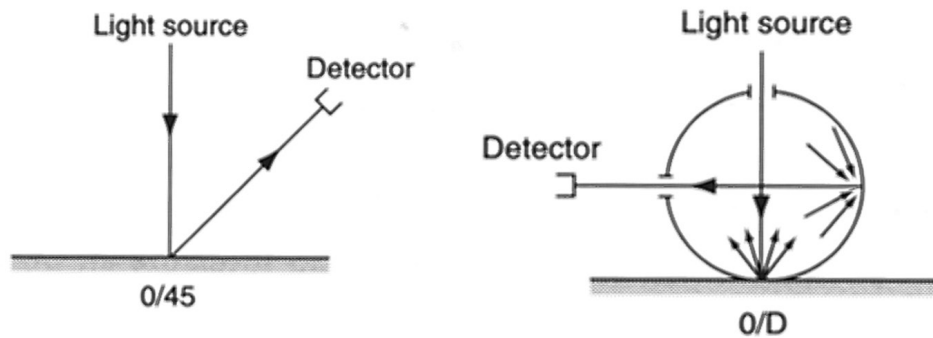
Figure 3.8: *Optical geometry recommended by CIE for two types of spectrophotometer: a 0/45 instrument and an integrating sphere 0/diffuse instrument. In practice integrating sphere spectrophotometers have an 8 degree angle from the normal for the light source, which allows specular reflections from the sample to be excluded by the inclusion of a specular trap.*

Both types of spectrophotometer integrate measurements from all parts of the surface placed in the aperture of the instrument. Most integrating sphere spectrophotometers allow the operator to choose between different sized apertures. The largest possible sample size is desirable so that the largest aperture of the instrument can be used and any inconsistencies can be averaged out across the surface.

The results of these measurements are reported in Table 3.1A in the Appendix (p 229). CIELAB values, L*, a* and b*, show consistent results for the two sets of samples with the variation in values between the two sets accounted for by the fact that different daylight illuminants were used for each set. The colorimetric values for **2J** set were computed from spectral reflectances using a D_{50} illuminant, as mostly used for printing and graphics on paper-based substrates, while the colorimetric values for the **2K** set were computed using a D_{65} illuminant, generally used for screen imaging. The measurements of the **2K** sample set were therefore shifted towards a higher value of b* and a lower value of a* compared with those for **2J.**

Figure 3.9 shows the plot of the values for a* against b* for sample sets **2J** and **2K**. a* values are plotted on the horizontal x-axis or red/green axis, where red is positive and green is negative. b* values are plotted on the vertical y-axis or yellow/blue axis, where yellow is positive and blue is negative. Although this two-dimensional graphical presentation cannot include the L* or lightness of the sample, the important attributes of the colour, hue and chroma, allow useful comparisons to be made. The greater distance a plotted point is from the zero point indicates a greater chroma or relative colourfulness. The integrating sphere

[18] McDonald, Roderick, ed. *Colour Physics for Industry,* 2nd Edition, Society of Dyers and Colourists, Bradford,, W. Yorks. 1997, p65.
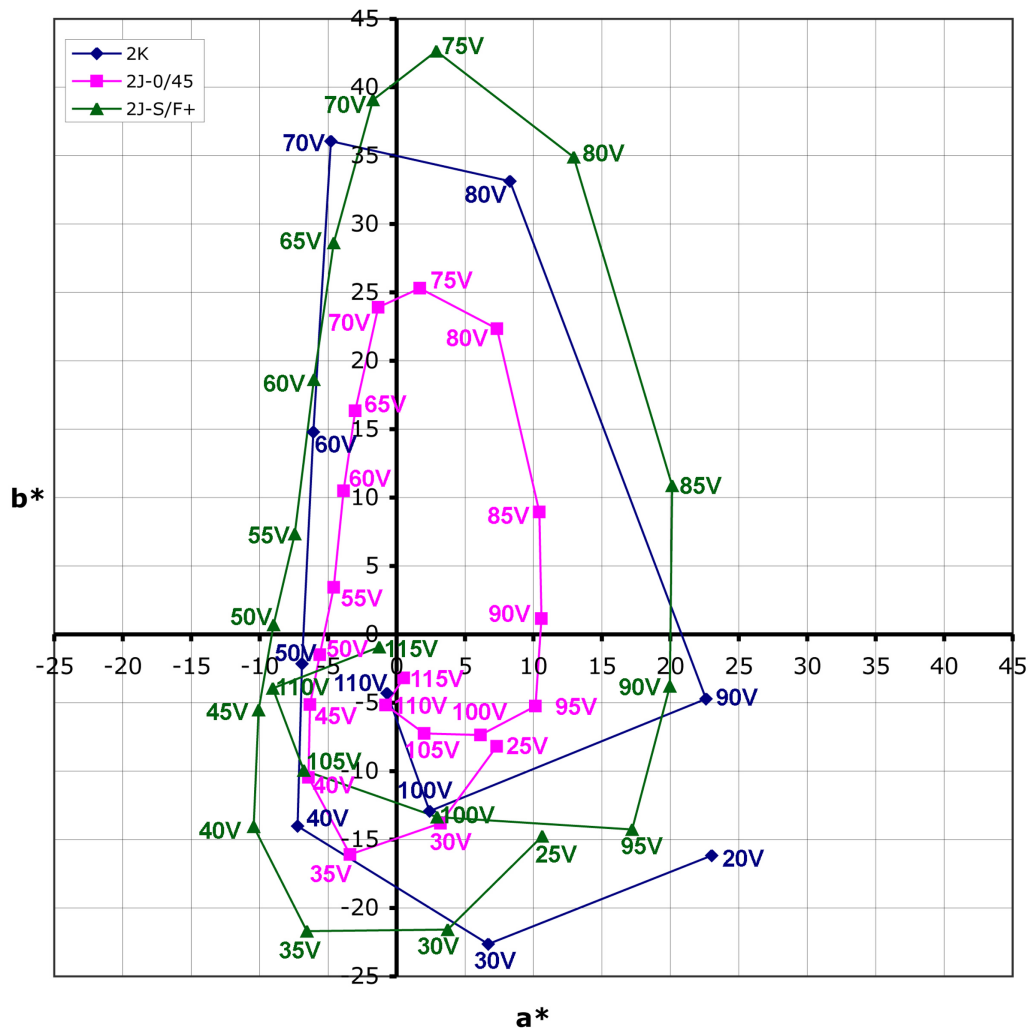
Figure 3.9: *Graphical projection of two measurements for sample set* **2J** *and one for* **2K**.

instruments, operating in the mode that includes specular reflection, record the highest chroma for a sample compared to the 0/45 type. However the angles formed by the lines drawn from points of apparently similar colour to the zero point show that the measured colours are of similar hue for each applied voltage.

The measurements of the **2J** sample set showed that both types of spectrophotometer could be used to measure colour on oxidised titanium and this was confirmed by the results for the **2K** set. The differences between the measurements for the two sets emphasised the need for the illuminant to be quoted for all such measurements. Having therefore demonstrated the feasibility of the proposed colour appearance measuring system, the next phase of this part of the experimental programme was undertaken to apply the system for titanium.

Application

This part of the experimental programme used two types of spectrophotometer with different geometry, a 0/45 and an integrating sphere, to measure the colour of specially prepared samples of anodised titanium. CIELAB values were calculated from the recorded measurements using the dedicated computer programmes for each instrument. In order to average out any instrumental or operator variation, an arimetic average of three measurements was recorded for each sample for both instruments used.

The GretagMacbeth Spectrolino 0/45 spectrophotometer (Spectrolino) has a small aperture only a few millimetres in diameter but its operation is simple and similar instruments are widely used and are portable. The illumination source is tungsten. The instrument was calibrated using a supplied standard white tile and then the samples were measured directly. From the three measuements of relative reflectance for one sample an average deviation was calculated at 0.8 percent of the mean of the three values.

The principle colour measurements of each sample in the four sets were made using a DataColor Spectraflash 8degree/diffuse(Spectraflash) instrument, Figure 3.10. The larger aperture of 3cm was used so that the maximum area could be measured and the colour integrated across the surface. The illumination source is a xenon arc. The Spectraflash was calibrated before use with a standard white tile and a black trap. Values were recorded first with specular included and then with specular excluded. As only the mean values were recorded the manufacturer's specifications are quoted for repeatability of measurements[19].

Inter-instrument Agreement for Reflectance (CIELAB) 0.15 (max) and 0.08 (avg).

For both instruments a D_{50} daylight illuminant was used to avoid the differences highlighted above in the feasibility phase caused by the use of different illuminants.

In order to use the largest available aperture on the integrating sphere spectrophotometer (3cm diameter), larger sample sizes (5 cm square) were required. Therefore an additional sheet of CP titanium (0.7 mm thick), designated **TA[20],** was acquired specifically for this phase of the experimental programme. The surface

Figure 3.10: DataColor Spectraflash 8degree/ diffuse spectrophotometer.

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[19] www.datacolor.com/spectrophotometers/600
[20] **T** denotes material supplied by Timet UK.

of this ground and etched sheet had a smooth, matt appearance, visually similar to that of material **2**, used in the feasibility phase, and was regarded as representative of the industry standard for sheet titanium. The manufacture and finishing processes that produce such a surface on titanium sheet are discussed further in Chapter 4.

Two sample sets of **TA** material were prepared, designated **TA1** and **TA2**. The larger number of samples in each set in this phase was used so that they could be anodised across the full voltage range in small incremental steps. Each set consisted of twenty-four samples but one sample of set **TA1** was left unanodised. Therefore only twenty-three samples of set **TA1** were coloured by anodising at 5V intervals from 10-120V and the full twenty-four samples of set **TA2** were anodised from 5-120V at 5V intervals.

In order to verify the applicability of the CIELAB system for measurement of colour appearance of anodised titanium consistent results must be obtained when using spectrophotometers with different optical geometry to measure the same samples so that the differences observed can be seen to be attributable solely to that geometry. The system should also be able to measure and differentiate the colours of different sample sets prepared from the same material by the same procedures. The tabulations and graphical representations of the measured data presented in the following paragraphs highlight these two facets of comparison.

Comparison of Instruments

The differences in measurements given by the two instruments, and both modes of the integrating sphere spectrophotometer, are illustrated in Table 3.2A in the Appendix (p 229), which compares the three sets of measurements for the **TA1** sample set, showing the effect of the differing geometry of the instruments. The highest chroma are recorded by the integrating sphere spectrophotometer with specular included and the lowest for the 0/45 instrument. A plot of a* against b* for the three sets of measurements for sample set **TA1**, shown in Figure 3.11, confirms that the CIELAB hue angles recorded for each sample are consistent. The plotted points for each sample, as measured by the different instruments, lie on a straight line drawn from the zero point. The apparently anomalous values observed in the lower voltage areas (15-25V), may be caused by the patchy colour of the samples (for details see the case study in Chapter 2). A recording error has resulted in the values for the 10V measurement without specular reflection being mis-recorded.

This comparison emphasises that for measurement of colour appearance it is essential to specify the type of instrument being used and the operating mode. As has been demonstrated, the most differentiated CIELAB values are recorded using an integrating sphere spectrophotometer with specular reflection included and it is proposed that this should be recommended as the preferred system for measuring the interference colours
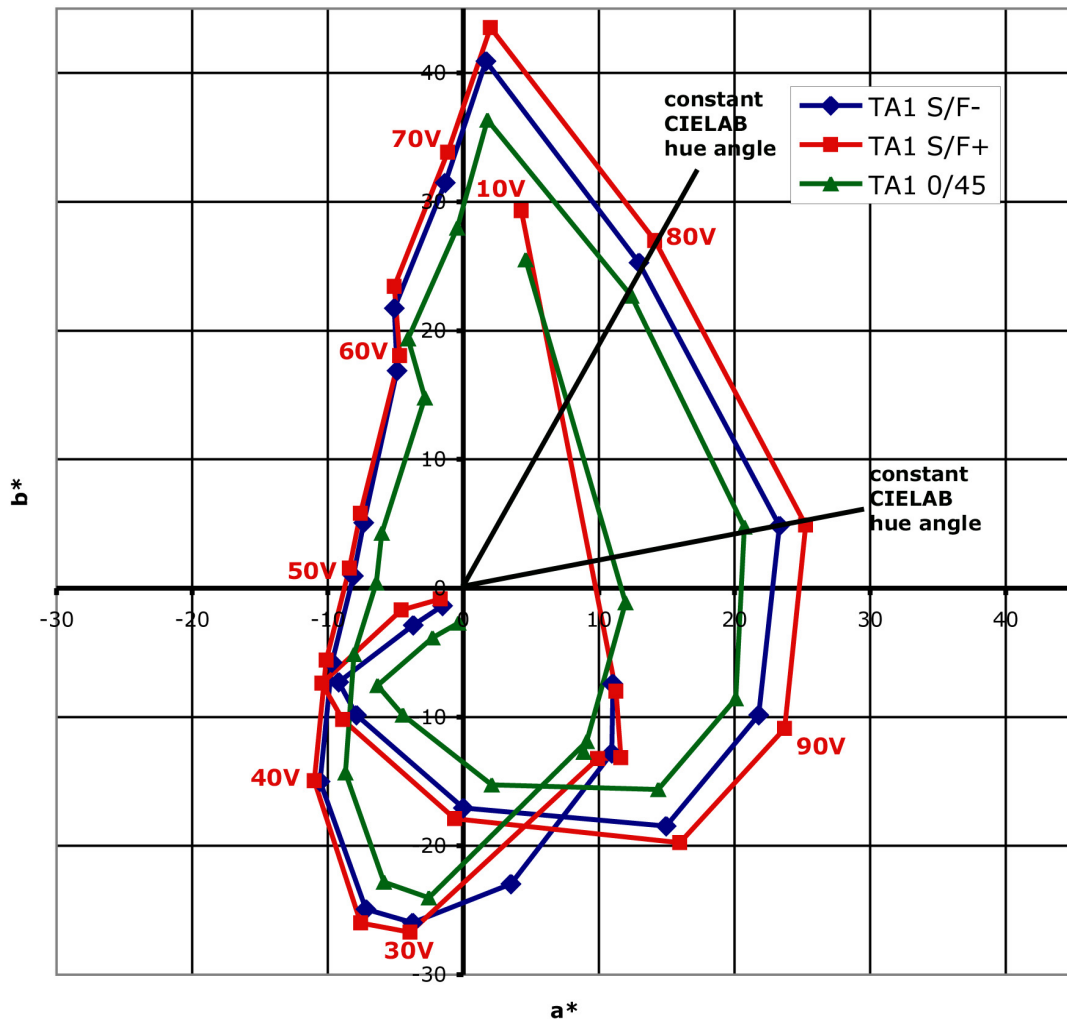
Figure 3.11: *Graphical projection showing variation in measurement attributable to different instruments and modes.*

on titanium. However while it is desirable to use an integrating sphere instrument, and essential in this phase of the experimental series for the validation of the colour appearance measurements, it can be seen that 0/45 geometry instruments give valid and useful data about the hue of a colour and may be more readily accessible for regular use.

Having illustrated the variations in measurements that are due to the different measuring instruments, the following comparison concentrates on measurements made with the integrating sphere spectrophotometer with specular included. The differences observed are due only to the colour differences of the sample sets.

Repeatability of Colouration

As stated above, the sample sets **TA1** and **TA2** were prepared from the same sheet of titanium and the calculated CIELAB values for measurements made with the integrating

sphere spectrophotometer with specular included are recorded in Table 3.3A in the Appendix (p 224). Apart from some anomalous values, which reflect the unexpected colour developments in the 15-25V region, as already indicated, Figure 3.12 shows that the two **TA** sample sets give comparable results. The graph confirms and categorises the small
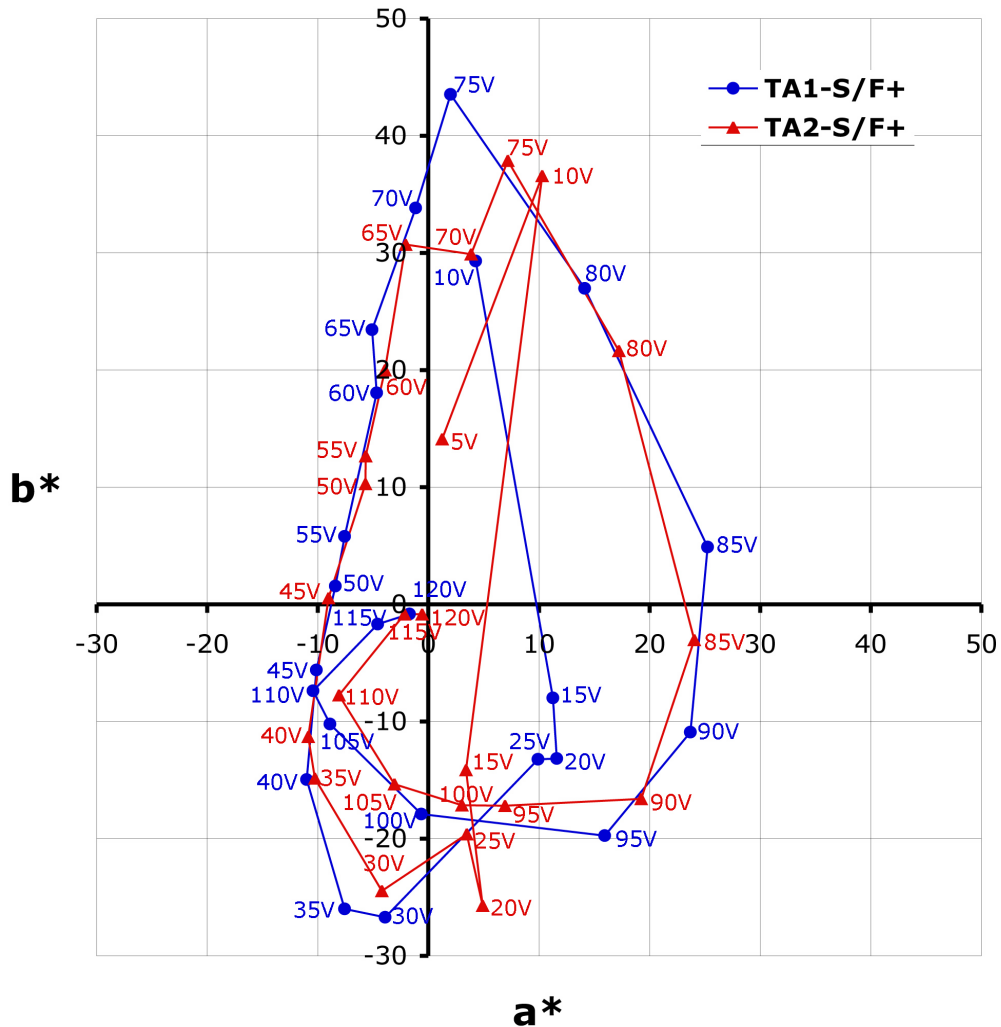
Figure 3.12: *Graphical projection showing variations between TA1 and TA2 sample sets measured with Spectraflash and specular included.*

differences in hue observed by visual inspection of the samples. Thus sample **TA2** anodised at 50V is shown to be more yellow than sample **TA1** anodised at the same voltage. It also differentiates between the samples where visual discrimination is difficult. Both the samples anodised at 80V fall within the red/yellow quadrant of the graph and are visually similar but the **TA1** sample has a more yellow hue than the **TA2** sample.

The difference in colour between two samples (delta E) can be quantified by using the following equation:

$$\text{Delta E }_{TA1/TA2} = ((L*_{TA1}-L*_{TA2})^2 + (a*_{TA1}-a*_{TA2})^2 + (b*_{TA1}-b*_{TA2})^2)^{1/2}$$

A Delta E value of 1 indicates a just perceptible difference. Typically, for printed colours, differences up to 5 are accepted within the industry[21] and are not easily visually distinguished unless placed side by side for comparison. The calculated difference values in Table 3.3A in the Appendix (p. 230) for the **TA2** sample set compared with **TA1**, illustrate how difficult it is to reproduce exactly the same colour on titanium using material from the same source and anodising to the same voltage. Disregarding the higher voltages, 115V and 120V, which give shades of grey, only five of the remaining twenty-one comparative samples would fall within the printing industry acceptable standard.

The two phases of experimental investigation have confirmed that CIELAB is a robust system for the measurement of colour on titanium. The following part of the programme uses this system to measure and compare the colour produced by anodising titanium sheet with different surface finishes.

Surface Comparison

The colour measurements made in the first part of the programme used samples of CP titanium sheet with a matt surface. The difference in colouring behaviour of differently finished titanium surfaces, reported in the literature, with polished titanium surfaces apparently oxidising more slowly than matt ones,[22] suggested that this should be confirmed in terms of colour measurement. A further two sample sets were therefore prepared for the comparison of colour development on differently finished titanium sheet, one rougher and one smoother than the sheet already used. The premise being that a similar colour would be produced at a lower voltage on the rougher surface and at a higher voltage on the polished surface in comparison with the previously measured matt surface.

The highly polished CP titanium foil, described in Chapter 2, designated material **3** was used to prepare one of these additional sets of samples. However the dimensional stability of this material in terms of flatness was a problem and the sample size was restricted to 3cm square. Thirteen samples of this material were prepared and anodised at 5V intervals from 30-90V.

For the rougher textured surface a fifth example of titanium sheet, designated **TB**[23] (0.5 mm thick), which had been prepared by shot blasting and pickling to give a uniform rough granular textured surface was acquired. A set of ten samples (5 cm square) was prepared from this material and anodised at 10V intervals from 10-120V.

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[21] Personal communication. Professor A Johnson, London College of Communications, December 2004.
[22] Hass, G, *Vacuum,* 2, 331, 1952.
[23] **T** again denotes material supplied by Timet UK and **TB** differentiates it from the **TA** sheet.

The colour of both these sample sets was measured using an integrating sphere spectrophotometer with specular reflection included. The recorded values are compared with those for the **TA** material previously measured and described above. Thus a total of three sample sets with substantially different surface finishes were compared: **TA1** (23 samples), **TB1** (10 samples) and **3K** (13 samples).

CIELab values from measurements on Spectraflash 600 - spec. inc

Anodising Voltage	10	20	30	40	50	60	70	80	90	100	110	120
TA1 Series												
L*	60.5	38.91	45.53	61.1	72.15	74.83	74.52	65.04	52.66	50.1	53.46	53.18
a*	4.29	11.62	-3.91	-11	-8.4	-4.68	-1.15	14.13	23.69	-0.64	-10.43	-1.7
b*	29.3	-13.15	-26.71	-14.95	1.55	18.06	33.84	26.98	-10.9	-17.9	-7.39	-0.83
TB1 Series												
L*	56.28	34.67	51.5	62.68	65.48	66.38	60.31	56.27	50.64	51.33	54.97	53.54
a*	7.04	11.03	-10.07	-10.46	-5.96	4.71	15.99	22.63	12.29	-4.04	-9.47	-1.65
b*	38.97	-35.34	-21.55	-0.99	15.53	23	7.57	1.23	-18.37	-13.04	-1.94	0.25
Differences	10.903	22.599	10.011	14.06	15.681	13.564	34.436	28.5	13.778	6.0574	5.7362	1.1395
3K Series												
L*			36.36	48.53	59.83	65.13	62.22	52.79	52.73			
a*			0.83	-4.52	-5.15	-0.1	8.73	9.29	1.98			
b*			-12.54	-9	2.34	24.41	25.4	3.05	0.19			
Differences			17.531	15.343	12.766	12.466	17.892	27.315	24.379			

Table 3.1: Comparison between three different titanium surfaces.

The results presented in Table 3.1, show that the colour produced by a particular voltage is significantly different for the three different surfaces of the **TA**, **TB** and **3** sample materials. The calculated differences refer to comparison with the **TA1** sample set in all cases.

As it has been noted above that polished titanium surfaces oxidise more slowly than matt ones, it would have been expected that, under similar anodising conditions the same colour would appear at lower voltages, i.e. more quickly, on the roughest surface, **TB,** followed by the matt surface, **TA,** and at the highest voltages on the more polished **3K** sample set. However no such correlation is apparent from these measurements presented graphically in Figure 3.13.

The samples of the three different surfaces when each is anodised at 30V do appear to indicate that there is a relationship between colour development and surface polish with the rough surface having a colour in the blue/green quadrant, the matt surface colour closer to the blue axis and the polished surface colour just on the red side of the blue axis. However this colour order is not maintained throughout the voltage range. For example the colour produced by the matt surface, **TA1,** when anodised at 70V falls almost on the yellow axis, while that for the rougher surface, **TB**, anodised at the same voltage is in the
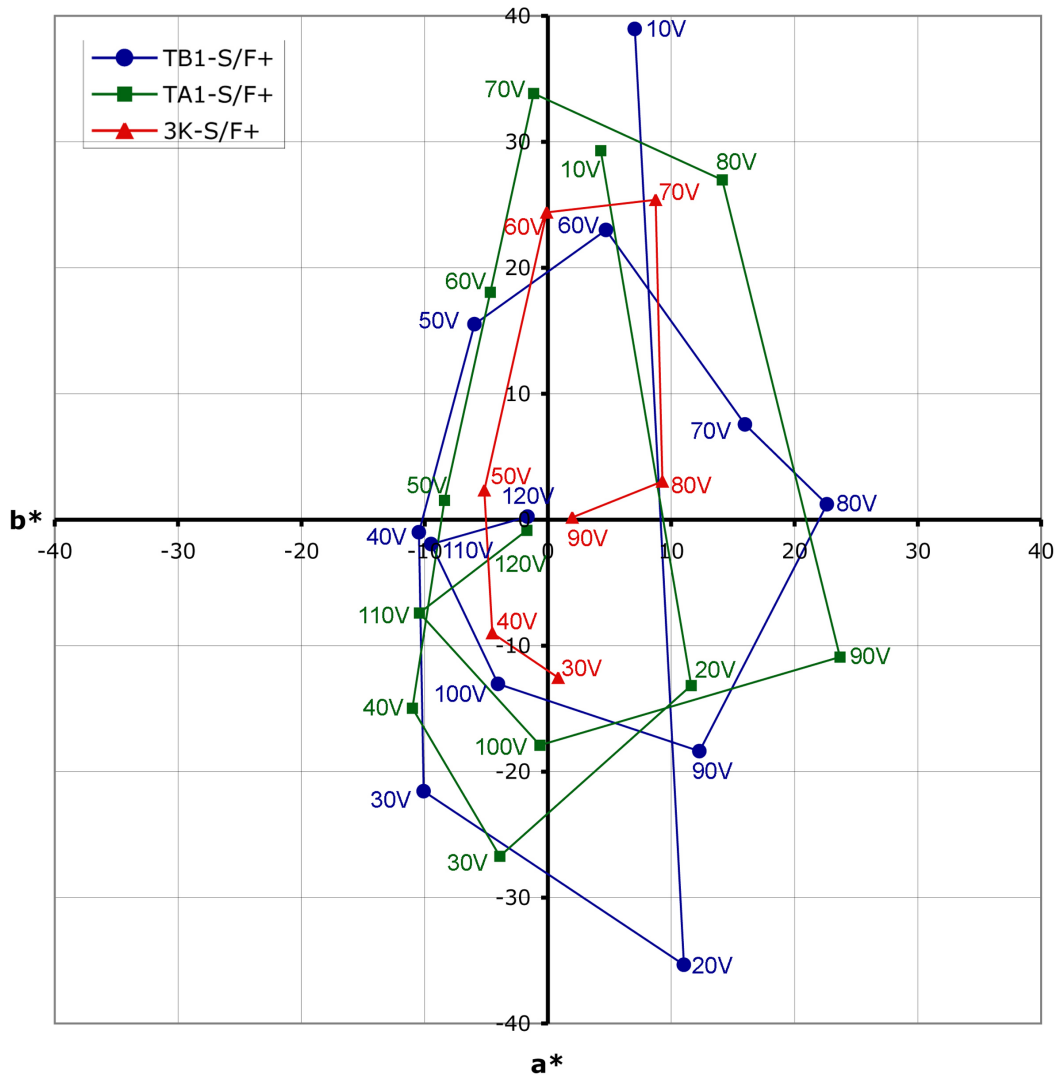
Figure 3.13: *Graphical projection of Spectraflash with specular included for* **TA, TB** *and foil sample set* **3K**.

yellow/red quadrant of the graph. It would therefore have been expected that the same voltage applied to the highly polished surface, **3K**, would have been in the yellow/green quadrant but it is almost mid-way between the other samples.

When anodised at higher voltages, the surface structure of the **TB** material produces samples with a parti-coloured appearance and areas of different colour which produced variations in the measured apparent colour.

3.3.3. Transmission of Colour Data for Titanium

The above section of the chapter demonstrated that CIELAB values could be successfully used to measure the appearance of coloured titanium surfaces. However while an expert in the field of colour measurement may be able to assess the comparisons from

the numerical values for L*, a* and b* and the graphical plot of a* versus b*, a visual method is needed for the transmission of the colour appearance data for titanium in the jewellery sphere.

One method is to feed the numerical values for L*, a* and b* into a computer graphics programme, such as 'Photoshop' and the chosen colour can be reproduced at any location worldwide within the consistency of the displays used. The method does not even depend on the recipient having a copy of the same software, as a file can be created displaying the chosen colours and transmitted as an attachment to an e-mail.

The procedure for the Photoshop programme involves selecting the rectangular tool from the tool bar menu and then setting the foreground colour using the L*, a* and b* values in the colour picker. A rectangle is then drawn using this colour. As the system has

Figure 3.14: *'Photoshop' created patches using L*, a*, b* values for different surfaces.*

to use whole numbers some rounding of the values is necessary. Any shape can be used within the menu of the tool. Figure 3.14 illustrates the colour patches produced using this method for the samples measured.

The actual colour of the visualisation depends on how the CIELAB data is converted to the values used within the transmission system (normally via an ICC profile) and also how these are subsequently converted within the devices used for screen display or printing. For the greatest consistency it would be necessary to ensure that all the devices to be used within a chain of communication are calibrated to the same standard.

3.3.4. Summary

A viable method has been demonstrated for the measurement of the interference colours produced on titanium and also a quick and convenient technique for their communication. This system will be used to define the colours of the samples produced for the experimental work presented in Chapter 5, on the oxide layer thickness and composition.

The final part of the chapter expands on the notion of comparing colours using the wavelength at which maximum absorbance occurs. Although the oxide layer on titanium grows steadily as the energy input is increased, the mechanism of development of colour on titanium means that, as can be seen from the chart above, some colour transitions occur more rapidly than others and the measured data will be used to consider these transitions.

3.4. Interference and Oxide Layer Thickness

The formulae presented in the discussion of thin film interference in the first part of the chapter show that information about the layer thickness may be deduced from knowledge of the wavelength in the visible spectrum at which maximum absorption occurs. This wavelength can be identified from the plot of the relative reflectance values for each sample. The measurement of colour appearances using the CIELAB system is based on the relative spectral reflectance values recorded by spectrophotometers at 10 nm bandwidths throughout the visible spectrum. Although minor variations occur most instruments record data from 380 nm through to 730 nm. The plotted data also highlight the differences between first and second order colours.

3.4.1. Relative Reflectance

A plot of the data for each sample across the wavelength range pinpoints the wavelength at which minimum relative reflectance and therefore maximum absorbance occurs. These values can be obtained from both types of instrument as demonstrated in Figures 3.15 and 3.16, which show the reflectance curves for the sample set **2J** as measured on the 0/45 spectrophotometer (Figure 3.15, Table 3.4A in the Appendix p. 231) and on the integrating sphere instrument, with specular included (Figure 3.16, Table 3.5A in the Appendix p. 232) . The different values for the relative reflectance data arise from the operating conditions of the respective instruments and the calibration standards that are used in each case.

The absorption curves illustrate how the interference colours develop as the oxide layer thickens, i.e. as the applied voltage is increased, and are practical examples of the
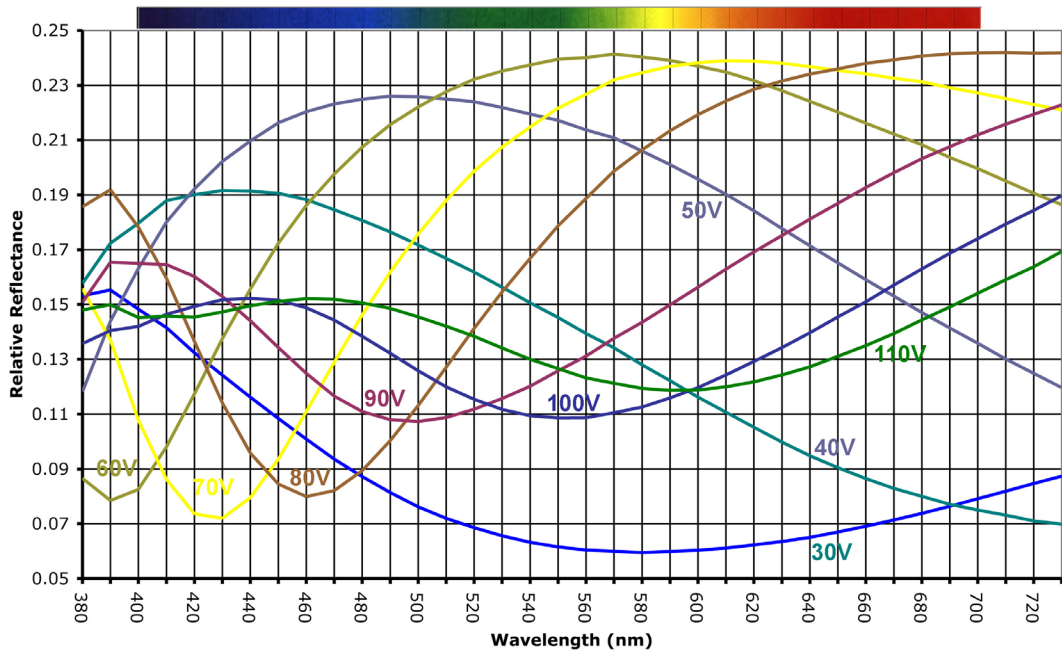
Figure 3.15: *Relative reflectance data for sample set **2J** measured with 0/45 spectrophotometer.*
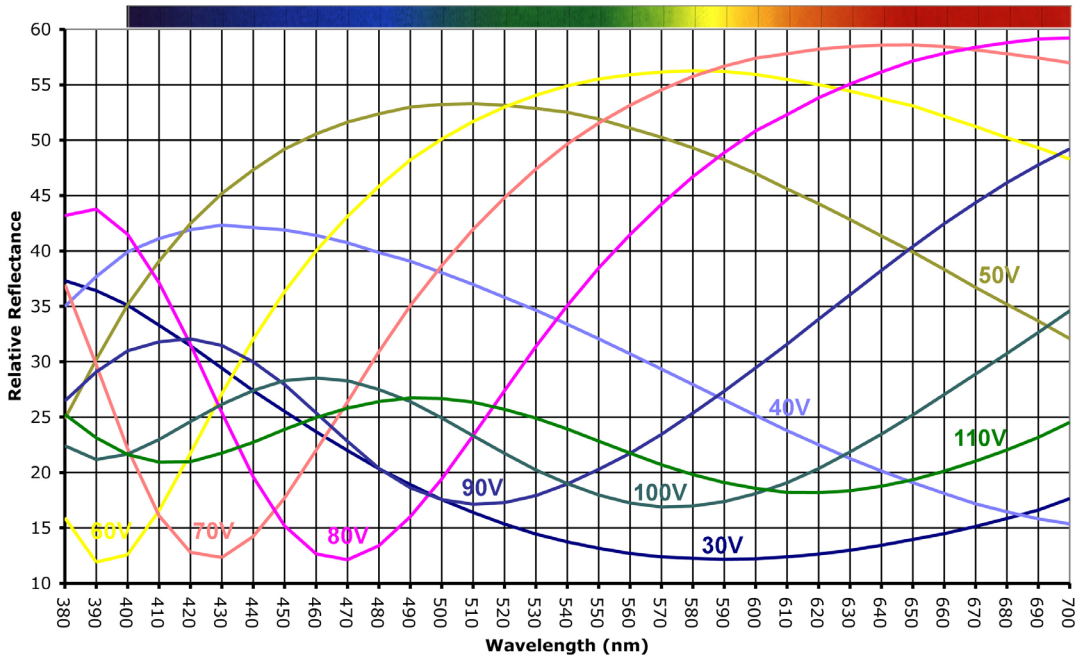
Figure 3.16: *Relative reflectance data for sample set **2J** measured with integrating sphere spectrophotometer with specular reflection included.*

theoretical sequence given in Figure 3.5 above. To take just two examples, for both sets of measurements the maximum absorption for the sample anodised to 70V is at 430 nm in the blue part of the spectrum, producing a yellow colour, and that for the 90V sample is at 510 nm in the green, with a resulting blue/red colour appearance. For the samples anodised to

40V and 50V, the maximum absorption occurs outside the visible spectrum, which is why the samples appear silvery with only a hint of colour.
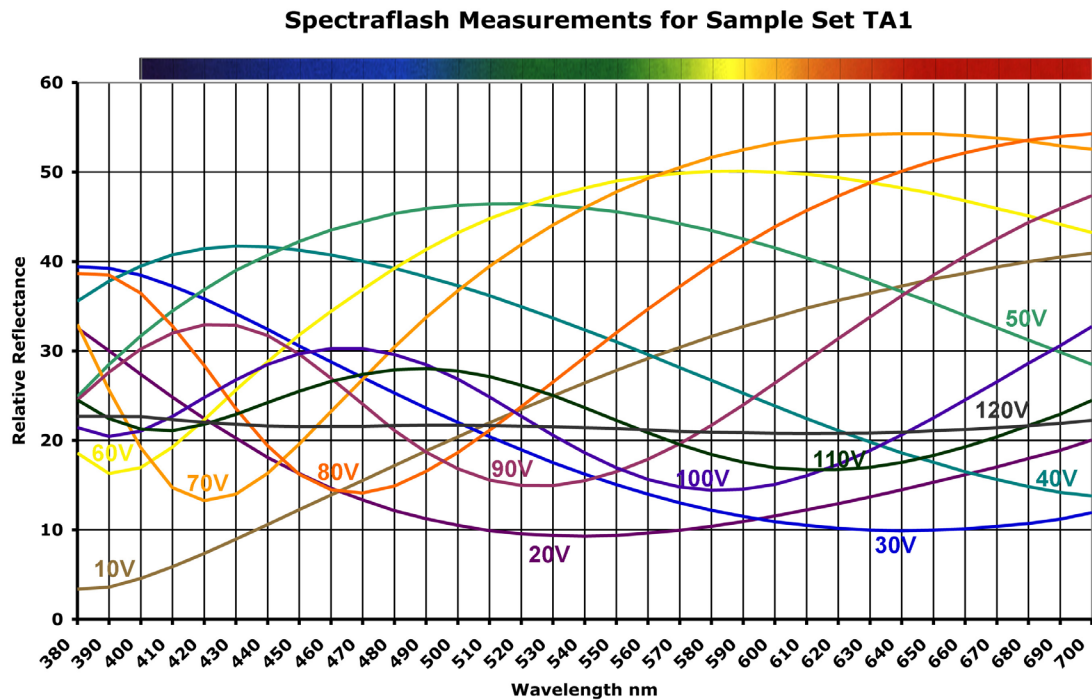
Figure 3.17: *Relative reflectance data for sample set **TA1**/Spectraflash with specular included.*

To confirm this sequence a full range of values is given for the sample set **TA1**, Table 3.6A in the Appendix (p. 233), and shown graphically in Figure 3.17, which shows the relative spectral reflectance values for the measurements made on the **TA1** sample set. It is interesting to note that the absorption bands for the first order colours, 10-40V, are broad, whereas the second order colours (60-90V), which appear clearer, have sharper troughs. It is also possible to observe that two absorption bands are present for the higher voltage samples at 100V and 110V. At 390 nm and at 580 nm for the 100V sample and at 410 nm and 620 nm for the 110V sample giving purple and green colours respectively. The virtually flat line recorded for the 120V sample shows that no interference colour is observable and the sample is dark grey.

Thus the measured data give values for the wavelength of maximum absorption that may be used to confirm the similarity of coloured titanium surfaces selected for further test procedures, see Chapter 4. Although preliminary visual comparisons give an indication of like colours, selection by identifying materials with reflectance minima of similar wavelength ensures that the comparison is as close as possible. This procedure may be used to compare samples of coloured titanium from third parties as discussed below.

3.4.2. Comparison of Anodised Titanium Samples

As the colour measuring experiments are non-destructive, the technique may be used to examine materials from third parties without risk of damage and may at some future date be used for jewellery items. To gain greater experience in the use of the technique and to extend the range of coloured titanium samples that had been measured, two further sets of anodised samples were measured. The materials used also extended the range of surface finishes by including a rougher (etched) surface and a smoother (polished) surface. These materials had been prepared in different countries and at substantially different dates. Both sets were thought to have been pre-cleaned by etching with a hydrofluoric acid (HF) mixture, as the colours appeared brighter than those of the sample sets created for colour measuring, but the preparative methods were only known in detail for one of the sets. As HF etching had not been used for sample preparation within the research project the inclusion of these sample sets permitted comparisons to be made between the coloured surfaces with and without this treatment.
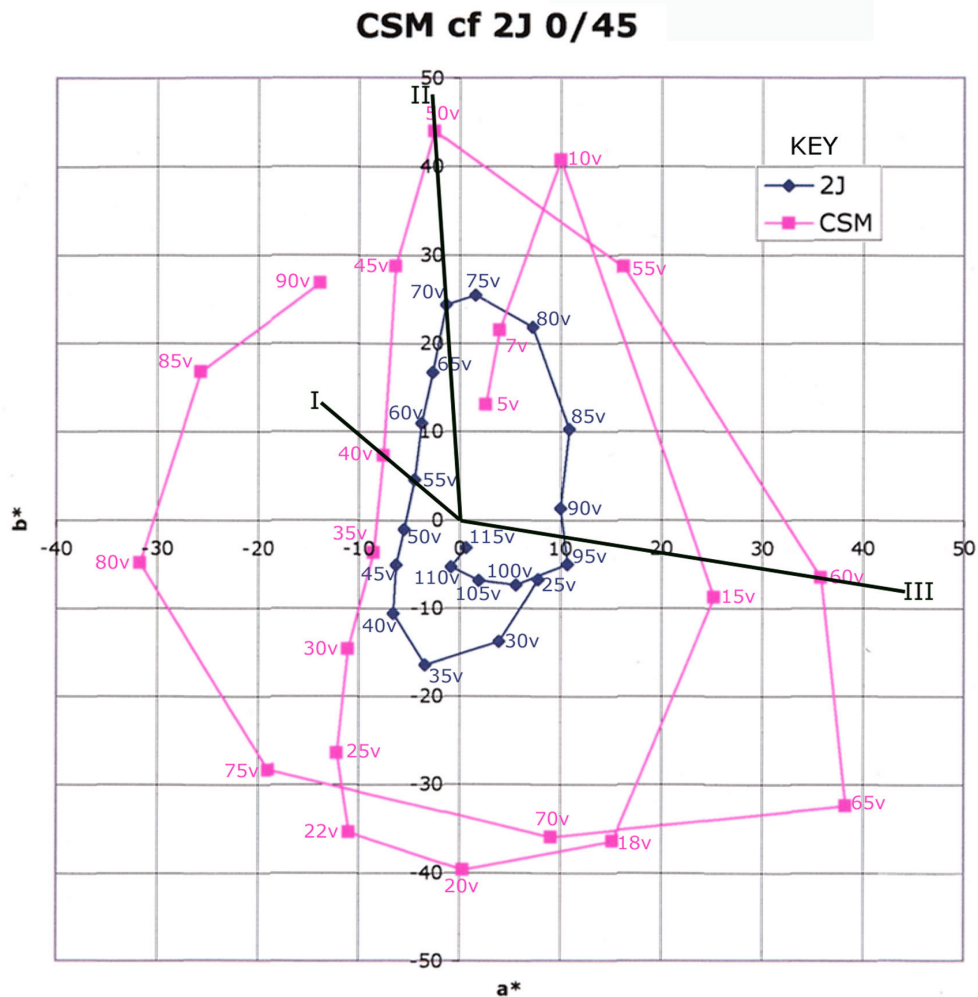
Figure 3.18: *Chart comparing a* and b* values for sample sets **CSM** and **2J** from 0/45 spectrophotometer.*

The first of these additional sample sets had been prepared in the early 1990s as workshop standards and had been continuously on display. This sample set called **CSM**[24] (21 samples) had been prepared from CP titanium sheet which had been etched with a hydrofluoric acid mixture, prior to anodising in an aqueous ammonium sulphate solution in the voltage range from 5V–90V. Measurements were made with a 0/45 geometry spectrophotometer, using a D_{50} illuminant and the spectral reflectance data and CIELAB values are recorded in Table 3.7A in the Appendix (p. 234).

The plot of the a* and b* values for the CSM sample set compared with the values for sample set **2J,** both measured using the same spectrophotometer, is given in Figure 3.18.

The lines shown on the chart designated **I**, **II** and **III** pass through points of constant CIELAB hue angle and demonstrate how the rate of colour development varies between the two materials. The hue achieved on the **CSM** material at 40V is the same as the hue for **2J** at 55V (line **I**). Similarly the same hues appear at 50V for **CSM** material and 70V for the **2J** set (line **II**). Line **III** passes through the point that shows the colour development for the **CSM** material at 60V and passes between the 90V and 95V colours for the **2J** material.

This comparison emphasises the much greater chroma or colourfulness of the sample set that was pre-treated with a hydrofluoric acid etch. The examination of the
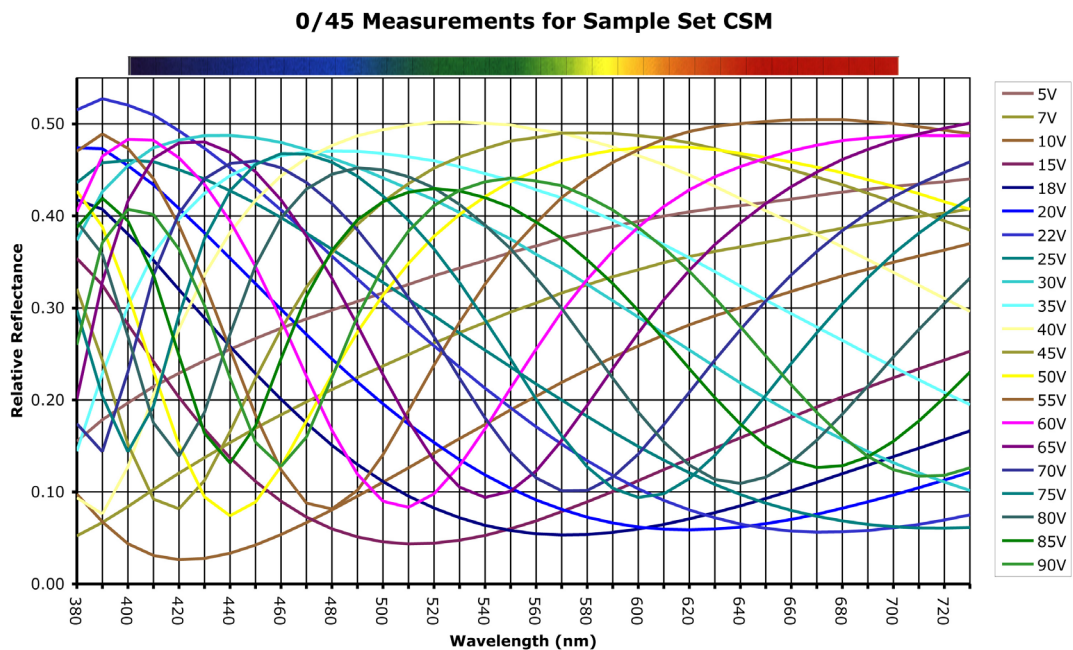
Figure 3.19: *Relative reflectance data for full range of CSM samples showing how wave minima move across the spectrum.*

relative spectral reflectance data allows further comparisons to be made between the two sample sets and also between the first and second order colours.

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[24] **CSM** denotes the set of samples prepared by technicians in the Jewellery Department at Central Saint Martins College of Art and Design.

The full range of samples illustrated in Figure 3.19 shows in greater detail how the absorption bands move across the wavelengths of the visible spectrum and are more sharply defined as the voltage of anodising and thus thickness of film increases.

Figure 3.20 shows the range of colours translated from the CIELAB values via Photoshop, emphasising the colourfulness of this sample set.

Using the colour comparisons **I**, **II** and **III** as shown in Figure 3.18 above, it can be

5v	7v	10v	15v	18v
20v	22v	25v	30v	35v
40v	45v	50v	55v	60v
65v	70v	75v	80v	85v
90v				
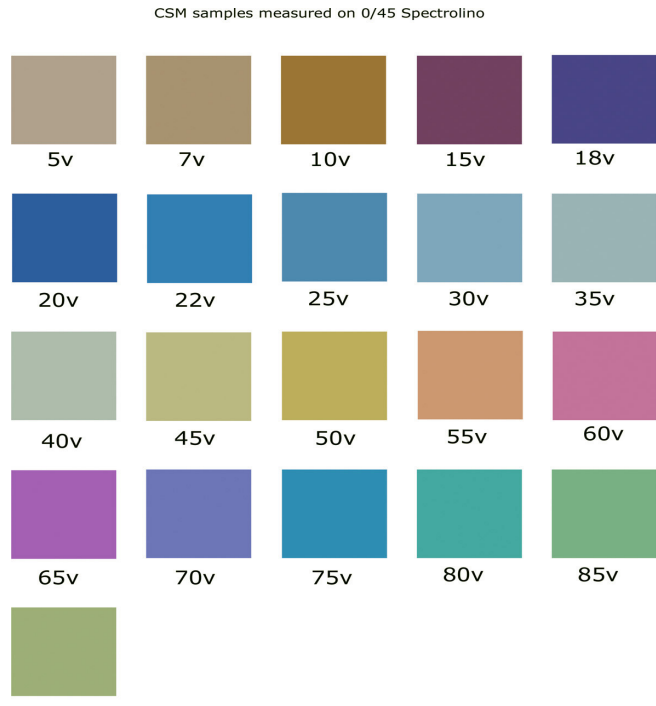
Figure 3.20: *Photoshop created patches using Lab values for* **CSM** *sample set.*

2J/CSM Comparisons I, II, III

CSM-40V

CSM-60V

CSM-50V

2J-55V

2J-90V

2J-95V

2J-70V

Relative Reflectance

Wavelength (nm)
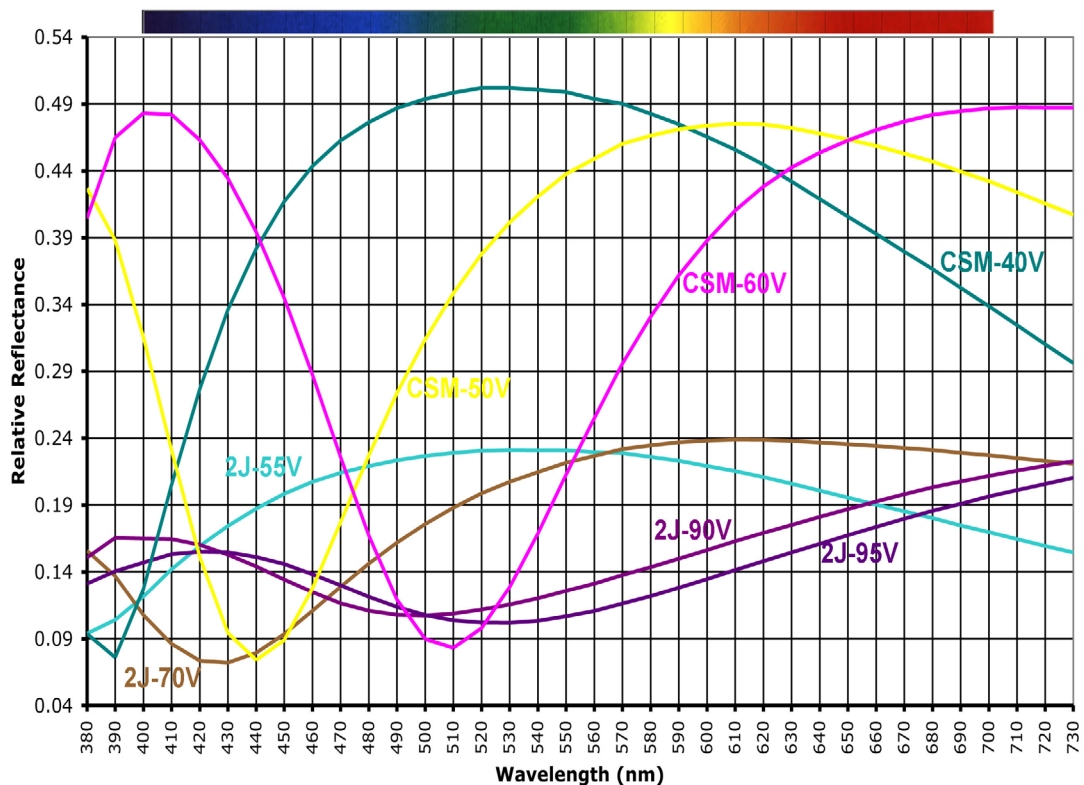
Figure 3.21: *Comparison of relative reflectance curves for similarly coloured samples from* **2J** *and* **CSM** *sample*

seen in Figure 3.21 that the minima for the colours of constant CIELAB hue angle are very close although the shapes of the curves differ.

The yellow samples **2J-70V** and **CSM-50V** have minima at 430 nm and 440 nm respectively and the purple/pink minimum for sample **CSM-60V,** at 510 nm, is between the minima for **2J-90V,** at 490 nm, and **2J-95V,** at 530 nm. It is particularly noticeable that the titanium sheet, which had been pre-treated with HF, the **CSM** sample set, exhibits greater clarity of colour, as evidenced by the sharper troughs in the reflectance curves, in comparison with the **2J** sample set which was not etched immediately before anodising.

Figure 3.22: *Comparison between 1st and 2nd order colours for **CSM** sample set.*

The measurements also permit comparison between the first and second order colours within the one sample set as shown in Figure 3.22. The first order colours have shallower curves than the second order colours indicating more muted shades.

Thus the relative reflectance curves not only define the wavelength of maximum absorption, which determines the colour observed, but also give an indication of the quality of the colour produced by the interference. This assessment was further expanded by the examination of a set of samples with an expanded colour range.

The second additional sample set of coloured titanium obtained from a Japanese supplier was of recent manufacture. The thin sheet had a bright polished finish and it was intimated that the material had been HF etched prior to anodising but the preparative

process details were not divulged. Similarly the numbering sequence of the samples appeared to indicate the anodising voltages but this was not confirmed by the manufacturer.

As the **CSM** sample set showed a wider range of bright colours compared with the samples created for the experimental programme, so this sample set designated **H**[25], expanded the colour range even further, including not only first and second order colours but also third order. The spectral reflectance values CIELAB values are recorded in Table 3.8A in thr Appendix (p. 235).

3 orders of colour tints
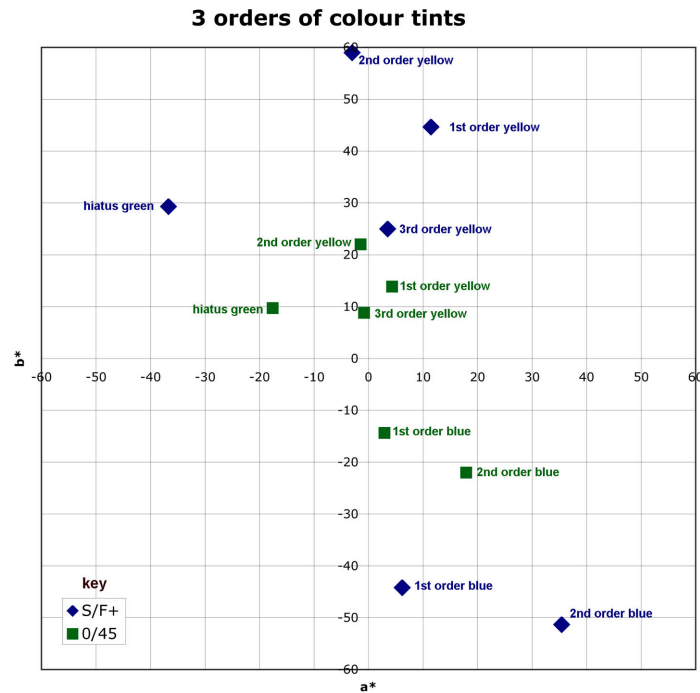
Figure 3.23: Plot of a*/b* values for three orders of colour tints seen in samples from Japanese supplier.

The a* b* coordinates for the three orders of tints, plotted in the graph in Figure 3.23 for measurements made on two spectrophotometers, demonstrate that first orders of colour are more diffuse than second order colours and that third order tints for titanium colour tend to be paler than the previous orders.

These differences are demonstrated in Figure 3.24, which compares the colour patches for these samples, and also by the relative reflectance curves in Figure 3.25.

The first and second order yellows have minima at 440 nm and the first and second order blues have minima at 590 nm. Two minima, at 440 nm and 670 nm, are noted for the sample estimated to be anodised at 90V, demonstrating that if substantial absorption occurs in both the red and blue parts of the visible spectrum the resulting colour is green. The third order colour which is a pale gold (ca 100V) has minimum at 470 nm and the third

[25] **H** is used to identify this sample set of material obtained from Horie Corp. in Japan.

order pink (ca 110V) has a minimum at 510 nm compared to the second order pinks at 490 nm (ca 60V) and 530 nm (ca 66V). Therefore it could be speculated that within the preparative conditions for this material a sample anodised at 62V might produce a

Three orders of colour tints from Japanese samples

Figure 3.24: Photoshop created patches for three orders of colour tint seen in Japanese samples.

second order colour with a similar hue to that of the third order sample.
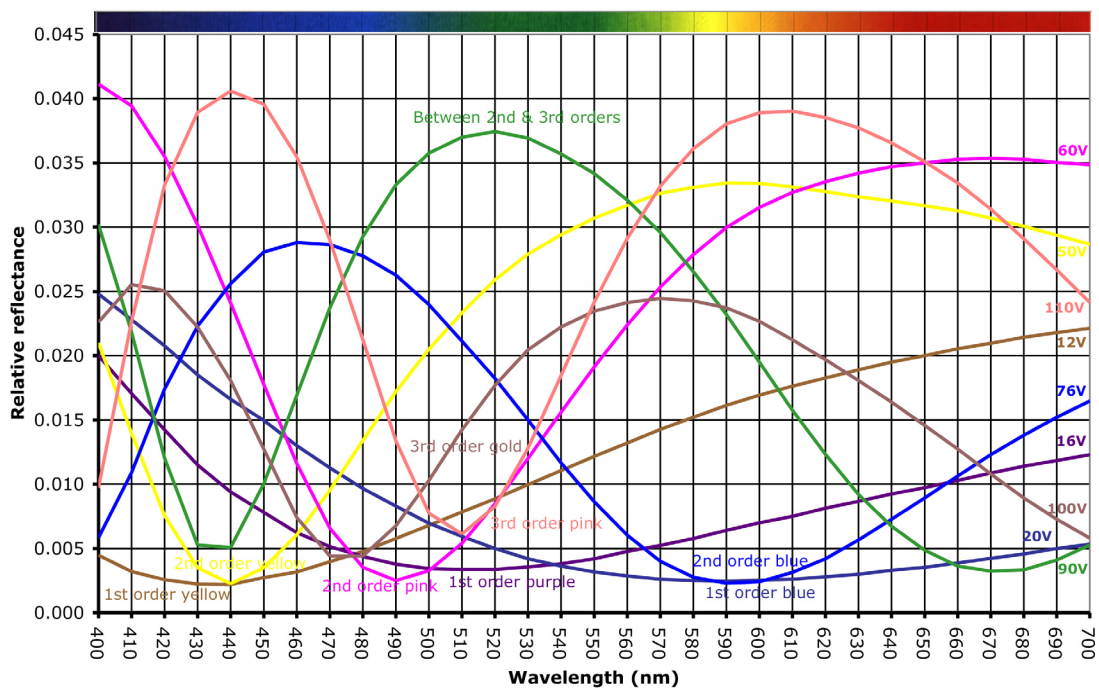
*Figure 3.25: Relative reflectance data for sample set **H** showing three orders of colour.*

The above examples demonstrate how the measurements from the spectrophotometers can be used to both compare materials from different sources and to predict possible colour outcomes.

3.4.3. Theoretical Oxide Layer Thickness

The conclusions from the first part of this chapter noted that calculation of the theoretical thickness of the oxide layer that produces a specific colour is possible from consideration of the theory of thin film interference. Therefore having demonstrated above how the colour measuring data may be used to characterise each of the colours produced by thin film interference in terms of the wavelength at which maximum absorbance occurs, the next step is to use the formula to calculate the thickness limits for the oxide layers that produce each of the colours. In order to do this assumptions must be made about the likely composition of the oxide layer in terms of the species present and their respective refractive indices.

As described in Chapter 1, titanium dioxide, which forms the thin layer on the titanium, occurs naturally in three crystal forms: rutile, anatase and brookite. All three polymorphs have high refractive indices: anatase 2.493/2.554, brookite 2.583/2.705 and rutile highest of all in the range 2.62/2.9. The majority of investigations[26], which will be examined in greater detail in Chapter 5, have shown that both anatase and rutile may be present on the surface of oxidised titanium. Table 3.2 illustrates the differences in calculated thickness of the film that could result if it was composed exclusively of either anatase or rutile.

Calculation of Film thickness, retardation and refractive index.

	Wavelength eliminated (nm) W	Retardation (nm) R	Refractive Indices				Colour	Anodising voltage
			Rutile n_o 2.62	Rutile n_e 2.9	Anatase n_o 2.493	Anatase n_e 2.554		
					Calculated thickness (nm)			
1st order colour R=W/2	380	190	36.3	32.8	38.1	37.2	ochre	10v
	540	270	51.5	46.6	54.2	52.9	purple	20v
	640	320	61.1	55.2	64.2	62.6	blue	30v
	700	350	66.8	60.3	70.2	68.5	mid-blue	40v
2nd order colour R=Wx3/2	380	570	108.8	98.3	114.3	111.6	silver	50v
	390	585	111.6	100.9	117.3	114.5	yellowish	60v
	420	630	120.2	108.6	126.4	123.3	orange	70v
	470	705	134.5	121.6	141.4	138.0	pink	80v
	530	795	151.7	137.1	159.4	155.6	violet	90v
	580	870	166.0	150.0	174.5	170.3	blue	100v
	610	915	174.6	157.8	183.5	179.1	greenish	110v

Calculated thickness = retardation/2xRI

Table 3.2: *Comparison of calculated oxide thickness for anatase and rutile for 1st and 2nd order colours.*

Figure 3.26 plots the different colour bands and shows the effect that the various refractive indices would have on the thickness of the layer needed to produce any particular colour. As an example the absorption centred at 530 nm (retardation 795 nm), which produces a second order purple, would be given by a layer 137.1 nm thick if the oxide were all in one form of rutile and 159.4 nm if all one type of anatase, i.e. a maximum variation of 22 nm.

[26] Aladjem, A, *Journal of Materials Science*, 8, 1973, p688.
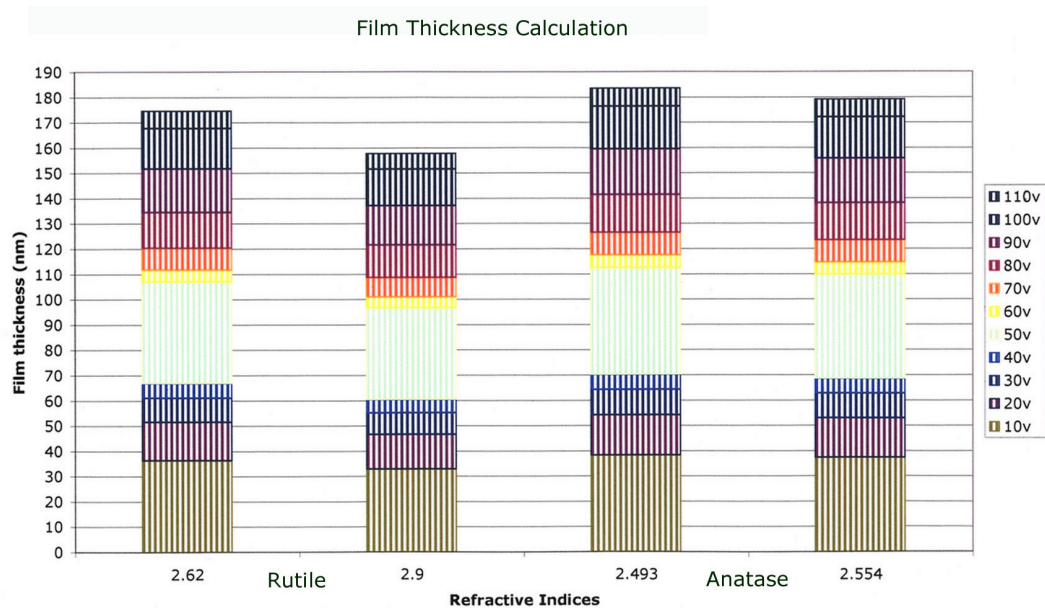
Figure 3.26: *Graphical representation of calculated film thickness and colour.*

Although, as stated, the calculations are greatly simplified, the figure quantifies the degree of uncertainty introduced into the titanium interference colour by the possible variations in the oxide crystal form. The conditions under which either anatase or rutile is preferentially formed and the methods of identifying these different forms are considered in the following chapters.

The example given outlines the method and presents the results for possible values of the limiting values of the refractive indices for the both the rutile and the anatase forms of titanium dioxide.

A similar calculation may be performed to identify the most sensitive colour transitions that occur when anodising titanium. When the voltage is increased during the anodising procedure there are regions where the colour appearance changes very slowly and others where small voltage increases lead to a rapid change in hue. As colour variability is most likely to occur in this latter region it is useful to identify the colour zones where such rapid transitions are to be expected. A simple calculation of the theoretical layer thickness for the second order colours of sample set TA1, assuming that the oxide is principally in one form, say anatase, with one refractive index, is presented in Table 3.3 and shown graphically in Figure 3.27.

The slope of the graph shows that for this sample set the most rapid layer thickening, and thus colour transition, occurs between the colours generated by 75V and 90V, i.e. the orange/pink region. Therefore any future explorations of workshop anodising procedures could usefully be carried out in this region.

Theoretical oxide layer thickness for sample set TA1, assuming an average RI for anatase of 2.524

2nd order colour	Visual Appearance	Anodising Voltage	Retardation (nm)	Absorbance (nm)	Calculated oxide layer thickness (nm)
	silver	50v	570	380	112.9
	silvery yellow	55v	570	380	112.9
	yellowish	60v	585	390	115.9
	pale yellow	65v	600	400	118.9
	yellow	70v	630	420	124.8
	gold	75v	660	440	130.7
	pink	80v	705	470	139.7
	cerise	85v	750	500	148.6
	mauve	90v	795	530	157.5
	violet	95v	825	550	163.4
	blue	100v	870	580	172.3
	greenish/blue	105v	900	600	178.3
	pale turquoise	110v	915	610	181.3
	greenish/grey	115v	945	630	187.2

Table 3.3: *Theoretical oxide layer thickness for second order tints of sample set TA1, assuming oxide to be anatase.*
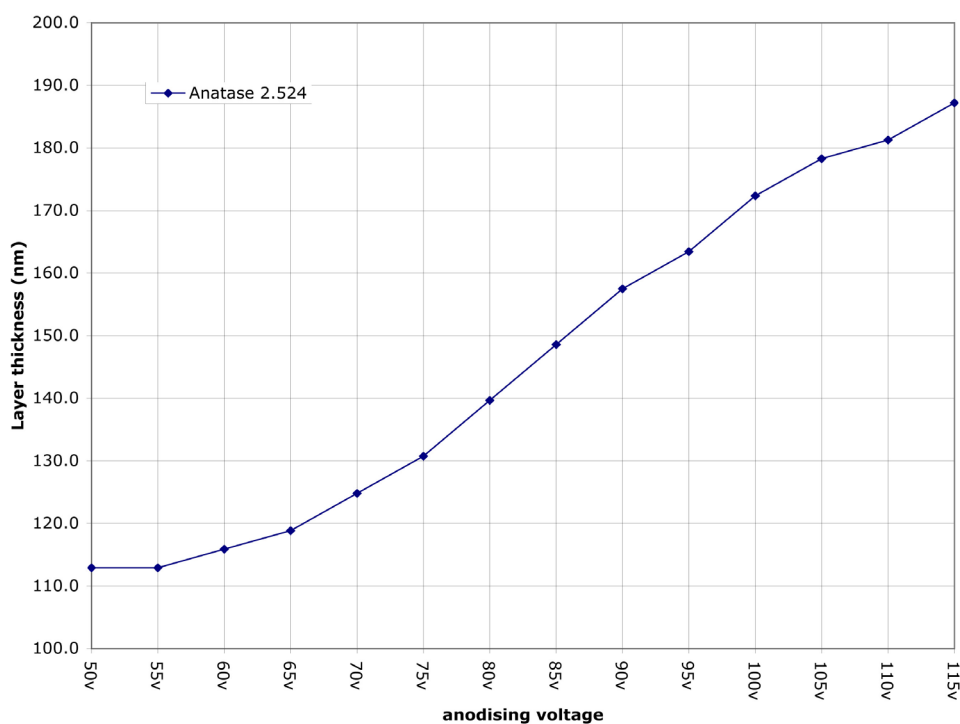
Figure 3.27: *Graph of theoretical oxide layer thickness against applied voltage for sample set **TA1**.*

3.4.4. Summary

This part of the chapter has shown examples of how data from colour measuring

may be used to compare different anodised titanium samples from any source, to predict voltages required to produce particular hues and to identify regions of rapid colour transition for any specific sample material.

3.5. Conclusions

The three parts of this chapter have presented the interference colour phenomenon as observed in the case of oxidised titanium, confirmed the utility of the proposed CIELAB colour measuring system for coloured titanium, demonstrated a simple method for communicating the results and explored further applications for the data obtained from the measurements made using the system.

In addition to the measurement and reporting of colour appearance, information from the relative reflectance data measured across the visible spectrum allows definitions of colour to be made in terms of the wavelength of maximum absorption. An estimation of the theoretical thickness of an oxide layer produced on titanium by anodising may be calculated and the difference in value attributable to different oxide species identified. Such calculations provide useful background for experiments to measure the thickness of the oxide layer and the oxide forms from which it is composed. These experiments are presented in Chapter 5.

The qualitative differences of the colours observed on the sample sets with different surface finishes emphasises the importance of the surface quality of the metal surface prior to colouring and this will be examined in the following chapter, Chapter 4.

Chapter 4

4.1. Introduction

The titanium metal surface on which the oxide grows is one of the most important potential sources of colour variability. While the composition of the bulk metal is important in terms of purity, it is the structure of the surface layer which plays the most significant role in the oxidation behaviour of the metal. The differential oxidation behaviour between matt and polished surfaces was reported in the early literature[1] on titanium oxidation. Hence a comparative evaluation of titanium sheet with a range of surface finishes is a crucial step in the analysis of the possible sources of colour variability within the system.

As the titanium surface underpins the total system that creates the thin film interference colours it is important to identify the different surface structures that are commonly available and to investigate their oxidation by heat and by anodising. Therefore a range of titanium surfaces are categorised in terms of their morphology. The structures of these metal surfaces are subsequently compared with the surface structures of the oxide layers created on each of them. The object of this comparison is to highlight differences attributable to each of the oxidation processes in order to identify anomalies or irregularities in the oxide growth patterns. The investigations presented in this chapter are designed to obtain the maximum amount of information about all the surfaces, both metal and oxide using non-destructive methods.

The first part of this chapter deals with methods of surface production. The industrial production of metal surfaces is outlined in terms of the processes used and the structures that are created, providing an introduction to the specific case of titanium. The introduction to the industrial production of titanium is followed by a brief review of the methods used by jewellery practitioners to manipulate titanium surfaces to achieve a desired design outcome.

The second part of the chapter presents the comparison of the surface morphology of different examples of commercially available titanium sheet with that of their oxidised, coloured counterparts. Increasing levels of magnification are used in order to explore the structures in greater detail. The methods used for surface examination and measurement include simple visual observation and the use of non-destructive tests including Scanning Electron Microscopy (SEM) and White Light Interferometry (WLI). Particular attention is given to different surface finishes commonly used by jewellers and to the comparison between the surfaces of heat-generated oxides and anodised oxide surfaces.

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[1] Hass, G, *Vacuum,* 2, 331, 1952.

4.2. Surface Creation

The finishing processes to which the metal has been subjected create the surface layer of titanium sheet, which may differ in crystal structure from the body of the metal. This section therefore presents a brief review of the metallurgy of titanium, in the context of the general structure of metals, with particular reference to surface finish and outlines how the processes to which the metal has been subjected influence its structure.

4.2.1. General Structure of Metals

A simplistic definition of a metal is a substance in which electrons are shared between atoms. The structure can be regarded as one in which positively charged spheres are surrounded by a cloud of negatively charged electrons. The mobility of the electrons results in a property possessed by many metals, good conduction of electricity.

Most metals are crystalline solids, at ambient temperature but the crystals are usually only visible under high magnification. The size and shape of the individual crystals, often called grains, are established by the refining processes and, in turn, are responsible for the strength and workability of the metal. In summary, *'There exists a close relationship between structure and properties of metals and the structure is established by the past history of the metal.'*[2]

Metallic crystals are formed by the arrangement of atoms into regular, highly symmetrical patterns or lattices. The commonest lattice structures for metals are cubic and hexagonal. There are two forms of the cubic lattice, face centre cubic (fcc), and body centred cubic (bcc). The high degree of symmetry of these structures gives metals their properties of ductility and malleability. As will be discussed in subsequent paragraphs titanium has a hexagonal structure at ambient temperature but a bcc structure at elevated temperature.

Grain size may be manipulated by casting molten metal, heat-treatment, hot and cold working and annealing. Mechanical working of the solid metal can strengthen it by work hardening and give the metal directional properties. The metallurgist employs a combination of these processes to achieve the shape, form, surface finish and properties required in a metal for a specific end-use.

In practice metals are considerably weaker (by a factor of 100-1000)[3] than they should theoretically be because under most refining conditions, crystal growth is imperfect and the resulting lattice may contain atoms of other elements or voids where atoms are missing. These are known as dislocations or point defects and may be responsible for failure of the metal in wear as is discussed below.

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[2] Rollason, E C, *Metallurgy for Engineers,* 4th Edition, Edward Arnold, London, 1980.
[3] Ibid, p 107.

4.2.2. General Forming of Metals

When metal ores are refined the resulting, purified metal is produced as a molten liquid mass, which is cooled into an ingot or billet, a convenient form for transportation or further processing. Alloys are also produced in a similar form, depending on the properties required, but are outside the scope of this study. The crystalline structure of the ingot in terms of the shape and size of crystals or grains depends on the nucleation of the crystals and the direction and rate of their growth. Slow cooling produces a coarse structure with large crystals and rapid cooling, small crystals. In most ingots the crystals solidify from the cooler outside surface radiating towards the centre. Further processing is needed to refine the grain structure and to produce metal in the form required, such as sheet.

For most purposes a fine-grained structure is desirable for increased strength, toughness and resistance to shock. Dislocations, described above, which may be caused by stress on the metal are blocked by grain boundaries and therefore work processes aim to achieve small grains.

Hot-Working

The first steps in fabricating metals from the ingot stage are hot forging or hot rolling to achieve good structure and an approximate shape. The majority of metals are softer at elevated temperatures and therefore less power is required for their working. Hot-working is used to:

- refine crystal structure,
- eliminate orientation from the ingot,
- promote uniformity of structure by facilitating diffusion of different elements within an alloy.
- improve mechanical properties.

Hot-working helps to homogenise the metal in terms of composition and crystal size, producing an intermediate form that usually requires further processing. Any corrosion products or scale on the surface of the metal as a result of the hot-working process have to be removed, either mechanically or chemically, before undertaking any cold formation.

Cold-Working

Cold–working is used to strengthen the metal by work hardening and to produce the final precise form and dimensions, such as thickness and surface finish for sheet metal.

All cold-working deforms the grain structure and grains are elongated, particularly in the surface layer. In heavily cold-worked material the grains are deformed and distorted to a fibrous texture. The stresses introduced into a metal by cold-working increase its strength but the resulting hardness limits the possibility for further processing. Excessive stress is

relieved by annealing the metal.

Annealing and Recrystallisation

In addition to relieving the stress built up in the metal by cold working, large grains in metal can be converted to small crystals by the heating process that anneals cold-worked material. As the temperature is raised above the minimum recrystallisation temperature new smaller crystals grow independently of the original structure of the metal. A combination of temperature and time is needed for recrystallisation. Extensive cold-working of a metal prior to recrystallisation lowers the required recrystallisation temperature and produces a smaller grain size.

4.2.3. Titanium Metallurgy

The specific metallurgical properties of titanium are presented in the context of its behaviour compared with the general properties of metals as discussed above. The refining of titanium is a batch process. The resulting titanium sponge is arc melted as a consumable electrode under vacuum in order to eliminate/minimise the absorption of oxygen, nitrogen and hydrogen. These gases are readily absorbed by the molten metal and embrittle the solid metal. Molten titanium is formed into billets in which, on cooling, columnar crystals grow from the base and sides of the ingot. The subsequent processing of the metal is similar to that of other metals with hot and cold forming and annealing. As for other metals, the amount of cold deformation and the time and temperature of annealing are of prime importance with respect to grain size.

Titanium may exist in two crystal forms or allotropes. Up to 882^0C it has a close-packed hexagonal structure known as alpha[4], which is strong but hard to work. Above 882^0C titanium has a body centred cubic form, known as beta. The beta form is more workable than the alpha but less strong. Alloys are designed to stabilise a specific alpha/beta ratio structure depending on the properties required in the finished metal.

Working

The working processes are usually carried out at elevated temperatures in the softer beta phase, hot-forging in the range $800\text{-}1000^0C$ and hot-rolling at approximately 100^0C below the forging temperature.[5] These processes, followed by annealing at 700^0C and air-cooling, ensure a fine grain structure in the metal. The beta phase transforms to the alpha phase during cooling. CP titanium is mostly alpha but some beta is present in most manufactured material.

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[4] McQuillan, A D, McQuillan, M K, *Metallurgy of the Rarer Metals, No. 4, Titanium,* Butterworths, London 1956, p.139.
[5] Ibid, p.86.

Grade Specification

Commercial purity (CP) titanium is available in four grades and defined not by the percentage of titanium (ca 99.5%) but by the maximum permitted percentages of the impurities present as a result of the manufacturing process. The grades shown in Table 4.1 are selected according to the analysis of the percentages of oxygen and iron present, which determines the hardness of the material[6].

Titanium Commercial Purity (CP) Grades

Grade/Composition	1	2	3	4
Nitrogen % max.	0.03	0.03	0.05	0.05
Carbon % max	0.10	0.10	0.10	0.10
Hydrogen % max	0.0125	0.0125	0.0125	0.0125
Iron % max	0.20	0.30	0.30	0.50
Oxygen % max	0.18	0.25	0.35	0.40
Total residuals % max	0.40	0.40	0.40	0.40
Timet grade	35A	50A	65A	75A
	MILT 9046			

Table 4.1: *Specifications from Timet for Commercial Purity (CP) titanium grades.*

Grade 1, which has the minimum percentage of both iron and oxygen, is therefore the most easily formable sheet and grade 4, with the greatest percentage of iron and oxygen, has the greatest strength.

Surface Finishing

Primary suppliers of titanium products, such as sheet, usually supply the material to the specified dimensions, thickness, length and width, in an annealed and cleaned state. The final annealing produces oxides, known as scales, on the surface of the metal. The oxides are initially removed by mechanical descaling methods such as sandblasting and grinding. These processes in turn leave residues of the abrasive materials used, and any lubricants involved in the process, as contaminants on the surface of the titanium sheet. Therefore mechanical cleaning is followed by alkaline washing and finally acid pickling. Material is cycled through the cleaning processes until the metal is scale free and visually clean.

Not all material is annealed at the final stage. Some forms such as thin foil are supplied in a worked state to retain the mirror finish achieved by the final rolling.

4.2.4. Jewellery Techniques for Surface Manipulation

Workshop techniques developed by jewellers for the surface preparation of

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[6] *ASTM titanium specifications*, Titanium Metals Corp., USA, 1999, p.3.

jewellery fabricated from titanium were presented in Chapter 2. Standard techniques for the finishing of all metal jewellery begin with removal of tool marks by filing, using a succession of smoother cut files, depending on the nature of the marks to be removed, to produce a visually homogeneous surface. For precious metal jewellery, often designed as highly polished finished pieces, there follows as succession of abrasion steps using a range of increasingly finer grade emery papers, with or without water as a lubricant. The final steps use polishing compounds such as jewellers rouge (powdered haematite in a wax matrix) on electrically driven polishing wheels to achieve a highly reflective finish. Thorough cleaning by washing with detergent and water between each grade of abrasive paper and each grade of polishing compound is essential to avoid contamination.

While all these processes may be followed to create uniform surfaces on titanium jewellery (it just takes more time for each step), practitioners have, as described, a noted preference for matt finishes and only the filing and abrasion steps are generally used. The direction of abrasion may be controlled for creative effect as exemplified by the work of Ed de Large, profiled in Chapter 2. The use of hydrofluoric acid (HF) etching mixtures to create a matt lightly granular surface, as described above in industrial metal-finishing procedures, has gradually declined in workshop practice.

Whatever level of surface polish a jeweller designs for a piece of titanium jewellery, each separate area of the finished surface must be at least visually homogeneous for a consistent colour to be achieved.

4.2.5. Summary

As with the majority of metals, the surface structure of titanium is the result of the working processes to which the metal has been subjected. A fine-grained structure is most desirable as it gives greater strength and is most likely to give an even colour appearance.

The following section considers how the roughness or polish of the surface, whether achieved by rolling, mechanical abrasion or acid etching, influences not only the appearance in terms of reflection but also the rate at which oxidation occurs. In Chapter 3 it was evident from the colour measurements that the degree of smoothness of the titanium surface appeared to influence the rate at which the oxide layer formed but no clear relationship between the surface polish of the metal and the speed of oxidation was apparent. The experimental programme, reported below, establishes a hierarchy of levels of surface smoothness and seeks to correlate this with the rate of oxide growth in terms of energy input. The quality of smoothness of the metal surfaces is also compared with the surfaces of their oxidised counterparts.

4.3. Surface Examination

This part of the chapter presents the experimental programme in which titanium sheet with different surface finishes is oxidised thermally and electrochemically and the resulting oxide surfaces are examined and compared with the original metal surfaces.

Following the introduction of the range of samples, prepared by the methods discussed in Chapter 2, the instruments and techniques used to examine the external morphology of the surfaces of these samples and the results obtained are discussed. Progressively higher levels of magnification are used, from simple visual observation, through optical microscopy to Scanning Electron Microscopy (SEM). The roughness of both the titanium surfaces and the oxidised equivalents are compared using White Light Interferometry (WLI).

4.3.1. Experimental Samples

Four different levels of surface finish that could be obtained or created by jewellers were selected for comparative examination in this phase of the project. The experimental samples were prepared from CP titanium sheet using the methods described previously in the third section of Chapter 2. Examples of titanium sheet with three different surface finishes designated **1**, **2** and **3** were purchased and a fourth surface was created by abrading the surface of materials **1** and **2** with 1000 grade polishing paper. Thus the coupons of these two materials were prepared so that half of the sample was as purchased and half polished. This meant that a direct comparison of the oxidation behaviour of these surfaces was possible.

As described in Chapter 2, materials **1** and **2** had matt surfaces with different levels of reflectivity and material **3** had a highly polished surface. Sets of samples were prepared from these chosen titanium surfaces and oxidised either by heat or anodising, using the methods described in Chapter 2, to produce visually similar colours. Initially two colours were chosen for comparison, royal blue and gold, but the results of the examination of the samples, as described below, required further investigation and therefore additional sample sets coloured pink and green were prepared from materials **1** and **2**.

The royal blue and gold sample sets were each made up of six sample coupons, three of which were heated and three anodised. It was noted that different heating times or different voltages were required to produce visually similar colours on the three different sample materials as shown in Table 4.2. Four of the blue coloured samples are illustrated in Figure 4.1.

Sample	Oxidation Method	Volt or time at 700°C	Surface finish half/half	Colour Variation
Samples coloured royal blue:				
1A	heat	3min	as supplied/polished	none
2A	heat	2min	as supplied/polished	none
3A	heat	1.5min	as supplied	indeterminate
1C	anodised	21V	as supplied/polished	yes
2C	anodised	23V	as supplied/polished	slight
3C	anodised	30V	as supplied	n/a
Samples coloured gold:				
1B	heat	4min	s supplied/polished	patchy
2B	heat	min	as supplied/polished	slight
3B	heat	10min	as supplied	patchy
1D	anodised	55V	as supplied/polished	gold/pink
2D	anodised	61V	as supplied/polished	pink edge
3D	anodised	61V	as supplied	n/a

Table 4.2: Sample sets with polished and unpolished samples of materials *1* and *2* and *3*, coloured blue and gold.
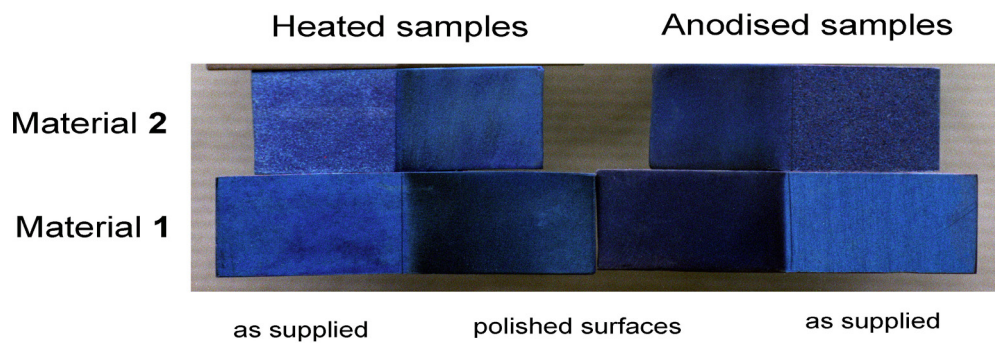
Figure 4.1: Sample set heated and anodised to get blue colour.
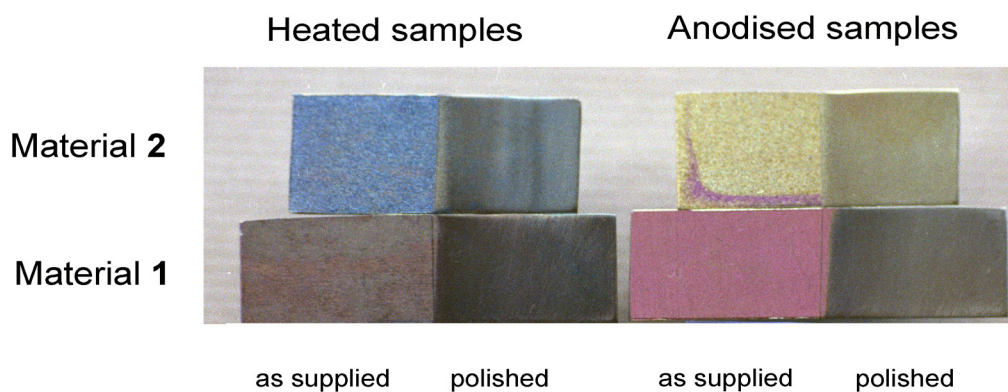
Figure 4.2: Sample set heated and anodised to get gold colour. These samples demonstrate the difficulty in producing heated colour.

It was also noted that the polished parts of the sample coupons produced different colours from the unpolished parts. The colour difference was particularly marked for material **1**, especially when it was anodised. The voltage required in order to achieve a gold colour on the polished part of the surface created a pink colour on the unpolished part of the sample coupon. These differences can be seen in the four sample coupons illustrated in Figure 4.2.

Investigation of these surfaces, reported below, revealed unusual features on the unpolished part of the surface of material **1**, when anodised. This was considered to be a possible consequence of the fact that this surface was pink, indicating a probable thicker oxide layer, and so a further two sample sets were prepared to investigate this feature using only coupons of materials **1** and **2**.

Four samples were oxidised, two heated and two anodised, with the aim to achieve a similar pink colour and four samples were oxidised to give a green colour. The preparation details are shown in Table 4.3 and the samples in Figure 4.3. The heated samples illustrate the difficulty in control of colour to this level by this method compared with anodising.

Sample	Oxidation Method	Volt or time at 700ºC	Surface finish half/half	Colour Variation
Samples coloured pink:				
1H	heat	10min	as supplied/polished	patchy
2H	heat	12min	as supplied/polished	gold/bluish
1F	anodised	87V	as supplied/polished	green/pink
2F	anodised	89V	as supplied/polished	none
Samples coloured green:				
1I	heat	15min	as supplied/polished	patchy
2I	heat	16min	as supplied/polished	patchy
1G	anodised	110V	as supplied/polished	purple/green
2G	anodised	112V	as supplied/polished	slight

Table 4.3: *Sample sets with polished and unpolished samples of materials **1** and **2** coloured pink and green.*

The surfaces of the sample sets, prepared as described above, were examined using a range of techniques commencing with visual examination and low magnification. In each case the oxidised surface was compared with the surface of the titanium sheet from which it had been prepared.

4.3.2. Visual Examination and Optical Microscopy

The human eye cannot distinguish the individual wavelengths that may form a colour, in contrast to the human ear, which does discriminate between the component frequencies of musical notes. The lack of colour wavelength discrimination is evidenced in the work of the pointillist artists who used fine points of 'pure' colour in close juxtaposition to create
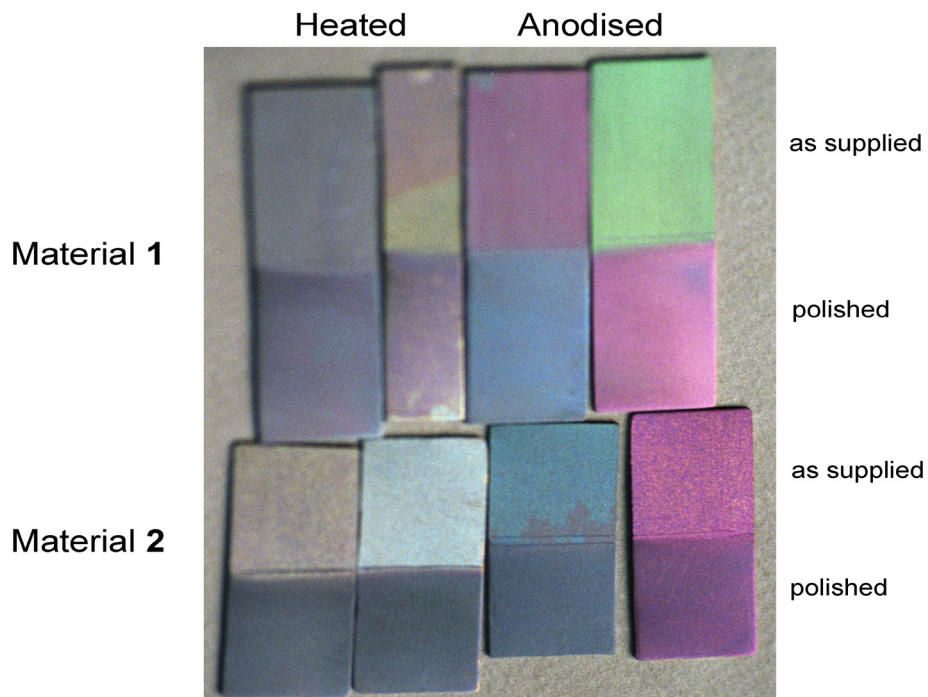
Figure 4.3: *Sample sets heated and anodised to get pink and green.*

apparent areas of different colours, and is the basis of much print media. In the case of anodised titanium, the eye integrates the colour across the surface of the oxidised metal and it is only when any discontinuities reach a particular size that differently coloured areas become apparent to the observer. Therefore visual examination with the unaided eye produces limited information about the sample sets. Following both electrochemical and thermal oxidation the samples appear to retain the different finishes of the original metal syrfaces in terms of abrasion or polish. Within the sample sets, which had been created to be of visually similar colours, it was not possible to distinguish from their external appearance which surfaces had been heated and which anodised.

As explained earlier in this chapter, commercially available titanium sheet is produced with a small grain size and such a grain structure is only visible under magnification. Examination of the oxidised surfaces under low magnification, such as with a x10 lens, reveals that the apparently uniform surface of the anodised titanium is in fact composed of small areas of differing colours. The surface resembles that of a 'shot' fabric, where lustrous fibres of different colours are used as warp and weft and woven together to create a fabric that changes colour with the angle of view. In place of the tiny areas of different colour created by the weaving process, the differently oriented grains of the crystalline titanium metal, when oxidised, provide 'dots' of different colours. This is observable with low magnification but is difficult to record with accuracy of colour using microscope-based techniques.

For most commercially available titanium metal the crystal grains are only visible at high magnification and many fall into the area of investigation between optical and electron microscopy. However some researchers have succeeded in using photography with optical microscopes to record the colour variations on anodised titanium[7].

Colour variation due to the grain structure of titanium may be demonstrated by manipulating the metal surface so that the individual grains become visible to the naked eye. This procedure known as grain-enhancement involves heating the titanium to the alpha/beta transition temperature in a vacuum and can produce fine or coarse-grained material. The technique was used by IMI to produce surface patterning on titanium sheet as reported in Chapter 1 and illustrated here in Figure 4.4.
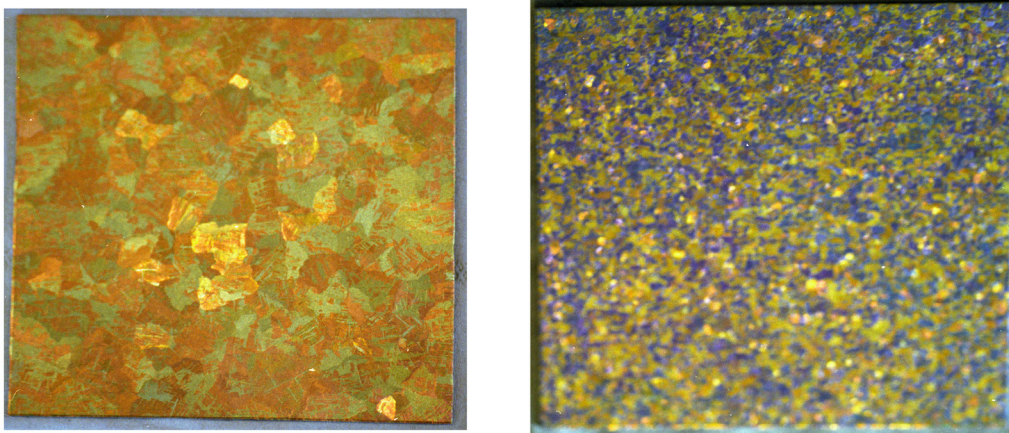
Figure 4.4: *Two examples of grain-enhanced titanium sheet, showing colour variation and different grain sizes.*

The metal grains exposed on the surface are at different orientations and the oxide grows preferentially on different crystal faces, as demonstrated by Davepon et al[8], reaching different thicknesses at different rates depending on the relative density of atoms on each face. The orientation of the hexagonal crystals of the alpha titanium varies across the surface of the metal and the growth rate of oxide on the crystal planes with comparatively low packing of atoms is higher than that of the planes with more closely packed atoms.

Although visual observation provided a comparison of the reflectivity of the different titanium surface finishes, the difficulty in recording the information obtained with optical magnification for the coloured oxidised surfaces meant that higher magnification

[7] Diamanti, MV, Del Curto, B and Pedeferri, MP, *Interference Colours of thin oxide layers on titanium,* Color Research and Application, 33, 3, 2008, p221-228.
[8] Davepon, B, Schultze, JW, Konig, U and Rosenkranz, R, *Crystallographic orientation of single grains of polycrystalline titanium and their influence on electrochemical processes*, Surface and Coatings Technology, 169-170, 85-90, 2003.

was required for detailed examination of surface structure. Therefore Scanning Electron Microscopy (SEM) was used for comparative analyses of the titanium surface finishes and the morphology of the oxidised layer and metal surfaces, to observe the changes wrought by the oxidation process.

4.3.3 Scanning Electron Microscopy (SEM)

Although the different surfaces of the titanium sheet could be visually separated into different degrees of roughness or polish, higher magnification was required to fully characterise their external surface morphology. The higher magnification, achieved by using SEM, separated the different surfaces and allowed detailed comparison between the metal surfaces and their oxidised counterparts. The first SEM examinations were carried out on a JEOL T200 electron microscope at magnifications of x350 and x2000 with features of particular interest studied at higher magnification. The results presented here analyse the four different surfaces of the sample materials oxidised by the two different methods, heating and anodising. The different microscopes used for SEM investigations of the metal surfaces and other oxidised titanium samples will be described below in the relevant sections.

Metal Surfaces

The SEM images, taken with a Hitachi S-2600N, presented in Figure 4.5, show the external surface morphology of the four different surfaces of titanium sheet used for sample preparation.

Material **2** has the typical appearance of an etched material showing the grain structure of the titanium, which is superficially removed by polishing with 1000 grade wet and dry paper as shown in the fourth image. The magnification reveals the irregularity of workshop hand polishing procedures but shows the directional nature of the process. A similar directional structure is shown for the foil **3** but in this case the surface has been achieved by rolling rather than abrasion. There is some directionality in the surface of material **1**, the scrap sheet, but it is not evident what processes it has been subjected to. Even at higher magnification as in Figure 4.6, apart from possible rolling or pressing, it is not possible to be sure of the previous history of the material but analysis in the SEM, presented as Figure 4.7, confirms that the material is CP titanium.

The analytical mode of the JEOL 5610, sampled at the point indicated on the metal surface produced only significant peaks for titanium and was confirmed by similar results obtained from other sampling points on the surface.

Material **1** scrap sheet
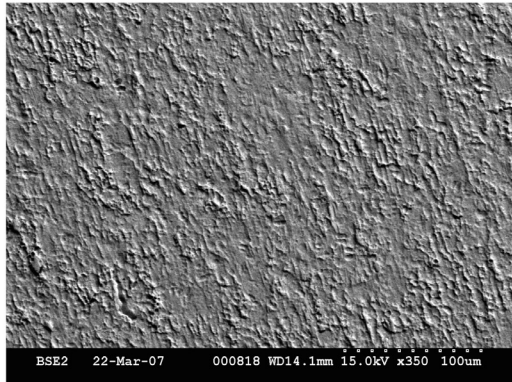
Material **2** purchased sheet
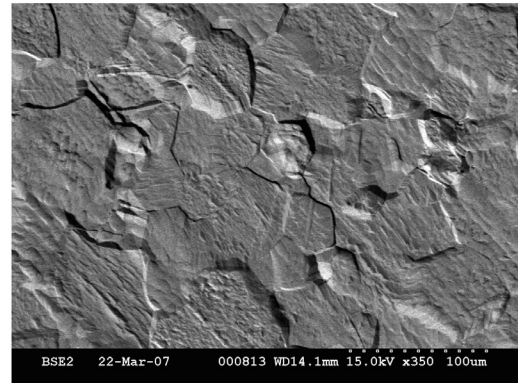
Material **3** purchased foil
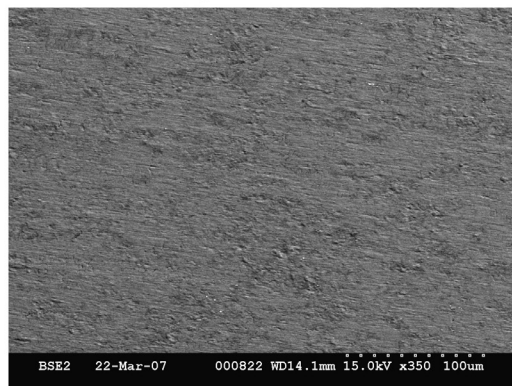
Polished material **2**
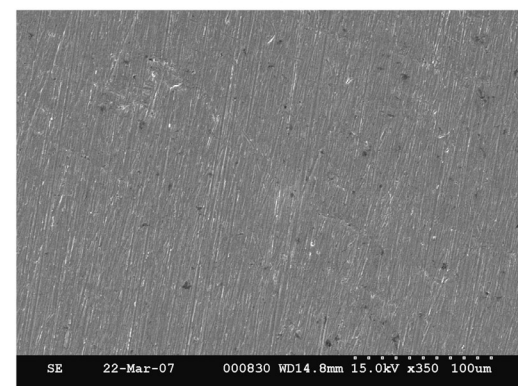
Figure 4.5: SEM images showing the morphology of the four different titanium metal surfaces used for sample preparation, at x350 magnification.
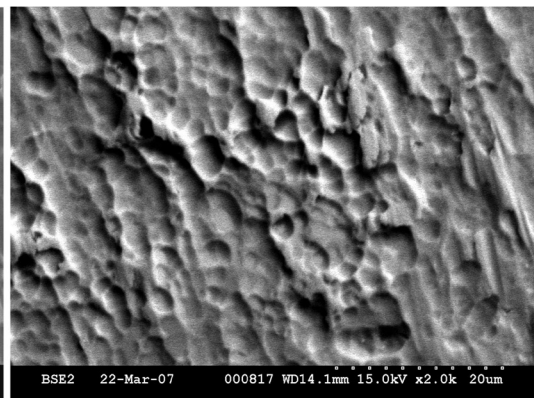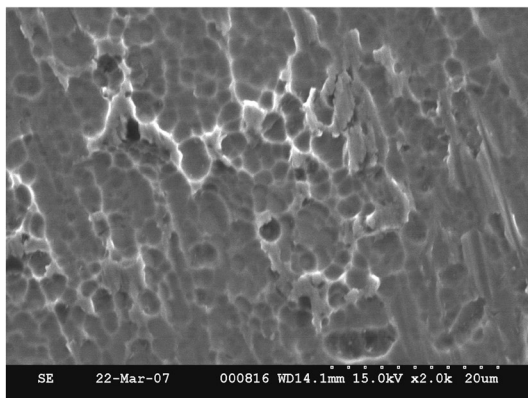
Figure 4.6: SEM images of scrap material (**1**) at higher magnification, (x2000).
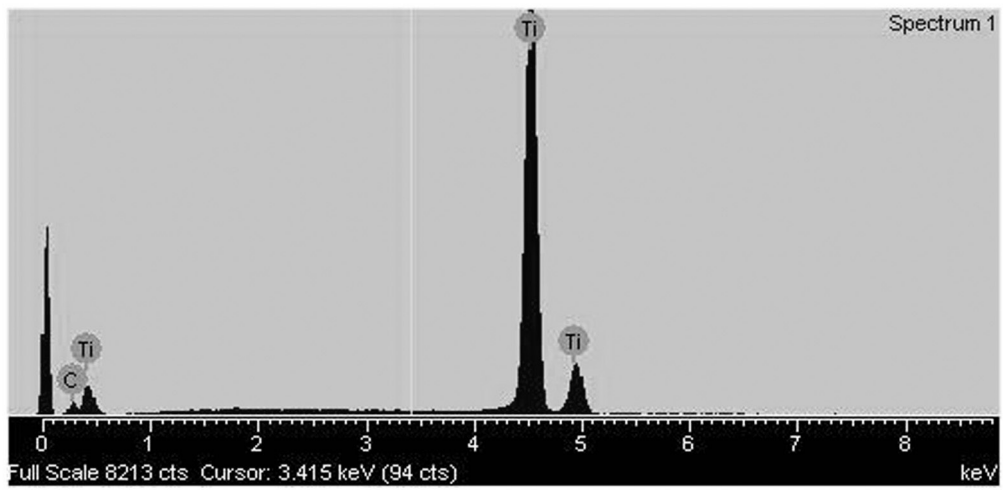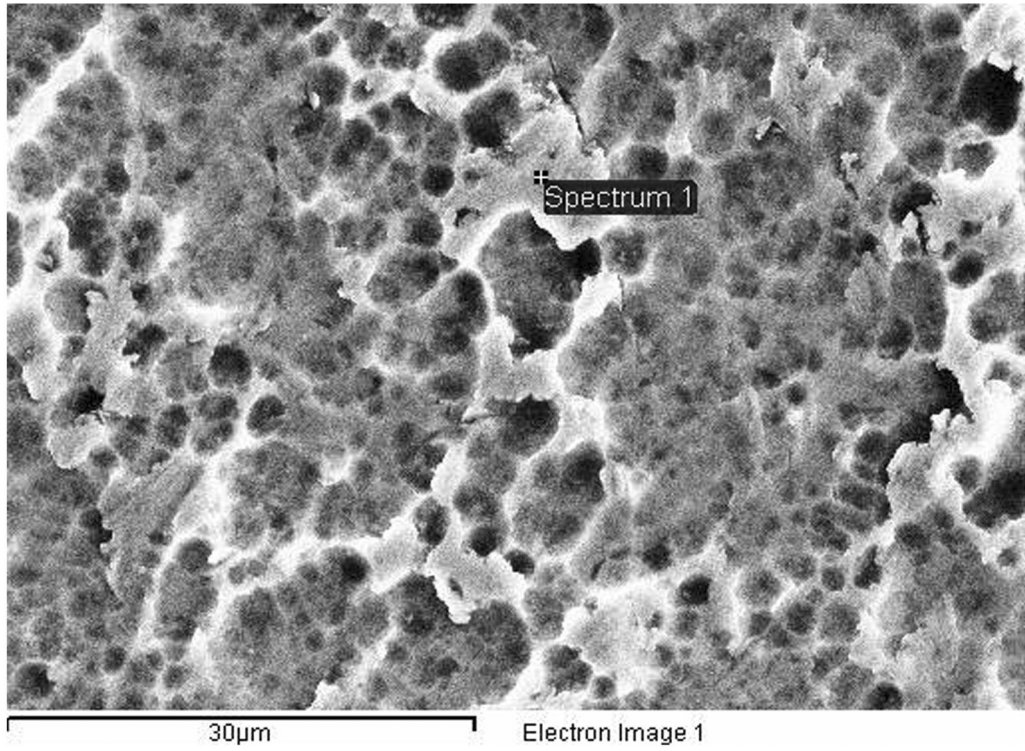
Figure 4.7: *SEM image of material 1 with analysis*

Oxidised Surfaces

The SEM images of the samples coloured royal blue are presented below. Comparison between the SEM images of the metal surfaces and the oxidised surfaces, created both by anodising and heat, show little difference in the external surface morphology either between the treated and untreated surfaces or between the two modes of oxidation carried out to produce observable blue colour. The topography of the oxide surfaces, viewed under magnification, is essentially that of the underlying metal surface as demonstrated in Figures 4.8, 4.9, and 4.10. These figures present images of the three different metal surfaces and their oxidised counterparts at the same magnification.

*Figure 4.8: SEM comparison of metal **1** and the oxidised samples coloured royal blue.*

The comparison between the abraded surfaces of materials **1** and **2** after oxidation, as presented in Figure 4.11, shows little significant difference in structure between the different samples. The surface of the oxide layers corresponded closely to the fourth surface shown in Figure 4.5 above, the abraded surface of the metal.

The SEM images recorded at higher magnification are presented for the comparison of the samples coloured gold and show that the thicker oxide layer appears to make no

Material 2

Secondary electron
SEM at x350

Titanium metal
as supplied

Samples oxidised to royal blue colour

Heated

Anodised

Figure 4.9: *Comparison between SEM images of metal 2 and of samples oxidised to blue at x350 magnification.*

Material 3

Secondary electron
SEM at x350

Titanium metal
as supplied

Samples oxidised to royal blue colour

Heated

Anodised

Figure 4.10: *Comparison between SEM images of metal 3 and of samples oxidised to blue at x350 magnification.*

Abraded examples of materials **1** and **2** oxidised to royal blue colour

Material **1**   Material **2**
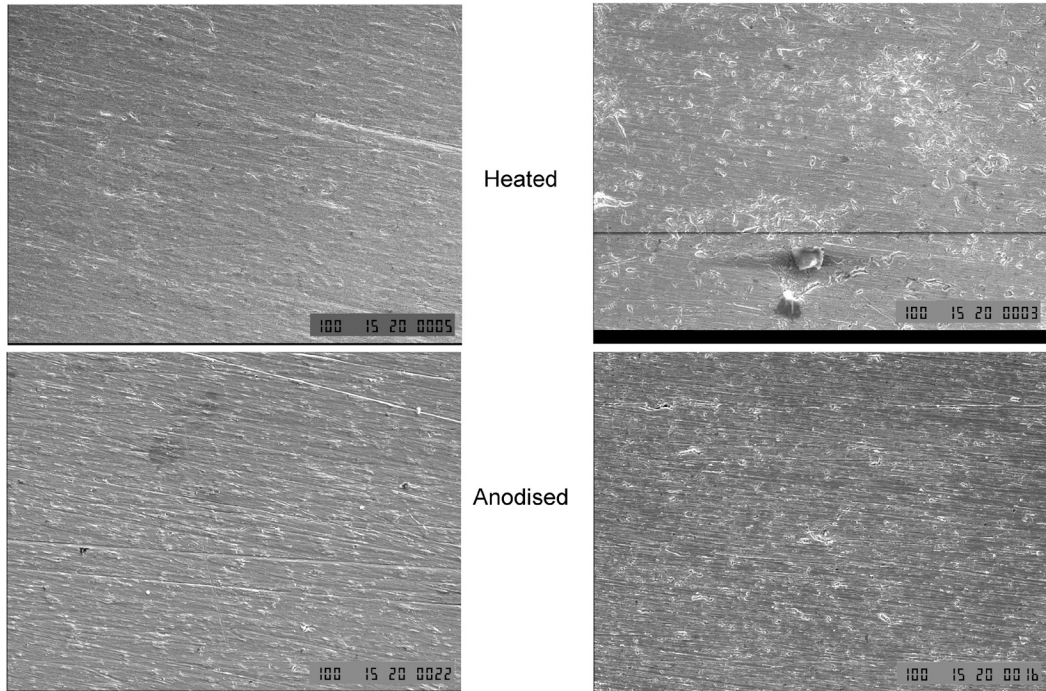
Heated

Anodised

Figure 4.11: Comparison between SEM images of abraded examples of metals **1** and **2** oxidised to blue at x350 magnification.

Material **2**

Secondary electron
SEM at x2000
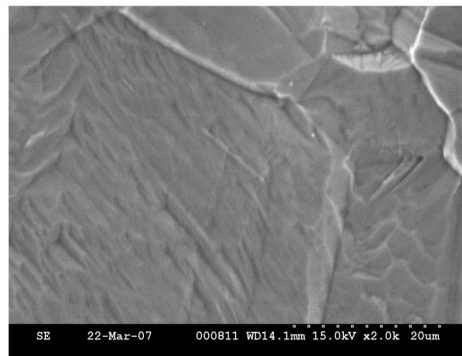
Titanium metal
as supplied

Heated   Samples oxidised to gold colour   Anodised
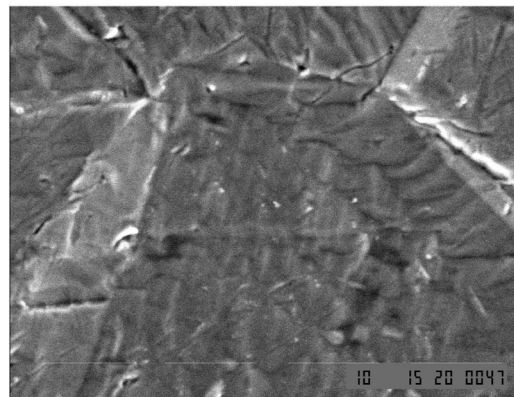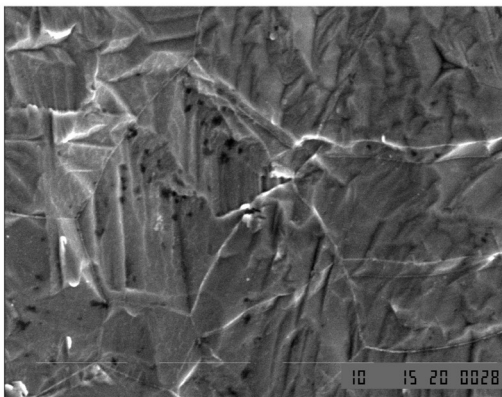
Figure 4.12: SEM images of gold samples at x2000 magnification.

difference to the surface appearance of the samples of material **2**, Figure 4.12. The surface structure of the oxide layer is essentially that of the underlying metal surface.

The SEM images of the samples of oxidised material **3** and the abraded materials **1** and **2** show no significantly different structures from those already presented in Figures 4.10 and 4.11.

However the SEM images of the oxidised samples of material **1**, Figure 4.13, record the appearance of hitherto undocumented structures. These novel structures, which have been given the designation 'Flower' oxides, were noted only on the anodised sample of

Figure 4.13: SEM images of gold samples at x2000 magnification, showing first appearance of 'Flower' oxides on pink areas.

material **1**, and are discussed in greater detail below.

As previously stated, it was speculated that the 'Flower' oxides were the result of the thicker oxide layer, evidenced by a 'higher' colour, on the unpolished, anodised part of the sample coupon of material **1**. In order to test this assumption a further sample set, see Table 4.3 above, was prepared to a similar pink colour appearance as the parts of the sample coupons where the 'Flower' oxides had been observed. Examination of these samples established that, contrary to expectations, the samples of materials **2** and **3**, when oxidised to achieve similar colours did not show this form of oxide. Whereas, as can be seen in the SEM images in Figure 4.14, 'Flower' oxides of differing sizes, perhaps indicating various

stages of formation, appeared in greater profusion on the unpolished part of sample **1G** which had been anodised to 110V. However the polished part of this sample showed 'coral-

SEM images at increasing magnification of anodised sample of material **1**

x350
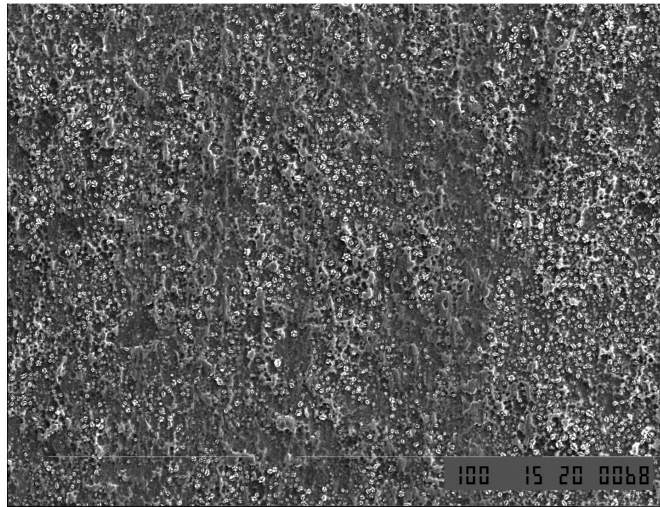
x2000
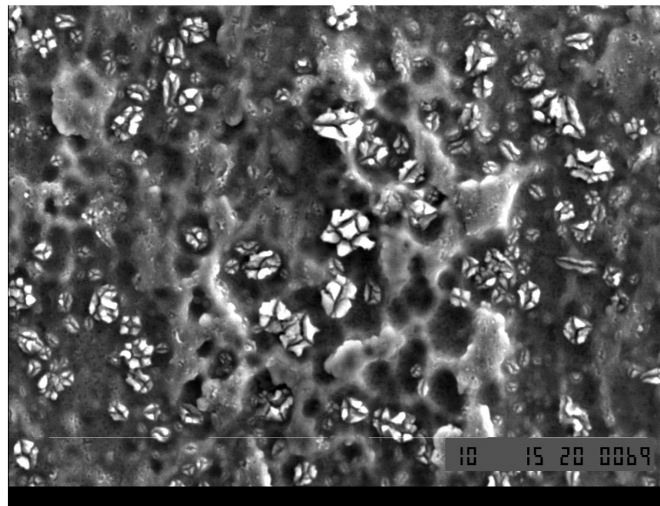
x10000
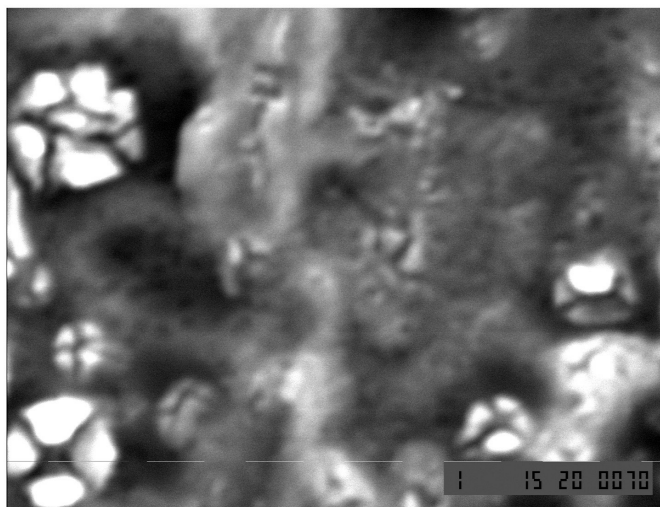
Figure 4.14: SEM images of unpolished sample of material **1,** anodised at 110V, showing a substantial number of 'Flower' oxides.

like' colonies of oxide as described below.

For all the other samples of titanium sheet, whether as supplied or polished, little oxide structure is discernible under SEM on the surface of any of the heated samples, including those heated for up to 20 minutes at 700⁰C. The heat-coloured samples **1H** and **2H** did not show any particular features that indicated anything other than the underlying metal surface structure.

For thicker oxide layers achieved by anodising at voltages over 100V all the titanium surfaces produce a porous coral–like structure. This is demonstrated for the polished half of

SEM images at increasing magnification of anodised polished samples of material **1**

x350
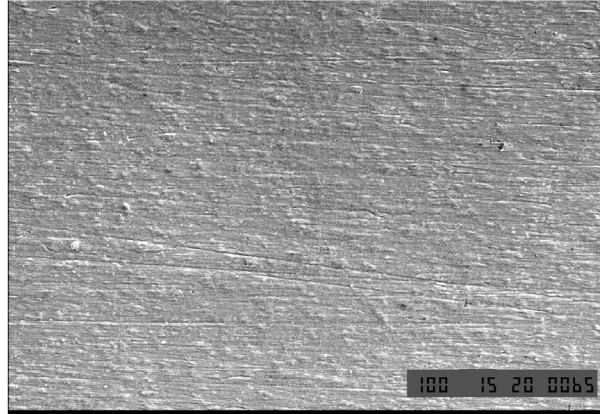
x2000
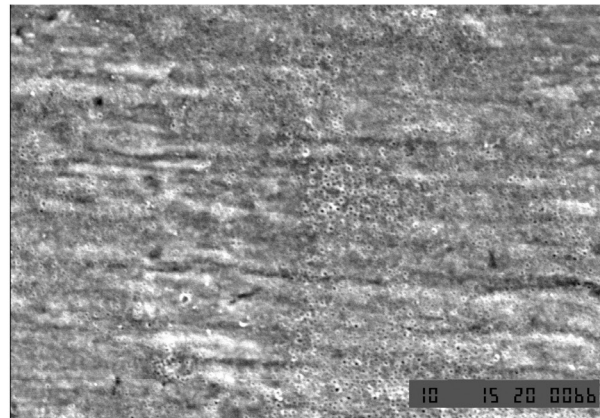
x10000
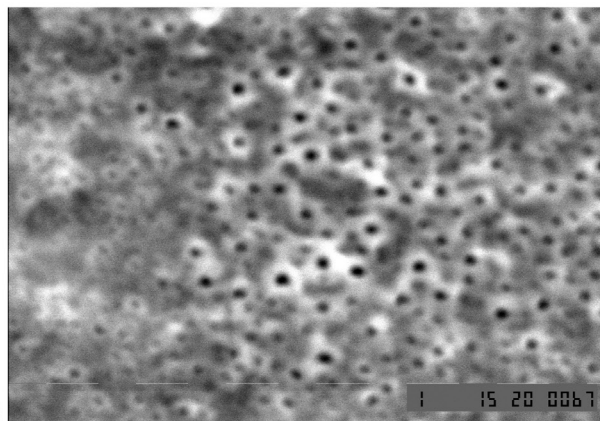
Figure 4.15: *SEM images of polished material **1** anodised to 110V showing thick oxide structure.*

the sample of material **1** anodised at 110V, shown in Figure 4.15.

A similar structure is also observed on both material **1** and material **2**, when the unpolished titanium is anodised at high voltages, Figure 4.16. The structures, which appear to show porous columnar growth, range up to 800 nm in diameter[9] with central pore sizes ranging from 100 to 300 nm in diameter, Figure 4.17. However the colour observed on this

SEM images of thicker oxide layer surfaces

Material 1 anodised at 110V

x10000
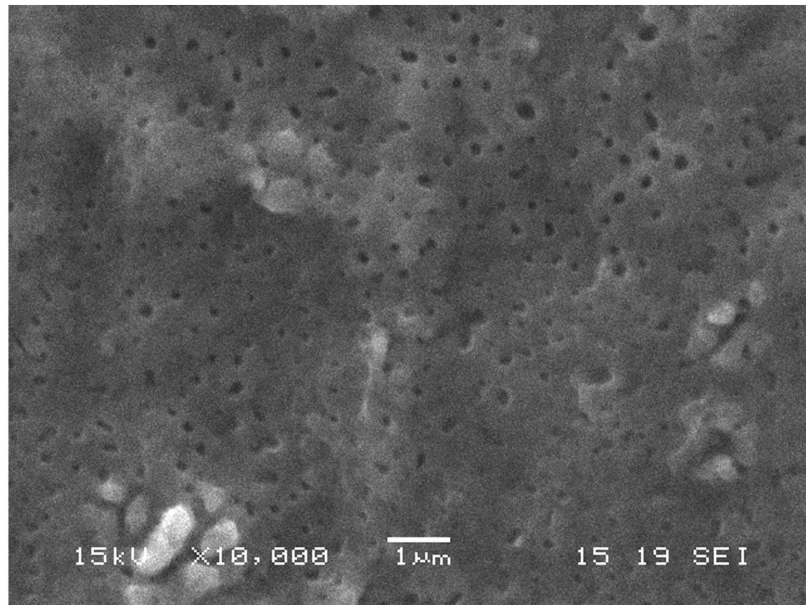
Material 2 anodised at 115V

x5000
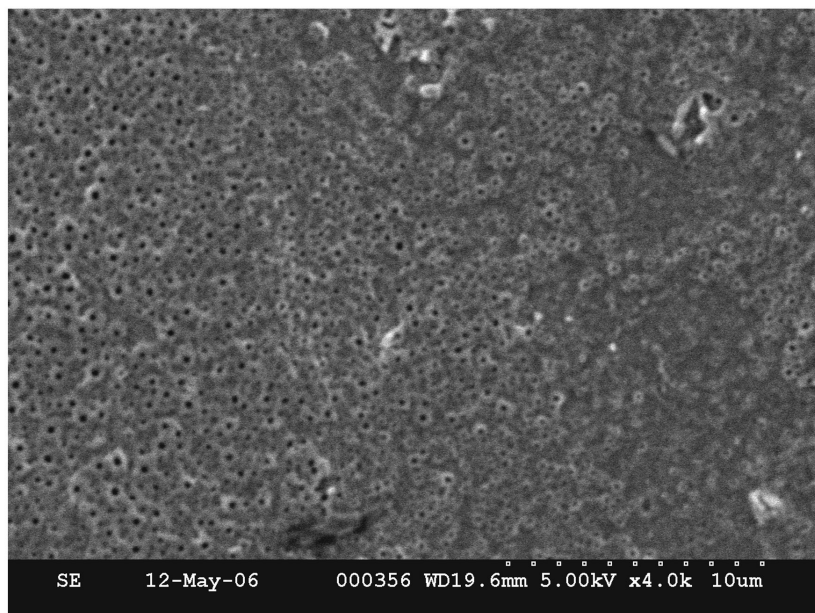
Figure 4.16: SEM images showing 'coral' type oxide structure on unpolished material **1** anodised to 110V and unpolished material **2** anodised to 115V.

[9] Measurements on the image are made using Image J software for details see Chapter 5, p 177.
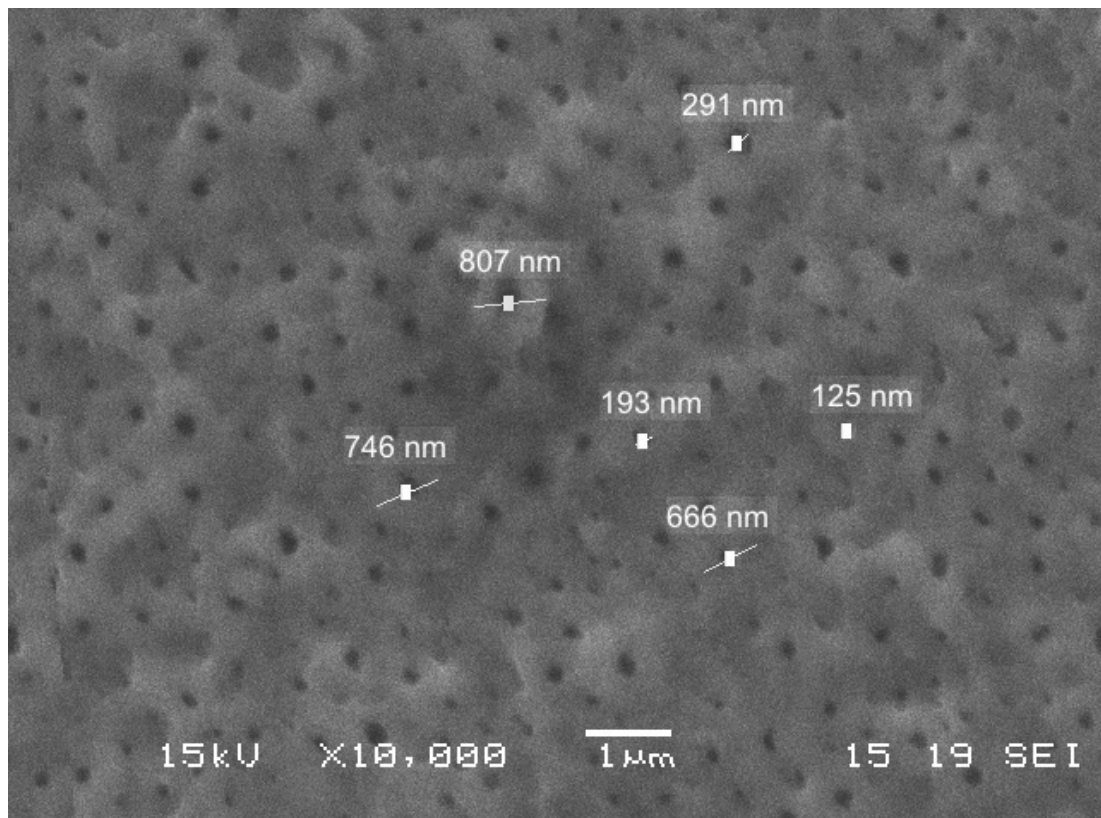
Figure 4.17: *SEM of polished sample of material 1 anodised at 110V showing 'coral-like' structure.*

material tends towards a greyish hue indicating that the oxide thickness has reached the limit for interference colour on these materials. In addition the apparent porosity of the surface structure reduces the reflectivity thus affecting the interference colour.

'Flower' Oxides

The phenomenon of 'Flower' oxides, mentioned briefly in the previous section, was first observed during the SEM examination of the sample set of titanium sheet oxidised, as described above, to a gold colour. The 'Flower' oxides appeared on the unpolished half of sample coupon **1D**, which was anodised at 55V, Figure 4.18.

The other samples anodised to pink, **2F** and the polished part of **1F** did not exhibit 'Flower' oxides but only fine nodules of oxide. However the unpolished part of **1F**, which had been anodised to a bright green, showed 'Flower' oxides scattered all over the surface with a an apparent 3-dimensional structure. Thus suggesting that the phenomenon was an attribute of the scrap titanium sheet when it was anodised.

In order to investigate this unexpected phenomenon a set of samples was prepared and examined by SEM to establish the voltage at which 'Flower' oxides were first generated on the titanium sheet designated material **1**.

The sample set consisted of twelve coupons of titanium sheet **1**, as supplied, which were anodised at intervals of 5V from 25V to 80V. The samples are shown in Figure 4.19 and
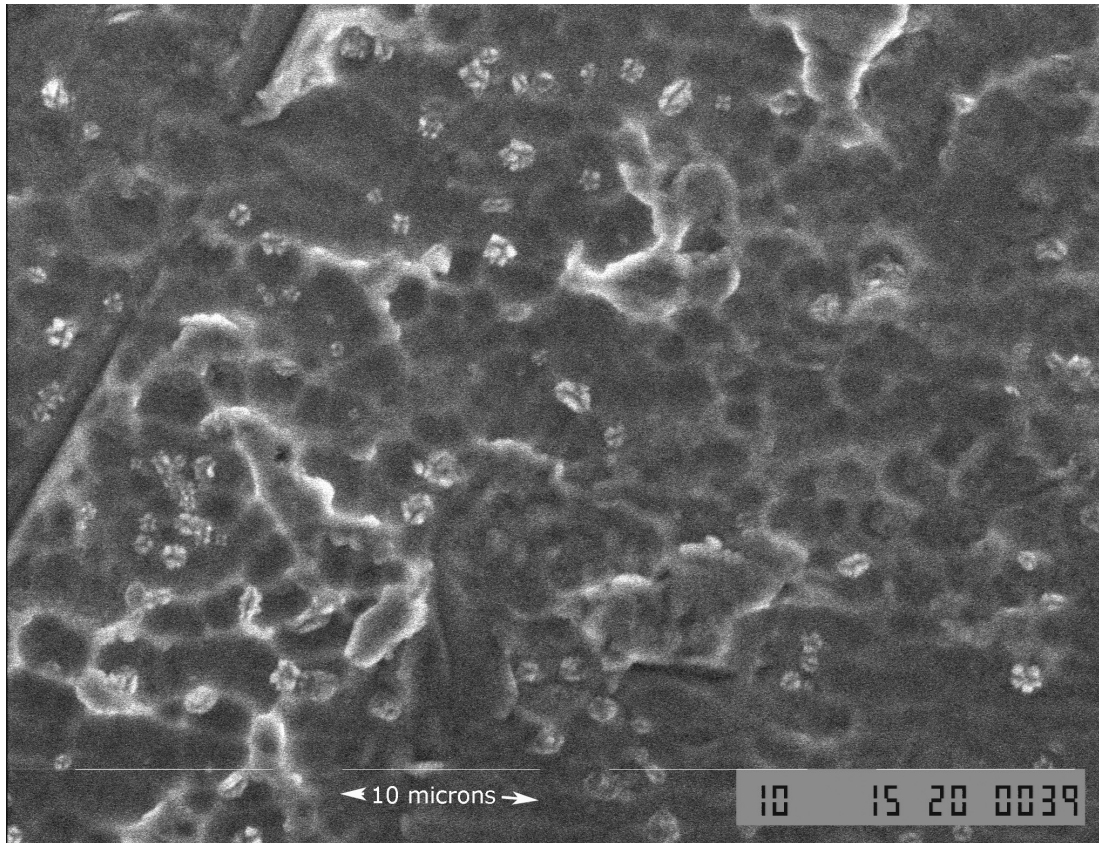
Figure 4.18: *SEM of first appearance of 'Flower' oxides on sample of material **1** anodised at 55V, (x2000)*

Table 4.4 summarises the visual appearance of the individual coupons.

Sample	Surface finish	Voltage (V)	Colour	L*, a*, b* Co-ordinates
1J	as supplied	25V	Cyan blue	48.14, -8.59, -20.8
1J	as supplied	30V	Pale turquoise	56.38, -8.12, -10.8
1J	as supplied	35V	Silver	65.54, -8.14, -3.43
1J	as supplied	40V	Pale gold	64.21, -5.76,10.97
1J	as supplied	45V	Yellow	61.3, -4.44, 25.83
1J	as supplied	50V	Gold	60.6, -0.51, 31.87
1J	as supplied	55V	Orange gold	65.81, 7.9, 6.18
1J	as supplied	60V	Pink	49.73, 26.84, -11.98
1J	as supplied	65V	Mauve	45.57, 13.51, -17.37
1J	as supplied	70V	Blue/gold patches	84.27, 0.69, -3.74
1J	as supplied	75V	Turquoise	51.19, -14.98, -15.27
1J	as supplied	80V	Green	54.46, -14.39, 4.69

Table 4.4: *Details of the sample set of material **1** prepared to examine the genesis of 'Flower' oxides.*

The SEM images presented in Figure 4.20 show the development of 'Flower' oxides proving that while none were visible on the sample coupon anodised at 25V, just one or two 'Flower' oxides were visible at x10,000 magnification on the sample coupon anodised to 30V. The 'Flower' oxides increased in profusion on the sample coupons of material **1** as the anodising voltage is increased.
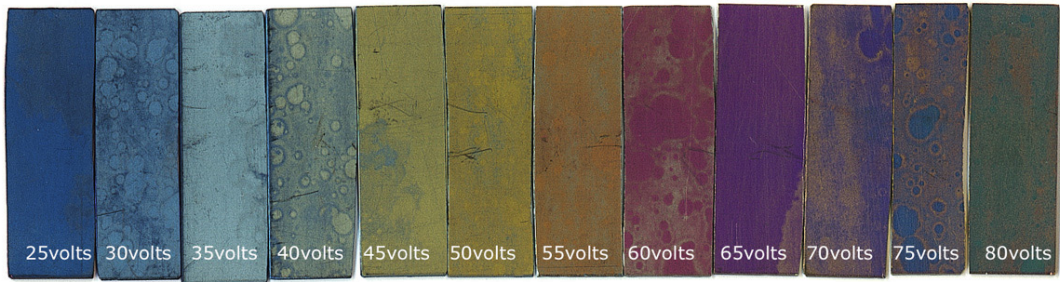
Figure 4.19: *Unpolished samples of titanium **1** anodised at 5V intervals from 25V - 80V.*

Scrap CP titanium, unpolished, anodised at various voltages. SEM images at x10000

lbti090
25v

blue

lbti099
30v

pale
blue

lbti091
35v

silver

lbti089
40v

pale
gold

lbti087
55v

dark
gold

lbti096
75v

blue/
green

lbti058
87v

green

lbti070
110v

purple
/pink
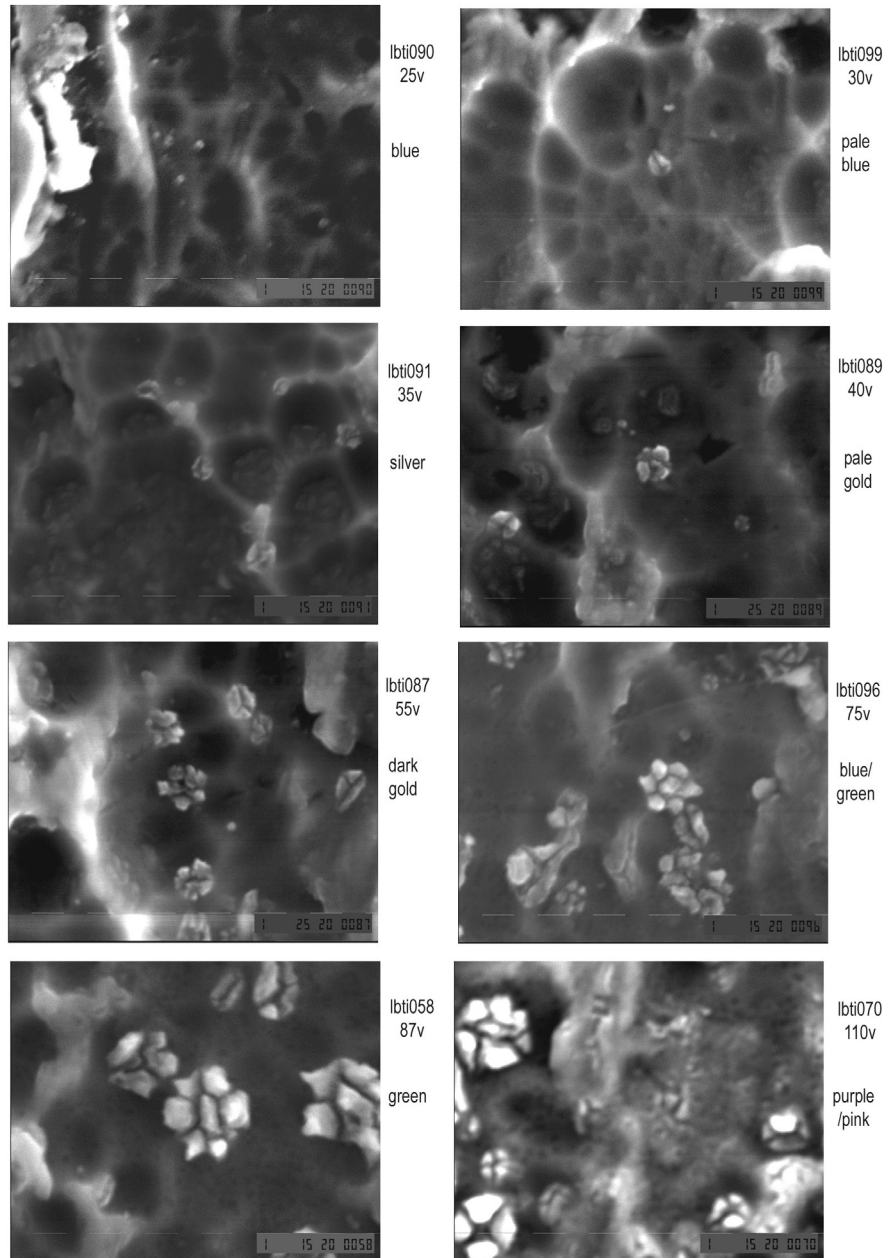
Figure 4.20: *SEM of scrap titanium showing development of 'Flower' oxides with increasing voltage.*

The possibility that the 'Flower' oxides were an artefact created by the anodising equipment was tested by using an alternative anodiser. Two new sample coupons of material **1** were prepared and anodised using the same electrolyte solution with a different anodiser. The samples, designated **1K**, were anodised to two different voltages, 89V and 110V respectively and examined by SEM using a JEOL 5610. Figure 4.21 shows that the 'Flower' oxides are randomly distributed across the surface and not associated with any noticeable features of the surface structure. The sizes of the individual 'Flowers' range from 700 nm to over 2 microns in diameter, as shown[10].
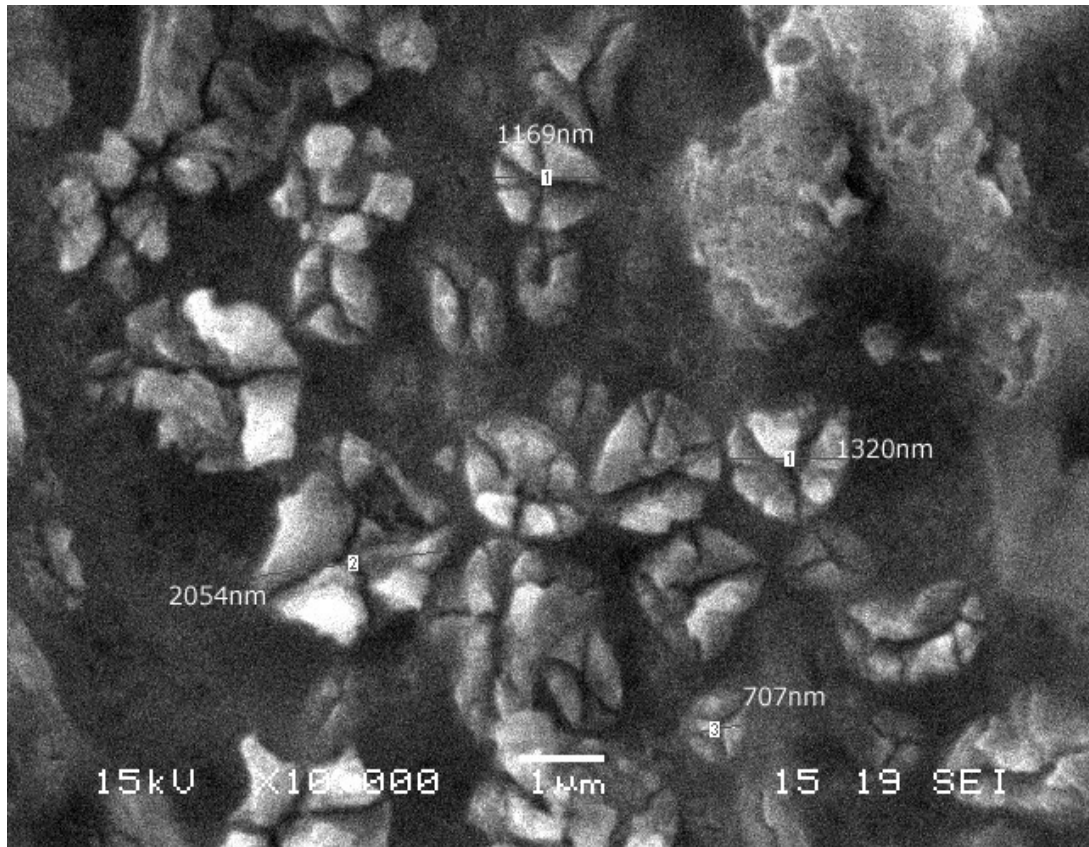
Figure 4.21: *Material **1** anodised to 89V using different anodiser and different SEM, annotated to show size of 'Flower' oxides.*

This small sub-set of experiments confirms that the 'Flower' oxides are a reproducible property of titanium sheet **1** when it is anodised above 25V and not an artefact of the anodising equipment.

'Flower' oxides on other Titanium Sheet

Although the phenomenon of the 'Flower' oxides was established as being associated with material **1** when it was anodised, the evidence that such oxide growths could be observed occasionally on other titanium sheet, as shown in Figure 4.22, meant that all other sample coupons of anodised titanium sheet were scanned by SEM for similar

[10] Measurements made using Image J software.

structures.

Magnification x2000

Magnification x10000
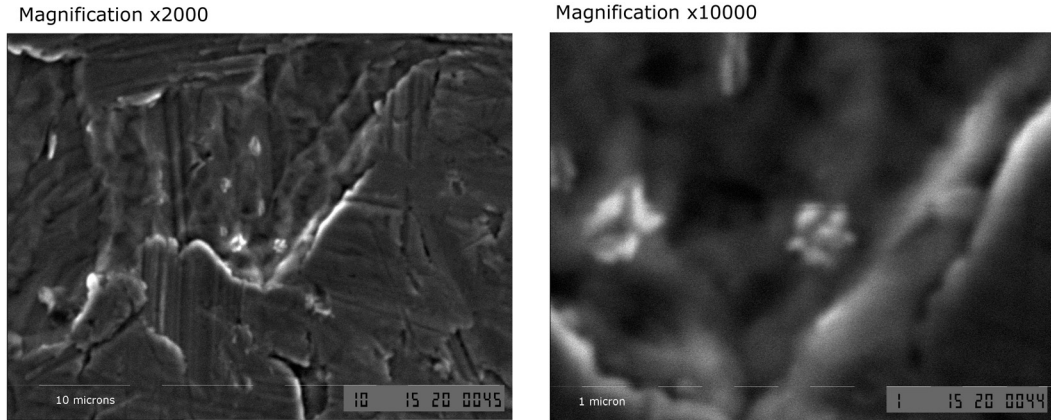
Figure 4.22: *Appearance of 'flowers' on material **2** anodised to 61V at magnifications of x2000 and x10000.*

Also included in these investigations were the two sets of anodised samples prepared by third parties introduced in Chapter 3 as part of the colour measuring exercise. As with colour measuring, the SEM examinations are non-destructive. The first of these additional sets was the workshop colour comparative set, which had been prepared in the early 1990s and was designated **CSM**. The second additional set was a chart of sample coupons of anodised titanium sheet, distributed by a Japanese manufacturer, which was designated material **H**. These two additional sets expanded the range of titanium surface finishes as material **CSM** was more heavily etched than material **2** and material **H** had a brightly polished surface. Before considering the oxidised material, the structure of the two new metal surfaces was established as shown in Figure 4.23.

Material **CSM** etched sheet

Material **H** sample sheet
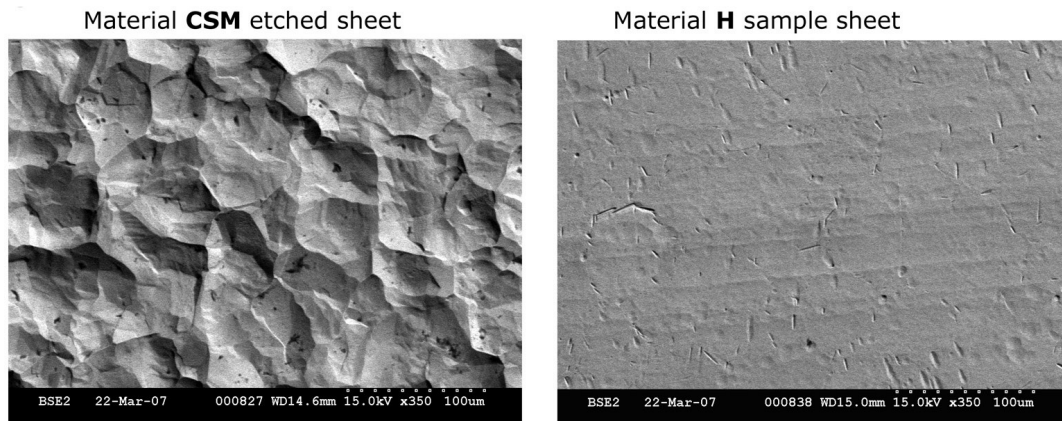
Figure 4.23: *SEM images of additional titanium metal surfaces, materials **CSM** and **H**, x350.*

The examination of the underlying titanium sheet, material H that had been used to prepare the second sample set was straightforward in that a coupon of the unoxidised titanium metal was included in the set. However no sample of the unanodised titanium sheet that had been used to create the CSM sample set was available. Bearing in mind

that all titanium metal develops an air-formed oxide layer almost immediately any fresh titanium surface is exposed to air, the assumption was reasonably made that the thickness of an oxide layer produced by anodising at 5V, ca 10 nm, was of an order of magnitude of the thickness of the natural oxide layer. Therefore, for comparative purposes, the sample anodised to 5V was considered to be representative of the etched metal surface.

The SEM image of the surface of the **CSM** sample coupon anodised at 5V , which had produced a barely perceptible yellow tint, shows the granular structure expected for highly etched metal. The image of titanium sheet **H,** which has a bright polished finish, shows some directional structure overlying an etched surface.

When looking for the presence of 'Flower' oxides on anodised materials other than material **1,** it was considered that the materials with thicker oxide layers would be those most likely to show the phenomenon. Therefore the CSM sample with the thickest oxide layer (anodised to 90V) was examined by SEM. This showed the expected granular structure for etched material as had been observed on the 5V anodised sample. There were also a few 'Flower' oxides. However examination of the sample anodised to 70V showed no 'Flower' oxides. The SEM images of both these sample coupons are presented in Figure 4.24.

CSM/90v sample at various magnifications
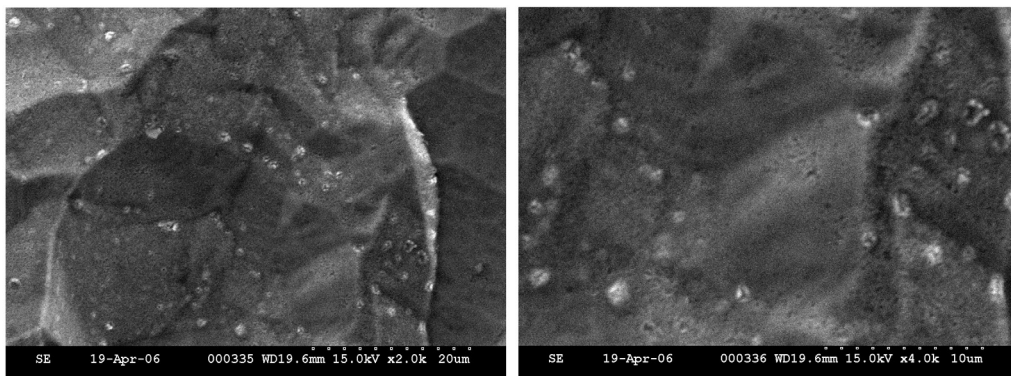
CSM/70v sample
no 'flowers'

Figure 4.24: *SEM showing 'flowers' on CSM material anodised to 90V but not on that anodised to 70V.*

The implication from this observation is that the 'Flower' oxides could either be produced when higher voltages are used or that a particular thickness of oxide is needed on this material for 'Flower' oxides to develop.

Although as demonstrated above a few 'Flower' oxides had been observed initially on one sample of material **2**, this had not been replicated on any of the other samples of this material. Having now observed the 'Flower' oxides on another form of oxidised titanium sheet, it was decided to re-examine sample coupons of material **2** that had been anodised to higher voltages in greater detail. The images in Figure 4.25 show possible 'Flower' oxides and also an underlying porous structure that has been observed on other samples anodised to high voltages as discussed above.

Sample 2J/90v

Sample 2G/112v

Sample 2J/115v
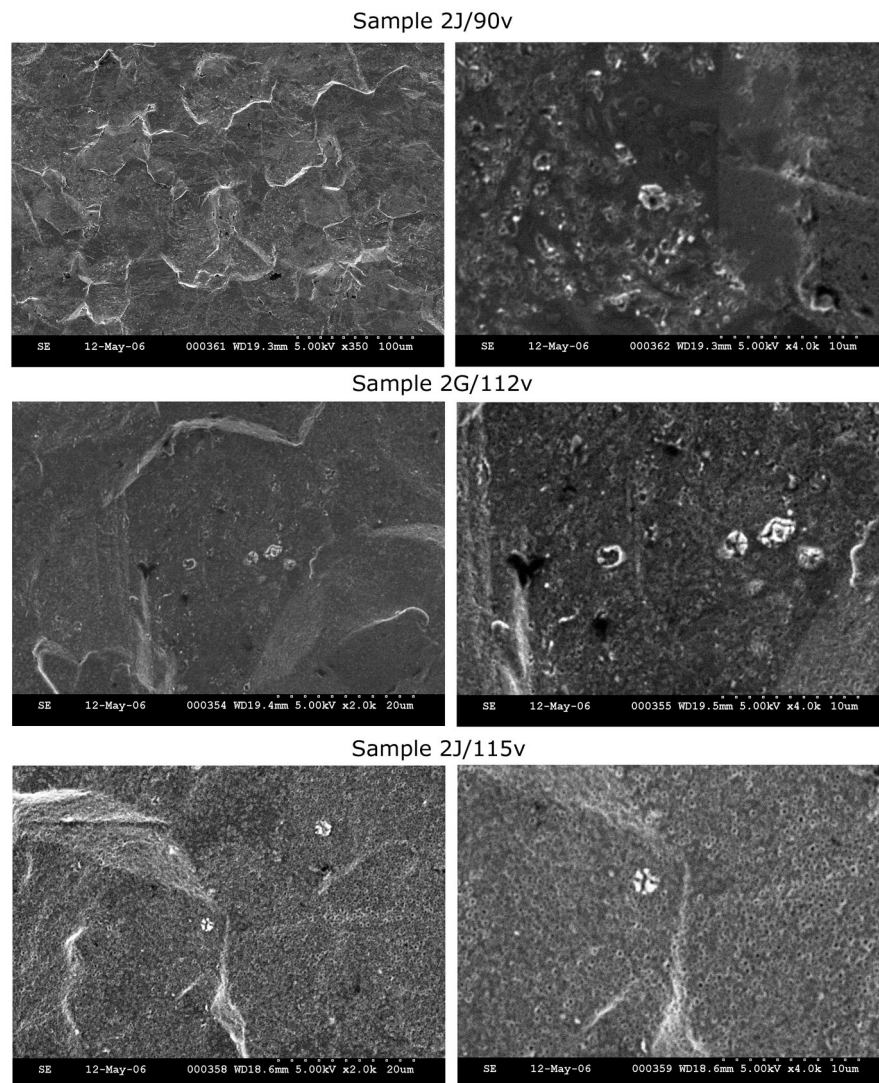
Figure 4.25: SEM images of material **2** showing just a few 'Flower' oxides on samples anodised at high voltages.

This work shows that 'Flower' oxides are not only produced on the scrap CP titanium of

unknown origin, material **1**, but may develop at higher voltages on other forms of titanium sheet but in much less profusion. They do not appear on the abraded or polished surfaces. The presence of 'Flower' oxides does not appear to influence the colour appearance of the material. An explanation of this observed phenomenon might be that the presence of nucleation sites results in inhomogeneous crystal growth. The further investigation of 'Flower' oxides needed to elucidate their genesis and structure are projects for further study.

   Summary

   The SEM enabled detailed examination of the surface morphology of six different surface finishes for titanium sheet that might reasonably be used or created by a jeweller. The six surfaces included the four chosen metal surfaces, which were oxidised by two different methods as part of the experimental programme, and two additional different metal surfaces, which had been anodised by third parties. The SEM examination of the surfaces of the oxides created on these metals showed that there was little observable difference between the surfaces of the oxidised layers compared with the surfaces of the underlying titanium metal. The exceptions were the porous oxide structure created by anodising at high voltages and the presence of 'Flower' oxides, which were particularly evident on material **1**.

   The speed at which an oxide layer grows on titanium metal when it is anodised is influenced by the surface roughness of the metal. This behaviour of the metal was recorded early in the literature[11] and has been observed in the experimental work carried out during the course of this project. A technique was therefore needed to quantify the texture or roughness of the differing surface finishes. White Light Interferometry was selected as a suitable technique for the examination and comparison of the topography of the six untreated titanium surfaces and the corresponding oxide surfaces.

4.3.4 White Light Interferometry

White Light Interferometry (WLI*)* is a microscope-based technique often used by manufacturers to measure fine surface textures as part of the manufacturing control process. A significant component of surface texture is the roughness, usually inherent in the manufacturing process, which is a measure of the structure at right angles to the plane of the surface. WLI is a technique that '*creates topographical height data from interference signals produced when white light is reflected off of a surface and interfered with the light reflected off of a high quality reference surface.'[12]* Data is recorded digitally and may be analysed in the instrument's software or with a separate software package. An image of

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[11] Hass, G, *Vacuum,* 2, 331, 1952.
[12] Metropro Films Analysis Application, Zygo Corporation Literature. USA

the surface is produced with the heights scaled in colour centred on zero. WLI is also a non-contact and therefore non-destructive method for examining the surface topography of a sample and hence a useful technique for the examination of the fine surface features of the titanium and oxide surfaces[13].

A Zygo Corporation NewView 200 White Light Interferometer, Figure 4.26, was used to examine the surfaces of samples of titanium metal with different surface finishes and oxidised examples of each of the different surfaces.

The objective of these measurements is to establish if there is any correlation between the roughness or texture of a surface and the rate at which the energy input, in terms of electricity or heat, was converted to the growth of the thickness of the oxide layer.

Figure 4.26: *Zygo Corporation NewView 200 white light interferometer at IC. (photo courtesy of Helena Tellez)*

Surfaces Compared

As the technique is non-destructive, it was possible to use samples that had been prepared for other tests and sample coupons from third parties. The six different examples of titanium sheet, as described above, namely: scrap of unknown origin **1**, commercially available etched sheet **2,** commercially sourced foil **3,** sheet **2** mechanically abraded with 1000 grit polishing paper, commercially produced titanium **H** and a sample designated **CSM** anodised to 5V, considered to be representative of the metal, were all examined.

Representative oxidised examples of these six different titanium metal surfaces were selected for the surface measurements. The samples chosen for these measurements were those with a reasonably thick oxide layer, which in all cases produced a pink/purple surface colour appearance with maximum absorption around 500 nm. Figure 4.27 records the absorption spectra for these samples. The majority of the oxidised samples were prepared by anodising but heated samples of material **2**, both polished and as supplied, were also

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[13] Reprodceability and reliability of WLI measurement and analysis is discussed in NPL_Guide to WLI.pdf produced by the National Physical Laboratory asNational Measurement Good Practice Guide No. 108.

included to extend the comparison.

The theoretical thickness of such an anodised layer with maximum absorption at 500 nm, calculated from the formula derived in Chapter 3 and assuming the titanium dioxide to be in the form of anatase, is ca 150 nm.
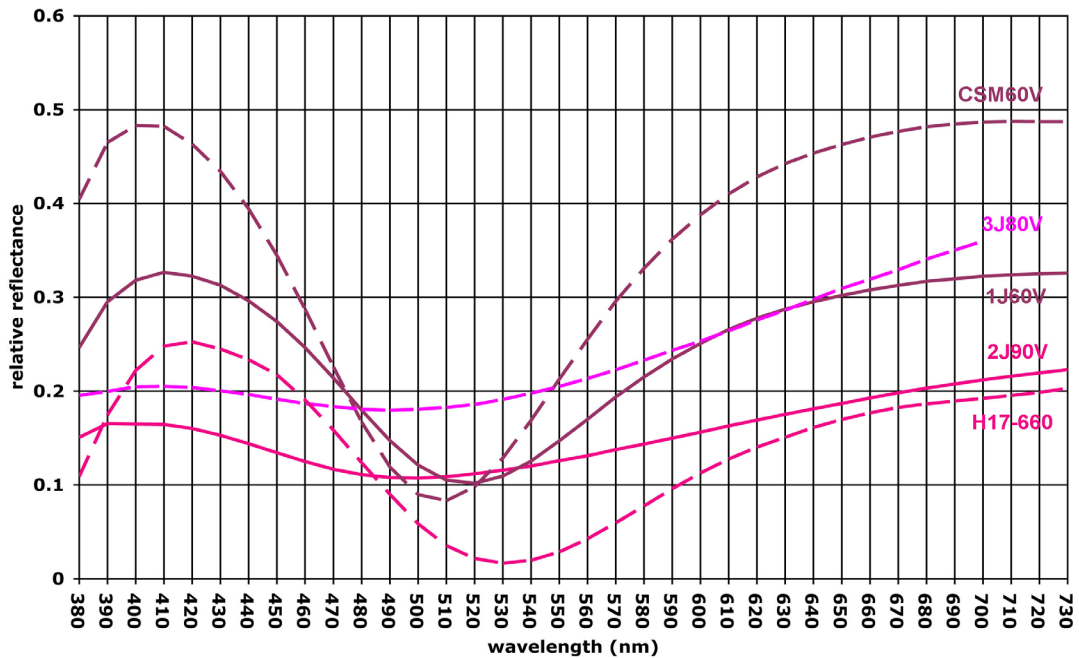
Figure 4.27: *Comparison of relative reflectance spectra of anodised samples used for Zygo investigations.*

- Sample **1J60V** maximum absorption at 520 nm
- Sample **2J90V** maximum absorption at 500 nm
- Sample **3J80V** maximum absorption at 490 nm (measured using a different spectrophotometer but this does not affect the wavelength of maximum absorption)
- Sample **CSM60V** maximum absorption at 510 nm
- Sample **H17-660** maximum absorption at 530 nm

Although the anodised samples showed similar colours, indicating a similar thickness of oxide layer they had been prepared by anodising at substantially different voltages to achieve these results. Both the **CSM** and **H** samples had been etched with a hydrofluoric acid mixture prior to anodising. In addition to these samples, measurements were made on two of the half-abraded sample coupons of material **2** that had been prepared for the SEM analysis as reported in the previous section. The colour of these sample coupons was not measured but that of sample **2F89V** was visually assessed as close to sample **2J90V.** The heated sample coupon **2H** showed a pinkish/grey on the polished part.

   Measurements

The basic result produced by the instrument is an optical micrograph of the surface under magnification, which is recorded as a topography map or image of the surface with the heights scaled in colour. A magnification of x25 was selected giving a field of view of 294 microns by 221 microns in area, which produced a good representation of the surface features of each sample. From the additional options within the Zygo programme, alternative views of the surface map; the solid plot, the profile plot, the oblique plot and the bearing ratio distribution plot were selected to highlight different aspects of the surfaces as discussed below. These five plots are illustrated below with examples from the measurement of the titanium sheet, sample **1**.

The solid plot, Figure 4.28, records the image that would be seen through the microscope, at the magnification selected, allowing continuity to be established with previous examinations. However, as the magnification is substantially below that

Figure 4.28: Solid plot for titanium metal **1**

of the previously discussed SEM data, little additional information is obtained from this plot for the majority of samples.

Figure 4.29 shows the more informative basic result from the instrument, the
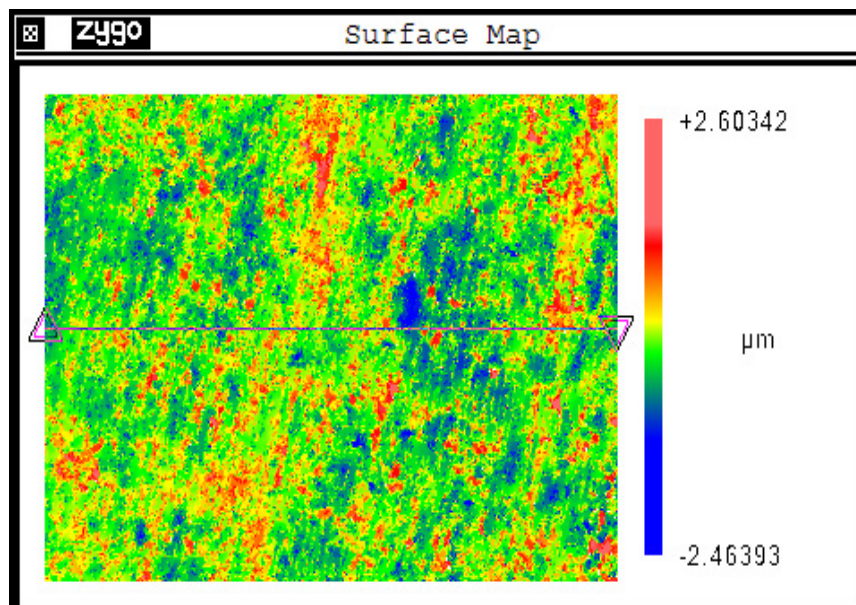
Figure 4.29: Topography map of 294 x 221 micron area of sample of titanium metal **1.**

topography map of the surface area with the height scaled in colour, centred on zero.

The profile plot, Figure 4.30, records the height distribution across the surface of the sample in a straight line, shown on Figure 4.29. It is a representation of a cross section of the surface at this particular direction. The height scale is selected within the programme and varies between samples.
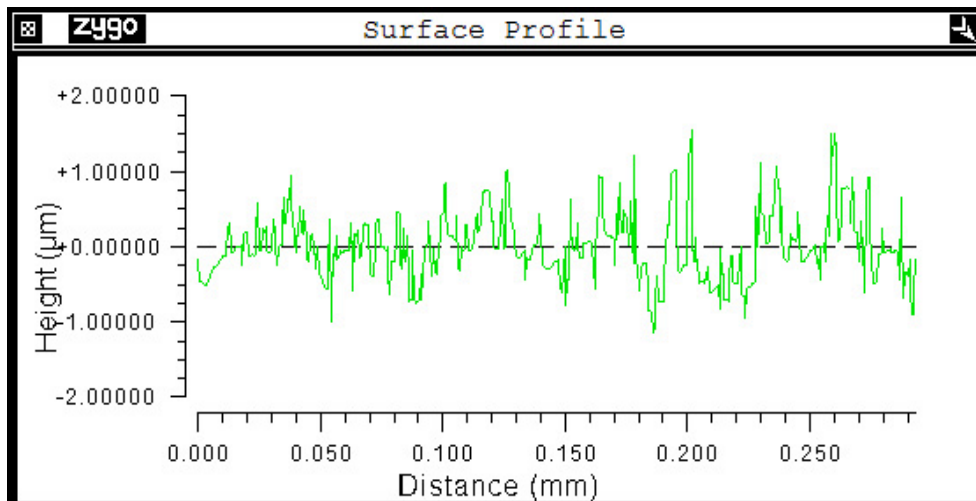
Figure 4.30: *Profile plot for titanium metal* **1**

An alternative view of the surface plot is the oblique plot, which is a 3-D image of the topography map, Figure 4.31. This plot gives a visual indication of the height distribution across the surface map but a detailed analysis of the measured data is best achieved by consideration of four moments height distribution, available within the programme of the
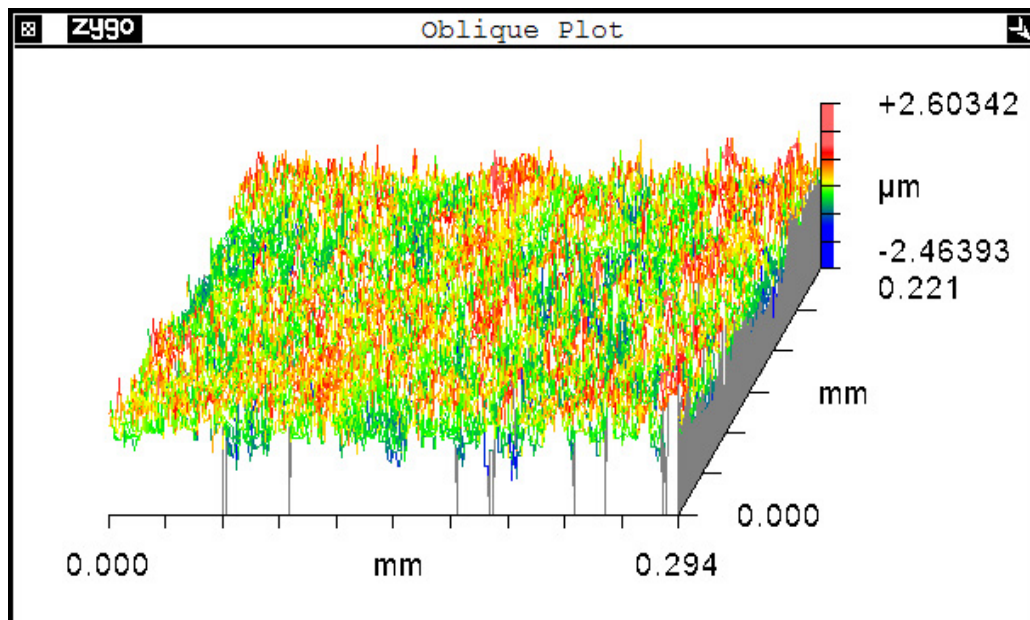
Figure 4.31: *Oblique plot for titanium metal* **1**
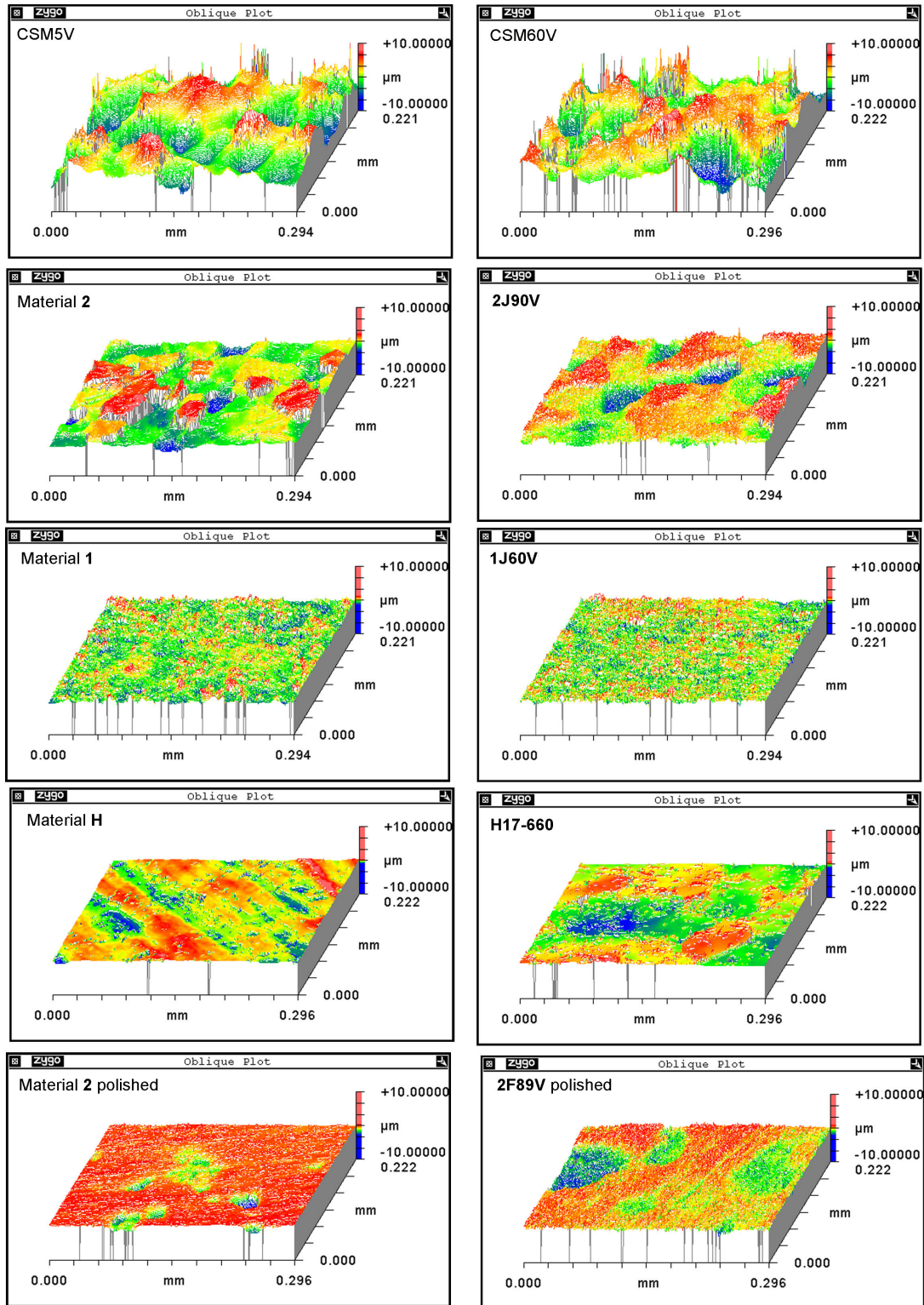
Figure 4.32: *Zygo oblique plots comparing metal and oxidised surfaces for five different surfaces and four different metals.*

instrument, as discussed below.

Although, as stated above, the height scale is usually selected automatically within the programme of the instrument, it can be adjusted so that all the data is plotted on the same scale, thus aiding comparison. An example of this is given in Figure 4.32, which presents the oblique plots for a selection of metal and oxidised surfaces, with a scale set to +10 microns to –10 microns.

This comparison shows that the surfaces of the titanium sheet can be clearly differentiated with **CSM** material showing the roughest surface and material **H** the smoothest.

The bearing ratio distribution plot, Figure 4.33, an alternative representation of a histogram of the height distribution data from the surface map, is a cumulative height data plot representing the percentage of each area of the map bounded by a given height contour.
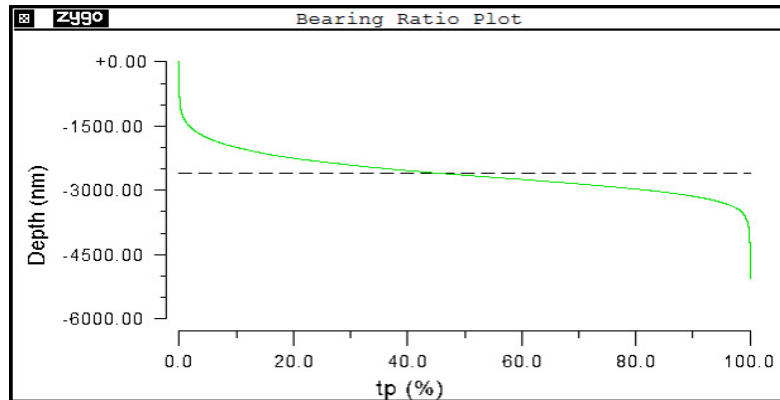
Figure 4.33: Bearing ratio plot for titanium metal *1*

While the previous plots produced quantitative measurements, this plot also gives a qualitative evaluation of the different surfaces. With the mean height of the fifty percent height contour set to zero this ratio allows direct comparison to be made between surfaces. Figure 4.34 compares a range of metal surfaces using this method[14].

Figure 4.34: Comparative bearing ratio plots for titanium metals *CSM* and materials *1*, *2* and *3.*

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[14] Graph courtesy of R Chater, Materials Department, Imperial College, 2006.

This graph confirms that material **CSM** has the widest height distribution and material **3** the narrowest. Two different examples of material **1** were included in this comparison and the resulting plots lie on top of each other confirming that the samples have similar surface textures.

The full set of images of the plots that were recorded for each titanium metal surface and its anodised equivalent are shown in the Appendix.

Moments of Height Distribution

As stated above, the plots produced from the recorded data illustrate various features of the measured surface area of the samples. In addition programmes are available to analyse the height distribution of these surfaces using data from the topography maps. Two of these moments of height distribution, Ra and RMS, are measures of the roughness of the surface comparing the highest and lowest points on the surface with a calculated average height. The other two moments, Rsk and Rku, analyse the type of roughness in terms of the degree of symmetry and regularity of peaks and troughs. These four moments of height distribution therefore provide quantitative comparisons between the titanium surfaces and also between the metal and the oxidised surfaces. The four moments of height distribution are defined in the following paragraph.

Ra is the arithmetic average deviation from the centre line. RMS or Root Mean Square also measures the average deviation from the centre line but by squaring each value and taking the square root of the mean. Rsk or skewness measures the symmetry of the profile about a calculated centre line. An Rsk of zero indicates equal number of sharp peaks and troughs on either side of the centre line. When the Rsk is negative the surface is characterised by sharp troughs and when the Rsk is positive by sharp peaks. Rku or Kurtosis is the measure of the randomness of the surface. An Rku value of 3 indicates a perfectly random surface and the further the value is from 3 the more repetitive the structure of the surface in terms of height distribution.

The measured data, for the differing titanium surfaces and their oxidised counterparts are presented in Table 4.5. The values for the four parameters permit direct comparison between the textures of the various surfaces in terms of roughness. The samples measured also include additional samples with thinner oxide layers, **2J70V**, an anodised sample of material **2**, and **2QE**, a sample of the same metal, heated to a similar gold colour.

Sample	Magnification	Ra (nm)	RMS (nm)	Rsk	Rku
Metal surfaces:					
CSM	x25	2396	3008	0.26	3.076
2b	x25	1183	1577	0.17	4.637
2a	x25	957	1224	0.17	2.842
1b	x25	391	508	0.447	3.924
1a	x25	355	457	0.417	3.592

2bpol	x25	309	488	-2.77	14.487
H1-000	x25	186	253	-0.75	4.482
3	x25	94	145	0.462	9.524
Oxidised surfaces:					
CSM60V	x25	2672	3314	-0.18	3.142
2QE	x25	1289	1613	-0.58	2.933
2H	x25	1132	1492	0.157	9.454
2F89V	x25	1091	1393	-0.3	3.057
2J90V	x25	1073	1361	-0.49	3.069
2J70V	x25	791	987	-0.11	3.026
2F89Vpol	x25	536	677	-0.73	3.448
2Hpol	x25	443	623	-1.62	17.991
1J60V	x25	390	499	0.121	3.648
H17-660	x25	302	378	-0.08	3.022
3J80V	x25	222	291	-0.6	4.138

Table 4.5: *Moments of height distribution for metal samples and anodised examples of each.*

The measurements of the metal surfaces confirm the visual observations, which are that the **CSM** material has the roughest surface of the materials under test, followed by materials **2**, **1**, abraded **2**, **H**, and finally **3**. The results for the oxidised samples indicate that while most aspects of the oxide surface topography are related to the topography of the untreated metal some differences are apparent. These differences are quantifiable using the four moments of height distribution, described above, Ra, RMS, Rsk and Rku.

The average height distribution parameters Ra and RMS, for all the metal sample coupons measured, are presented graphically in Figure 4.35, in order of decreasing value.
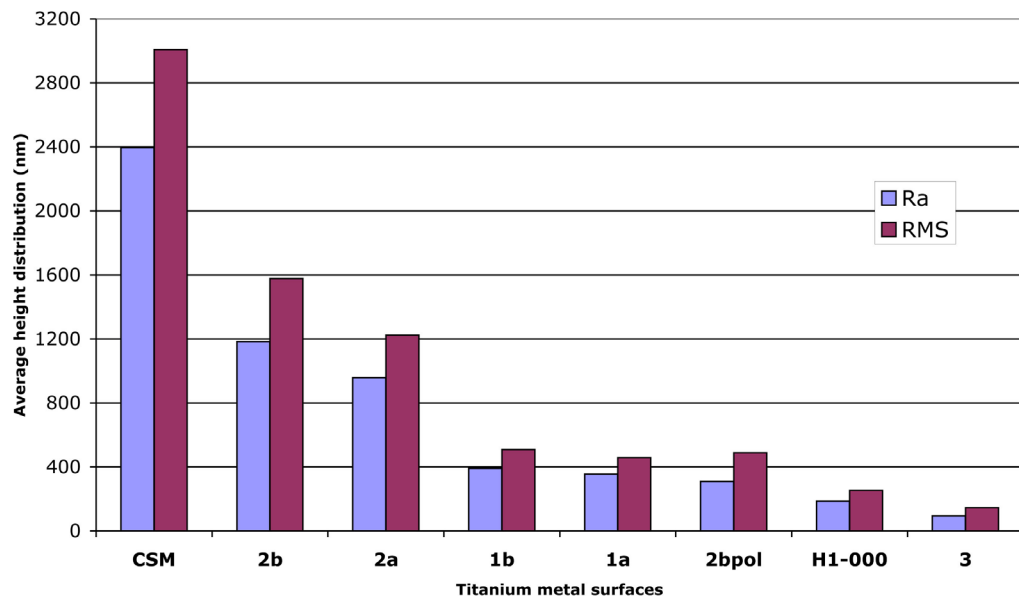
Figure 4.35: *Comparison of Ra and RMS values for the different metal surfaces.*

For the majority of samples both moments Ra and RMS produce similar comparisons between the metal surfaces and therefore the results are discussed in terms of the most differentiated measure, RMS. The height distribution for the CSM material, the titanium with the visually roughest surface is twice that of the next roughest surface, which is the commercially etched metal **2** and this in turn is over twice that of the scrap material **1.** There are however variations in the measurements for the two sample coupons of material **2**. Such differences may be within the expected range of the commercially available titanium sheet but a larger number of samples would be required to establish such a variation. As the focus of the project is the comparison of the different titanium surfaces no further investigation is planned into the variation within sample types other than to note that there is a small variation between samples of material **1**, **1a** and **1b**.

The polishing of the etched metal surface **2b** to create sample **2bpol** reduces the RMS roughness by a third, producing a similar surface roughness to that of metal 1, even though the surface is shown not to have been abraded to a uniform structure. The lowest RMS value for height distribution is given by the smoothest surface, that of the rolled foil **3**, which is a tenth that of metal **2**. The metal surface **H** has a roughness nearly double that of foil **3** and half that of metal surface **1**.

A similar ranking in terms of the RMS parameters is seen for the oxidised samples of the different materials shown in Figure 4.36.
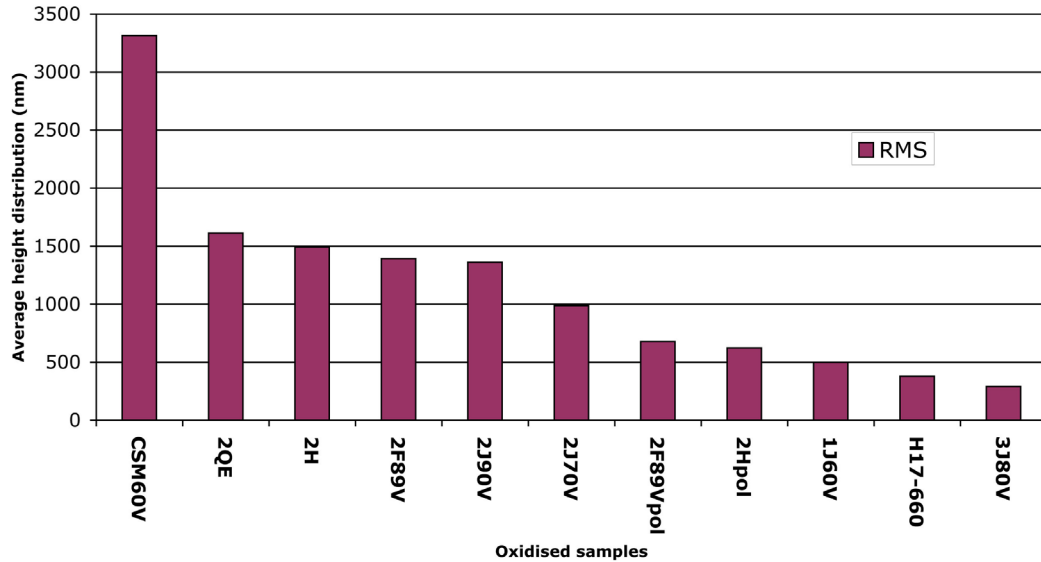
Figure 4.36: *Comparison of RMS values for the different metal surfaces after oxidation.*

The anodised example of the **CSM** material, **CSM60V** is approximately twice as rough as the oxidised examples of material **2** but the heated samples, **2H** and **2QE**, are slightly rougher than the anodised samples, **2F89V** and **2J90V.** The thicker oxide layers created at

voltages of ca 90V are substantially rougher than the sample anodised to a lower voltage, **2J70V,** which was anodised to 70V, implying that surface roughness increases with oxide growth. In contrast to the observations for the metal surfaces, the oxidised samples of the polished surfaces, **2F89Vpol** and **2H** are rougher than the anodised sample of material **1**, **1J60V**.

The effect of oxidation on the surfaces roughness of the range of titanium surfaces can be assessed from the graph, Figure 4.37. The graph uses RMS measurements to compare the metal and oxidised surface for all six different finishes of titanium sheet, including both heated and anodised samples.
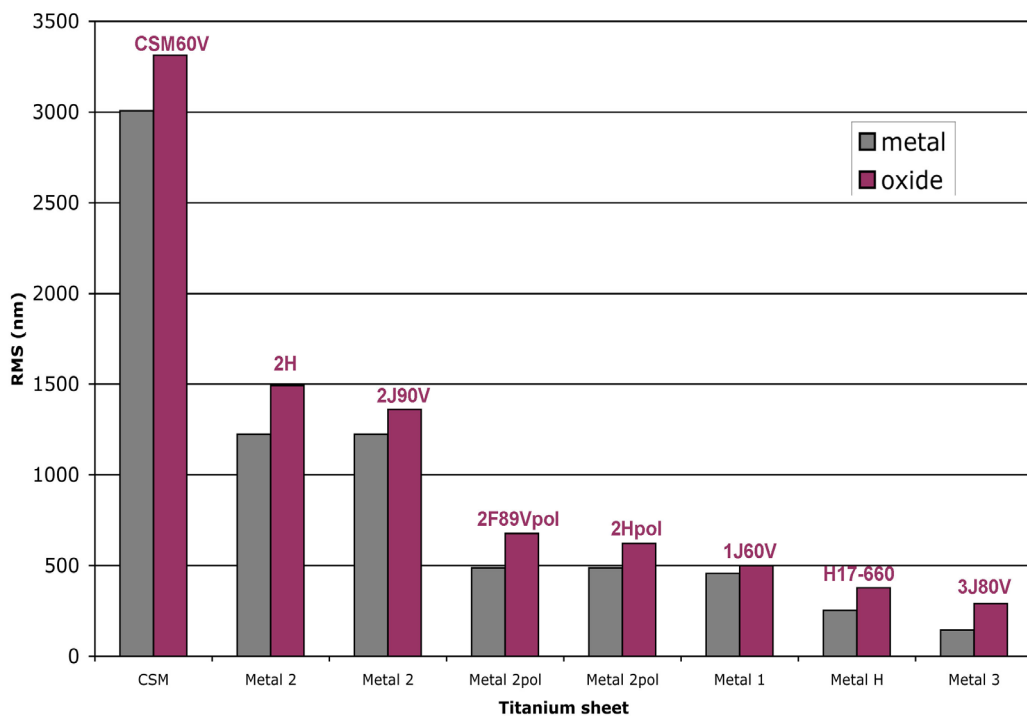
Figure 4.37: *Comparison of RMS values for the six different metal surfaces and the oxidised equivalents both heated and anodised.*

The graph demonstrates that in all cases, for the samples measured, oxidation produces an oxide layer with a rougher surface than that of the metal that has been oxidised. An analysis of the results shows that there is a comparatively small increase in surface roughness for the materials designated **CSM** and **2** after anodising but heating of surface **2** produces a slightly larger effect. Conversely the heated sample of the polished surface of material **2**, **2Hpol**, exhibits a slightly lower increased roughness than the anodised sample, **2F89Vpol.** There is no significant difference between the scrap titanium metal surface **1** and the anodised equivalent. However the roughness of the anodised titanium foil surface is double that of the metal surface and the roughness of the anodised polished titanium over a third greater than that of the polished metal itself.

The height distribution parameters considered so far have confirmed and quantified the roughness of the different metal surfaces and demonstrated how it is affected by both methods of oxidation.

The two additional moments of height distribution, Rsk and Rku, described above, allow an assessment of the quality of the surfaces in terms of symmetry about the notional centre line of the profile and the randomness of the surface. The symmetry of the surface is measured by Rsk, with a zero value indicating an equal number of peaks and troughs about the notional midpoint. The randomness of the surface topography is indicated by Rku, where a value of 3 is that of a 'perfectly' random surface, which exhibits no regular repetitive surface features. The Rsk and Rku values for the oxidised sample coupons, both anodised and heated, compared with the metal surfaces are presented graphically in Figure 4.38.
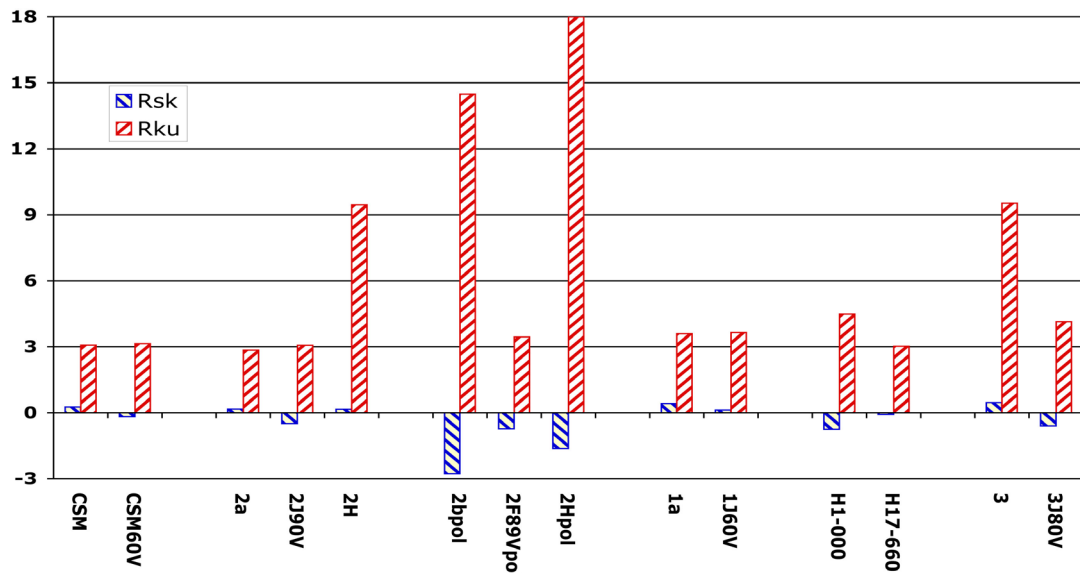
Figure 4.38: *Comparison of Rku and Rsk values for metal and oxidised surfaces.*

From the analysis of the data it can be seen that the majority of the sample coupons have Rsk values close to zero and Rku values close to 3, indicating symmetrical surfaces with random structure. Only the polished metal surfaces, **2bpol** and **3** show significant variation. However it is likely that the Rsk value of −2.77, measured for the abraded metal surface, **2bpol,** is due to the unpolished pits in comparison with the much flatter surface produced by the polishing process. This value is reduced when the surface is oxidised, which could suggest that the oxide layer grows preferentially within the troughs of the metal surface but may just indicate that a relatively flatter part of the surface has been measured. The effect is more noticeable for the anodised sample, **2F89Vpol**, than for the heated sample, **2Hpol**. The polished metal surface also has a high Rku of 14.487, indicating a non-random surface due to the directional polishing lines.

High Rku values are also measured for the titanium foil sample coupon, **3**, which can be attributed to the more regular directional surface structure produced by rolling. In this case, as indicated by the small positive Rsk value, the surface has more peaks than troughs. A similar small positive Rsk value for the metal sample, **1a**, may indicate that the titanium sheet was flattened by rolling but the Rku value of just over 3 suggests that further processing acted to normalise the surface. The small negative Rsk value for metal **H** together with an Rku value >3, is indicative that a fine abrasive polishing procedure was used to create the surface of the titanium sheet. This brief analysis indicates how information about the surface preparation of the titanium sheet may be deduced from these two moments of height distribution.

The overall comparison between the metal and the oxidised surfaces is summarised in Table 4.6.

Sample	Mag	RMS (nm)	Rsk	Rku	Surface
CSM	x25	3008	0.26	3.076	metal
CSM/60v	x25	3314	-0.181	3.142	pink oxide
1a	x25	457	0.417	3.592	metal
1J/60v	x25	499	0.121	3.648	pink oxide
2a	x25	1224	0.17	2.842	metal
2J/90v	x25	1361	-0.492	3.069	pink oxide
2H	x25	1492	0.157	9.454	pinkish oxide
2bpol	x25	488	-2.772	14.487	metal
2F/89vpol	x25	677	-0.728	3.448	pink oxide
2Hpol	x25	623	-1.62	17.991	pinkish oxide
3	x25	145	0.462	9.524	metal
3J/80v	x25	291	-0.596	4.138	pink oxide
H1-000	x25	253	-0.751	4.482	metal
H17-660	x25	378	-0.075	3.022	pink oxide

Table 4.6: *Tabulation of the parameters comparing the roughness of titanium metal samples with oxidised surfaces.*

As previously stated, for most of the titanium metal surfaces measured, oxidation produces a slightly rougher surface compared to that of the underlying metal. This is particularly evident for thermal oxidation of any surface and for electrochemical oxidation of the smoother, polished surfaces. However no apparent linear correlation has been established between the roughness of a surface and the rate at which the oxide layer grown on the surface increases in thickness. The roughest surface, **CSM**, when anodised

at 60V, produces a similar colour to the second roughest surface, **2**, when anodised at 90V. The third roughest surface, **1** needs only 60V to achieve a similar hue. The smoothest surface, **3** needs 80V and the next smoothest **H1-000** only an estimated 66V for a similar hue and hence assumed oxide thickness, to be achieved. The conclusion must be that some other factor besides or in addition to the surface roughness is responsible for the different colouring rate exhibited by these materials.

4.4. Conclusions

This chapter has examined the role of the titanium metal surface in the oxidation process. The factors that contribute to the structure of the surface of titanium metal and the techniques used by jewellers to manipulate these surfaces, to achieve a desired design outcome, have been investigated. Working with samples generated using workshop practices, described in Chapter 2, titanium sheet with different surface finishes has been oxidised by both heating and anodising and the resulting surfaces have been compared with those of the underlying metal using SEM and WLI.

SEM analysis has demonstrated that the external morphology of the oxide surfaces, however generated, is predominantly that of the original metal surface in each case. Exceptions occur for thicker layers, created by anodising at voltages above 110V and for the previously unrecorded phenomenon of 'Flower' oxides. The latter discovery has been published[15] and a copy of the paper is attached in the Appendix.

More qualitative information about the texture of the surfaces was obtained by the use of WLI. The measurements of the roughness of the metal surfaces and their oxidised counterparts have confirmed the differential oxidation rate between different surfaces but no correlation between the degree of roughness or polish of a titanium surface, as measured, and the speed at which it is oxidised has been established. It has however been demonstrated that the oxidised surface is rougher than that of the corresponding unoxidised metal. There is a small effect when the rougher metal surfaces are oxidised but a substantial one when the smoother surfaces are oxidised and heating produces a rougher oxide surface than anodising.

However while this increased roughness may produce a greater scattering of the incident light, resulting in a more diffuse colour, it does not account for the degree of colour variation experienced in practice. The implication follows that having eliminated the surface structures of titanium metal and titanium dioxide as major causes of colour variability, the remaining possibility is that variability arises from within the oxide layer. This oxide layer is important in establishing the observed colour of the titanium surface by

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[15] Bartlett, L: *Optics and Laser Technology*, **38** (2006) pp440-444.

virtue of the critical role it plays in producing the interference colour and therefore variation in its chemical and physical structure could produce variability in the observed colour.

Variations in the layer that could produce colour variation include the presence of the different crystal forms of titanium dioxide, which have different optical properties, variable thickness of the layer across the surface and a lack of homogeneity within its structure. Therefore to determine the causes of the observed colour variability it is essential to look below the surface of the oxide and above the surface of the metal and examine in detail the oxide layer adherent to the metal surface. The following chapter, Chapter 5, examines in detail the composition, structure and thickness of the oxide layer.

Chapter 5

5.1. Introduction

Comparison of the surfaces of thermally and electrochemically oxidised titanium sheet, presented in Chapter 4, showed that although the surfaces of the oxide layers were slightly rougher than the surfaces of the underlying metal, this difference could not account for the degree of colour variation experienced in practice. Therefore the logical next step in the search for the causes of variability is the detailed examination and analysis of the oxide layer adherent to the metal surface. As was discussed in Chapter 3, it is the presence of the oxide layer on the metal surface that produces the thin film interference and thus the observed colour of the titanium.

This chapter considers and measures the attributes of the oxide layer, in order to assess the likely impact that their individual variation may have on the observed colour of the oxidised titanium surfaces. In summary the important areas to be investigated are the thickness of the layer and its refractive index, both significant factors in the determination of the thin film interference colour.

As considered theoretically in Chapter 3, the thickness of the oxide layer determines the distance travelled by the refracted light rays, which leads to colour change as the layer thickens. But theoretical assumptions consider only a uniform thickness and colour variation may be caused by variation in thickness across the surface. Hence it is important to measure not only the thickness of the layer but also any variations in layer thickness.

Theory also assumes that the oxide layer has a uniform composition in terms of its chemical nature and crystalline form, i.e. an homogenous material with a single refractive index. Colour variation may be due to differences in the degree of crystallinity of the oxide and/or the presence of different polymorphs of titanium dioxide, which would affect the overall refractive index of the layer. Therefore the detailed composition and physical structure of the oxide layers need to be analysed and the nature of the species present identified.

Information about the nature and composition of the thin oxide layers formed on the titanium metal surface has been sought from the extensive body of scientific literature, created since the early 1940s covering all aspects of titanium, its production, properties and structure. The most relevant studies on the formation of oxides on titanium have been in the context of the corrosion resistance of the metal, discussed in Chapter 1, because oxidation is the most common corrosion process affecting metals. Oxidation can be a progressive process such as for iron where, under certain conditions, it continues until all

the metal is reacted or it can be a process where the formation of a thin film of oxide on the metal surface acts as a barrier to further corrosion. Titanium is in the latter category and is known as a 'valve' metal. Other examples are aluminium, zirconium, niobium and tantalum. It is the thin oxide layer that gives titanium its corrosion resistant properties as well as producing the interference colour.

The first part of this chapter therefore reviews the literature in the field of titanium corrosion studies with particular emphasis on the creation and composition of the oxide layer. From the review it is possible to identify which aspects of the study of titanium oxidation are widely accepted within the scientific community and which areas are the subject of continuing debate. For example, as described below, it is accepted that the bulk of the oxide layer created by oxidising titanium is titanium dioxide but the morphology of the oxides formed under both oxidation methods has not been unambiguously identified and all the possible crystal forms of titanium dioxide and also amorphous material have been reported.

The review also identifies techniques suitable for the microscopic examination of the thin oxide layer on titanium, generally accepted to be of a thickness in the range 10-300 nm in order to show interference colours[1]. The use of these techniques, specifically aimed at the identification of the crystal form of the titanium dioxide and the measurement of the thickness of the oxide layer and its composition, together with the results of their use are presented and discussed in the second part of this chapter.

5.2. Scientific Literature Review

This section reviews published studies of the layer structures formed when titanium is oxidised, the mechanisms proposed for the oxidation processes and the measuring techniques used within the field of corrosion studies to examine the morphology of thin films.

5.2.1. Oxide Form and Structure

The majority of studies of titanium oxidation were concerned with either its behaviour when heated or under anodising conditions. The corrosion resistance of titanium and its alloys in acidic media made it an ideal candidate for use in the chemical and other process industries and much work was carried out in this context. The review by Aladjem[2] in 1973 gives a comprehensive listing of papers covering the anodic oxidation of titanium and its alloys under a wide range of conditions and in a vast range of electrolytes. Most of these

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[1] Nassau, K, *Scientific American,* 243, 4, 124, 1980.
[2] Aladjem, A, *Journal of Materials Science*, 8, 1973, p688.

materials are unsuitable for workshop use, involve difficult to achieve conditions in terms of temperature and pressure and produce films that are too thick to show interference colours. The paper does however highlight the controversy as to the precise nature of the oxide film, which continues to this day.

Early studies of the corrosion behaviour of titanium sought to identify the oxidation products present in the oxide film and their crystal form. Initially studies such as that of Harrington and Nelson[3] in 1940 were simply to determine whether the films formed by anodisation were crystalline or amorphous. Their results showed both forms depending on the conditions of anodisation. Subsequent researchers have identified all the possible variations of crystalline titanium dioxide; rutile, anatase and brookite, present in the oxide film. Rivolta[4] found both anatase and rutile after anodising titanium in a sulphuric acid solution to produce a yellow interference colour. However under similar conditions Yamaguchi[5] identified brookite in an oxide layer of 300 nm that showed a blue interference colour but Jouve and Severac[6] observed anatase crystals when anodising titanium in an acidic medium.

More recent work has shown that different oxide forms develop under different rates of growth. Pang et al[7] show that anodised films tend to be amorphous when grown quickly but have a crystalline anatase structure when grown more slowly. Later studies such as that of David et al[8] conclude that the oxide films are not homogeneous and have a layered structure. More sensitive techniques, described in the following section, employed by Gueneau de Mussy et al[9] show that on anodising up to 120V in sulphuric acid solution, a ca 300 nm layer of fine polycrystalline anatase is formed at the metal oxide interface with a thicker layer from 300 nm to the outer oxide surface composed of mostly columnar crystals of anatase and rutile. The majority of the larger crystals show the anatase structure. Such a layered structure, with both the rutile and the anatase forms of titanium dioxide present within the oxide layer, could explain why previous researchers had identified the presence of either rutile or anatase on anodised titanium.

Fewer studies have researched the heat oxidation of titanium and in the majority of cases, heating of titanium results in the formation of titanium dioxide as rutile. This is

[3] Harrington, R A and Nelson, H R, *Trans. American Inst. Min. Met. Engr., Inst. Met. Div.,* 137, 62, 1940.

[4] Rivolta, B, *Metallurgia Italia,* 50, 173 and 255, 1958.

[5] Yamaguchi, S, *J. Electrochemical Soc.,* 108, 302, 1961.

[6] Jouve, G and Severac, C, *5th International Conference on Titanium 1984*, Lutjerling, G, Zwicker, U and Bank, W,(ed) Deut. Gesellschaft fur Metallkunde e.V. Oberursel, 1985, p. 2589,

[7] Pang, M. et al, *Structural and Mechanical Characteristics of Anodic Oxide Films on Titanium,* Corrosion, 57, 523, 2001.

[8] David, D, et al. *4th International Conference on Titanium 1980*, Kyoto, Kimura, H and Izumi, O,(ed) AIME, New York, 1980, p.2811,

[9] Gueneau de Mussy, J-P. et al, *TEM and X-ray diffraction investigation of the structural characteristics of the microporous oxide film formed on polycrystalline Ti,* Scripta Materialia, 48, 23 2003.

reported in the early work of Gulbranson and Andrew[10] and confirmed by the findings of Hass[11] that air oxidation of a thin film of titanium at 400-450 ^{0}C produced rutile. Hass also observed that a slower rate of titanium film deposition allowed the metal to pick up oxygen and nitrogen. The oxidation of this film gave anatase. Heating of the anatase film for two hours at 600 ^{0}C gave equal proportions of anatase and rutile and further heating at 800 ^{0}C converted all the anatase to rutile. He concluded from this that '*Rutile is the only stable modification of titanium dioxide and that the other modifications brookite and the frequently appearing anatase are unstable transition forms.*' Another observation he made was that the rate of oxidation depended on surface quality. Abrasively polished titanium oxidises faster than evaporated films that have mirror-finish surfaces.

Many of these studies looked at the oxide films when they had been removed from the metal substrate but Flower and Swann[12] in 1974 examined titanium oxidation in situ in a high voltage electron microscope and reported the growth of a porous rutile film developed at 450-850 ^{0}C.

A possible combination of anodising and heating is reported by Yamaguchi et al[13], who anodised titanium in a phosphoric acid solution at 25V to give a blue colour. The oxide was analysed as titanium dioxide but no crystalline form was detected until after an unspecified treatment which resulted in a decrease in layer thickness and the observation of anatase.

5.2.2. Layer Thickness

The few studies that have attempted to measure oxide thickness in relation to the colour produced have used calculated methods to determine the oxide thickness rather than direct measurements. Techniques for the precise measurement of the thickness of the oxide layer have not been readily available until recent years when methods of preparation of sufficiently fine cross sections for examination by Transmission Electron Microscopy (TEM) have become possible.

The most comprehensive study concerned with colour on titanium is that of Cotton and Hayfield[14]. The relationships between the applied voltage, colour and the thickness of oxide, as measured by ellipsometry are quoted. Fukuzuka et al[15] used ellipsometry to

[10] Gulbranson, E A and Andrew, K F, *J. Electrochemical Soc.,* 96, 364, 1949.

[11] Hass, G, *Vacuum,* 2, 331, 1952.

[12] Flower, HM and Swann, PR, *Acta Metallurgica*, 22, 1339, 1974.

[13] Yamaguchi, H, et al, *6th World Conference on Titanium 1988,* Lacombe, P, Tricot, R and Beranger, G, (ed) Les editions de physique, France, 1988, p. 1823,

[14] Cotton, J B and Hayfield, P C S, *Decorative Finishes on Titanium*, Transactions of the Institute of Metal Finishing, 45, 48,1967.

[15] Fukuzuka, T, et al, *4th International Conference on Titanium 1980*, Kyoto, Kimura, H and Izumi, O,(ed) AIME, New York, 1980, p.2783,

give a correlation between film thickness, colour and thermal oxidising temperature by examination of the isolated film formed at 600 ⁰C, which indicated a rutile structure. Ellipsometry[16] is an optical technique often used to estimate the thickness and optical constants of thin films by observing the polarization changes caused by reflection or transmission of light from materials. In 1963 Sibert[17] in the course of a study on the factors influencing film formation concluded that in a phosphate electrolyte film formation was at a rate of 20 Angstroms (2 nm) per volt up to 200V although the thickness of the films were not directly measured. This value is now accepted as a 'standard' within corrosion studies of titanium.

5.2.3. Oxidation Mechanism

Another category of studies investigates the mechanisms of titanium oxidation. The mechanism as proposed by Evans[18] is as follows: *'Oxidation of titanium is largely a process of oxygen passing inwards through the film – probably by oxygen anions taking advantage of vacant anion sites in the lattice. When it reaches the metal – oxide interface part of it enters the metal in solid solution and part of it is used to form fresh oxide.'* Armanet et al[19] propose different mechanisms depending on the oxidation method. Thermal oxidation proceeds by the diffusion of oxygen through the oxide layer to the metal surface while anodisation involves the diffusion of titanium outwards from the metal surface to the electrolyte.

It is now accepted by researchers that for titanium oxidation by anodising a dual mechanism takes place, Marsh et al[20] note *'anodic film growth takes place at both the metal/film and film/solution interfaces,'* while Habazaki et al[21] summarise the process, *'The distribution of the crystalline oxide can be correlated with ionic transport during film growth. The transport number of cations in amorphous anodic titania is 0.35-0.38. Thus the outer 35-38 percent of the film formed at the film/electrolyte interface by migration of Ti^{4+} ions outward, with the remaining film formed at the metal/film interface by migration of O^2/OH^- ions inward.'* Their studies presented in a series of papers[22],[23],[24] confirm the mechanism by looking at

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[16] www.jawoollam.com/ellipsometry tutorial

[17] Sibert, M E, *J. Electrochemical Soc.,* 110, 65, 1963.

[18] Evans, U R, *The Corrosion and Oxidation of Metals,* Arnold, 1961.

[19] Armanet, F, et al. *6th World Conference on Titanium 1988,* Lacombe, P, Tricot, R and Beranger, G, (ed) Les editions de physique, France, 1988, p. 1941,

[20] Marsh, J, and Gorse, D, *A photoelectrochemical and ac impedance study of anodic titanium oxide films,* Electrochimica Acta, 43, 659, 1998.

[21] Habazaki, H, et al, *Crystallization of anodic titania on titanium and its alloys,* Corrosion Science, 45, 2063, 2003.

[22] Habazaki, H, et al, Influence of molybdenum species on growth of anodic titania, Electrochimica Acta, 47, 3837, 2002.

[23] Habazaki, H, et al, Ionic transport in amorphous anodic titania stabilised by incorporation of silicon species, Corrosion Science, 44, 1047, 2002.

[24] Habazaki, H, et al, Influences of structure and composition on growth of anodic oxide films on Ti-Zr alloys,

various alloying elements and electrolytes and tracing the presence of the ions from the alloy element and from the electrolyte in segments of the film. However in a comparative study of anodic and thermal oxidation of a titanium alloy, Zorn et al[25] noted that for heated samples diffusion of oxygen into the substrate metal occurred with consequent roughening of the metal surface as well as the oxide surface.

5.2.4. Analytical Techniques

In the majority of investigations X-Ray Diffraction (XRD) is used to identify the crystallinity and form of the oxides.

Other studies have tended to use novel techniques for either preparing specimens for examination or for measuring the properties of the films. The preparation of samples for examination of the cross section of thin films adhering to a metal substrate include ultramicrotomy, Furneaux et al[26], and Ion Beam Thinning, Morris[27]. Gueneau de Mussy used an FEI Company Focused Ion Beam system (FEI FIB) to prepare samples by a 'lift-out' technique[28]. All three techniques provide suitable specimens for Transmission Electron Microscopy (TEM), which in previous studies had to be undertaken on films that had been removed from the metal substrate thus introducing possible distortions in the film.

TEM has largely superseded the other thin film measurement techniques quoted by King and Talim,[29] which include ellipsometry. Ellipsometry has been used, as already mentioned, in the study of thin films on titanium but the calculations involved assume a homogeneous layer, which as discussed above, has been shown not be the case in practice.

Focused Ion Beam (FIB), as discussed above, which uses a beam of gallium ions as a milling tool, can be used for sample preparation but can also be used to cut into the surface of a sample, exposing the cross-section of the layer structure for microscopic examination.

5.2.5. Conclusions from Literature Review

The literature confirms that the method of oxidation plays a significant role in determining the crystal form in which the titanium dioxide layer grows and hence the refractive index of the layer. Thermal oxidation under laboratory conditions is reported to produce titanium dioxide in its rutile form whereas both amorphous and crystalline areas are reported within electrochemically formed oxide layers. The latter forms include the anatase and rutile polymorphs of titanium dioxide. Heating is also reported to produce

Electrochimica Acta, 48, 3257, 2003.

[25] Zorn, G, Lesman, A, and Gotman, I, *Oxide formation on low modulus Ti45Nb alloy by anodic versus thermal oxidation,* Surface and Coatings Technology, 201, 612, 2006.

[26] Furneaux, R C, Thompson, G E, and Wood, G C, *Corrosion Science,* 18, 853, 1978.

[27] Morris, F W, *Practical Metallography,* 16, 222, 1979.

[28] Gueneau de Mussy, J-P. et al, Op Cit.

[29] King, P J and Talim, S P, *Optica Acta,* 28, 8, 107, 1981.

rougher oxide surfaces and to cause a roughening of the underlying metal surface. The majority of studies in which values for the thickness of the oxide layer are quoted have used indirect measurement techniques. However, with improving sample preparation procedures, TEM has been increasingly used to examine the cross-sections of anodised titanium surfaces.

Drawing on the findings from the literature review the following part of this chapter presents the experimental programme, which has been designed to compare in detail the structure and composition of oxide layers created in the workshop by either thermal or electrochemical oxidation of titanium.

5.3. Investigation of the Oxide Layer

This part of the chapter presents the sequence of experiments devised to explore in increasing detail the composition and structure of the oxide layers that give rise to interference colour on titanium. The complexity of these structures, as indicated in the literature review in the first part of the chapter, means that increasingly sophisticated techniques are required to analyse them. Three principle methods have been selected for the analysis of the oxide layer as outlined here: XRD to determine the crystal species present, FIB for an initial examination of the cross-section of the layer and TEM for the final detailed structural investigation.

The literature review suggests that, as there is an on-going debate about the crystal form of the titanium dioxide created by the two main oxidation methods, it is important to establish whether rutile or anatase is present in the oxide formed on the titanium surface. The varying refractive indices of these polymorphs, as outlined in Chapter 3, may be instrumental in causing the variability of colour observed. Hence the study begins with XRD, a non-destructive technique, which identifies the crystal forms present in the different oxide layers. However more intrusive investigations are needed to examine the cross-sectional structure of the layer and to measure its thickness.

Therefore the Focused Ion Beam (FIB) instrument is used to cut into the oxide film, exposing the depth of the layer attached to the metal surface and allowing both its thickness and structure to be explored under magnification. Different electron microscopes are used, as outlined in the relevant sections, to obtain increasingly higher levels of resolution for the detailed examination of the layer structure.

Finally the most recent technique for sample preparation, presented in the literature review above, *'FEI FIB by lift out'*, is used to cut sections, which include both the oxide layer and the underlying metal surface, that are thin enough for examination by Transmission

Electron Microscopy (TEM). The TEM analysis records the detailed structure of comparative oxide layers at the nanometre level.

5.3.1. Crystal Species

The object of this part of the investigation is to confirm the findings from literature, as discussed in the first section of this chapter, that each of the two methods of titanium oxidation produces predominantly one crystal form of the oxide. Analysis of laboratory-prepared samples confirmed that heating produces the rutile form of titanium dioxide and anodising produces anatase, but this needs to be investigated to confirm if this distinction holds true for samples prepared under workshop conditions. The possible influence on colour variability attributable to the presence of the different crystal forms is also considered.

As outlined above, XRD is a non-destructive technique used principally to determine the crystallography of a material, based on the diffraction of monochromatic X-rays by crystal lattices. The X-rays penetrate the oxide layer and produce XRD spectra that encompass both the titanium metal and any oxide species present at over 5 percent within the surface layer. (The limits of detection of the technique mean that the presence of any species cannot be detected if it is below 5 percent of the composition of the layer.) The measured spectra are compared with reference spectra for the crystalline species that are expected to be present in the layer under test and the spectra for the underlying titanium metal. Reference spectra are published for a wide range of crystal species by the International Centre for Diffraction Data (ICDD). Each species has a unique reference code and the published data is continually reviewed and updated as new and more sensitive measurements are made. The most significant measurement for comparison of spectra is the angle of diffraction, which can be diagnostic for the species. The relative intensity of the peaks provides information about the orientation of the crystals.

As the XRD analysis was intended to compare the crystallinity of the oxides generated by the two different methods of oxidation, only one of the titanium sheet materials, **2,** was used to prepare sample coupons. The dimensions of the sample chamber of the equipment necessitated an amended coupon size, 1.5 cm x 1.5 cm, and, as the technique works best with thicker oxide layers, additional sample coupons were required. Two sample coupons, **2L100V** and **2L120V**, were prepared by anodising to higher voltages, 100V, and 120V, respectively and a third, **2Mb**, by heating in a kiln at 700^{0}C to achieve a green/blue colour, estimated to be produced by a layer thickness similar to that of the anodised sample coupons.

Figure 5.1 presents the results of the XRD analysis for the anodised sample coupons. The standard graph for XRD spectra plots the angle of diffraction along the x-axis, measured

as $2^0\Theta$, and the intensity in counts per second along the y-axis. The comparison of several spectra means that the values shown on the y-axis do not apply to all the spectra presented. The objective is to compare the positions of the stronger peaks, which are diagnostic for
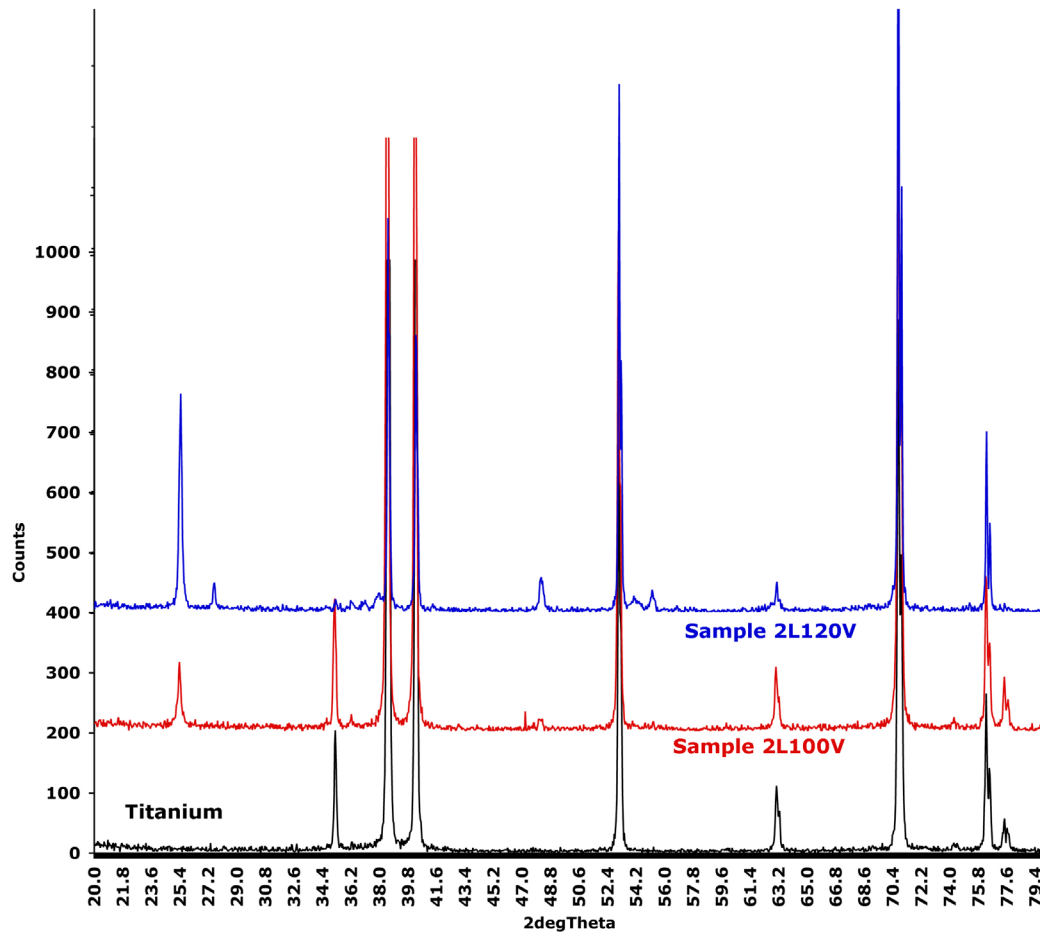
Figure 5.1: *XRD analysis comparing titanium metal sample with samples anodised to 100V and 120V.*

the specific crystal forms.

The base line shows a typical XRD pattern for titanium with peaks at 35.2, 38.52, 40.28, 53.08, 63.04, 70.72, 76.28 and 77.44 recorded at $2^0\Theta$, matching the International Centre for Diffraction Data (ICDD) code 00-005-0682 for titanium.

The coupon anodised to 100V, **2L100V**, shows not only the peaks associated with titanium but also additional peaks at 25.36 and 48, which are the two major peaks for the anatase form of titanium dioxide (ICDD code 00-004-0477). However the sample coupon anodised to 120V, **2L120V**, shows both the two major peaks for anatase with increased intensity and also peaks at 27.56 and 54.04 indications of the presence of rutile (ICDD code 00-021-1276). The peak at 35.2, one of those due to the titanium substrate appears for both the titanium sample and for the anodised sample, 2L100V, but is very much reduced for sample, 2L120V. The most likely explanation for this is that the thicker oxide layer generated

by 120V would mask this particular titanium peak.

The XRD analysis of the heated sample coupon, **2M(b)**, presented in Figure 5.2, shows that while the predominant form of titanium dioxide present is in the rutile form with major peaks at 27.48, 36.08 and 54.4, there is also a trace of anatase evidenced by a small peak at
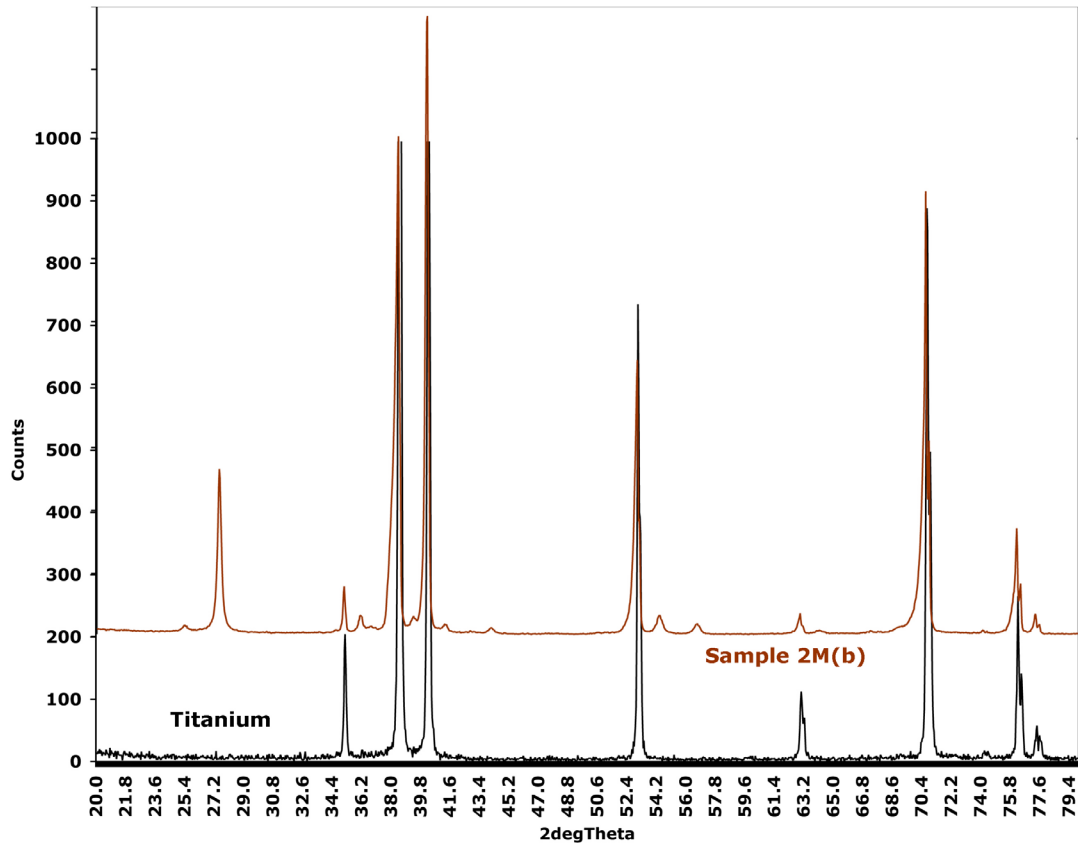
Figure 5.2: *XRD of heat-coloured sample showing both anatase and rutile present.*

25.36.

An additional XRD analysis was carried out on two further sample coupons that had been anodised to 100V and 120V respectively and then further processed by heating in a kiln at 700 ^{0}C for one minute, **2L100V+H** and **2L120V+H**. This procedure produced a change in the colour appearance of the samples, particularly marked in the sample anodised initially to 100V, which changed on heating from purple to green, as illustrated in Figure 5.3.

The postulated theory was that heating an anodised surface might have changed the crystal form of the titanium dioxide from anatase to the more stable rutile form. However the results of the XRD analyses showed that the crystal species present in the anodised and heated samples were the same as for the samples that had only been anodised. In particular, as presented in Figure 5,4, there was no indication of the rutile form of titanium dioxide on the sample that had undergone heating after anodising to 100V.

This confirms that the crystal form is determined by the anodising voltage and that

Anodised cf anodised + heat
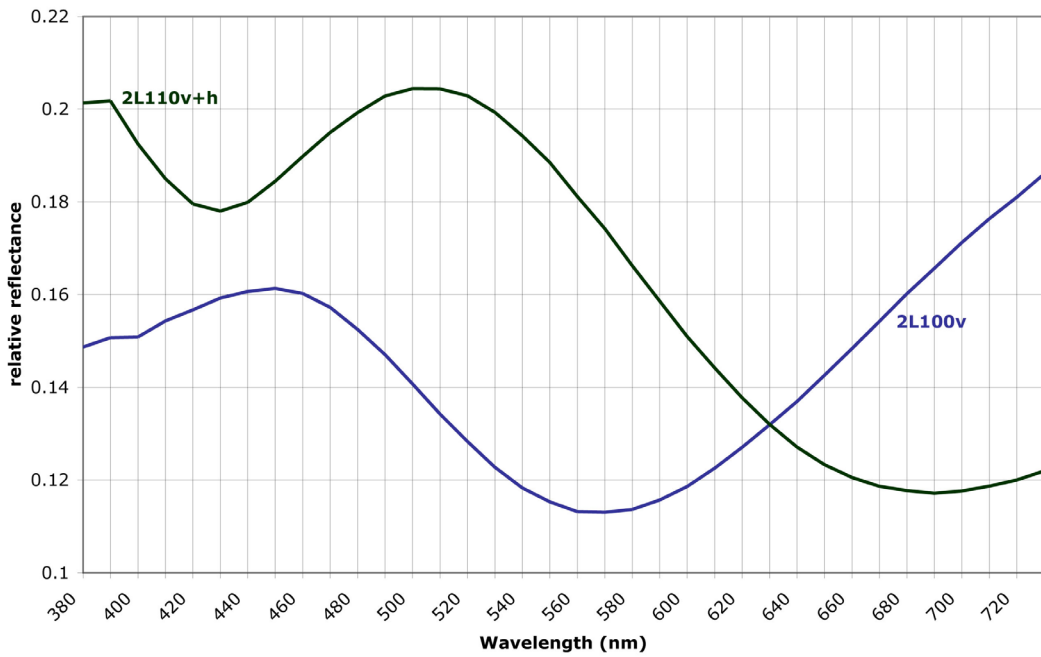
Figure 5.3: *Relative reflectance curves of samples anodised to 100V and anodised to 100V and heated showing significant colour change.*
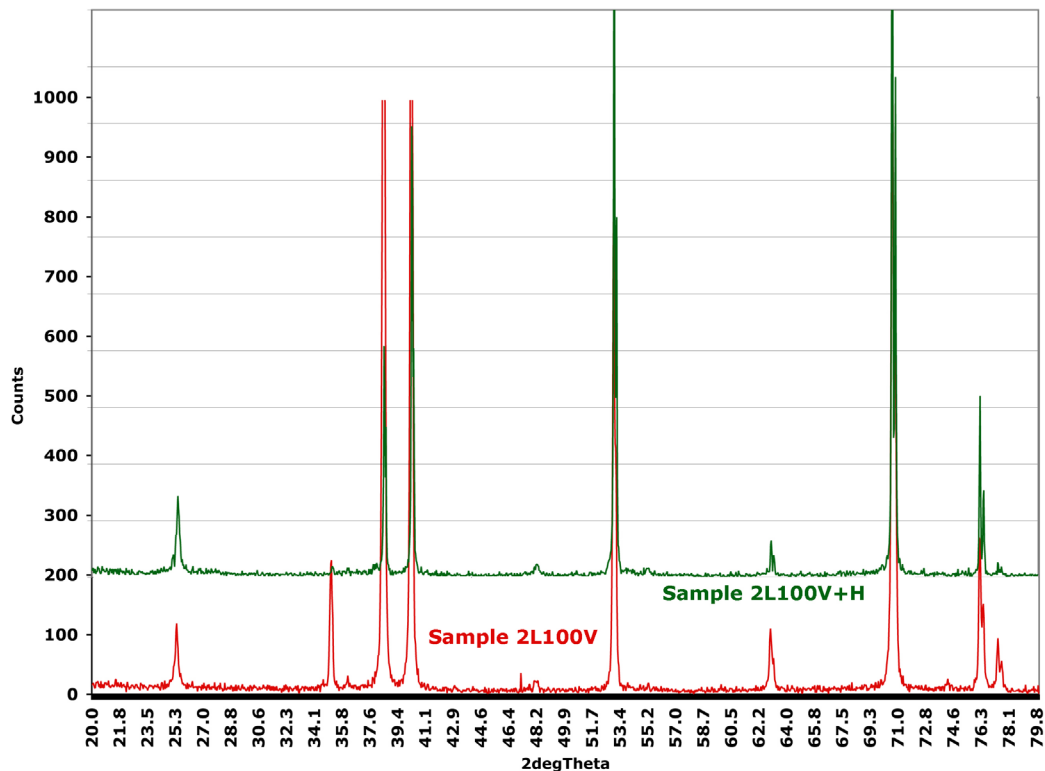
Figure 5.4: *XRD of anodised sample **2L100V** compared with sample **2L100V+H** which had been anodised and then briefly heated showing no change in the peaks associated with the anatase form of titanium dioxide.*

subsequent brief heating, although changing the colour appearance, does not change the crystal form. Again it should be noted that the titanium peak at 35.2 is much reduced in the spectrum of the sample **2L100V+H,** compared with that of sample **2L100V**, either indicating a thicker oxide layer or an orientation difference in the underlying titanium surface. Reference spectra for titanium are based on a very fine crystal structure but Material **2**, which was used for the sample preparation had a granular surface structure, as shown in Chapter 4. Therefore the relative intensity of the titanium XRD peaks would vary compared with the reference data, although the position of the peaks would remain as quoted. Hence the major peak for the reference data is at 40.2 but the major peak for the base titanium material used for sample preparation is at 38.5.

Consideration of alternative possibilities for the observed change, as described above, suggested that heating might have removed the water of crystallisation from the anatase, producing a more transparent layer. An attempt to verify this was made using infrared spectrometry but the method did not identify any water molecules present in the surface oxide layer of either the anodised sample coupon or the anodised and heated sample coupon. This therefore remains an area for further experimentation outside the scope of this project. However, from the perspective of the jewellery practitioner in the workshop, it is clear that the combination of anodising and heat allows for a more precise and subtle control of the oxide layer and thus the colouring achieved and this technique is worthy of further exploration. A further evaluation of this procedure is discussed in Chapter 6.

The conclusion from the XRD analysis is that the crystal form of the oxide is largely but not entirely determined by the oxidation method. As, for example, the titanium dioxide present in the oxidised layer on titanium sheet, which has been anodised at voltages up to and including 100V, is in the anatase form. But both the rutile and the anatase forms of the oxide are present in oxide layers formed by anodising at higher voltages or by heating. Therefore any variation in colour of the oxidised surface produced electrochemically, with voltages up to 100V, cannot be attributed to the different refractive indices of the two crystal forms of titanium dioxide.

It is also possible by consideration of the theoretical layer thickness calculated from the formulae presented in Chapter 3 to quantify the likely maximum thickness difference that could be attributable to the potential variation in refractive index of the two species. The colours are identified by the wavelength at which maximum absorption occurs and the calculations are made using an average refractive index for rutile of 2.76 and for anatase of 2.524. The results for a range of first and second order colours are presented in Figure 5.5.

The graph shows that for a first order yellow with absorption at 420 nm the thickness difference is calculated at 4 nm, while for a second order yellow with the same absorption,
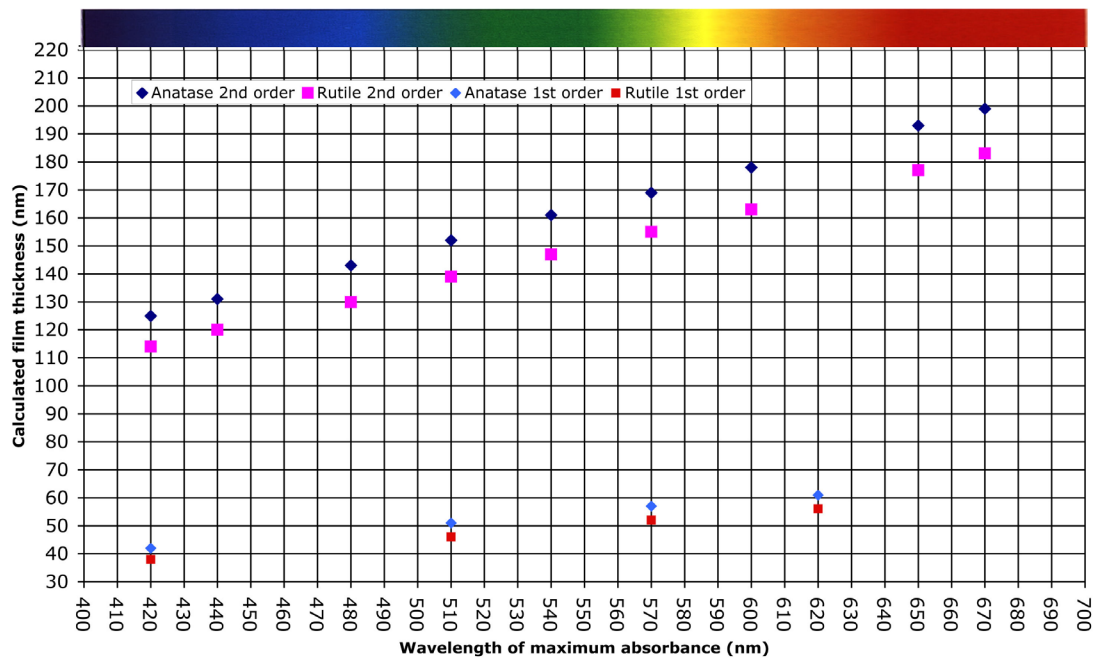
Figure 5.5: *Theoretical oxide layer thickness for different colours, identified by the wavelength of maximum absorbance, assuming oxide is either all anatase or all rutile.*

the difference is 11 nm. Even for the thicker, second order layers with absorption at 670 nm, showing a blue/green colour, the maximum difference would be 16 nm. Therefore even if the oxide layer is a mixture of the anatase and rutile forms of titanium dioxide, it is unlikely that this would be responsible for the level of observed colour variability and an explanation must be sought within the structure and measured thickness of the oxide film.

5.3.2. Oxide Film Structure and Thickness

The XRD analysis**,** described above, gives some information on the crystal species present in the oxide layers formed by heating and by anodising, but other techniques are needed measure the thickness of the oxide layers and to view and examine their internal structure in detail. These techniques are presented below in order of increasing resolution.

Focused Ion Beam System (FIB)

A Focused Ion Beam (FIB) system, a FEI Company FIB 200 TEM Workstation, Figure 5.6, was used to mill out a small section of the oxidised titanium surface, cutting through into the titanium substrate and exposing the cross-section of the oxide layer attached to the underlying metal. The thickness and structure of the oxide layer was observed in situ by recording images of the sample tilted through 45 degrees.

Although there are some similarities in the operation of SEM and FIB systems, the major difference is that the electron beam used for imaging in the SEM is non-destructive

whereas the beam of gallium ions used in the FIB is destructive. The focused gallium ion beam bombards the surface of the sample producing a signal when an atom is removed. The intensity of the
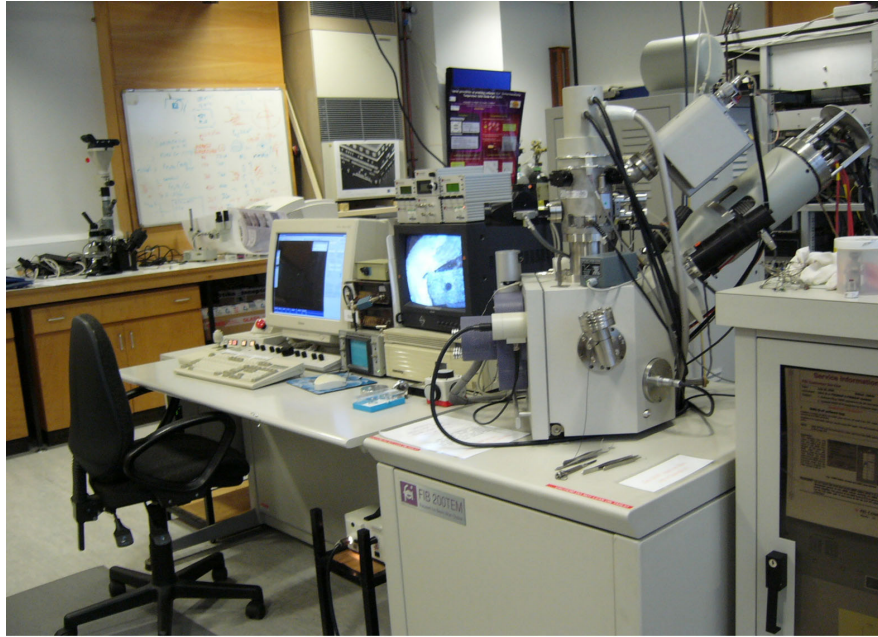
Figure 5.6: *FEI company FIB 200 TEM Workstation at IC. (Photo courtesy of Helena Tellez)*

beam can be varied for imaging or for milling to cut into the surface of the sample.

Experimental Conditions

In order to establish the experimental conditions for the measurements a coupon of material **2, 2J90V,** anodised at 90V to produce a reasonably thick oxide layer, ca 150 nm, was used. Two trial trenches (5 microns x 1 micron) were milled in this sample but although the metal surface was clearly visible, it was difficult to distinguish the upper surface of the oxide layer. It was therefore deemed necessary to protect this surface during the milling process by deposition a thin layer of platinum on the surface of the oxidised material, a procedure included as a feature of the FIB workstation. Figure 5.7 shows images of the first trial trench, the stages of the platinum deposition and the subsequent milling and polishing with the ion beam.

This procedure produced a clear image of a well-defined oxide film whose thickness could be measured, as shown in Figure 5.8.

However measurement of the layer thickness produced variable results from the two images, of 180 nm and 140 nm. Examination of the images revealed an unexpected feature; the presence of apparent lenticular voids within the oxide layer. Such inhomogeneity within the oxide layer could produce unexpected colour variation as the refractive index of the gas within the voids would be considerably lower than that of the surrounding oxide and the resulting interference colour would be affected.

'Gold' Sample Coupons
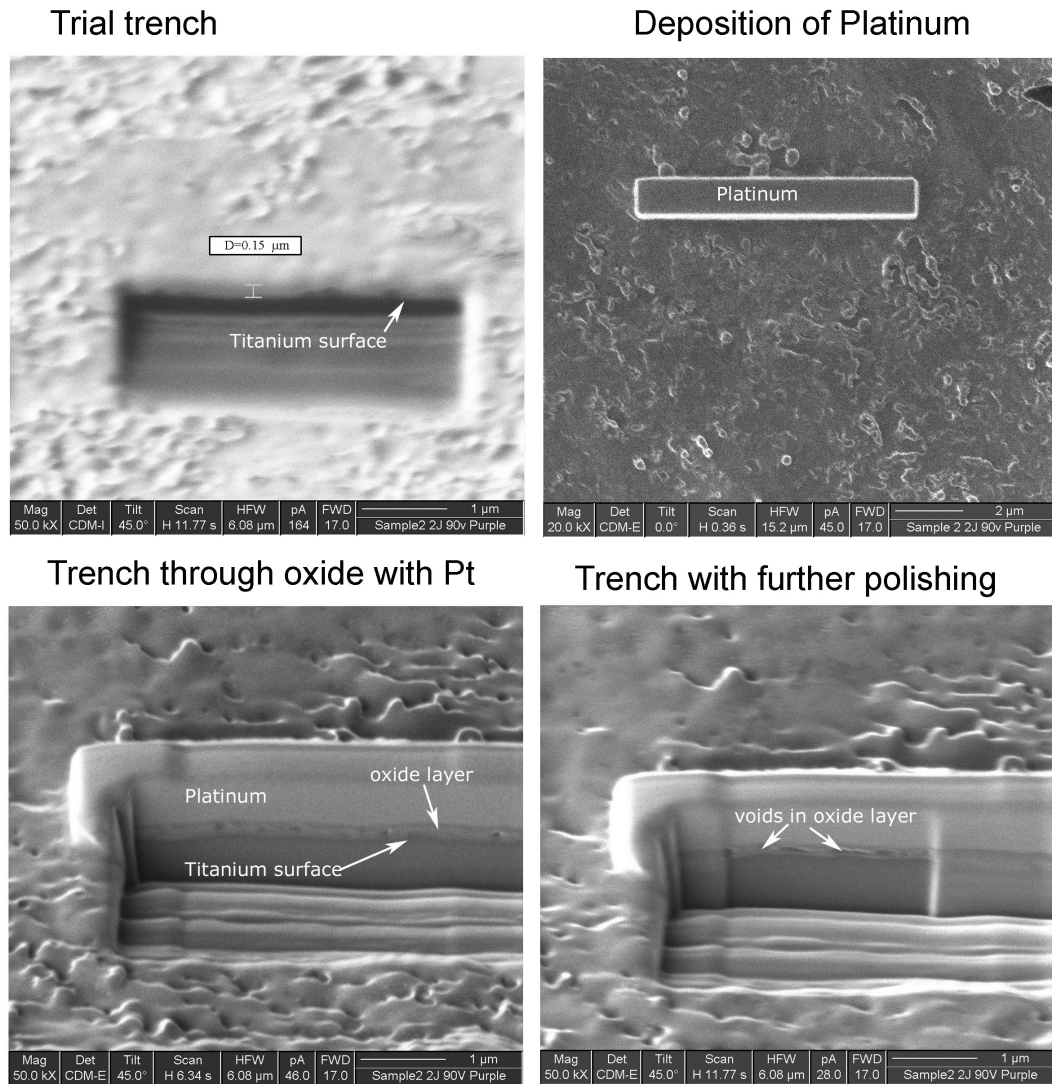
Figure 5.7: *Stages in determining the operating conditions from first FIB trial trench, subsequent platinum deposition and successful trench.*

The initial intention for the measurement of the structure and thickness of the thermally and electrochemically produced oxide films on titanium had been to compare samples coloured blue and gold and sample coupons of material **2**, (1.5 cm x 1.5 cm) were prepared accordingly. However the difficulties in obtaining valid results for the thicker, purple-coloured sample meant that the blue coloured samples were judged to have been created by oxide films that were too thin for satisfactory results from this technique. Therefore only the sample coupons coloured gold, **2J70V** and **2QE,** were examined with FIB and the results are given in Figure 5.9. The theoretical thicknesses of the gold samples were calculated to be 128 nm for the anodised sample, **2J70V,** which as shown above was likely to be composed of anatase, and 120 nm +/- 5 nm for the heated sample, **2QE,** assumed to be a mixture of anatase and rutile**.**

For the anodised sample **2J70V**, it is just possible to determine the edges of the oxide
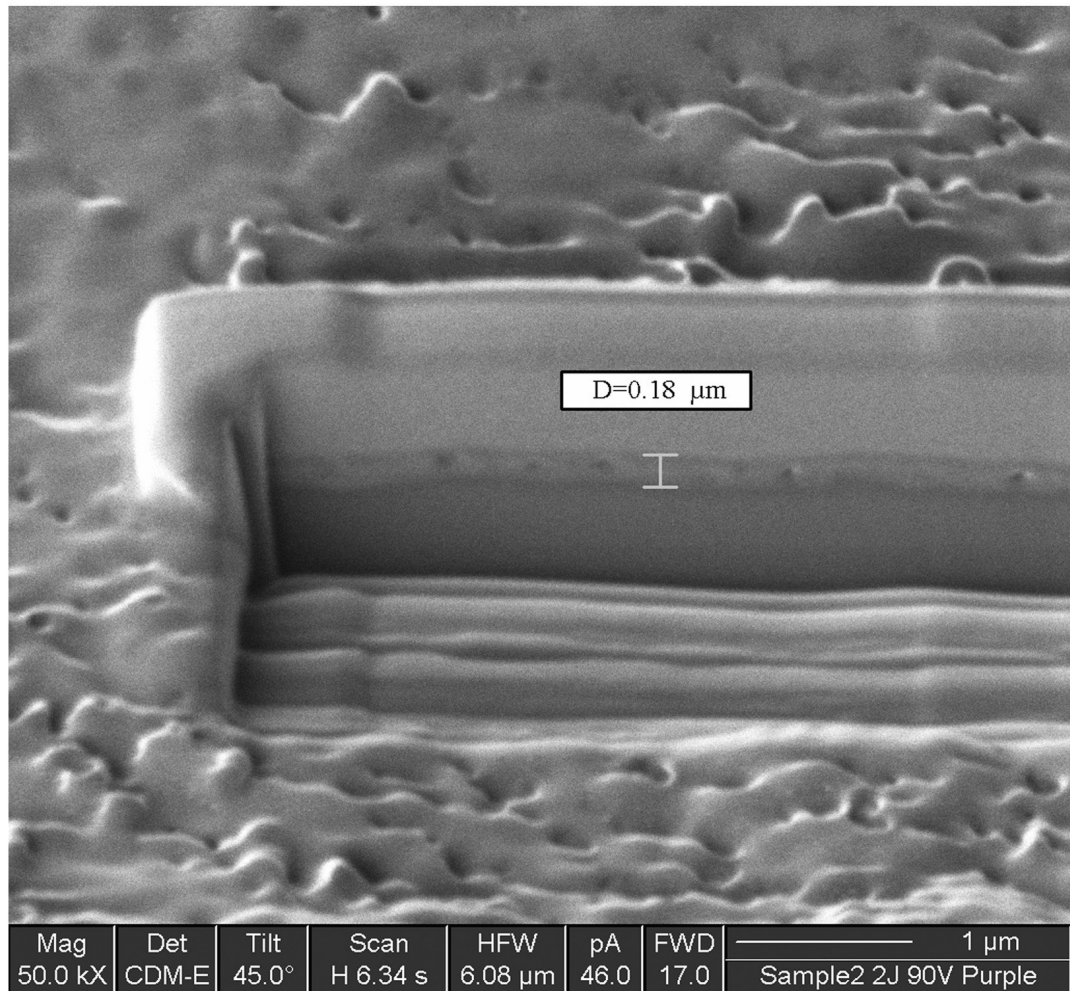
Figure 5.8: *FIB trench through thicker anodised oxide layer showing the layer measurement at 180 nm and the presence of voids.*

layer, which appears to have a uniform structure with no obvious voids. The thickness of this layer is consistent along the length of the trench and measures only 80 or 90 nm. In contrast, the micrograph of the trench through the heat coloured sample, **2QE**, gives a clearer image showing the metal surface to be irregular at the sub-micron level with an attached oxide layer varying in thickness along the trench, measured at one point as 90 nm.

Thicker Layers

The unexpected structure, with voids observed in the thicker anodised oxide layer but not in the thinner gold colour sample, prompted examination of available samples of other titanium sheet that had been anodised to a similar colour and therefore a presumed similar thickness of oxide layer. The objective of these examinations was to determine if the anodisation of other samples of titanium sheet produced similar structural features which included voids. FIB was therefore used to examine anodised sample coupons of materials **CSM**, **H** and **1**.

Sample **2J70V** anodised gold   Sample **2QE** heated gold
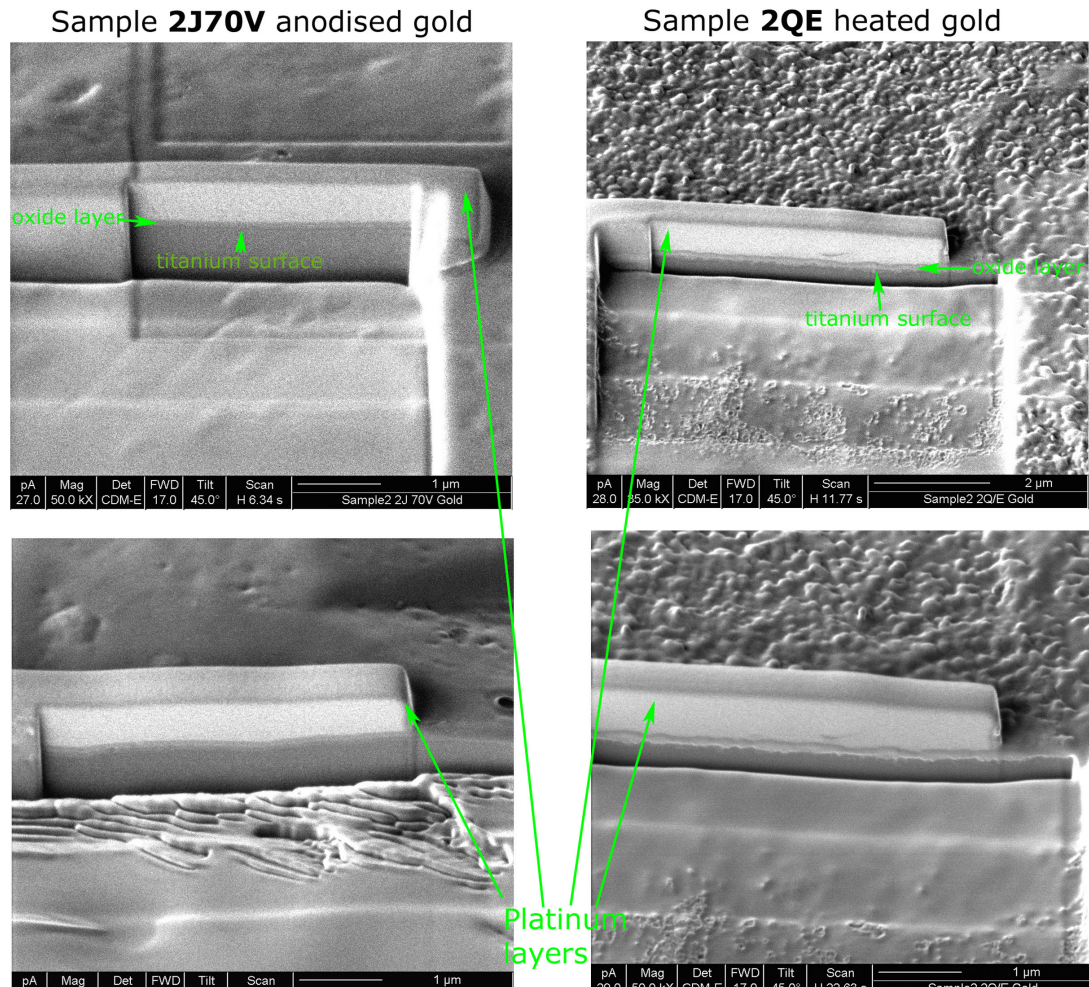
Figure 5.9: FIB images showing comparison between anodised and heated samples of metal **2** coloured gold.

Examination of sample **CSM60V** with FIB showed the structure expected for an etched titanium surface and although some parts of the surface appeared rough at magnification of x2000, these looked much smoother at higher magnification, x20000. Two trenches were milled on the same area situated in a smoother and a rougher part of a single grain and the oxide layer was clearly visible on the tilted sample, Figure 5.10.

The images show an undulating metal surface and an oxide layer of variable thickness with lenticular voids as observed for sample **2J90V** but in greater profusion throughout the layer. The frequency of voids appeared to be slightly greater in the smoother area compared to that in the slightly rougher part. The measurement of the layer thickness in the two separate trenches, observed in the FIB showed the same value at 130 nm.

In an attempt to achieve an improved image of these trenches, the sample coupon was subsequently viewed at higher resolution using the Leo Gemini 1525 FEGSEM. The resulting images are presented in Figure 5.11 and discussed below.

Even though the images were taken at approximately twice the previous
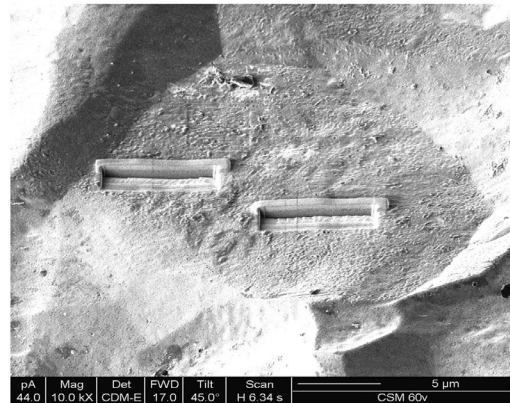
Figure 5.10: *Stages in preparation of trenches on sample **CSM60V**, which show the presence of voids in the oxide layer.*

magnification, little further information was obtained from this higher magnification and the greater resolution of the Leo SEM. But the presence of the voids was confirmed, indicating that these appear to be a feature of workshop anodised material. Although the **CSM** sheet had been etched with an HF mixture immediately before anodising, the presence of voids in the oxide layer of this material and the sample **2J90V** proved that such pre-treatment did not influence this phenomenon.

Trench in rougher area

Platinum layer

Titanium surface

voids

oxide layer

200 nm   EHT = 5.00 kV   Signal A = InLens   Date :27 Sep 2006   ZEISS
          WD =   7 mm   Mag = 126.55 K X   Time :12:56:49

Trench in smoother area

200 nm   EHT = 5.00 kV   Signal A = InLens   Date :27 Sep 2006   ZEISS
          WD =   7 mm   Mag = 124.81 K X   Time :12:50:47
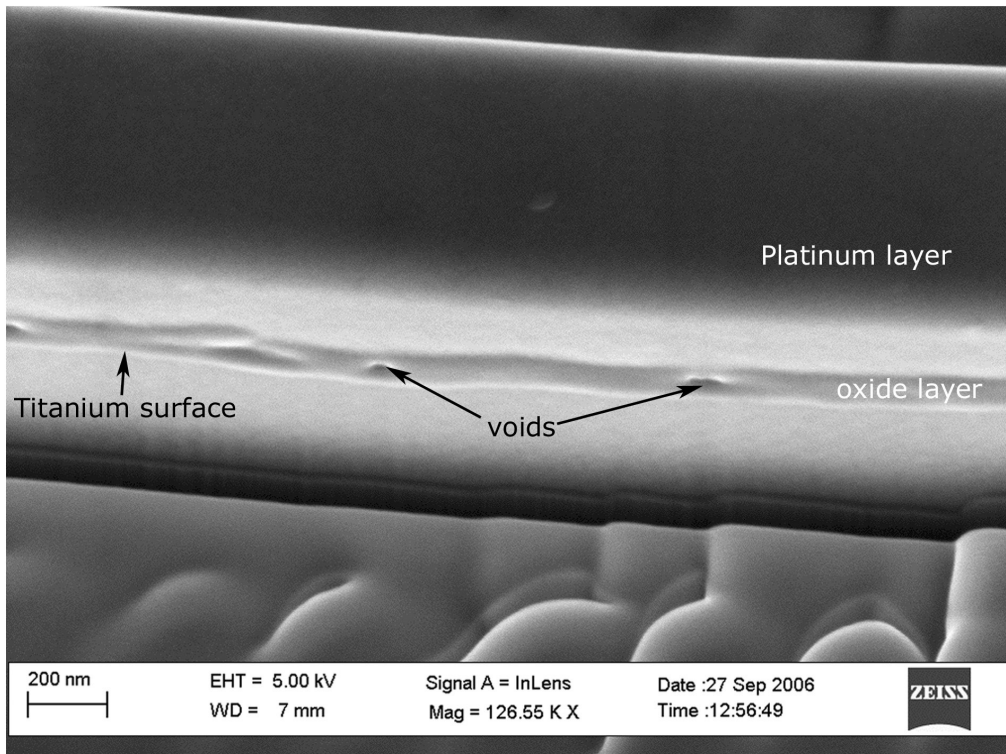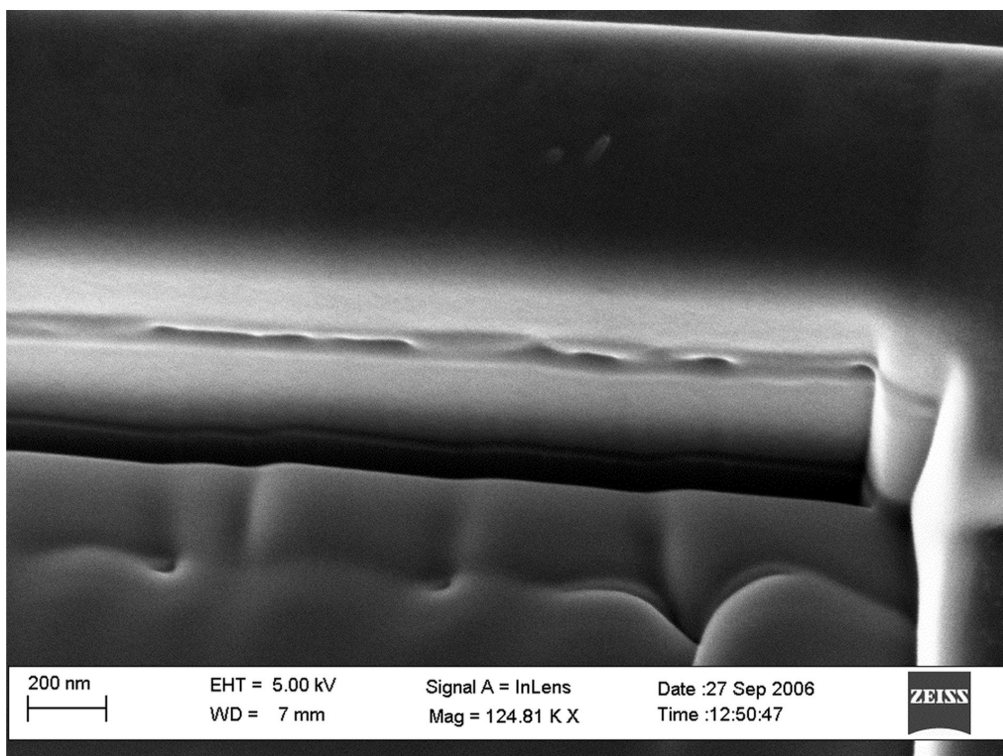
Figure 5.11: *FIB cut trenches on anodised sample* **CSM60V** *viewed with Leo at higher resolution.*

However examination of the anodised sample H17-660, whose colour was similar to that of CSM60V and 2J90V, showed no evidence at all of the presence of voids within the oxide layer, as shown in Figure 5.12.

FIB Images of H17-660 sample

First trench   Second trench
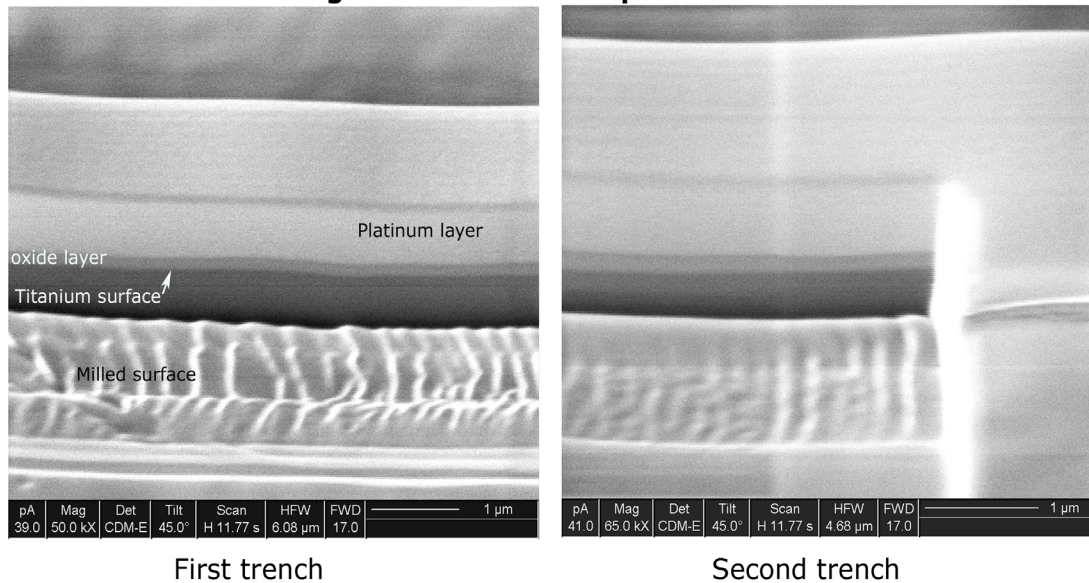
Figure 5.12: *FIB images of two trenches cut into anodised sample H17-660.*

The preparation details of this sample are not precisely known but the titanium was said to have been prepared by HF etching. Examination, at two levels of magnification, of two different trenches cut into the surface oxide reveal a clearly defined oxide layer of even thickness.

The final sample examined with FIB was a sample coupon of material **1,** anodised at 60V to produce a pink colour. The phenomenon of 'Flower' oxides had been discovered when this material was anodised and the imaging capability of the FIB system was used to select an area of particular interest for examination. Imaging with the ion beam as shown in Figure 5.13 gives greater detail of the surface topography of the sample and confirms that the 'Flower' oxides are three-dimensional features.

The area within the green box on the upper ion-beam image at x10,000 is further magnified to x35,000 imaged both with the ion beam and the electron beam. The images show the undulating nature of the underlying titanium surface which is mirrored by the overall oxide layer and also that the 'Flower' oxides appear to be formed from below the oxide surface, breaking through the surface layer and pushing back areas of the oxide to form the 'Flower' structures. Examples, indicated with arrows, can be seen of all stages of this process. These range from what appears to be the first eruption with a simple cross split, designated 1, via the intermediate stage, 2, to fully formed 'Flower' oxides, 3 and 4.

The protective platinum layer was deposited in an area across a group of 'Flower'
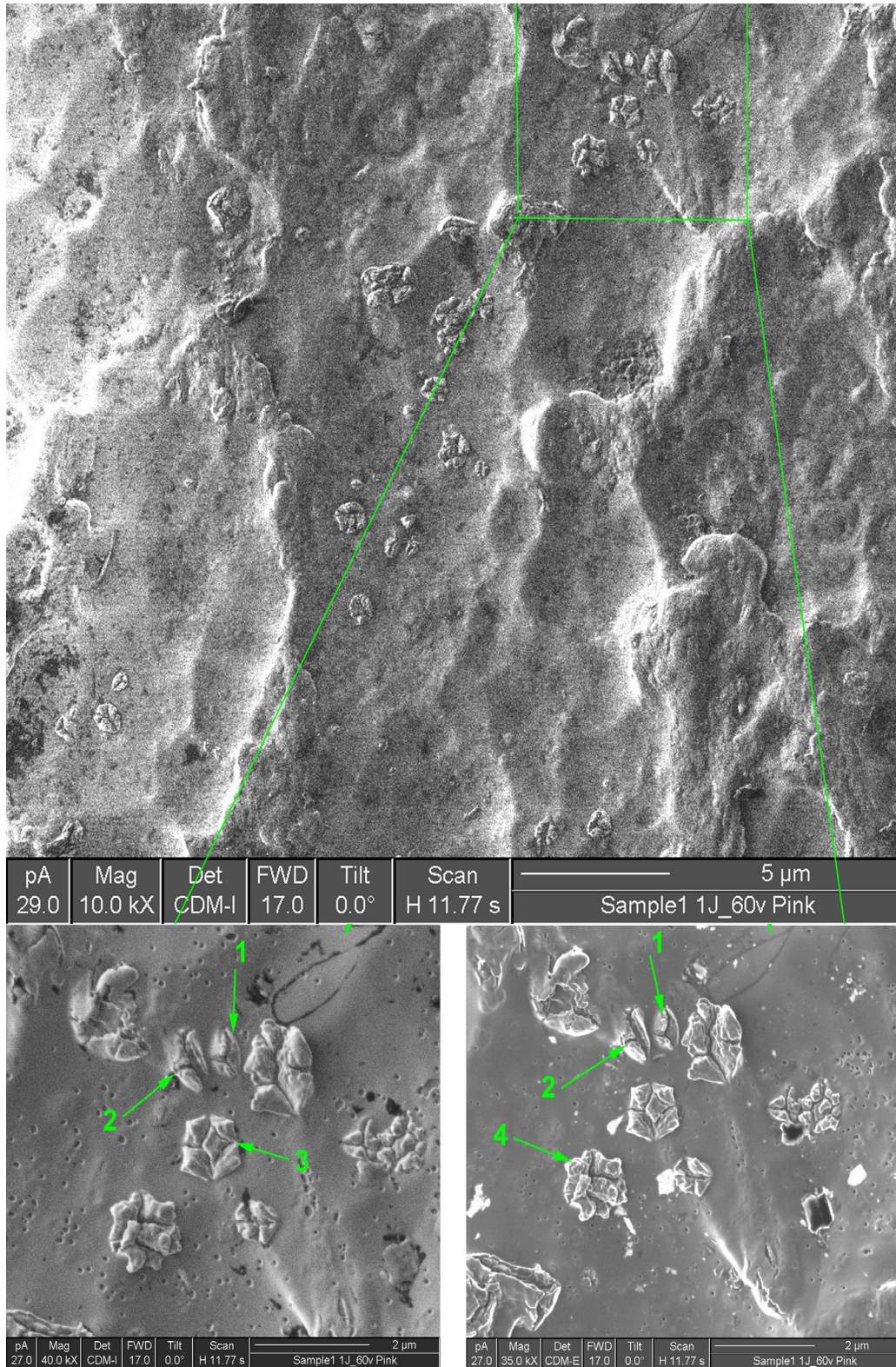
Figure 5.13: *FIB images of 'Flower oxides' on anodised material **1** using ion-beam images to show 3-D aspects of the surface.*

oxides so that the subsequent ion-beam milling would cut through the oxide layer containing the 'Flower' oxides as shown in Figure 5.14.

Same area flat and tilted
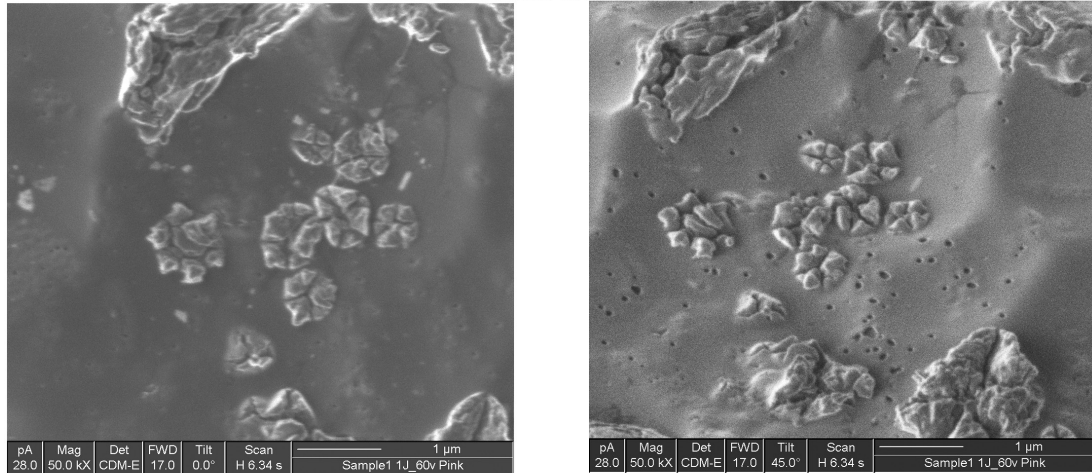
Pt deposited across 'flowers' and trench cut
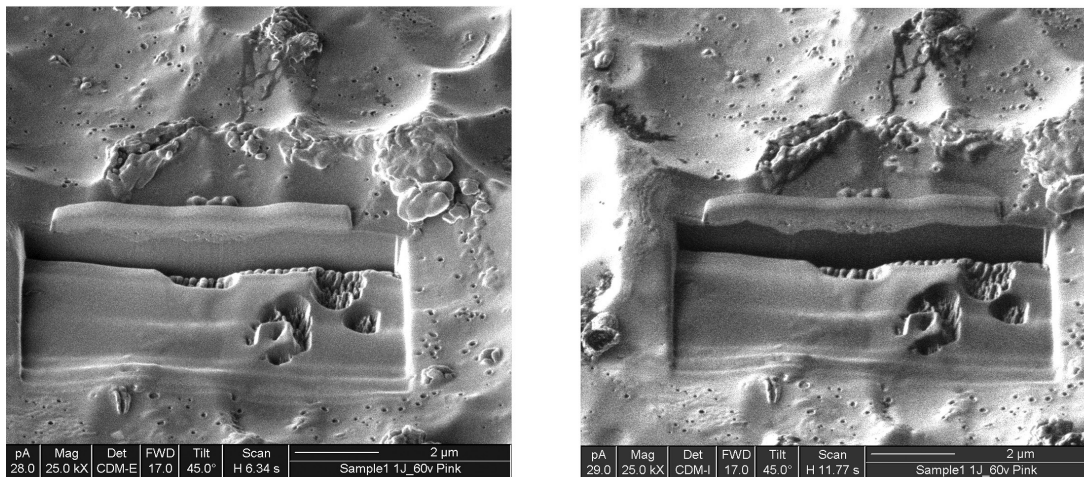
Figure 5.14: *FIB images of area of 'Flower' oxides before and after trench cut some structure evident but not sufficiently resolved.*

The resultant trench confirms the undulating metal surface and the wide variation in the thickness of the oxide layer. The section through the 'Flower' oxides gives an indication of structure although the upper surface of the oxide layer is not well defined and further resolution of the images, not possible with the current system, is needed to clarify the structures observed. Further investigation of the 'Flower' oxides could contribute to the understanding of the phenomenon but it is outside the scope of this study.

The FIB investigations revealed a great deal of information about the oxide layers, especially the presence of voids within those produced electrochemically in the workshop, but the measurements of the thickness of the layers were inconsistent. This may have been due to the fact that the images were at the limitations of the resolution of the FEI FIB system. The viewing of the trenches cut by FIB in one of the samples, using the higher resolution Leo microscope, while confirming the presence of the voids did not substantially add to the structural information and produced conflicting values for the measurement of the

layer thickness. The trenches in the other sample coupons proved difficult to locate when the samples were transferred from the FIB system, where they were prepared, to the Leo microscope. Therefore in order to generate a higher resolution image of the sample, which would be expected to permit a more accurate and consistent measurement of the layer thickness, an instrument with the combined facilities of an FIB milling system and a higher resolution electron microscope was sought. The 'gold' samples were therefore examined using a 'Cross-Beam' instrument, which combines the milling properties of FIB with a high-resolution scanning electron microscope.

'Cross-Beam'

In order to view and compare the oxide layers on titanium prepared by either anodising or heat, at higher resolution, the same sample coupons that had been oxidised to give a gold colour, **2J70V** and **2QE** were examined in a Carl Zeiss XB1540 "Cross-Beam" focused-ion-beam microscope an *'instrument equipped not only with an in situ field-emission scanning electron microscope for gallium-free imaging, but also an in situ low-voltage argon-ion-miller for gallium-free nanofabrication'*[30]. The Cross-Beam combines an FIB system with a high resolution SEM and the set-up is designed for the preparation of the sample and its examination in the same chamber.

Trenches were milled in the sample coupons, using the FIB operating mode of the system and conditions similar to those previously established, as presented above, i.e. milling with the argon ion beam was preceded by the deposition of a platinum layer to protect the oxide surface as shown in Figure 5.15.
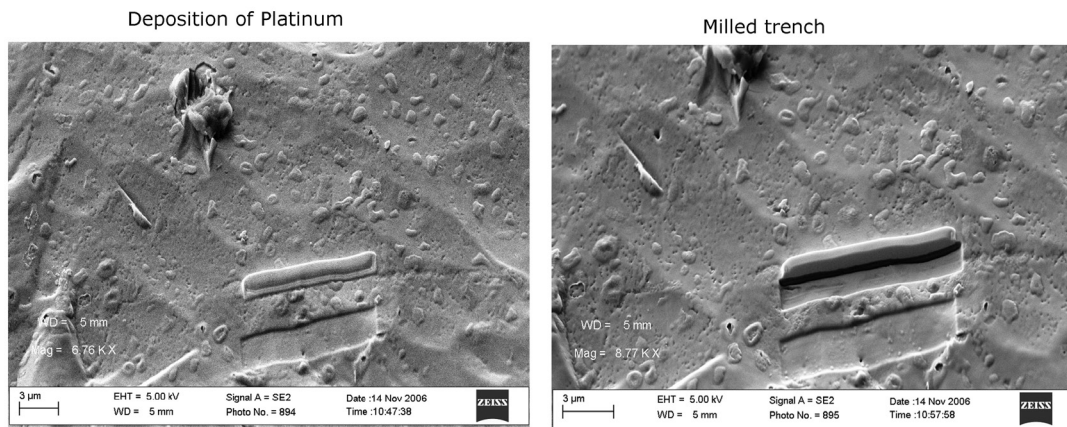
Figure 5.15: *CrossBeam images showing deposition of platinum and milled trench for anodised sample of metal **2, 2J70V**, coloured gold.*

The samples were subsequently tilted within the microscope chamber so that the sides of the milled trenches could be viewed with the SEM operational mode of the

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[30] London Centre for Nanotechnology website, www.london-nano.com

instrument. The angle of tilt dictated by the geometry of the instrument was 54^0. The resulting images from sample 2J70V are presented in Figures 5.16 and 5.17.
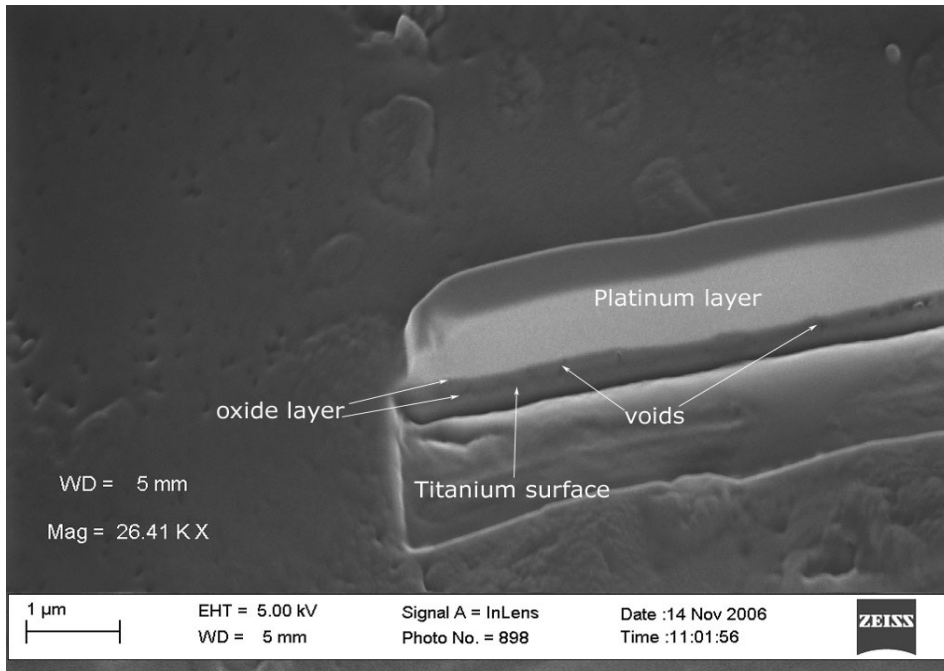
Figure 5.16: CrossBeam image showing the oxide layer of anodised sample *2J70V,* coloured gold with indication of voids in the layer.
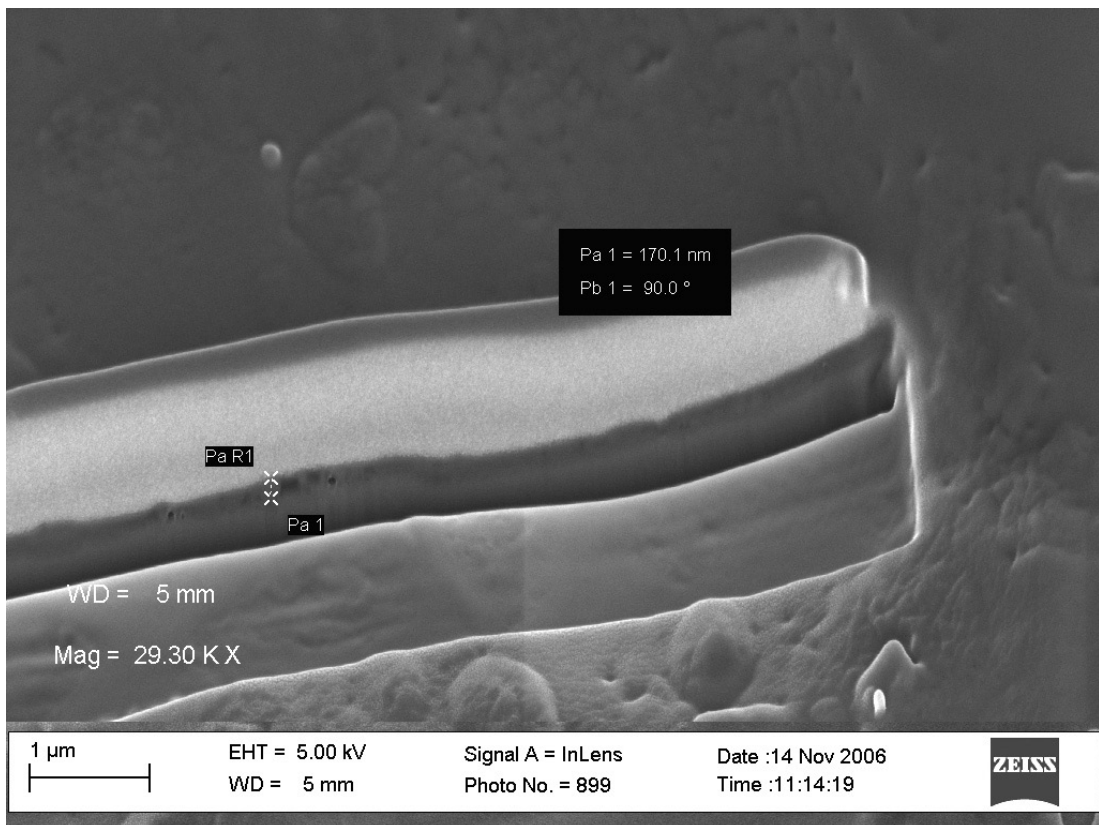
Figure 5.17: CrossBeam image of anodised sample **2J70V,** coloured gold with marker showing layer thickness of 170 nm. .

The CrossBeam images of sample **2J70V** in Figures 5.16 and 5.17, reveal much more detail of the oxide layer than had been observable with the FIB system alone. The clearly delineated layer showed more variation in thickness along the length of the trench and an indication of possible voids within the layer, which had only been observed previously in the thicker oxide layer. The measurement of layer thickness gives a value of 170 nm, which varied substantially from the previous measurements and also from the theoretical value of 128 nm.

The CrossBeam image of the platinum protective layer deposited on the heat coloured sample, **2QE**, presented in Figure 5.18, indicates that thermal oxidation creates a very different oxide surface. The overall surface is much rougher than that produced by electrochemical oxidation, as shown in Figure 5.15 above.
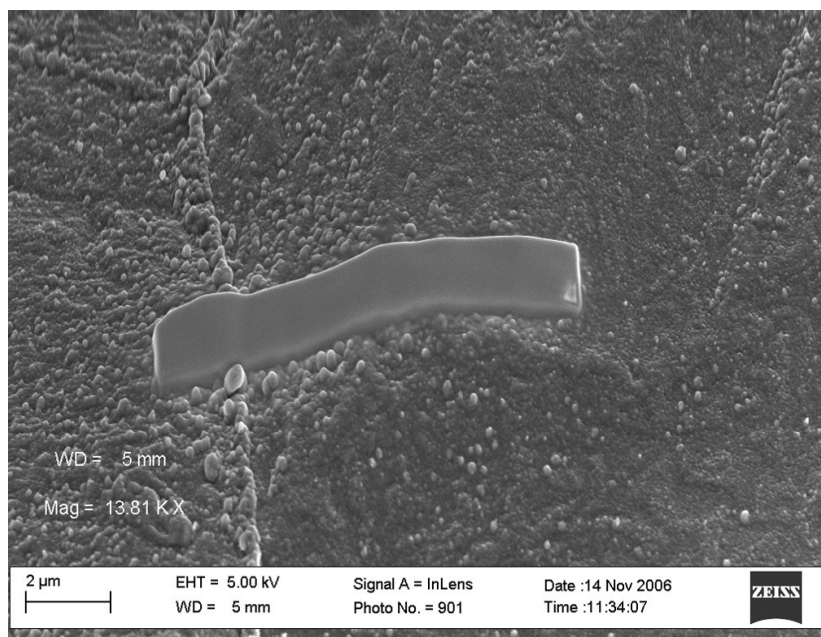
Figure 5.18: CrossBeam image showing heated sample of metal 2, 2QE, coloured gold with platinum deposited across a grain boundary.

The pronounced thickening of the oxide layer and coarsening of its structure at the grain boundaries of the underlying titanium surface is particularly noticeable. The cross-section, which shows substantial variability in the thickness of the layer along the trench, peaks at the point where the trench cuts through the grain boundary as shown in Figures 5.19 and 5.20. However thickness measurements made at other points of the layer show some consistency at 132.7 nm and 130.8 nm. Unlike the anodised layer, no voids are discernible.

For both samples additional information about the oxide structures was given by the CrossBeam images but the resolution of the instrument did not allow the structure to be clearly identified. Also the measurements made of the thickness of the oxide layers were inconsistent and before moving to the next step of the oxide layer investigation it is worthwhile to summarise the measurements made with all three different microscopes.
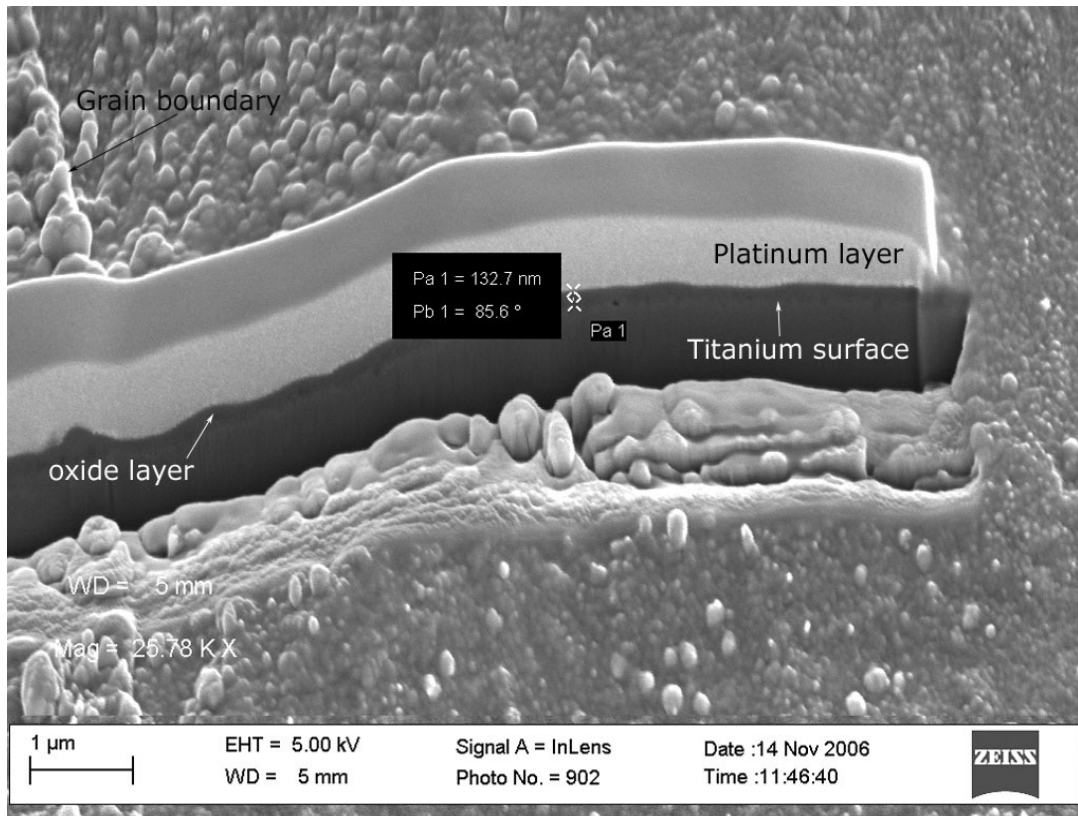
Figure 5.19: CrossBeam image of heated sample 2QE, coloured gold showing layer thickness measurement of 132.7 nm.
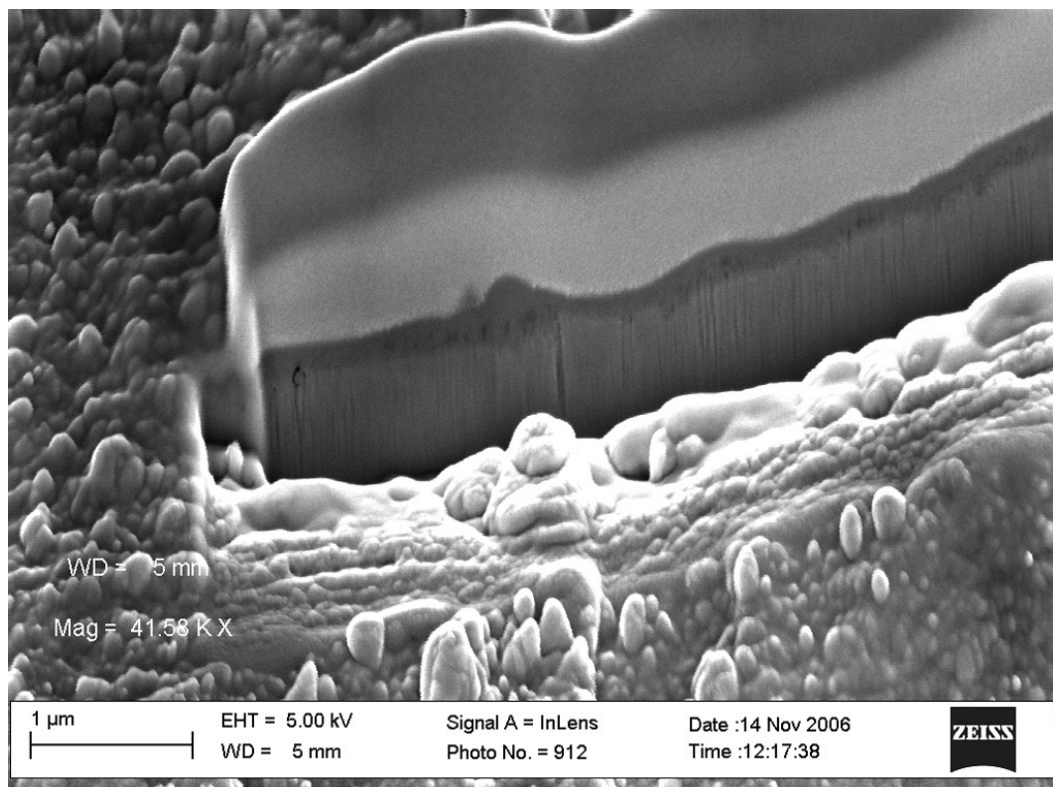
Figure 5.20: CrossBeam image of heated sample 2QE, coloured gold showing variation in layer thickness at the grain boundary of the underlying titanium.

Summary of Thickness Measurements

The measurements made of the thickness of the oxide layers on the different samples, viewed in situ attached to the metal surfaces, have yielded ambiguous results as presented in Figure 5.21.
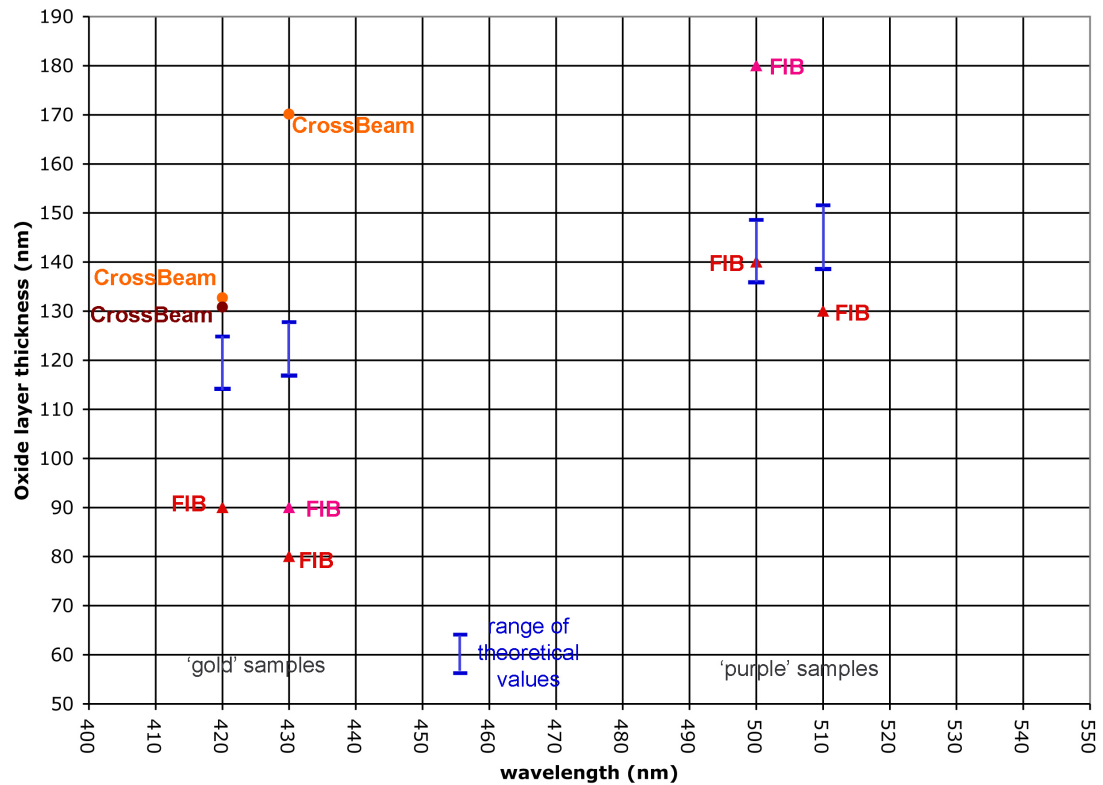
Figure 5.21: *Graph comparing theoretical thickness measurements for anatase and rutile oxide layers with values recorded in FIB and CrossBeam.*

The calculated values assume that the colours are second order interference colours with maximum relative absorbance at the wavelengths shown and that the oxide species present could be either rutile or anatase. Having established that the anodised sample coupons for the voltages shown produce only anatase, the theoretical value for **2J70V** is 128 nm compared with FIB measurements of 80 nm and 90 nm and a CrossBeam measurement of 170 nm. Similarly **2J90V** should have a theoretical thickness of 149 nm but FIB measurements give 140 nm and 180 nm. **CSM60V** with maximum absorption at 510 nm has a theoretical thickness of 152 nm and a measured thickness of 130 nm in the FIB. For the heat coloured sample **2QE** both species may be present in the oxide layer and therefore the theoretical thickness should be in the range 115-125 nm whereas measurement in the FIB is 90 nm and in the CrossBeam 132.7 nm and 130.8 nm.

Although the resolution of the different FIB systems does not allow the detailed structure of the oxide layers to be elucidated or the thickness of the layers to be measured accurately, the presence of voids, of varying profile, has been confirmed in the anodised

oxides created in the workshop. A few voids were detected in the thinner 'gold' layers with the CrossBeam but a greater profusion of voids were visible in the thicker layers produced at higher voltages. The further investigation of the voids within the oxide layers and accurate measurement of the oxide layer structures and thickness, in order to determine their possible effect on colour variability, requires a further increase in microscope resolution, which can be achieved by moving from Scanning to Transmission Electron Microscopy (TEM).

5.3.3. Transmission Electron Microscopy (TEM)

The microscope-based techniques using FIB and SEM yielded valuable information about the oxide layers formed on titanium by heat or anodising, where the layers on the different sample coupons have been viewed in situ attached to the metal surfaces. However the resolution of the microscopes used does not allow the detailed structure of the oxide layers to be elucidated or the thickness of the oxide layers to be accurately measured. Transmission Electron Microscopy (TEM) provides an appropriate technique to decipher the oxide layer structures. Whereas SEM provides images across the surface of a sample under test, TEM uses the electron beam to penetrate through the sample and image its structure. A crucial factor in TEM examination is the preparation of a cross-sectional sample, which is sufficiently transparent to the electron beam and stable within the vacuum chamber of the microscope, without damaging the structure of the layer.

The specimens for examination by TEM, known as foils, were milled from the two comparably coloured, gold sample coupons prepared from the known titanium sheet coloured by anodising and by heat, namely **2J70V** and **2QE** respectively, in the FEI FIB 200 TEM Workstation by the 'lift out' technique[31]. Prior to milling the oxide surface was protected by depositing a very thin gold layer and then a platinum layer. Two foils**, j13** and **i11** were lifted from sample **2J70V,** which had been prepared from titanium sheet of known origin, anodised at 70V to give a gold colour with a maximum absorption at 430 nm. But only one foil, **k9**, was cut from the sample **2QE**, which had been prepared from the same titanium sheet, heated in a kiln to obtain a similar gold colour appearance with a maximum absorption at 420 nm. The relative reflectance curves for these samples are shown in Figure 5.22.

These three foils were examined with a JEOL 2000FXII TEM at different levels of magnification and the cross-sections of the sample foils were tested for diffraction patterns to identify the degree of crystallisation of the material within the layers and the attached

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[31] Gueneau de Mussy, J-P. et al, *TEM and X-ray diffraction investigation of the structural characteristics of the microporous oxide film formed on polycrystalline T*i, Scripta Materialia, <u>48</u>, 23, 2003.

**Comparison of relative reflectance curves for 'gold' samples
measured on 0/45 spectrophotometer**
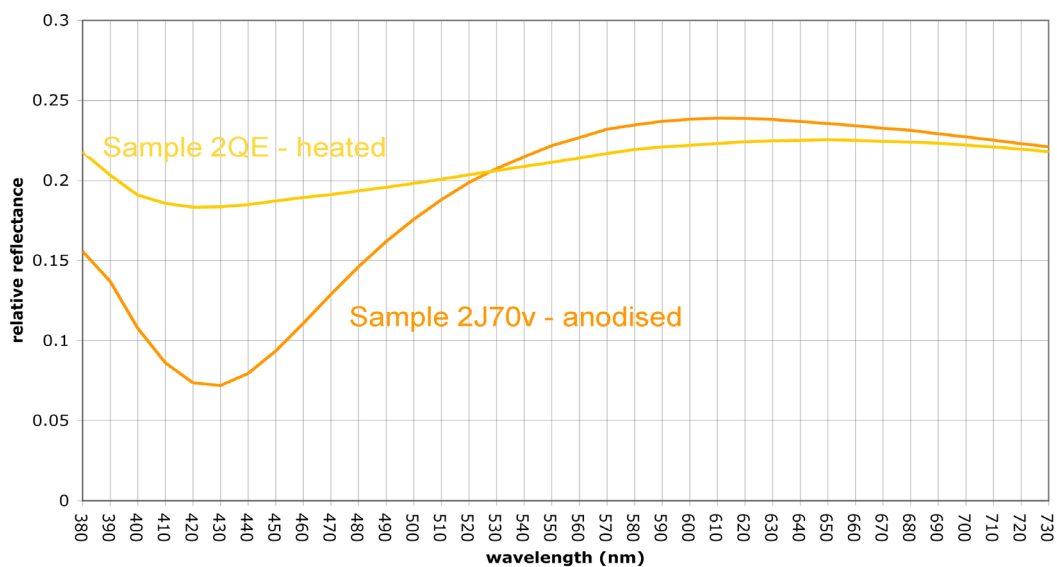
Figure 5.22: *Relative reflectance spectra for gold samples used for TEM.*

titanium. Information from the micrographs was analysed using an ImageJ[32] software programme. Repeat measurements made for one dimension on each of two different micrographs showed that the error in measurement by this technique was 0.25 percent[33].

Sample 2J70V

Two foils, **j-13** and **i-11** were lifted from the anodised sample coupon **2J70V** and Figure 5.23 shows the overview of the cross section of the oxide layer, 4110 nm in length, attached to the titanium sheet for foil **j-13**.

For over half of the length of the foil, the layer appears to be of a regular thickness but just over a third shows the presence of voids within the layer, as had been suspected from the CrossBeam images.

Higher magnification of the more regular part of the layer, Figure 5.24, confirms the presence of a 'sandwich' structure with three distinct layers.

Adherent to the titanium metal surface is an amorphous layer, confirmed by electron diffraction measurements, Figure 5.25, which shows no evidence of crystalline structure. Then there is a layer which is crystalline but whose electron diffraction measurement is not clear enough to identify the crystal form. Finally the top layer, which appears to be the thickest, is an amorphous layer with no structure visible in the electron diffraction measurements.

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[32] http://rsb.info.nih.gov/ij/
[33] The average deviation calculated from ten measurements of the same distance as a percentage of the average of the measurements.
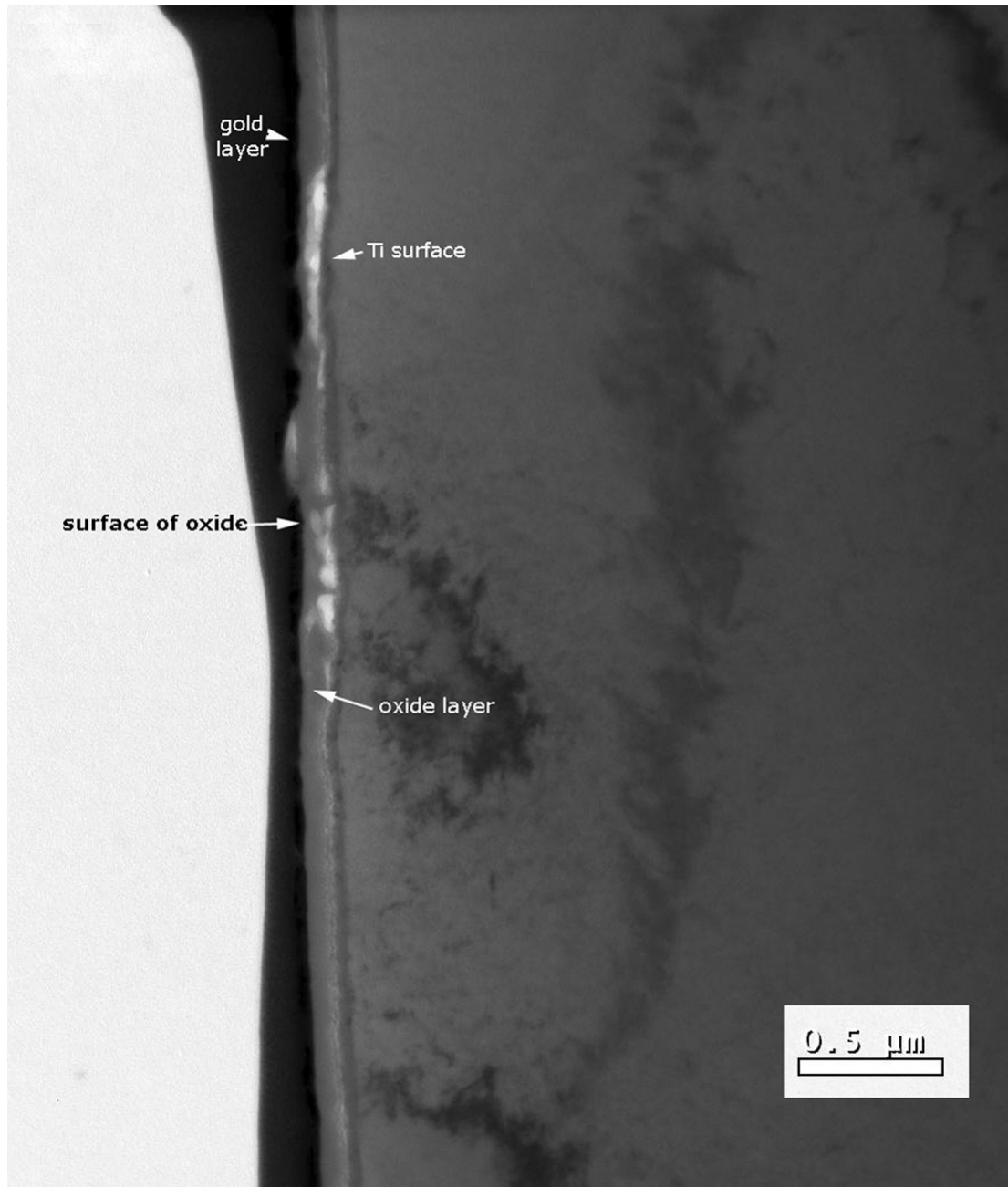
Figure 5.23: *TEM of anodised sample of material **2**, foil j-13 showing area with voids and regular area.*

Measurement of the total layer thickness shows it to be 139+/-4 nm for most of its length but increasing to 160 nm in the region where there are voids, Figure 5.26. As can be seen, the amorphous layer closest to the metal surface is the thinnest part of the overall layer ranging from 20-35 nm. The edges of the middle crystalline part of the layer are diffuse but an approximate width for this part of the structure is 60 nm. The final surface amorphous layer has a relatively smooth edge and varies in thickness between 42-55 nm.

As shown in Figure 5.26, the voids are situated within the middle crystalline layer and the largest one measures 136 nm at its maximum length and 56 nm at its widest point.
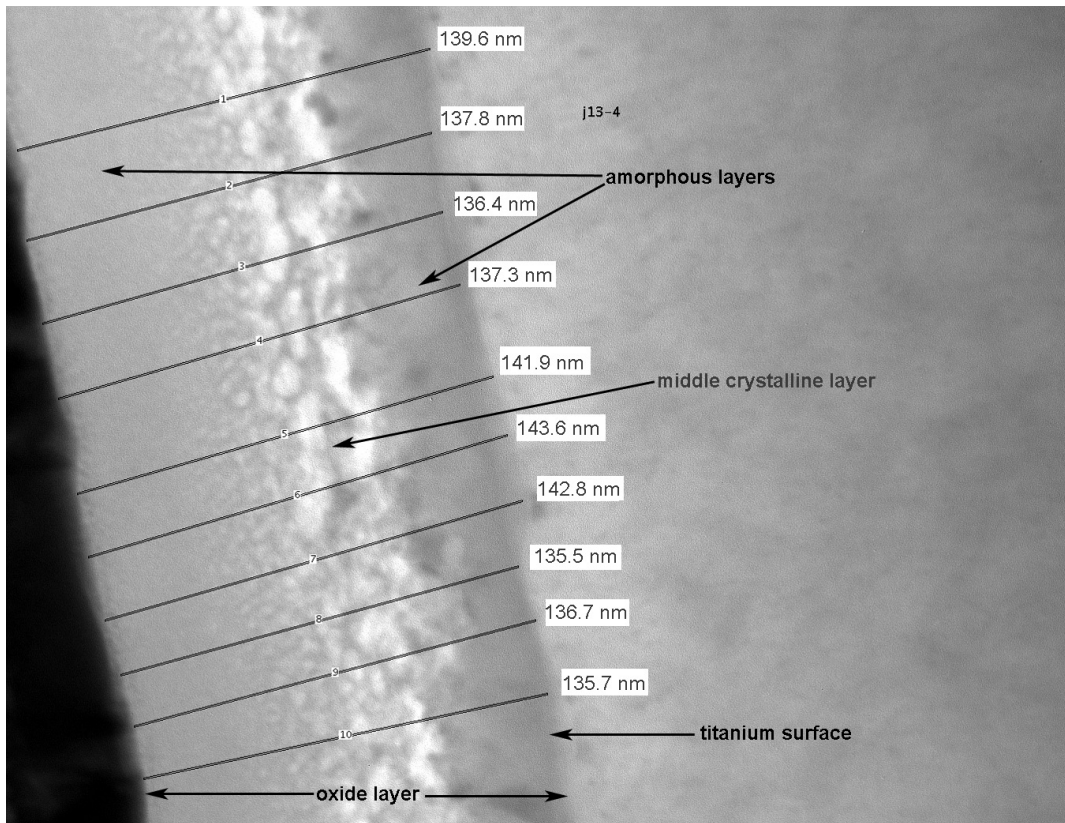
Figure 5.24: *Higher magnification of the uniform area with annotations measuring the thickness of the layer at regular intervals.*
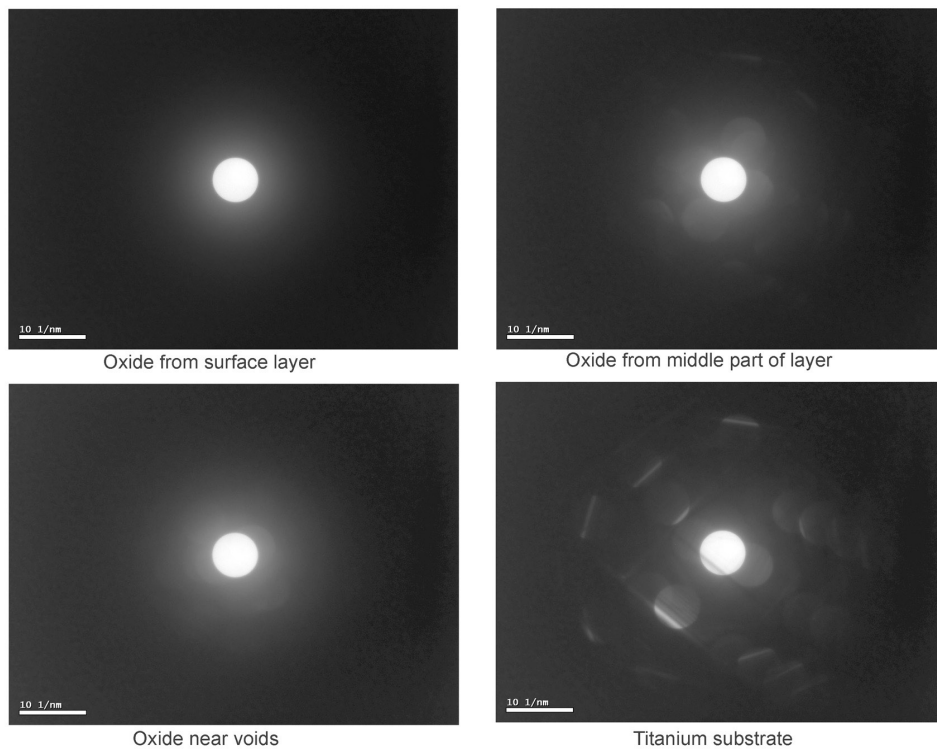
Figure 5.25: *Diffraction patterns for foil **j-13**, showing the amorphous structure at the surface of the oxide layer, an indication of crystalline structure in the middle of the layer and adjacent to the voids and the crystalline structure of the titanium metal.*
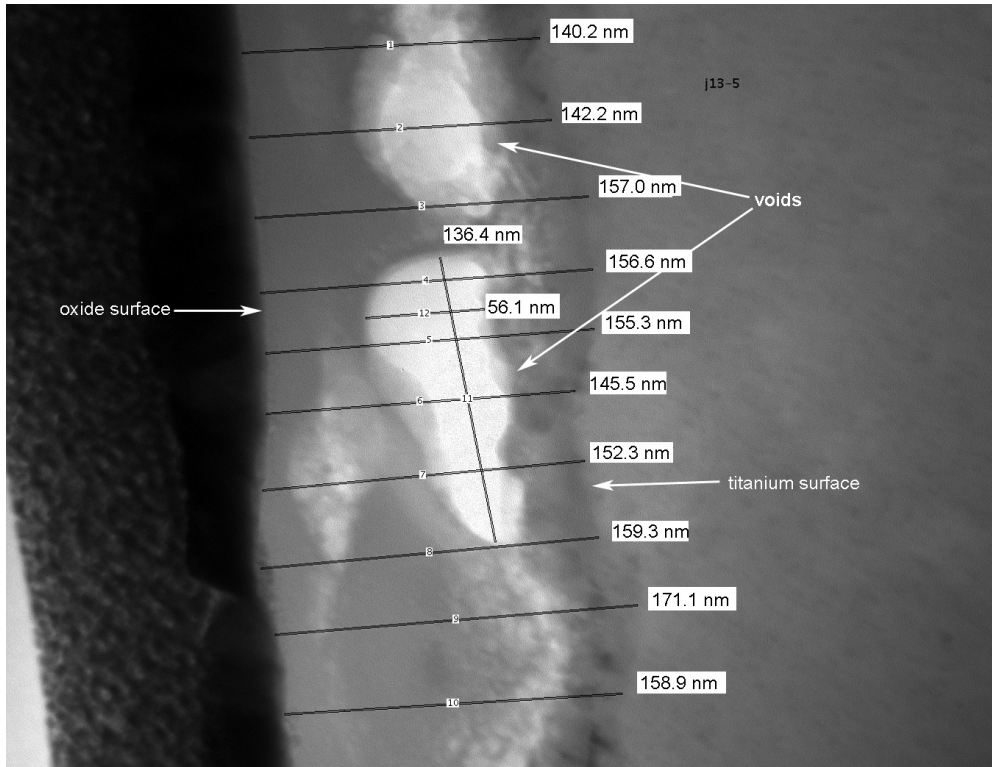
Figure 5.26: *Higher magnification of the area which includes voids with annotations measuring the thickness of the layers and the size of the voids.*
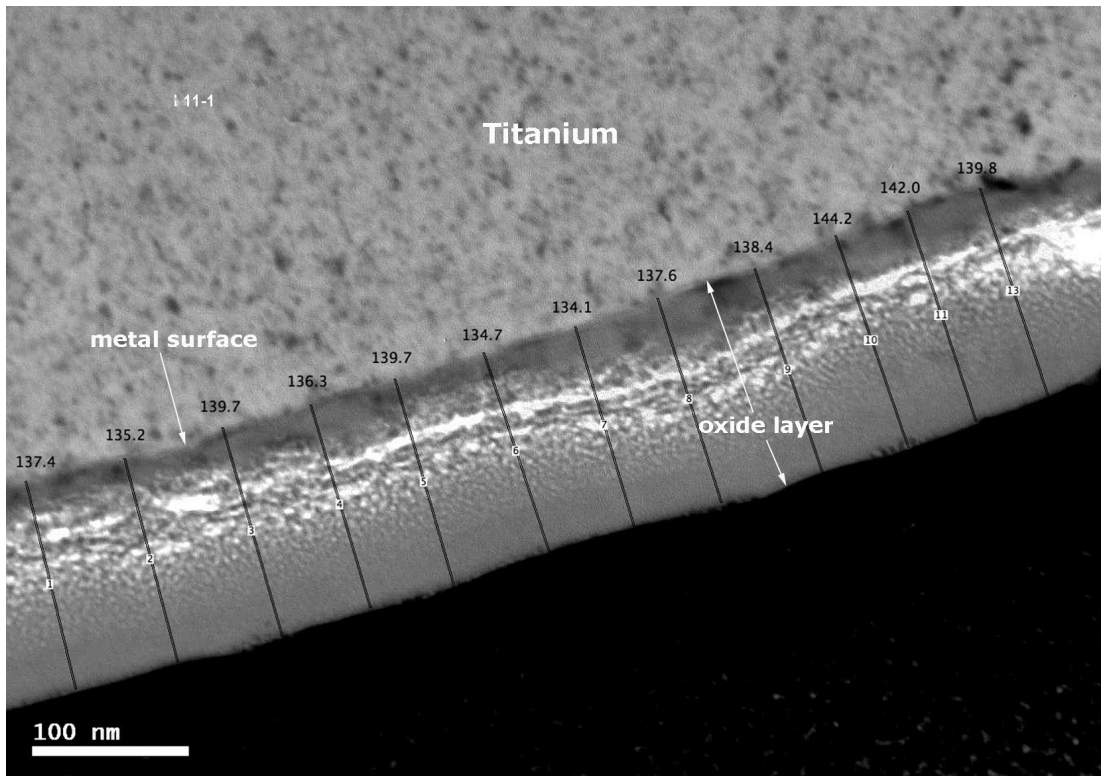
Figure 5.27: *TEM of foil i-11 cut from anodised material 2.*

The image from foil **i-11**, Figure 5.27, confirms the general structure of the oxide layer that was shown in foil **j-13**, taken from the same sample coupon, but has no significant

voids.

The overall measurement of the cross-section of this layer is consistent with that for the previous foil at 139+/-4 nm. However the inner oxide layer is slightly thinner, 13-24 nm, and the crystalline area somewhat thicker, in a range 61-67 nm.
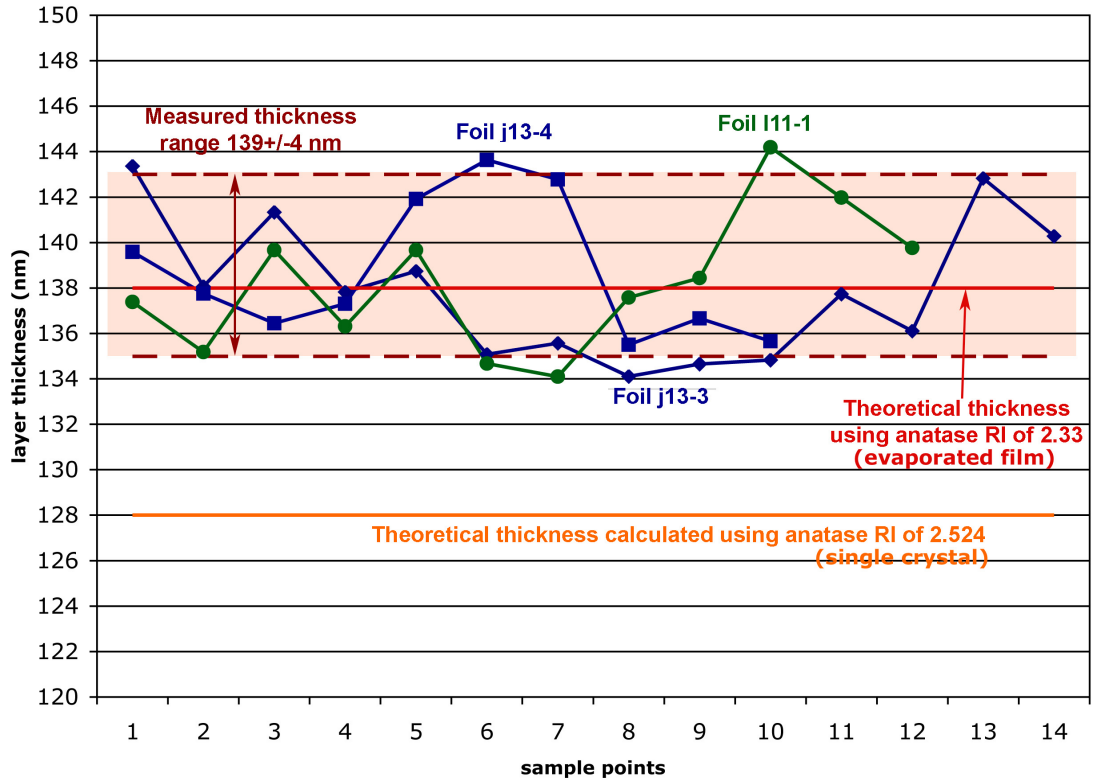
Figure 5.28: *Layer thickness measurements made using ImageJ software and the TEM images of the foils **j13** and **l11**. The average measured thickness is 138+/-4 nm compared with theoretical values of 128 nm or 138 nm.*

The layer measurements made using the ImageJ software programme and recorded on Figures 5.24, 5.26 and 5.27 are summarised for the regular sections of the anodised sample **2J70V** in Figure 5.28.

The average measured film thickness at 139 nm, for regions without voids, is somewhat thicker than would be predicted from the thin film interference calculation for anatase with an average refractive index (RI) of 2.524, i.e. ca 128 nm. But RI values are usually quoted for single crystals and, as discussed by Holland[34], anatase films have a lower refractive index than that of single crystals; unlike rutile which has similar values for both forms. It could therefore be argued that an electrochemically produced thin film of anatase is likely to be similar in structure to an evaporated film and the measured RI value of 2.33[35] for such films could be used to calculate the theoretical thickness. Using this lower

[34] Holland, L, *Vacuum Deposition of Thin Films,* Chapman and Hall, London 1963, p516.

[35] Blackwood, DJ, Greef, R, and Peter, LM, An ellipsometric study of thegrowth and open-circuit dissolution of the anodic film on titanium, Electrochimica Acta, 34, 875, 1989.

RI value, the calculated thickness for an anatase layer with a maximum absorption at 430 nm becomes 138 nm, which is in close agreement with the actual measurements. Whether or not the extra thickness of the layer incorporating the voids compensates in part for the change in RI due to the oxygen within the void is not possible to determine but the voids would almost certainly be a possible source of colour variability.

From these investigations it can be seen that anodising titanium produces a layered structure where the oxides generated at the metal/film interface and at the film/electrolyte interface are effectively amorphous but become crystalline in the intermediate region. This type of structure has been reported by Habazaki et al[36], where the oxide layer was grown anodically in sodium pentaborate on aged, sputter-deposited titanium. They also report the presence of voids in the crystalline area of the film. However there is a difference in that they detect the presence of nano crystalline anatase in the region of the oxide film adjacent
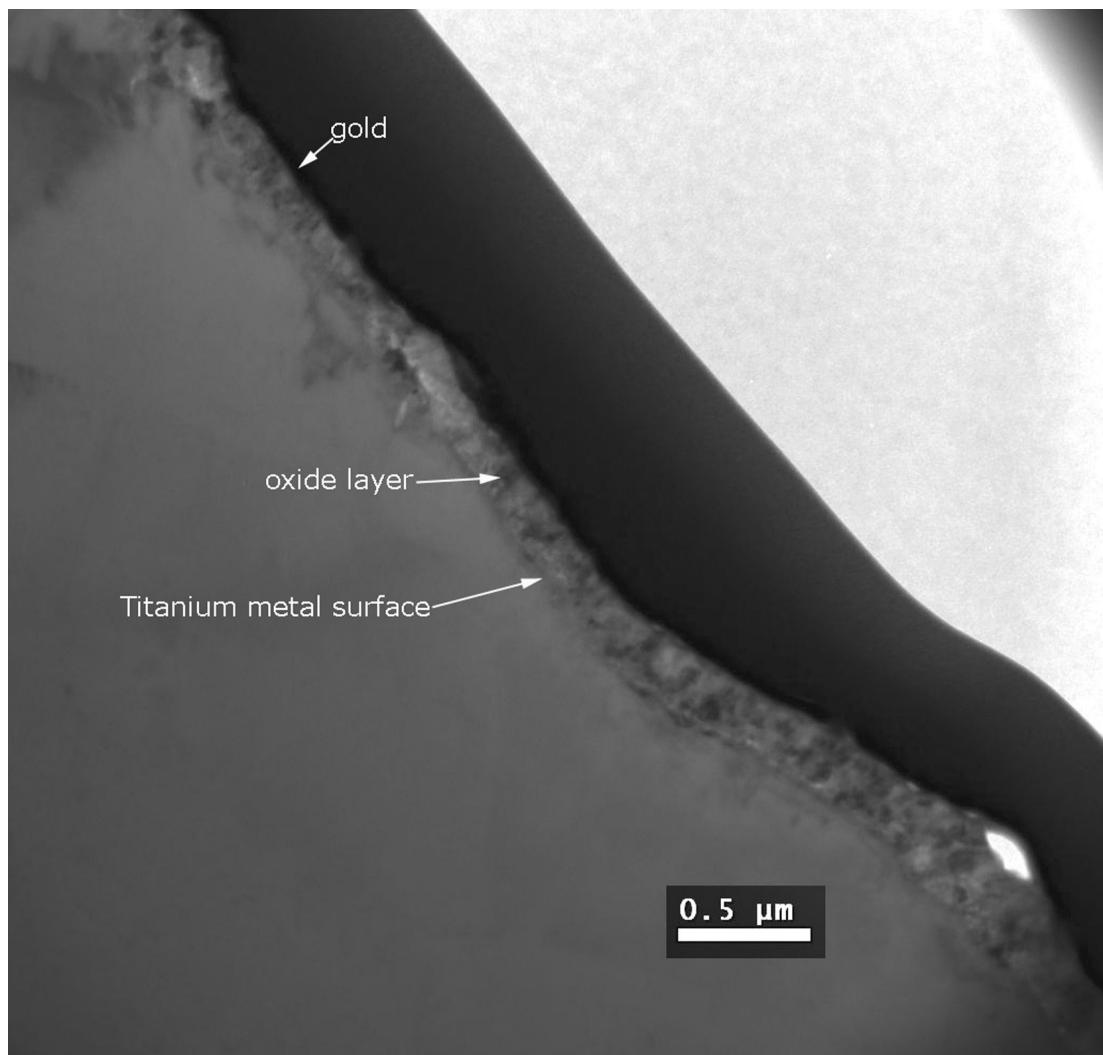
Figure 5.29: *TEM of foil k9 cut from heat-coloured sample of material **2** showing more irregular surface for both metal and oxide.*

[36] Habazaki, H, et al, Crystallization of anodic titania on titanium and its alloys, Corrosion Science, 45, 2063, 2003.

to the metal surface whereas there is no evidence of any crystalline structure in that region from these TEM observations.

Sample 2QE

Only one foil, **k-9**, was cut and lifted from the heat-coloured sample coupon **2QE**, and the TEM image of this foil is presented in Figure 5.29.

From the image it is clear that both the surface of the metal and the outer edge of the oxide layer are much rougher than similar parts of the anodised layer. The oxide
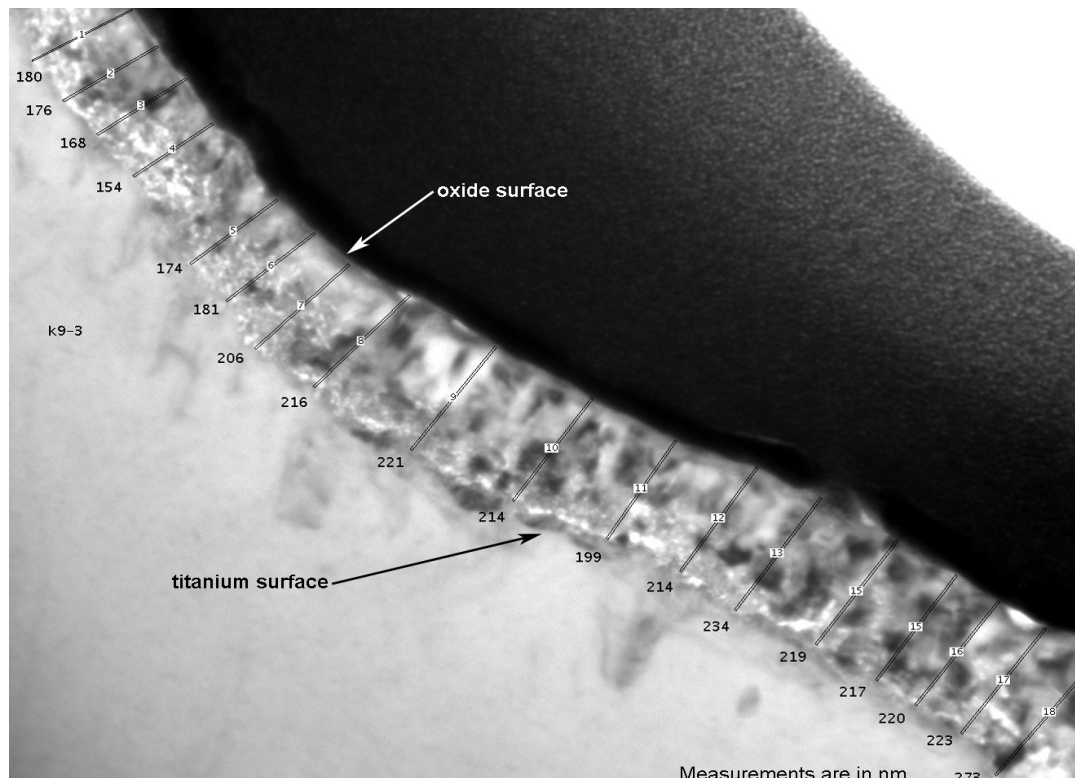
Figure 5.30: *Areas of foil **k9** at higher magnification, showing measurements of the layer made with ImageJ software.*

is completely crystalline with variable thickness ranging from 135 nm to 255 nm. The thickness appears to increase steadily along the length of the foil, ca 5500 nm. At the higher magnification shown in Figure 5.30 it is possible to discern finer crystals at the metal oxide interface and more columnar structures in the outer region of the layer near the surface but even at further increased magnification, Figure 5.31, it is not possible to fully resolve the possible distinct regions within the overall oxide layer.

In complete contrast to the anodised layer presented in the images of foils **j-13** and **i-11**, the oxide layer created by heat is entirely crystalline. The structure most closely resembles that reported by Gueneau de Mussy et al[37] but in their experiments the oxide

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[37] Op cit
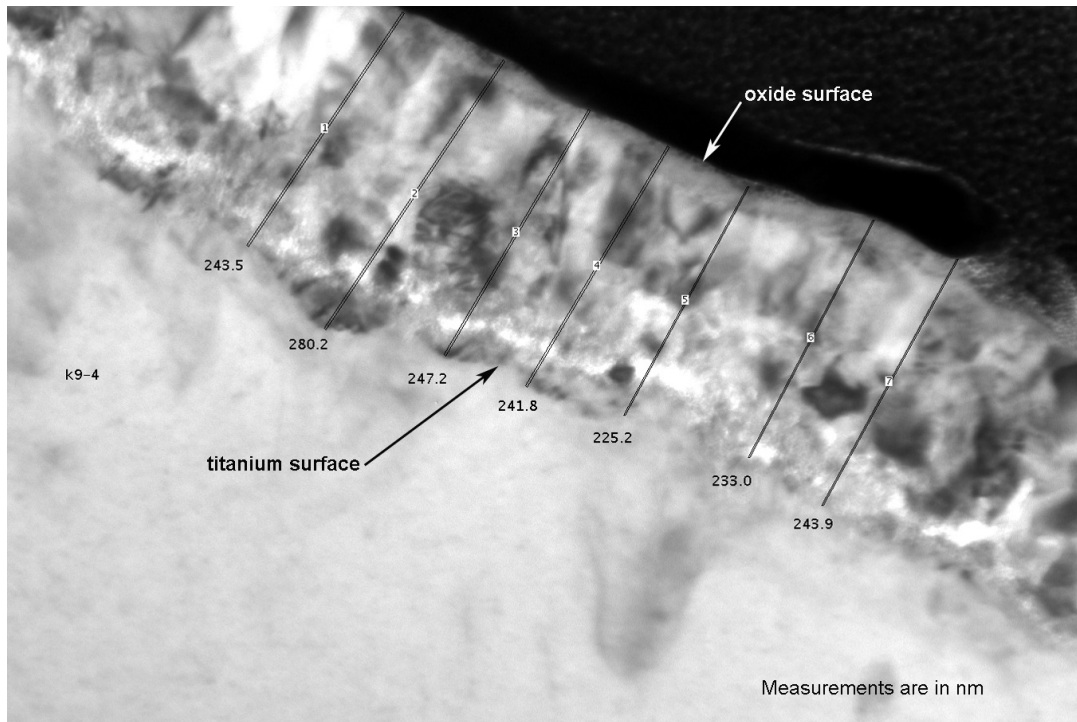
Figure 5.31: *Further detail of foil **k9** at increased magnification.*

layer was generated by anodising to a high voltage, 120V, where they have assumed that the sparking observed at voltages above 80V has a major impact on the oxide layer structure. They report both rutile and anatase in the structure, which is consistent with the XRD scan, reported previously, for a sample anodised to 120V. It may be that the sparking generates sufficient heat to produce a surface layer similar in structure to one generated solely by heat. Further work is needed to clarify these issues as part of a future project.

The variation in thickness of the layer from 135 nm to 290 nm is considerably thicker than calculated for rutile with an average RI at 2.66, i.e. 114 nm layer thickness; even if anatase is present the theoretical thickness would only be 128 nm. As the thickness of the layer seems to increase along its length it could be that an unevenness in heating resulted in a thickening layer. It is clear that the approximate layer thickness calculation for interference colour, which could be demonstrated for an anodised surface does not hold for a heat generated layer.

Summary of TEM

For the first time a direct comparison has been made between similarly coloured, oxidised samples of commercially manufactured titanium sheet produced in the workshop by different techniques. The images obtained from TEM analysis have allowed the examination and measurement of the cross-section of the oxide layers showing the very different oxide layer structures that are created by anodising and by heating the metal.

The samples analysed were created from the same titanium sheet and either thermally or electrochemically oxidised to a similar gold appearance.

The presence of voids in the anodised layer, first detected in thicker oxide layers on two different materials, is confirmed and is in agreement with recently published research[38], thus linking a workshop produced sample with one produced in the laboratory. A similar multi-layered structure with a central crystalline region and amorphous regions attached to the metal surface and at the electrolyte interface is confirmed for the oxide film produced by anodising. The total thickness of this layer, where no voids occur, is consistent with the theoretical thickness of a layer of titanium dioxide in the anatase form whose refractive index gives a second order gold interference colour. Confirmation of the correlation between colour and thickness of anodised layer thus established for one colour would be a useful area for future experiment for other colours.

In contrast the heat-generated oxide layer, which produces a similar colour, exhibits a completely different, fully crystalline structure and the cross-sectional measurement is much thicker than would be predicted for rutile or anatase. This structure has not previously been published and study in this area would be a worthwhile future project.

5.4. Conclusions

The experimental procedures have succeeded in directly measuring the thickness of the oxide layers created by both thermal and electrochemical oxidation of titanium. The very different structures of the two films, revealed during the experimental programme, provide substantial evidence of the possible causes of colour variation.

The literature reviewed in the first part of the chapter confirmed that while researchers had produced theoretical models linking the thickness of the oxide layer with the colour produced and the temperature or voltage used to produce it, few direct measurements had been made of the thickness of the oxide layer, which produced interference colour, while it was still attached to the metal surface.

The initial attempts to measure the thickness of oxide layers, created by heat and by anodising, used FIB to cut through the layer and SEM to observe the walls of the resultant trench. The images recorded revealed interesting features about the structure of the layers, indicating voids in those produced by anodising in the workshop, but gave variable and inconsistent results for the thickness of the layers. An exception was noted for the commercially anodised material, whose oxide layer examined by FIB showed no voids.

Subsequent preparation of cross section samples or foils for TEM examination, allowed

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[38] Habazaki, H, et al, Crystallization of anodic titania on titanium and its alloys, Corrosion Science, 45, 2063, 2003.

both the direct measurement of the thickness of the oxide layers and their structures. Thus permitting direct comparison between the thickness and structures of the oxide layers, created under workshop conditions by heating and anodising, which produced a similar colour appearance. TEM also confirmed the presence of voids in the anodised oxide layer, which had first been observed in the FIB examinations.

The experimental procedures confirmed that, although some colour variation may be due to the presence of different oxide forms within the layer, the effect was minor in comparison to that which could be attributable to the presence and size of voids in the oxide layer.

The heat-generated layer was shown to be completely crystalline but it was considerably thicker than predicted by interference theory and of variable thickness. This suggests a reason for the inherent colour variation generally experienced for this method of colouring. The anodised oxide layer was shown to be of a more consistent thickness than the heat-coloured layer but included voids at some parts within the layer.

The inclusion of voids within structures, especially in nature, is known to affect the colour appearance, due to the differing refractive indices between the material of the surrounding structure and the voids. It could even be argued that the 'play of colour' seen in precious opal is created by the presence of voids between the silica spheres but the colours displayed are the result of diffraction as well as interference and therefore not directly comparable with oxidised titanium. However it is known that colour variation in some bird feathers is attributable to the presence of regularly spaced voids within the structure and consequent changes in refractive index. Three dimensional nanoscale structures that include voids are also found in other living species, notably butterflies and moths[39] but within these structures the voids are of a uniform size and very regularly spaced. The colour variation is thus produced evenly across the surface in these well-known and well-ordered structures. In contrast to these structures the oxide film on titanium has been shown to include irregularly spaced voids of varying size, which could produce random patches of different colour on the surface. Therefore the presence of apparently randomly spaced voids within the anodised oxide layer is likely to be a major cause of the observed colour variation. This is confirmed by the observation that the commercially produced anodised samples appear to be free from colour variation problems and that no voids were detected within the oxide layer when one of the samples was examined by FIB.

Finally it is worth considering the possible consequences that the markedly different oxide layer structures may have in practical applications. It is noticeable that, as will be investigated in the following chapter, thermally oxidised titanium jewellery has a more robust surface in wear than anodised material. The fully crystalline structure produced by

[39] Vukusic, P and Sambles, JR, *Photonic structures in biology,* Natrure, 424, 14th August 2003, p862.

heat-oxidation would be expected to be stronger and more firmly adhering to the metal substrate than the largely amorphous anodised oxide film.

Chapter 6

6.1. Introduction

Observations about the behaviour of coloured titanium surfaces in a jewellery context and individual technical modifications, which were introduced in Chapter 2 in the Summary of Practice, may throw light on how and why variability occurs and suggest ways in which techniques may be improved to get good results in practice. Therefore this chapter examines briefly issues in relation to practice, in terms of colour creation or maintenance, that have arisen during the course of the study. Technical modifications, which warranted further investigation, have been noted from both workshop and industry practice. The model introduced in Chapter 3, which related colour to layer thickness and refractive index has been adapted in the light of experimental discoveries to produce a graph of anodising voltage in relation to the wavelength of maximum absorption.

The topics covered can be grouped into three parts. The first part concerns the wear characteristics of the oxide surface and hence the preservation of the colour appearance of the oxidised titanium. The second part explores minor modifications to the workshop oxidation procedures, with the aim of reducing colour variability. The final part draws together results from experimental investigation in order to produce a practical guideline for jewellers for the coloration of titanium electrochemically in the workshop. Each of these three parts is considered in the following three sections of this chapter.

6.2. Consequences of Structural Differences

The conclusion to Chapter 5 postulated that the different structures produced by the electrochemical and thermal oxidation of titanium, could be responsible for the difference in surface wear characteristics observed for the coloured surfaces which had been reported in Chapter 2. Therefore this part of the chapter considers briefly the evidence gathered with respect to the robustness of the oxide layer in terms of its resistance to abrasion and strength of adherence to the titanium surface for both methods of oxidation.

Consideration of the different oxide layer structures, identified in Chapter 5, would reasonably lead to the supposition that they would exhibit different wear characteristics. The robustness of the oxidised titanium surface can be manifest in two ways; resistance to abrasion in wear and stability in terms of adherence to the metal surface. Durability in wear, particularly the preservation of the original colour of a piece of jewellery is an important issue for jewellery customers and therefore for jewellery makers. The designer/

maker may also be concerned that the aesthetic of a piece in terms of colour and form is maintained. The removal of all or part of the oxide layer from an anodised titanium surface can be regarded as a problem in manufacture but could also provide an option for surface patterning. Both these aspects are considered briefly in this section.

6.2.1. Surface Wear

As discussed in Chapter 2 it has become a traditional practice within the jewellery industry to avoid the use of oxidised titanium for items that are subject to continual abrasion and knocks in wear, such as rings and bracelets. Consideration of the different oxide layer structures, identified in Chapter 5, suggests that it would be reasonable to suppose that they would exhibit different wear characteristics. Therefore it is possible that the heat-coloured oxide layer, because of its crystalline structure, would be more resistant to abrasion than the largely amorphous anodised oxide layer.

This is confirmed by the researcher's own experience of making chain from oxidised titanium links. The wear on the links that had been anodised was more apparent than the wear on the heat-coloured links when both were combined with silver links. The inner surfaces of the anodised links, where they were in contact with the other links of the chain, whether titanium or silver, became abraded to expose the underlying metal but the outer surfaces retained their colour. The effect was most pronounced for the thinner anodised pink colour than for the thicker anodised green coloured links, while the heat oxidised links were unaffected.

More work would be needed to fully confirm the tentative findings, outlined above, that the heat-generated surfaces are more resistant to abrasion than the electrochemically created surfaces. A future project would need to address both the degree of difference and how this is influenced by the different structures.

6.2.2. Film Adhesion

This part of the chapter considers the removal of part or all of the oxide layer from the titanium metal surface, whether intentionally or by accident. Research papers[1] mention the relative ease with which an anodised oxide film may be removed from the titanium substrate for further examination. Anecdotal evidence cites a case where the removal of a protective film on an anodised titanium sheet, used architecturally, also removed part of the oxide layer.

A practical example of this phenomenon occurred when samples of commercially

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[1] David, D, et al. *4th International Conference on Titanium 1980*, Kimura, H and Izumi, O, (ed), Kyoto, AIME, New York, p.2811, 1980,

produced anodised material were removed from a display chart. Part of the oxide layer
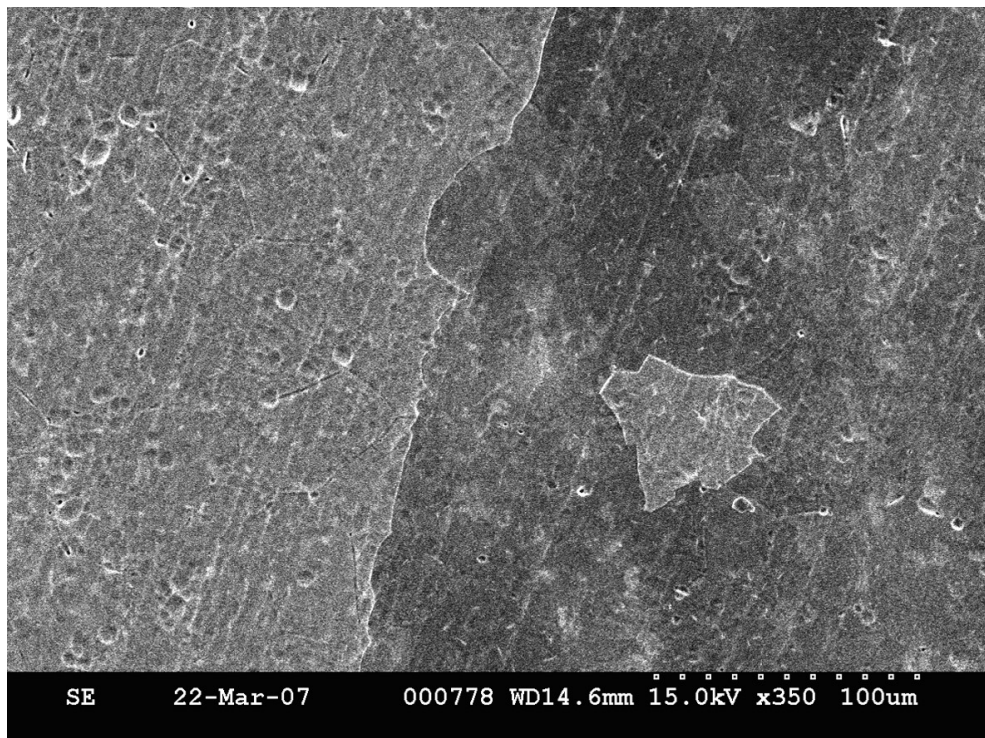
Figure 6.1: *SEM image of anodised pink coloured sample showing removal by adhesive tape of part of the oxide layer on the right side of the image.*

of each sample remained attached to the double-sided adhesive tape used to hold the samples in place. The oxide layers adhering to the tape showed the corresponding transmission interference colours. Thus the film removed from the pink sample appeared to be blue/green in colour and that removed from the gold coloured sample appeared to be pink. Figure 6.1 shows an SEM image of the sample with the lifted oxide. The image also illustrates clearly how the morphology of the oxide layer surface follows that of the underlying metal.

This exfoliation of an anodised titanium surface by adhesive tape is also shown by the commercial stock

Figure 6.2: *Titanium earring from 1980s' stock showing removal of oxide by adhesive stock label.*

of earrings from the 1980s, where removal of stock number labels removed the coloured surface, Figure 6.2.

A common feature in both these practical examples is that the adhesive tapes had been in place for some time, as had the protective film. A preliminary trial using standard double-sided Sellotape on an anodised titanium surface showed no effect after 30 minutes. Therefore a small experimental programme comparing anodised and heated titanium was undertaken using stronger adhesive tape, which was left in place for a longer period. As the examples of exfoliation, quoted above, were all observed on material that had been acid etched immediately before colouring, an unblemished earring part, which had been similarly prepared, was also used for comparison.

Adhesion Trials

The factors considered to be significant for these trials were the strength of the adhesive, the time that the adhesive was stuck to the oxide surface and the methods used to oxidise the titanium. Four proprietary adhesive tapes were selected, which were generally used for heavy-duty fixing: Duck tape, double-sided tape, Magic tape and Velcro. The results are presented in Table 6.1.

Sample	Tape				Time/Effect	
	Duck	Double-sided	Magic	Velcro	1day	1week
Material **2** Anodised:						
Blue **2T40Vs**	--	--	--	√	No	No
Gold **2T55Vs**	--	--	--	√	No	No
Material **2** Heated:						
Blue **2QA**	--	--	--	√	No	No
Gold **2QD**	--	--	--	√	No	No
TA Material:						
TA390V	√	√	√	--	No	Partial
TA324Vsc	√	√	√	--	No	Partial
TA5H2	√	--	√	--	No	No
Earring	√	√	√	--	--	Patches

Table 6.1: Summary of adhesion trials listing materials and adhesives used together with the time for which the adhesive patches were applied.

In one trial a single Velcro adhesive circle was placed across four sample coupons of material **2**, which had been coloured either blue or gold by either heating or anodising. Thus the same adhesive pad was used for all four samples. The pad was removed after one day but no removal of the oxide was observed and therefore it was replaced for a longer period. The oxide layers remained intact when the adhesive was removed after seven days as shown in Figure 6.3.

Tack trials
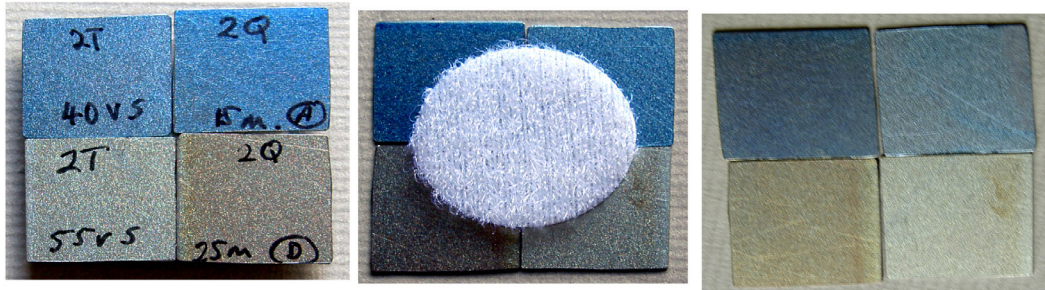
Figure 6.3: *Examples of 'tack' trials using a Vecro pad on thermally and electrochemically oxidised samples of material **2**, showing no exfoliation after removal of the adhesive disc.*

Partial removal of the oxide layers was observed when the TA material that had been anodised was tested with 'Magic' tape, Figure 6.4. No effect was observed when similar trials were carried out with heat-coloured examples of the same titanium sheet. In the final trial a patch of oxide was removed from the titanium earring that had been acid etched before anodising.
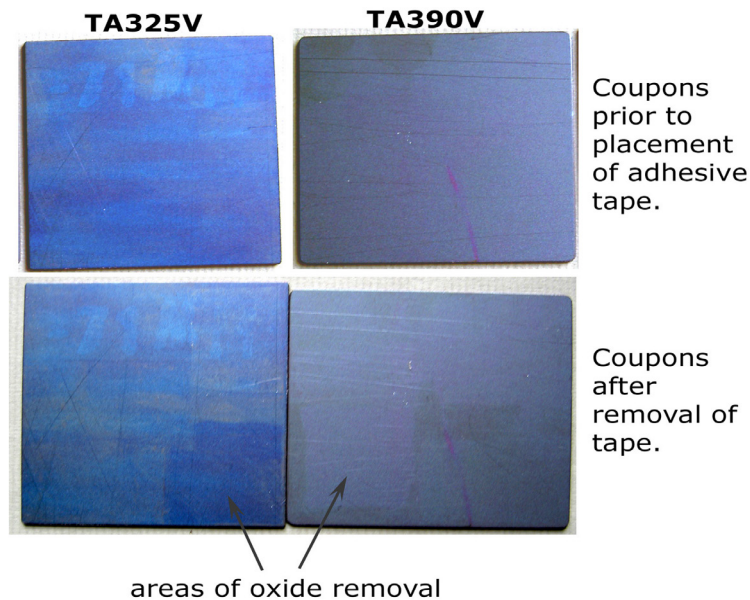
Figure 6.4: *Coupons of anodised TA material showing partial removal of oxide after seven days.*

This limited programme of experiments confirmed that some removal of the oxide layer from anodised titanium could occur and indicated the conditions under which further investigations should be undertaken as a future project.

The different behaviour of the anodised and the thermally created oxide layers indicated in the above experiments supports the evidence revealed in Chapter 5 that the layered and partly amorphous structure of the anodised oxide layer might make it more susceptible to damage from externally applied forces. Whereas the fully crystalline

heat-generated oxide layer has been shown to be more resistant to removal. Amorphous structures are not as strongly bonded as crystalline materials. An extreme example would be a comparison between carbon in the form of charcoal and as diamond. But further investigation, outside this project, would be required to establish this.

6.3. Oxidising Experiments

This part of the chapter reports the investigations into process modifications aimed at better control of the colour outcomes when oxidising titanium in the workshop. These process modifications were indicated in the course of the investigations of practice in Chapter 2 and the corrosion literature in Chapter 4. The results of the small programme of experiments are presented below. The experiments examined aspects of the anodising and heating procedures in the workshop in order to test the feasibility and utility of the suggested process modifications.

6.3.1. Anodising Experiments

The discussion of technical practice in Chapter 2 concluded that oxidation of titanium by anodising was a more controllable colouring method than heating. The standard anodising procedure selected for use throughout the project, for the preparation of the sample coupons, was described in the final part of Chapter 2 in terms of the time of anodising, and the rate at which the voltage was increased. It is the variation of these two aspects of the anodising procedure that will be examined in this chapter.

Investigation of other anodising variables was deemed to require either substantially different equipment or a significant programme of additional experiments, which could not be encompassed within the current project. These variables included the nature of the electrolyte, the temperature of the electrolyte bath and the positioning of the sample for anodising. A commonly used electrolyte, aqueous ammonium sulphate, was selected for the project and, as the anodising behaviour of titanium in a wide range of electrolytes had been examined and published elsewhere, this variable was not addressed in this study.

Literature indicated that temperature variation had a minimal effect on the titanium electrochemical oxidation reaction and workshop anodising equipment is not usually equipped with temperature controls. Hence the electrolyte temperature in the anodising bath was operated at the ambient temperature in the workshop. Also the anodising bath did not permit significant variation in positioning of the sample coupons.

Therefore only process modifications involving the anodising equipment and its capabilities, including evidence of its stability, are examined. The variations to the procedure

that have been studied, in order to determine their effects on the colouring outcome, include the rate of voltage increase and the total residence time in the electrolyte bath.

Also considered within the scope of general anodising procedural modifications are two suggested electrical pre-treatment techniques. The effects of both reverse and two-stage anodising, and combinations of these techniques with extended anodising times, are examined in the final part of this section.

Anodising Time

The following modifications can be considered under the general heading of time: the behaviour of different surfaces in relation to anodising time, the time taken for different sized samples to reach a particular voltage, the colour outcomes of different rates of increase of voltage and the effect of extended anodising periods on the colour achieved.

Surface Difference

A noticeable feature of titanium has been the apparently different rate of build up of thickness of the oxide layer on surfaces of different roughness. When polished and matt surfaces are anodised at the same voltage for the same time, different colours are observed. This was confirmed in Chapter 4 when the half-polished sample coupons were anodised and was particularly evident for titanium sheet **1.** The matt section of the sample coupons reached a 'higher' colour than the polished part, i.e. pink and gold at 55V or green and pink at 87V.

Assuming that the rate of oxide growth on the polished surface is slower than on the matt surface, a possible explanation for this difference was considered to be that the removal of the sample immediately the desired voltage was reached, did not allow for the polished part of the surface to achieve its full colour potential at this voltage. Therefore a small set of three sample coupons of material **1** was prepared (each half polished) to test this proposition by anodising for an extended period.

These sample coupons, designated **1L,** were each immersion anodised by ramping the voltage to the designated value and holding it at this level for an arbitrarily chosen time of 30 minutes. The three voltage levels selected were those previously employed in the preparation of the sample sets, described in Chapter 4. The results are summarised in Table 6.2.

Sample	Voltage	Increase	Fluctuation	Col./Polished	Col./Unpolished
1L40V	40V	0.2V	+/-0.1V	Blue	Gold
1L55V	55V	0.2V	+/-0.1V	Gold	Pink
1L87V	87V	0.8V	+/-0.2V	Greenish	Purplish

Table 6.2: *Extended anodising period for polished and unpolished titanium **1** samples.*

For all three samples, regardless of the final voltage, the colours of the polished and unpolished parts of the coupons remained distinctly different. However it became apparent that, although the voltage was not increased by further adjustment of the dial, the recorded voltage value drifted upwards by increasing amounts in an erratic manner. The drift was particularly marked at the higher voltage.

When the voltage dial was unchanged at 40V or 55V the voltage drifted up by 0.2V over the thirty-minute period but when the dial was at 87V the drift was 0.8V. In all cases the voltage value showed cycling about the increasing level. For the samples anodised at 40V and 55V, the final colours achieved were similar to those observed previously for this material at these voltages but for the third sample, anodised at 87V, the colours seemed to indicate that the oxide layer had continued to grow on both polished and unpolished surfaces, reaching an appearance nearer to that of an earlier sample anodised at a much higher voltage, 100V.

As the colours on the two parts of each sample coupon did not become uniform it was concluded that the differential rate of oxidation of polished and unpolished titanium surfaces was maintained over time and the difference was not eliminated by extended residence time in the electrolyte bath. However the experiment highlighted the variability of the anodising equipment and the possible effect of the speed of ramp of voltage which merited further investigation.

Sample Size Variation

The total anodising time for each sample includes both the time taken to reach the desired voltage (rate of ramp) and the period for which this voltage is maintained.

Examination of the first step in the procedure revealed that the time taken to ramp the voltage to the required level had to be varied with the size of the sample coupon to avoid the risk of blowing the protective fuse on the anodiser, i.e. for complete current decay to occur.

Little difference in anodising behaviour, in relation to sample size, had been observed in terms of the minor variations in size of the samples prepared for the first phase of experiments as outlined in Chapter 2. For example, for a sample coupon of material **2** (1.5 cm x1.5 cm x 0.4 mm), the slow ramp of voltage in the equipment used required 1.5 minutes to reach a level of 80V. However for the larger, thicker titanium sample coupons of material **TA, (**5 cm x 5 cm x 0.7 mm), the controlled slow ramp, allowing for complete current decay, took 5 minutes to reach the same 80V level.

This difference is an inherent property of the anodising equipment, and as such is not a controllable variable, but the other component of the total anodising time, namely the

period for which the voltage is maintained, can be controlled. Therefore an experimental programme was undertaken to examine the effect of variation in anodising time on the final colour outcome.

Extended Anodising Time and Voltage Stability

In order to observe the greatest possible effect of extended anodising periods, a region of colour transition that would be most sensitive to small variations in oxide layer thickness was chosen. Figure 3.26, presented in the final part of Chapter 3, illustrated graphically how
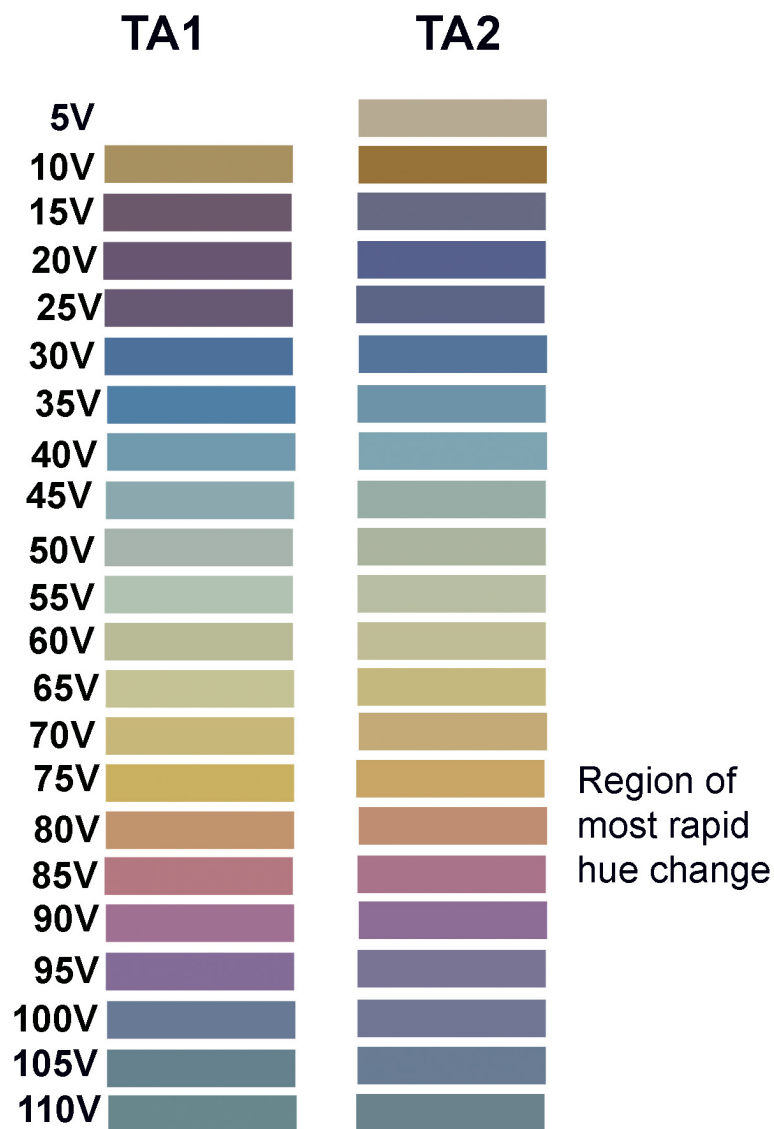
Figure 6.5: *Photoshop created patches from Lab values for anodised samples of **TA** material at 5V intervals, highlighting region of rapid change in hue.*

the theoretical rate of increase in layer thickness varies across the colours of the interference spectrum. The most rapid increase in theoretical layer thickness with applied voltage, and consequently colour transition, occurs as the observed colours change from orange through to purple and this region is deemed the most sensitive to the rate of energy input. For material **TA**, as illustrated by the Photoshop images shown in Figure 6.5, this colour transition occurs as the voltage levels increase from 75V to 85V. Therefore an anodising voltage of 80V, in the middle of this region was selected for the anodising trial programme.

The graph of the plot of the a* and b* coordinates for the samples anodised at 75V, 80V and 85V, Figure 6.6 shows that the majority of the samples fall within the yellow/ red quadrant of the CIELab space.
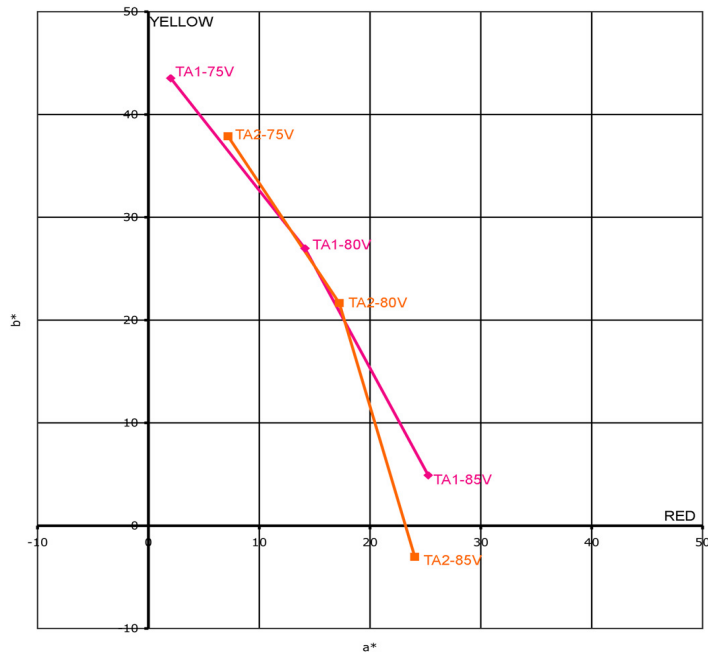
Figure 6.6: Graph of a*, b* values for samples of **TA** material anodised at 75V, 80V and 85V.

The programme of time trials was conducted using 5 cm square sample coupons of the **TA** material, chosen to allow comparison with the sample coupons prepared for the colour measuring experiments, with a target voltage level of 80V, as discussed above. The longest time period at which the sample coupons were held at a steady voltage was thirty minutes, based on the first experiment reported above. The other timings that were examined included immediate removal of the sample once the voltage was achieved, a one minute anodising period and an intermediate time of ten minutes.

Both fast and slow ramp of the voltage were used initially but, because of continuing current decay, a fast ramp to a nominal level of 80V resulted in a higher final voltage at 81.1V, as shown for sample **TA4-80Vf**. Therefore in an attempt to minimise this overshoot, a slow ramp was used for most of the time trials, as shown in the results presented in Table 6.3.

Sample	Ramp Speed	Voltage volts	Time min	Temp. °C	Drift volts	Colour
TA4-80Vf.	fast	81.1	2	10		patchy pink/or.
TA3-80Vs	slow	80	1	20		pink/orange
TA3t-10	slow	80	10	20	1.4	orange/pink
TA3t-30	slow	80	30	20	1.9	even pink
TA4-80V	slow	80	1	10		pink/orange
TA4-80Vt-10	slow	80	10	10	1.2	pink/orange
TA4-80Vt-30	slow	80	30	10	0.7	pinker
TA5-80V-c	slow	80	1	20	0.6	pink/orange
TA5-80V-cf	fast	80	0	20		pink/orange

Table 6.3: *Anodising time trials for extended periods using 5 cm square samples of **TA** titanium.*

Voltage drift was observed in all the extended anodising periods, an extreme example being sample coupon **TA3t-30** where the voltage increased erratically by 1.9V during the 30-minute period. With experience, and a very careful increase in voltage, it was possible to minimise the magnitude of voltage drift, as exemplified by the sample coupon **TA4-80Vt-30**, where the drift was limited to 0.7V over the 30-minute period, but not to eliminate it completely.

An inadvertent additional variant was the temperature of the electrolyte bath, which varied with the ambient temperature by 10°C from mid-August to late October. This cannot be addressed with the current set-up but it would be beneficial to eliminate such a variable by siting the equipment in a workspace less subject to ambient temperature fluctuation. However, as previously stated, the literature does not suggest that such variations in temperature would have a significant impact[2] on colour development.

Visual comparison of the nine sample coupons listed above showed similar overall shades of pink/orange, which were consistent with the previously measured samples of **TA1** and **TA2** anodised at 80V and 85V. However the extended anodising periods did not appear to have had any beneficial effect in eliminating the overall patchy colour of the sample coupons.

Therefore, as no benefit in terms of reduced colour variability could be observed, it was concluded that extended anodising periods were not to be recommended. Moreover the disadvantage in colour control associated with the voltage drift, inherent in the available equipment, suggests that extended anodising times should be avoided.

The following sections assess the efficacy of possible novel pre-treatments, which were identified from both the survey of jewellery practice and the corrosion studies literature.

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[2] Shibata, T, and Zhu, Y-C, The effect of film formation conditions on the structure and composition of anodic films on titanium, Corrosion Science, 37, 253,1995.

Pre-Treatments

The commonly used industrial pre-treatments for titanium, prior to anodising, chemical etching and/or electro-polishing are no longer techniques readily available to jewellery practitioners. Evidence from jewellers, reported in Chapter 2, indicates that the use of chemical etching has been discontinued in workshops. The literature suggests two other possible pre-treatment techniques that, in addition to any previous mechanical abrasion, may help to homogenise the surface of the metal prior to the final anodising and thus achieve a more uniform appearance of the coloured anodised surface.

Both corrosion literature and information from the survey of jewellers, as described below, suggest that a brief reversal of the polarity of the current in the anodising bath before the main anodising has a beneficial effect on the final colour produced. Other sources, also described below, indicate that carrying out the anodising procedure in two-steps reduces the incidence of colour variation. Variants of these two pre-treatment methods, both individually and in combination, using a variety of sample coupons, prepared from titanium sheet **1, 2** and **TA,** are presented here.

Reverse Current

Ohtsuka and Nomura[3] applied a small reverse current (>1V) which they claimed removed oxide film from the surface of the titanium and then anodised at a low voltage for an extended period before the final anodising step to the final voltage. While there is little evidence that any oxide would be removed by reverse anodising and their claim has not been supported by other researchers, such a procedure may remove contaminant residues from the titanium, creating a more homogeneous surface for subsequent anodising. A similar reversal of polarity was mentioned during the course of an interview with Eric Spiller, advice that he had been given by an industry contact, but the precise conditions were not recorded.

It was postulated that at high voltages a reverse anodising procedure would lead to substantial hydrogen evolution[4] at the titanium surface which could be absorbed by the metal and embrittle it, especially if the bath was very acidic. Therefore, before undertaking the experimental programme, the pH of the bath was measured and found to be weakly acidic at 5.7.

A research paper[5] had suggested a reverse current of –10V as a pre-treatment but trialling this with a small sample of material **1** proved that such a level was not possible within the capability of the anodiser and the minimum achievable voltage was –6V. This

[3] Ohtsuka, T, and Nomura, N, The dependence of the optical property of Ti anodic oxide film on its growth rate by ellipsometry, Corrosion Science, <u>39</u>, 1253, 1997.
[4] Personal communication from Dr M Ryan, Materials Dept IC
[5] Shaw, Marilyn, *Photographic Images on Refractory Metals*, Metalsmith, p32, Summer 1984.

was held for 1 minute and then the sample was anodised to 80V giving a patchy green coloured sample, similar to a previous sample of this material at this voltage. However there was considerable gas evolution at –6V and also at –4V, which was observed with a further test sample. A level of –2V was found to be achievable without gas evolution, unless the sample was held at the level for an extended period (12 minutes). To confirm the procedure a small coupon of material **1** was pre-treated at –2V for two minutes before subsequent anodising to 25V. This material appeared to have a more even colour in comparison with a coupon of the same material, which had been simply anodised to 25V.

Following these initial investigations an experimental procedure was devised which involved the use of –2V held for 2 minutes followed by removal of the sample coupon from the bath and rinsing in running water before finally anodising to the desired voltage level. A programme of work was undertaken to explore this 'reverse anodising' pre-treatment procedure over a range of voltages.

Seven pairs of sample coupons (1.5 x 1.5 cm) of titanium **2** were anodised from 10V to 100V at intervals of 15V. One sample coupon from each pair was anodised by slowly ramping the voltage to the desired level and then switching off the current. The coupon was then removed from the bath, rinsed and dried. The other sample of the pair was pre-treated by holding it at –2V for 2 minutes, removing it from the bath and rinsing it in water before replacing it in the bath and anodising it to the required voltage using the same method as for its pair. Table 6.4 summarises the results.

Sample	Final Anodising Voltage	Colour	Pair Difference
2T	10V	ochre	some
2T	25V	dark blue	some
2T	40V	mid blue	none
2T	55V	pale yellow	slight
2T	70V	gold	none
2T	85V	orange/pink	none
2T	100V	purple	none

Table 6.4: Reverse current experiments with known titanium sheet *2*.

For these samples the technique showed some beneficial effect in the lower voltage range but not at higher values. In order to test whether similar results would be observed for larger sample coupons, a repeat of the reverse current procedure was carried out using sample coupons of material **TA**.

Rather than examine the full range of colours it was decided to produce samples that could be compared with those in the previously reported anodising time trials and focus on a final voltage of 80V. Taking into account the size of the sample coupons (5cm X 5cm), the procedure was slightly amended by holding each sample at –2-2.4V for 3 minutes.

The sample was rinsed and then anodised by slow ramp to 80V and held for 1minute Two sample coupons were prepared in this manner on two different occasions and finally this procedure was repeated with the final step at 10 minutes. The results are summarised in Table 6.5 and show that there was little substantive difference between these samples and those produced by simple anodising.

Sample	Pre-treated	Voltage	Time(min.)	Drift	Colour
TA3-80Ve	Yes	80V	1	0	even orange/pink
TA4-80Ve	Yes	80V	1	0.4V	orange
TA4-80Vet-10	Yes	80V	10	1.1V	pinker

Table 6.5: *Reverse current experiments with known titanium sheet* **TA**.

No trace of the sheet markings as discussed in Chapter 2 were seen on these sample coupons after anodising and the possibility was considered that the reverse anodising step had removed the manufacturer's markings from the titanium sheet. This would have recommended the procedure as one to ensure the removal of residual chemical contaminants from the surface after thorough washing. However the sample coupons of **TA** material had not been segregated according to the previously observed marks but had been used randomly for the colouring trials and the anodising experiments, presented above. Hence it was also possible that these particular sample coupons had been free from identifiable marks initially.

To clarify this aspect, a small set of sample coupons was investigated to assess the utility of such a procedure for the cleaning of titanium, in particular the removal of sheet markings, prior to anodising.

Further samples of the **TA** material, designated **TA5,** were obtained and a total of six sample coupons, all with sheet markings were processed. After thorough washing and degreasing, during which the markings appeared to be removed, the sample coupons were oxidised as described here. Two of the sample coupons were used as controls and anodised by straight anodising; one with a fast ramp to 80V and immediate removal from the bath and one with a slow ramp to 80V, where it was held for one minute. The results for these two sample coupons are included in Table 6.2 above and both showed the reappearance of the sheet markings as higher colour images on the anodised surfaces.

Three of the remaining sample coupons of the **TA5** sheet were pre-treated by reverse anodising at –2V for periods of 1, 2 and 3 minutes and a fourth was held at –3.5V for 3 minutes. All four samples were then anodised by slow ramp to 80V, which was maintained for 1 minute before they were removed from the bath and washed and dried.

The sheet markings on these sample coupons reappeared after anodising but the colour difference was less pronounced than the samples anodised without the pre-

treatment. The indication was that some of the marking material may have been removed and that the technique might merit further investigation in a future study.

Two-Stage Anodising

Three references to two-step anodising procedures, presented below, suggest that such a method could be used to ensure more predictable results when colouring titanium anodically.

As quoted above, Ohtsuka and Nomura, in addition to the reverse anodising step for sample preparation, also applied a two-step anodising procedure to ensure a smooth homogeneous oxide layer. However as they were essentially looking at very low voltages (<5V) and small samples, their procedures need modification for application in a workshop.

An advice sheet on the anodising of titanium issued by Timet UK[6], ca 1995, suggests a two-stage anodising process that can be used when components need to be matched for colour. The procedure advises that the anodising is performed as usual for each component up to a voltage below that required for the final colouration. Then it proposes that the voltage is pre-set to the final value and the pieces returned to the bath where the power supply is switched on at the desired voltage. However the recommendations are very general, referring to a voltage below the one finally required but giving no indication of the voltage range.

The Pedeferri patent[7] indicates a two-stage anodising procedure with use of two different electrolytes to obtain a bright uniformly coloured surface, although he suggests acid etching of the surface prior to anodising.

As none of the methods mentioned in the above references give workable precise details for these techniques, procedural details for a two-stage process had to be developed.

An initial trial was carried out using a sample of **TA** material with a final voltage aim of 80V so that the result could be compared with the previously reported anodising trials. For the first step the sample was anodised at 5-6V for a period of 5 minutes, producing a barely perceptible colour. An estimated oxide thickness would be 10-15 nm. The sample was removed from the bath, rinsed in water and dried. It was then wrapped in a clean paper towel and stored overnight. On the following day the sample was replaced in the electrolyte bath and anodised at a slow ramp to 80V and held steady for 1 minute. The colour produced on this sample coupon **TA3-80Vd** was closest to that of the pre-treated sample **TA3-80Ve** see Table 6.4 above. It is therefore evident that the first anodising did not 'add' to the overall anodising period in terms of oxide layer thickness, as this would have been expected to give a colour closer to that achieved by anodising in one step to 85V.

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[6] Personal communication from Dr Andrew Wilson at Timet UK

[7] Del Curto, B, Pedeferri, MP and Rognoli, V, *Titaniocromie, il titanio e I suoi colori,* Epitesto srl, Milan 2004.

Reverse Current Plus Two-Stage Process

Having examined the effects of each pre-preparation process individually, i.e. reverse anodising or a two-stage anodising procedure, a further small set of experiments was undertaken using a combination of both. A set of five sample coupons of titanium, **TA,** was used to test the combined reverse current and two-step anodising procedure under different conditions. In all cases the final anodising step was a slow ramp to 80V, which was then maintained at this level for one minute.

All the samples were first prepared by reversing the current in the anodising set-up. The first three samples were reverse anodised at -2-2.4V for three minutes, and the fourth sample at –2.5V for 1minute and the final sample at –6V for 2 minutes. Thus examining possible variations in the time of the reverse anodising and the voltage.

Each of these five sample coupons was then subjected to a first anodising step at a different voltage. A further variable was tested by using different periods between the first anodising step and the second. These periods were four days, twenty four hours and a few minutes, the latter with and without removal from the electrolyte bath.

The first sample coupon was then anodised by slow ramp to 10V and held for 1minute (10-10.4V), producing a brownish purple colour. The sample was rinsed and dried and stored until the following day when it was anodised to 80V, (79.9-80.6V) **TA4-80V3-s**.

For the next two samples, the first anodising step was varied in terms of voltage and duration; 7V for 5minutes gave a clear gold colour after the first anodising step and 5V for 1minute a barely perceptible yellowish tint. These two sample coupons were rinsed, dried and stored for four days before the second anodising step.

The fourth sample, which had had a reduced time of reverse current pre-treatment, was given an intermediate first anodising step at 6V (6-6,4V) for 1 minute, which produced a pale gold colour. The sample coupon was then rinsed but not dried and replaced in the bath where it was anodised to 80V. The final sample coupon which had been prepared by reverse anodising at –6V was anodised as a first step at 6V for 2minutes and left in the bath while the anodiser was reset to zero, the sample was then finally anodised by slow ramp to 80V. The results are presented in Table 6.6.

Sample	1stAnodising	Time mins	2nd Anodising	Time mins	Colour
TA4-80V3-s	10V	10	80V (79.9-80.1)	1	lt orange
TA4-80V3-sa	7V	5	80V (79.9-80.2)	1	lt orange
TA4-80V3-sc	5V	1	80V (80.0-80.6)	1	orange
TA4-80V3-sl	6.4V	1	80V	1	lt orange
TA4-80Vrev6	6V	2	80V (79.9-80.2)	1	orange
(-6V for 2mins)					

Table 6.6: *Combination of reverse and two-stage anodising with **TA** material.*

As all the experiments in this mode were undertaken at a similar ambient temperature, no differences could be attributable to variations in the temperature of the electrolyte bath. In all cases, as had been noted for the two-stage anodising trial, the second anodising step had to be continued to a final value of 80V, indicating that the first anodising step was not additive, as might have been expected. The procedure also indicated that the elapsed time between the two anodising steps had no discernable effect on the final colour outcome, as similar colours were observed on sample coupons where the interval varied from a few minutes to four days.

For three of the sample coupons, **TA4-80V3-s, TA4-80V3-sa** and **TA4-80V3-si**, the resulting colour was a similar clear orange, slightly pinker than that of **TA1-80V** but less so than that of **TA2-80V** and with less variation than previously observed. An estimation of the L*, a*, b* coordinates would be: 64, +15.5, +24. The remaining two sample coupons, **TA4-80V3-sc** and **TA4-80Vrev6** were more patchy in colour and rather more pink. The major differences between the first three samples and the latter two was the first anodising time, which in both cases was at or below 6V. This suggests that the first anodising voltage should be at least 7V but that the timing does not need to be more than one minute at this level.

The reverse anodising step combined with the two-stage anodising process, and the more practised control of the voltage of the anodising equipment used, produced a more even, but slightly lower colour and this procedure could be further explored in a future project.

Summary of Anodising Trials

Investigation of the selected amended procedures, reported above, did not indicate major beneficial effects in the majority of cases. Indeed extending the anodising period beyond one minute was shown to increase the possibility of colour variability. Similarly the period between various steps in the modified anodising regimes did not appear to be significant as an interval of a few minutes was equivalent to an interval of several days between the two anodising steps.

The most promising outcome in terms of uniformity of colour was obtained when a reverse anodising step of -2.5V for one minute was followed by a first anodising step at 7V, before the final anodising. The range of sample coupons of **TA** material is presented in Figure 6.7, visually ranked from orange to pink, with procedures noted and compared in Table 6.7.

Examination of the samples indicates that the most influential factor in determining the final colour appearance, in terms of hue, is the ultimate voltage level, whether achieved

Anodising Experiments

Sample	Ramp Speed	Pre-treatment Voltage volts	Pre-treatment Time min	First Anodising Voltage volts	First Anodising Time min	Time lapse	Last Anodising Voltage volts	Last Anodising Time at V min	Ambient Temp. °C	Drift volts	Final Voltage volts	Colour	L*,a*,b*(0/45)
TA1-80v	slow						80	0		nr		orange	58.43,12.39,22.69
TA2-80v	fast						80	1		nr		orange	57.67,14.6,20.81
TA3-80vt-30	slow						80	30	20	1.9	81.9	even pink	
TA3-80vs	slow						80	1	20	nr		pink/orange	
TA3-80vt-10	slow						80	10	20	1.4	81.4	pink/orange	
TA4-80vt-10	slow						80	10	10	1.2	81.2	pink/orange	
TA4-80vet-10	slow	-2-2.6	3				80	10	10	1.1	81.1	pinker	
TA4-80vt-30	slow						80	30	10	0.7	80.7	orange/pink	
TA5-80v-r3	slow	-3.5	3				80	1	20	nr		orange/pink	marks not removed
TA4-80v	slow						80	1	10	0.7	80.7	pink/orange	
TA4-80vf.	fast						81.1	2	10	nr		patchy pink/or.	
TA5-80v-cf	fast						80	0	20	nr		pink/orange	
TA5-80v-r2	slow	-2	2				80	1	20	0.2	80.2	pink/orange	
TA4-80ve	slow	-2-2.4	3				80	1	10	0.4	80.4	orange	
TA4-80v3-sc	slow	-2-2.7	3	5	1	4 days	80	1	10	0.6	80.6	orange	
TA5-80v-c	slow	-2	1				80	1	20	0.6	80.6	pink/orange	
TA5-80v-r1	slow						80	1	20	0.3	80.3	pink/orange	
TA3-80ve	slow	-2-2.8	3	5-6	5	1 day	80	1	20	nr		orange/pink	
TA3-80vd	slow			6	2	0	80	1	20	nr		orange/pink	
TA4-80vrev6	slow	-6	2				80	1	10	0.5	80.5	orange	
TA4-80v3-s	slow	-2-2.4	3	10-10.4	10	1 day	80	1	10	0.2	80.2	lt orange	
TA4-80v3-sa	slow	-2-2.2	3	7	5	4 days	80	1	10	0.3	80.3	lt orange	
TA4-80v3-l	slow	-2.5	1	6-6.4	1	0	80	1	10	nr		lt orange	
TA5-80v-r4	slow	-2-2.1	3				80	1	20	nr		orange	marks not removed
TA4-80v2-s	slow			10-10.4	10	1 day	80	1	10	nr		anomalous	
TA4-80v3-sb	slow	-4.7	3	10.6-11	5	4 days	80	1	10	0.3	80.3	anomalous	

Table 6.7: *Table of **TA** samples anodised by various methods to ca 80V, ranked by visual appearance from pink to orange.*

Figure 6.7: *Image of samples from anodising trials (80V)*
by design or by accident due to the voltage drift inherent in the anodising equipment.

6.3.2. Heating Experiments

Fewer possible process modifications with respect to heat colouring of titanium were identified in the course of the study. Evidence from the review of practice and the preparation of sample coupons confirmed that oxidation of titanium by the application of heat is inherently more variable than anodising. However two areas were indicated that merited further investigation that would possibly produce information about the oxidation behaviour of titanium as well as introducing useful technical modifications to practice.

One technique involved a combination of anodising and heat, which appeared to improve the overall control of colour development. The other arose from a phenomenon that was encountered with respect to deliberate surface 'contamination' using permanent marker pens prior to heating which suggested a simple patterning procedure. The following paragraphs describe the preliminary investigation of these two procedures and suggest future areas for experiment following on from this project.

Anodising Plus Heating

Chapter 5 quoted the work of Yamaguchi et al[8], whose process for colouring titanium may have involved an anodising step followed by heating. A tentative trial of such a procedure was carried out in the course of investigations into the crystal species of titanium dioxide present on surfaces created both thermally and electrochemically, reported in the second part of Chapter 5. As explained it was postulated that heating an anodised surface would change the crystalline form of the oxide but this was shown not to be the case and the mechanism for the distinct change of colour has still to be confirmed.

However, as stated in Chapter 5, such a procedure may be used by studio jewellers to extend their control of the titanium colouring process, as described below.

A total of six sample coupons of titanium sheet **2** were prepared to test the procedure. The coupons were divided into three pairs and both samples in each pair were anodised by the standard methods to 100V, 105V and 110V. Then, after cleaning and drying, one of each pair was placed in a kiln controlled to 700°C for a few minutes. For each pair a substantial colour difference was recorded between the anodised and the anodised and heated coupons, as shown in Figure 6.8, which plots a* and b* coordinates for the sample coupons.

The plot illustrates how the hues of the sample coupons have been shifted across the blue/green quadrant of the CIELab space and the colour patches created in Photoshop,

Anodised plus Heat (0/45)
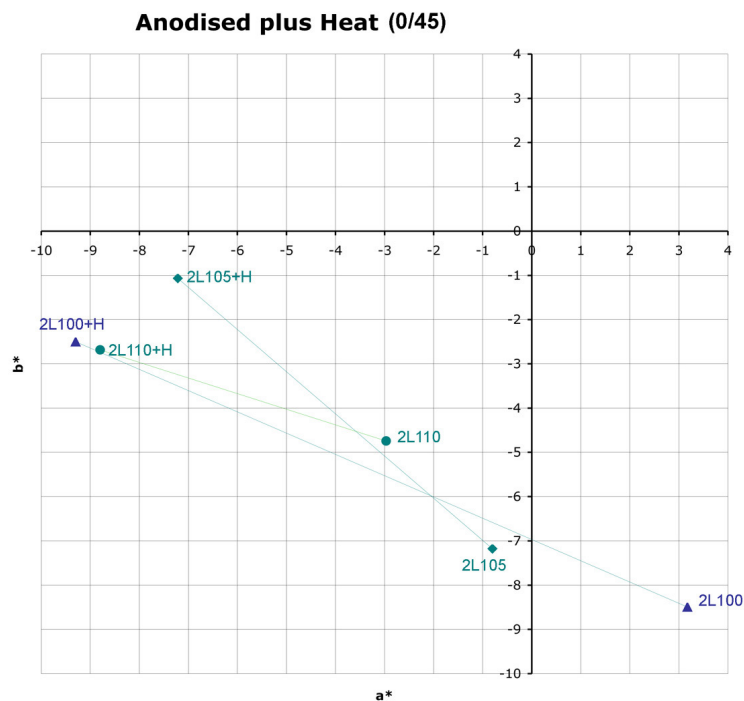
Figure 6.8: *Plot of a* against b*, showing the substantial shift in hue achieved by brief heating of the anodised samples.*

[8] Yamaguchi, H, et al, *6th World Conference on Titanium 1988,* Lacombe, P, Tricot, R and Beranger, G, (ed) Les editions de physique, France, 1988, p. 1823,
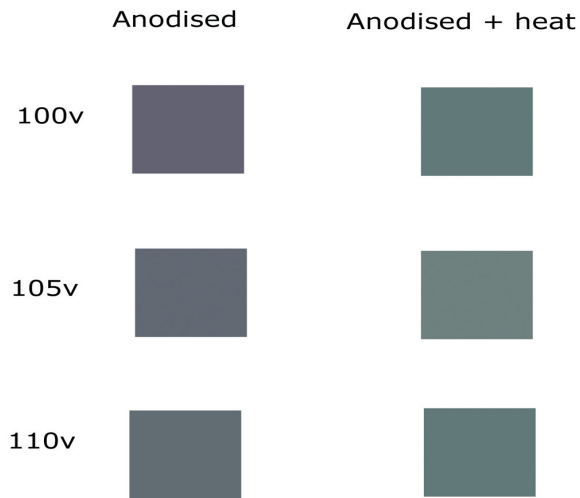
Figure 6.9: *Photoshop created colour patches, using Lab values from measurements made with the Spectrolino 0/45 geometry spectrophotometer.*

Figure 6.9, show the difference in appearance between the samples.

The substantial hue change is confirmed by relative reflectance curves, Figure 6.10, which demonstrates the significant change in the reflectance minima.
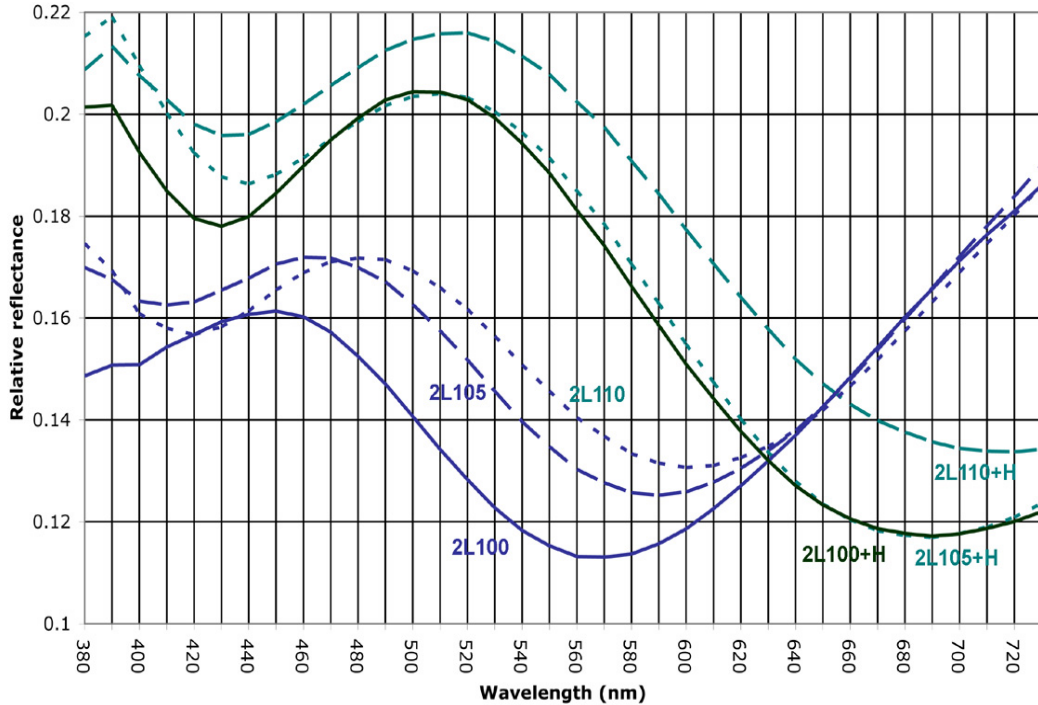
Figure 6.10: *Graph of relative reflectance curves comparing the anodised and anodised plus heated samples.*

From the graph it can be seen that the single minimum at 570 nm for the sample anodised to 100V is replaced by minima at 690 nm and 430 nm when such a sample has been heated at 700⁰C for 1 minute, changing the colour from blue to blue/green.

A practical use of this technique is demonstrated in the colouring of titanium links for chain making. The cleaned CP titanium wire was anodised in a spiral to a specific voltage, 85V, producing a pinkish gold colour. The individual links were then cut from the spiral and a few of them were heated in a kiln at 700⁰C for 2 minutes to blue green as shown in Figure 6.11.

The use of anodising followed by heating has been demonstrated to be particularly effective for brightening colours after anodising at higher voltages and for allowing the practitioner to create a wider range of colours. The future examination, by TEM, of a sample prepared in this way may reveal interesting changes in the structure of the oxide layer, particularly whether the voids in the anodised layer are affected

Figure 6.11: Titanium wire links anodised to orange/pink and some subsequently heated to blue/green.

by the subsequent heating. The testing of the robustness of these multi-modal generated layers would also be worth future investigation.

Patterning with Heat-Colouring

One of the phenomena encountered with the heat-colouring of titanium was that marks made on a titanium sheet prior to heating produced a different, higher hue in contrast to the surrounding area after thermal oxidation. The use of permanent felt-tipped marker pens to create contrasting patterns on heat-oxidised titanium sheet was introduced in Chapter 2 in the context of a review of the work of Debbie Moxon. The mechanism of the process could be one where the substance deposited on the surface acts as an initiator for the oxidation reaction producing faster growth in these specific areas.

Also from a practical standpoint as there are a limited number of resists that will withstand the high temperatures used for thermal oxidation of titanium, as discussed in Chapter 2, any procedures that can be used in the workshop to create pattern for heat-colouring of titanium are of interest and worth investigation. In order to establish the

conditions required and assess the repeatability of the procedure a limited number of trials were carried out, as follows.

Two sample coupons of **TA** material were used to test the efficacy of this method. A permanent black Stabilo pen was used to make the marks on the titanium coupons. After scribbling on one surface of the first sample it was heated in the kiln at 700⁰C for 3 minutes. When it was removed from the kiln the sample showed a pale blue surface with gold coloured markings. The sample was then returned to the kiln for a further 10 minutes. After removal from the kiln the surface was a pale patchy gold colour and the markings shaded from deep gold to mauve/pink, indicating the temperature gradient within the kiln. The inked lines were clearly visible and were of a 'higher' colour than the surrounding sample.

The second sample was marked on both sides and heated in the kiln for 3 minutes. The resulting coupon showed a very pale yellowish area where the ink had been used and a mid-blue on the remaining unmarked area, demonstrating that not only single line marks were possible to colour differentially in this way but also that complete areas could be affected. Figure 6.12 shows both samples.

These limited Investigations confirmed the applicability of the method but further
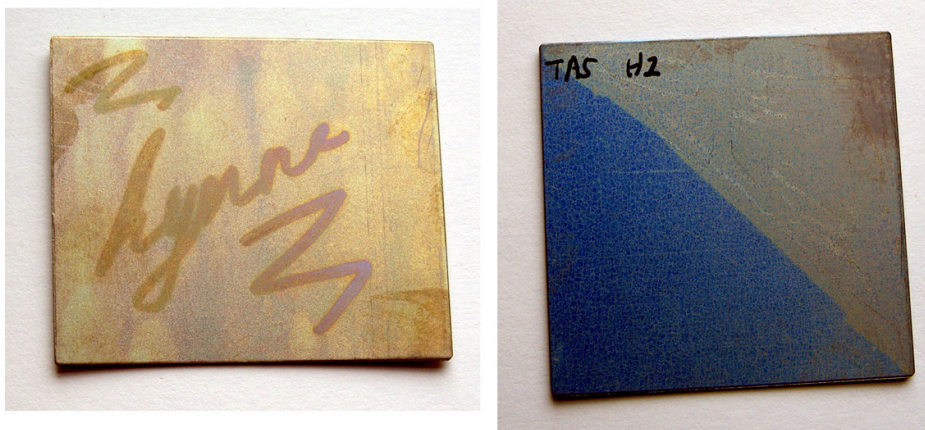
Figure 6.12: *Two samples of* **TA** *material showing ink-marked patterning for heat colouring of lettering and areas*

experiment, as part of a future study is recommended to test the limitations of the procedure and its underlying mechanism.

6.4. Relationship between Colour and Anodising Voltage

In Chapter 3 an equation, derived by application of thin film interference theory, was used to assess the differences in colour that could be attributable to the presence of either the rutile or anatase forms of titanium dioxide in the oxide layer on titanium.

Following from the experimental observations reported in Chapter 5, this equation may also be used to produce guidelines for anodising voltage/colour relationships for use in the workshop. The equation as set out below relates the colour of the oxidised titanium to the thickness, **t**, and refractive index, **n**, of the oxide layer.

$$t = Y (m-1/2)/2n$$

In the equation the colour of the surface is represented as the wavelength in nanometers, **Y**, that is eliminated in order to produce destructive interference, in practice the wavelength of maximum absorption, and **m** is an integer denoting the order of interference tint, 1,2, etc.

In Chapter 5 it was shown that the oxide layer produced on anodised titanium at voltages up to and including 100V is composed of the anatase variant of titanium dioxide. The layer thickness measurements carried out on anodised material, also reported in Chapter 5, are consistent with the refractive index of 2.33, which has been reported[9] for evaporated anatase films. Therefore these factors can be used together with actual voltage/colour observations to construct a table of anodising voltage against wavelength, giving guidance for colour development when anodising titanium sheet, Table 6.8. The transition between first and second order tints, i.e. **m**=1 and **m**=2, where the wavelength minimum is

TA1		RI Ev.Anatase 2.33		
Max absorbance (nm)	Integer (m)	Calculated film thickness (nm)	Anodising Voltage	Colour
1st order colour		1	5V	
380	1	40.8	10v	ochre
520	1	55.8	15v	puce
540	1	57.9	20v	purple
540	1	57.9	25v	purple
640	1	68.7	30v	blue
670	1	71.9	35v	mid blue
700	1	75.1	40v	pale blue
700	1	75.1	45v	silvery blue
2nd order colour	380	2	122.3	50v	silver
380	2	122.3	55v	silvery yellow
390	2	125.5	60v	yellowish
400	2	128.8	65v	pale yellow
420	2	135.2	70v	yellow
440	2	141.6	75v	gold
470	2	151.3	80v	pink
500	2	160.9	85v	cerise
530	2	170.6	90v	mauve
550	2	177.0	95v	violet
580	2	186.7	100v	blue

Table 6.8: *Calculated film thicknesses for 1st and 2nd order colours.*

[9] Blackwood, D J, et al, *An ellipsometric study of the growth and open-circuit dissolution of the anodic film on titanium,* Electrochimica Acta,34, 875, 1989.

outside the visible range, produces an area of uncertainty and discontinuity.

The calculations of layer thickness against voltage presented in Table 6.8 are for one type of titanium sheet, **TA**. Similar calculations performed for a range of different titanium sheets, used during the project, are shown graphically in Figure 6.13. The graph shows clearly that for etched material, such as that designated **CSM** or **H**, the layer thickness and

Theoretical layer thickness/voltage for different Ti sheets
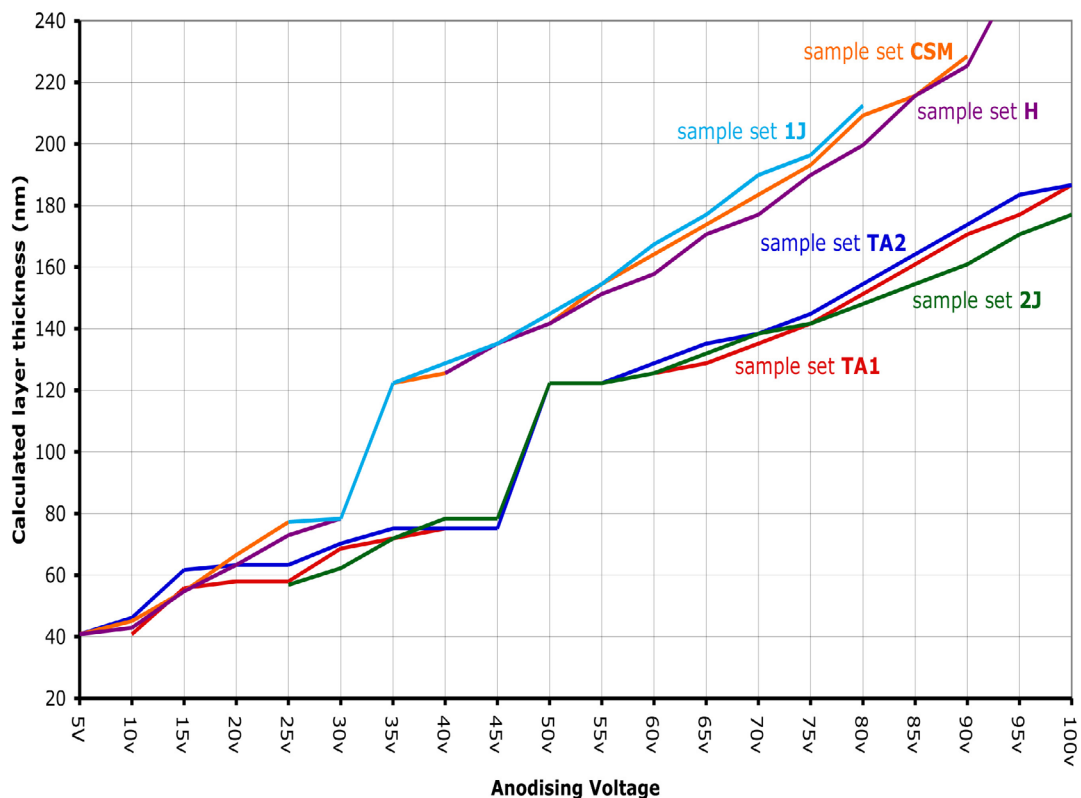
Figure 6.13: *Graph of calculated film thickness, assuming anatase RI of 2.33 against anoding voltage.*

hence colour development proceeds at a 'faster' rate than for unetched metal.

When titanium is anodised the colours develop, with increasing voltage and therefore increasing layer thickness. The hues start from yellow and move through purple to blue as the wavelength that is absorbed moves across the visible spectrum as described by Evans[10] and illustrated in Chapter 3 (page 76). Each order of tint represents the transit of the absorbed wavelength across the visible spectrum and, in terms of colour appearance measurement, describes a full circle of CIELAB hue angles. In the CIELAB colour space the plots of a* against b* move in a clockwise direction with increasing anodising voltage from the yellow/red segment through the red/blue and blue/green segments into the green/

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[10] Evans, U R, *The Corrosion and Oxidation of Metals-Second Supplementary Volume,* Arnold, London, 1976, p.378.
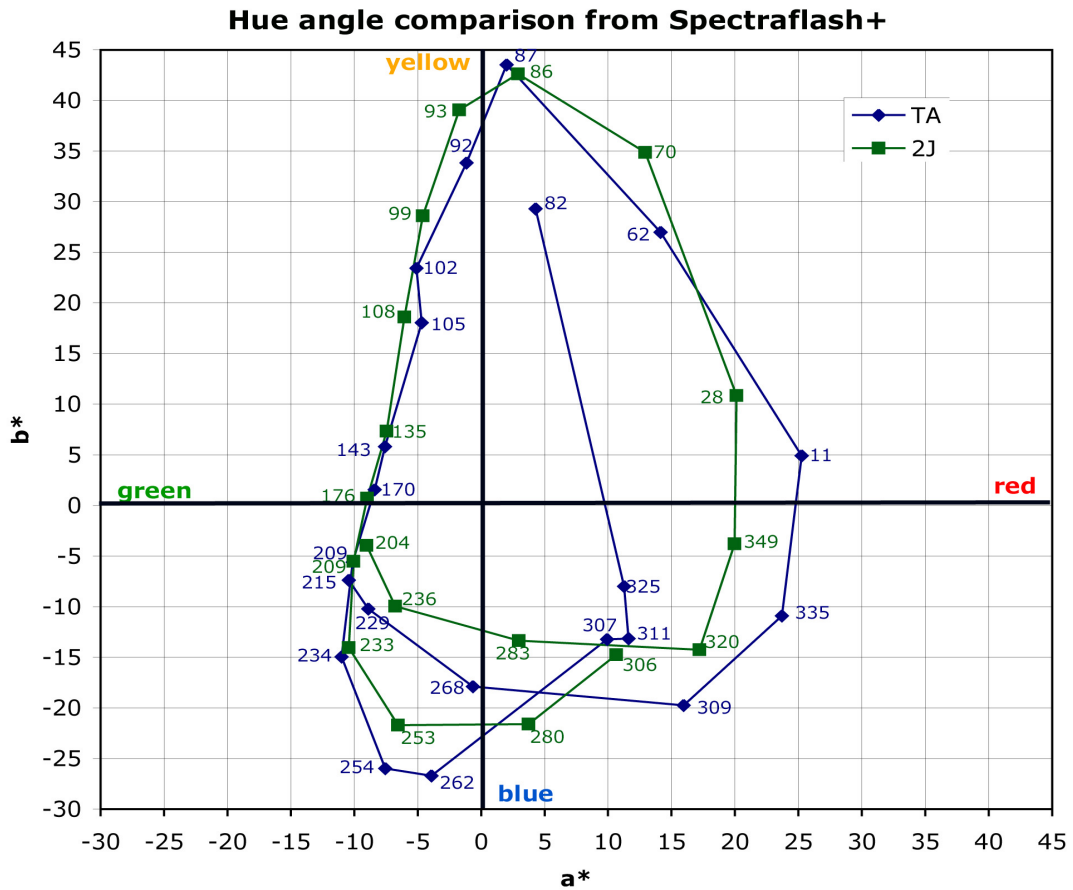
Figure 6.14: *Plot of a* against b* showing CIELAB hue angles for sample sets TA1 and 2J.*

yellow segment for each order of tint. The plot for the second order tints commences almost on the yellow axis and completes a similar circle as shown in Figure 6.14.

The plot shown in Figure 6.15 utilises the published[11] interference colour sequence
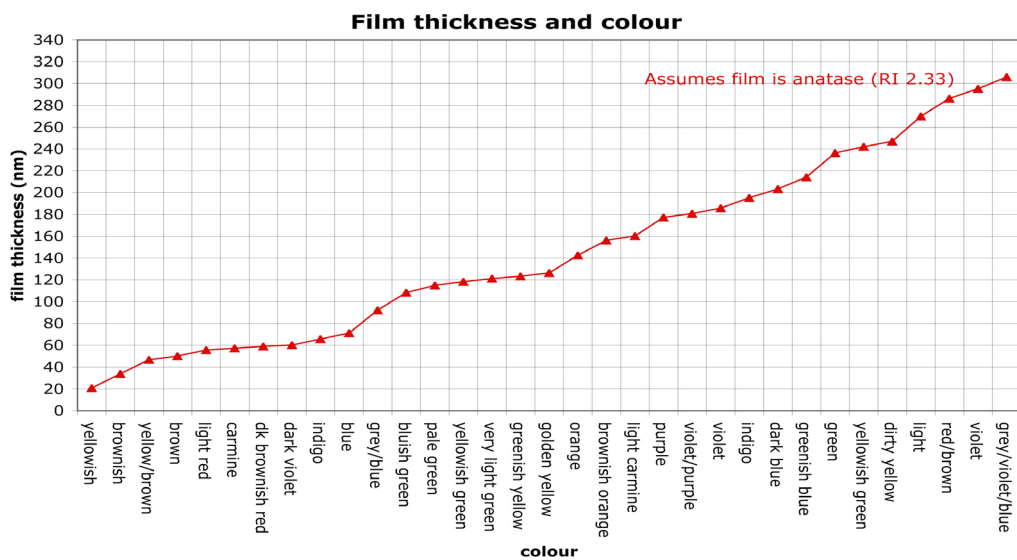
Figure 6.15: *General correlation between film thickness and interference colour.*

[11] Bruhat, G, *Optique, 5th Edition,* Masson et Cie. 1959, p.128.

and the calculated layer thickness needed to produce each colour, assuming the layer acts as evaporated anatase.

As the colours repeat for each order of tint an alternative variant is a plot of the layer thickness for first and second order colours against the wavelength of maximum absorption, Figure 6.16. Thus from this graph it can be seen that a first order indigo colour with maximum absorption at 540 nm, as shown in Figure 6.15, will be produced by a layer thickness ca 60 nm. Similarly a second order indigo, which has maximum absorption at 590
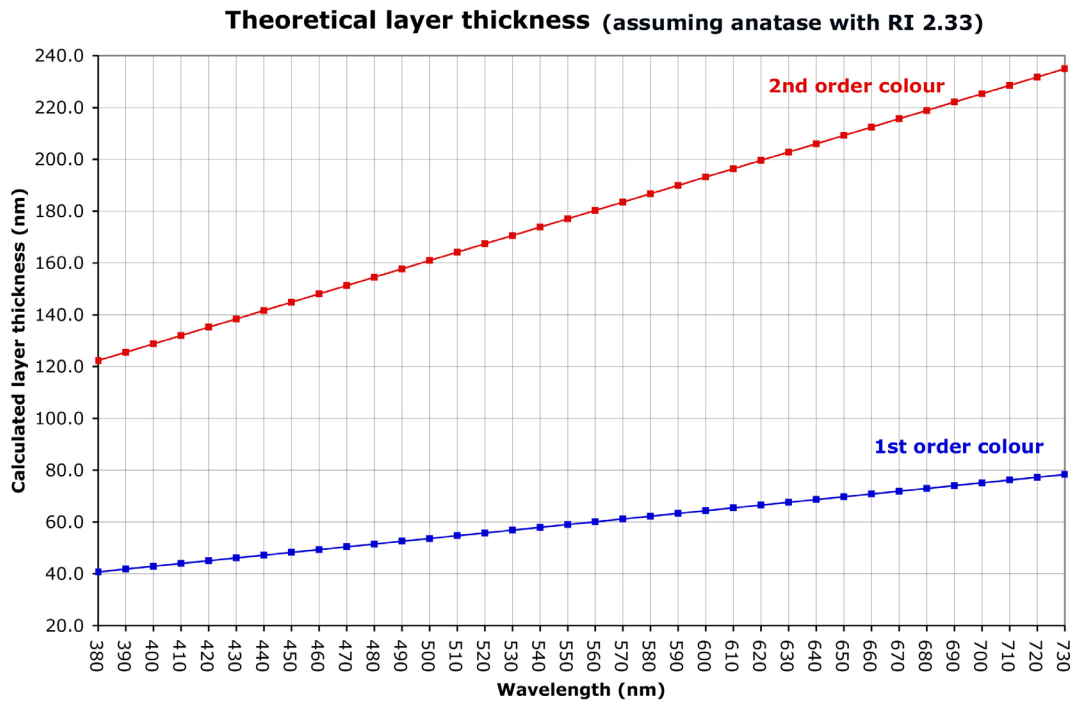
Figure 6.16: *Theoretical layer thicknesses for first and second order interference colours for titanium.*

nm, will be produced by a layer thickness of 190 nm.

The most useful plot compares the wavelength of maximum absorption, which defines the colour against the anodising voltage, Figure 6.17. This permits an assessment of the voltage needed to produce a specific hue for titanium sheet with a particular surface finish. This plot shows the anodising voltages and the wavelengths of maximum absorption for first and second order colours of the interference spectrum. Both first and second order colours fit well with linear trend lines but there are significant differences between titanium that has been etched prior to anodising and sheet that has a 'factory' finish.

This graph can be used to determine the anodising voltage required to achieve the colours quoted above. For standard CP titanium a first order indigo, with absorption at 540 nm, would be produced by a voltage of 20V and a second order indigo, with absorption at 590 nm, would need 104V. For etched material the voltages would be ca 17V and 73V respectively.
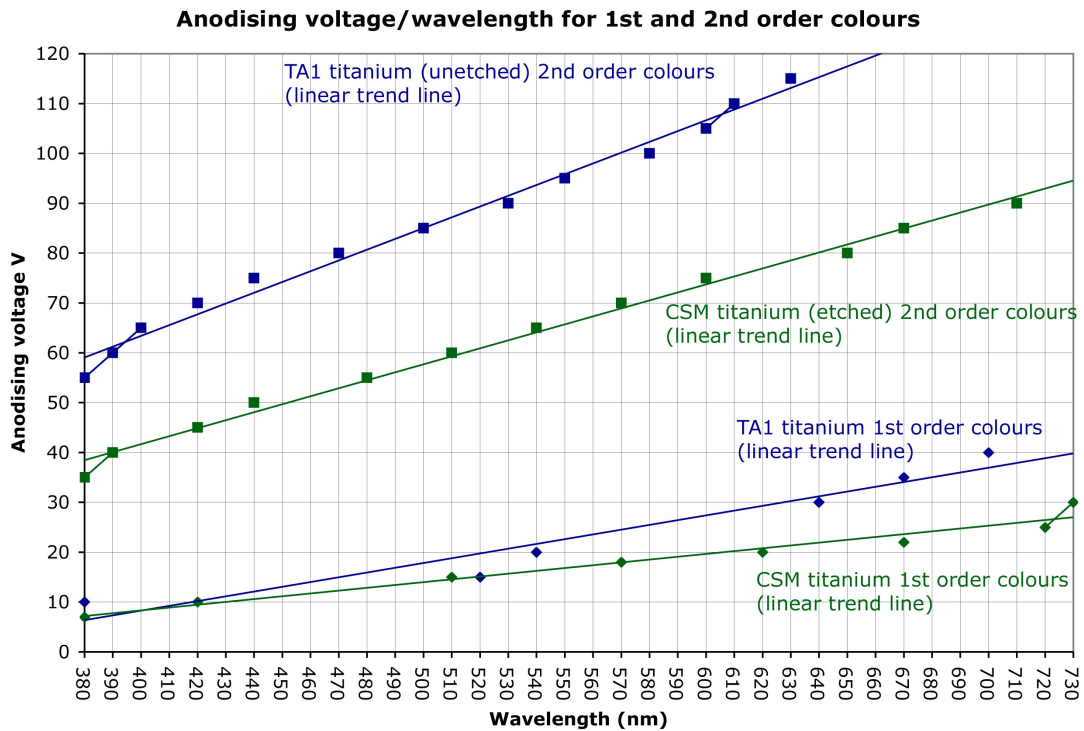
Figure 6.17: *Graph of anodising voltage against wavelength for first and second order interference colours.*

The utility of this comparison can be shown by comparing data from other sample sets. The **2J** sample set has a second order blue with absorption at 580 nm created by a voltage of 105V and the **H** sample set has a second order blue with absorption at 590 nm given by an estimated voltage of 76V, thereby confirming the probability of an acid etch prior to anodising.

6.5. Conclusions

The first part of the chapter confirmed the differential strengths of the oxide layers created by anodising and by heat in terms of abrasion resistance and adhesion to the underlying metal surface. This difference may be attributed to the substantial difference in oxide structure revealed by the TEM examination presented in Chapter 5 but needs further study, outside the scope of this project for verification.

The anodising procedural experiments, outlined in the second part of the chapter did not produce conclusive proof of their efficacy in reducing the variability problems experienced when colouring titanium in the jewellery workshop. However the negative aspects of extended anodising times were highlighted, together with the possible benefit of a reverse anodising pre-treatment followed by two-stage anodising.

One inference that could be drawn from the work was the overriding importance in the process of the precise control of the voltage. Although the exact nature of the process is not disclosed by the producer, it is probable that a commercial company in Japan uses a computer controlled anodising system to regulate the voltages used, but the failure rate of the process is also unknown.

In this part of the chapter it was also demonstrated how a combination of anodising and heat could give the studio jeweller a greater control over the colouring process and the future investigation of the structure of such an oxide layer could yield valuable information. The effect of the use of ink on titanium with subsequent heat colouring was confirmed as a mechanism for producing differential oxidation rates with added pattern making potential.

The experiments reported in the first two parts of this chapter suggest avenues of future exploration for the development of workshop practice and scientific examination. In particular it would be important to establish if the pre-treatment anodising processes could prevent the build-up of voids in the anodised oxide layer and if the brief heating of the anodised oxide layer acts to remove such voids.

The final part of the chapter demonstrated the utility of the theoretical relationship betweena the anodising voltage and colour, in terms of the wavelength of maximum absorption. The resulting graph may be used as a guide by the studio jeweller in workshop practice.

Chapter 7

7.1. Introduction

This chapter presents and discusses the conclusions from the study which set out to answer the principal research question: what factors lead to the occurrence of variability when titanium is coloured in the jewellery workshop? The principal outcomes of the research and its contribution to knowledge are identified and recommendation for further study arising from this research project are proposed

7.2. Conclusions and Discussion

The overview[1] of the impact that the new metal, titanium, had in the diverse fields of materials science and contemporary jewellery in the second half of the twentieth century established the context of the project.

The initial establishment[2] of the history of early titanium use in jewellery, pioneered in the United Kingdom (UK), was published in conference papers[3], lectures and an on-line exhibition[4] as an early part of this research. The study of the historic development of titanium jewellery proved that it was an initiative from the metals production company, IMI, in the UK which prompted the use of titanium in a decorative design context. Sources from both IMI and the jewellery[5] industry supplied confirmation of the route by which titanium was introduced as a jewellery material. The industry initiative coincided with changes in the education of jewellery designers, which produced an expanded cohort of students eager to experiment with and exploit new materials. This conjunction of events was responsible for the rapid adoption of titanium for jewellery fabrication from the mid 1960s onwards.

An overall picture of the range of responses to the new metal and its potential was drawn together from information obtained by questionnaire and in a series of informal[6] interviews with a representative number of jewellers active in the use of titanium in the UK. The colour potential of the metal was confirmed to be its principal attraction for all jewellery practitioners as tabulated in the Appendix.

The study of workshop practices, developed for the creation of titanium jewellery, confirmed that the methods recommended by industry researchers for oxidising titanium, i.e. heating and anodising, continued to be used by jewellers with only minor

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[1] Chapter 1, p6..
[2] *Ibid*.p13.
[3] Appended
[4] www.reflectionandrefraction.co.uk.
[5] Chapter 1, p15.
[6] Chapter 2, p36.

modifications[7]. Both methods create thin film interference colours, which are related to the thickness of the oxide layer developed. However heating produces inherently variable colour because of poor heat conduction in titanium metal. The thermal conductivity of titanium, as defined[8], is twenty-five percent that of steel and only five percent of that of the highly conductive metal, silver. Anodising gives the jeweller greater control of colour development but anodised titanium surfaces are still subject to variability. Exploration of types of colour variability, using examples from the researcher's own practice[9], confirmed that such variability is random and unpredictable.

The proposition was advanced that an assessment of the relative contribution to colour variability attributable to the component parts of the oxidised titanium surface could provide the evidence required as a basis for process modification. Hence the study focused on the use of scientific analytical techniques to examine coloured titanium samples prepared by standard workshop techniques[10]. An index of the component parts of the oxidised titanium system was constructed[11], and the areas to be investigated defined as:

- the titanium surface on which the oxide grows
- the oxide layer surface
- the composition of the oxide layer
- the homogeneity of the oxide layer
- the thickness of the oxide layer (including variation in thickness)

The study established a method of colour definition for oxidised titanium surfaces using the CIELAB colour measuring system[12]. A simple method for communicating the colour appearance of oxidised titanium, by the creation of colour patches, using Photoshop, was demonstrated. Although this method involves 'rounding up' values, with inevitable loss of precision, it provides a rapid approximation for communication of colour appearance, which had not been available previously.

A method of colour definition was established using the relative reflectance data to identify each colour in terms of the wavelength of maximum absorption. This value was derived from graphs plotted from the relative reflectance measurements across the visible spectrum, which were the raw input values for the CIELAB measurements[13]. The wavelength at which the minimum value of relative reflectance or maximum absorption for each coloured sample was identified from the plots. A colour could thus be defined by the wavelength, in nanometres, at which the maximum absorption occured.

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[7] Chapter 2,.p52.
[8] *Ibid*.p54.
[9] *Ibid*, p61.
[10] *Ibid, 53.*
[11] *Ibid, p66.*
[12] Chapter 3, p80.
[13] *Ibid, p95.*

Using this form of colour definition, a method for calculating the theoretical thickness of the titanium dioxide film was devised based on the theory of thin film interference. This method was used to estimate the theoretical thickness of an oxide layer produced on anodised titanium and calculate the difference in thickness attributable to the presence of either rutile or anatase within the layer.

Measurement of colour appearance also confirmed that differently finished titanium surfaces colour at different rates. This factor was demonstrated[14] by comparing the energy input required to produce similar colours, as defined by the wavelength of maximum absorption, on five surfaces with visually different degrees of surface roughness.

The morphology of oxidised titanium surfaces, created both thermally and electrochemically, was shown to replicate that of the underlying titanium sheet in the majority of cases. Analysis by Scanning Electron Microscopy (SEM)[15], confirmed that the observation was valid for titanium sheet with different surface finishes. Exceptions were noted for thicker layers, created by anodising at voltages above 110V, when a porous, columnar structure was observed. A further exception was the discovery of the phenomenon of 'Flower' oxides.

The discovery of this novel form of oxide growth, hitherto unrecorded, was published[16] and the structures were named 'Flower' oxides. The phenomenon was investigated to establish the conditions under which the 'Flower' oxides were formed but this discovery was not pursued within the project because the presence of these oxide forms in large numbers was only manifest on one type of titanium sheet and did not appear to affect the colour appearance.

The measurements of the roughness of the metal surfaces and their oxidised counterparts using White Light Interference (WLI)[17], confirmed that in all cases oxidation produced an oxide layer whose surface was rougher than that of the corresponding unoxidised metal. A small effect was observed when the rougher or more textured titanium surfaces were oxidised but a greater effect was noticeable when the smoother surfaces were oxidised. When comparing the effect of the different oxidation methods on the same titanium sheet, heating was shown to produce a comparatively rougher oxide surface than anodising of the same titanium surface. However the increased scattering of the incident light produced by the increase in surface roughness, while reducing the colour intensity, could not account for the degree of colour variation experienced in practice.

The variation of the rate of oxidation of titanium sheet with variation in the nature of the surface finish was confirmed by two methods. One method recorded the voltage

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[14] Chapter 3, p98
[15] Chapter 4, p117.
[16] Paper Appended
[17] Chapter 4, p134.

required to produce similar colours, as measured by the wavelength of maximum absorption (derived from relative reflectance), on differently finished surfaces. The results demonstrated that substantially different[18] voltages were required to produce similarly coloured anodised surfaces on the different titanium surfaces. In the alternative method one voltage value produced different colours on differently finished surface parts of the same sample coupon. However surprisingly no linear correlation was detected, as may have been expected, between the degree of roughness or polish of a titanium surface, as measured by WLI, and the speed at which it oxidised, as shown by the voltage required to produce a particular hue.

The presence of two polymorphs of titanium dioxide, anatase and rutile, in thermally created oxide layers and in anodised oxide layers created by voltages in excess of 100V was confirmed by X-Ray Diffraction measurements[19]. But for specimens anodised at 100V and below only anatase was indicated. The different refractive indices of these crystal species had been expected to contribute significantly to colour variation but calculations of theoretical layer thickness[20] proved that negligible colour difference could be attributable to the presence of titanium dioxide as either all anatase or all rutile.

Having eliminated surface roughness and variation in crystal species as major causes of colour variability, the conclusion was that the controlling factor must be derived from the thickness of the layer and the oxide layer structure.

The images from the Focused Ion Beam (FIB)[21] investigations gave indications of the structures of the oxide layers, produced either by electrochemical or thermal oxidation of titanium. A gallium ion beam was used to cut through the oxide layers and into the underlying titanium surface and the tilted samples were scanned. The images obtained from this technique suggested the presence of voids in the anodised layer. However it was only by further magnification that these initial observations could be confirmed. Fine cross-sections of the oxide layers, or foils, were prepared and examined by Transmission Electron Microscopy (TEM)[22], which permitted the structures of the oxide layers to be clearly observed and accurate measurements of the layer thicknesses made. These are the first direct measurements of the thicknesses of comparably coloured oxidised surfaces and publication is planned.

This research has demonstrated[23] that anodised oxide layers have a complex three-layered structure with regions of amorphous oxide either side of a central crystalline region, which may contain voids. The voids, lenticular shaped spaces within the layer, were shown

[18] Chapter 4, p136.
[19] Chapter 5, p156.
[20] Chapter 3, p102.
[21] Chapter 5, p162.
[22] *Ibid*, p176.
[23] *Ibid*, p177.

to be of variable size, randomly distributed along the length of the crystalline regions. The content of the voids was not analysed but judging from their reaction to the electron beam, as shown in the images, assessed to be gaseous. Where voids were not present, the thickness of the anodised oxide layer was uniform and consistent with interference theory. This was the first instance of the identification of the presence of voids in the oxide layers of workshop-generated anodised titanium samples.

TEM examination of the heated oxide layers showed that the layer was completely crystalline in structure but of variable thickness along its length. The crystalline layer produced by thermal oxidation of titanium was seen to be much thicker than would have been predicted by interference theory. This structure has not been previously published.

7.3. Principal Outcomes

The principal outcomes of this research project have been the identification of the structure of the oxide layer on thermally oxidised titanium, a comparison between the structures of the oxide layers generated in the workshop by different oxidation methods, to produce a similar colour, gold, and the direct measurement of the thickness of the oxide layers while still attached to the metal surface.

Consequences attributable to the markedly different oxide layer structures created by anodising and by heat could be differences in the layer strength, manifested in terms of abrasion resistance and adhesion to the underlying metal surface. The greater strength of a fully crystalline matrix compared with an amorphous structure would be a logical deduction. Therefore the fully crystalline structure produced by heat-oxidation would be expected to be inherently stronger and more firmly adhering to the metal substrate than the largely amorphous anodised oxide film. This is evidenced by the observation that thermally oxidised titanium jewellery is more robust in terms of surface wear than anodised material[24].

The significant conclusion from the analysis of the oxidised titanium systems is that the root cause of colour variability for anodised surfaces is discontinuity attributable to the presence of the voids distributed randomly within the layer. Other individual factors that might have produced variation such as the increased roughness of the surface caused by oxidation or the presence of both anatase and rutile forms of titanium dioxide within the layer have been shown to produce no significant colour variability. Their effect is so slight that it is unlikely that their combination would produce the type and degree of colour variation observed.

The presence of voids within the oxide film would not necessarily lead to variability.

[24] Chapter 6, p189...

Observation of natural systems, such as bird feathers, demonstrates that the presence of regularly spaced voids within a structure can be part of a systemic variation that produces a designed colour variation across a surface, depending on the angle of view. However it is the random nature of the distribution of the voids within the anodised oxide layer that is deemed to be the crucial factor in determining the observed colour variation in anodised titanium.

7.3. Contributions to Knowledge

The contributions to knowledge offered by this research programme and thesis can be summarised as follows:

A concise history of the use of titanium in jewellery in the UK.

An overview of the development and explanation of workshop practices.

A method for defining the colour of oxidised titanium surfaces by reference to the wavelength of maximum absorption.

A detailed microscopic analysis of the thin films of titanium dioxide created on different titanium surfaces by jewellery workshop oxidation practices to produce colour.

The measurement of the thickness of the electrochemically and thermally created oxide layers.

The verification by microscopic examination that the oxide layer on thermally oxidised titanium has a completely crystalline structure.

The confirmation of the presence of voids within the anodised films created under workshop conditions.

The discovery of the phenomenon of 'Flower' oxides.

A model based on interference theory that permits correlation between the wavelength of maximum absorption and the anodising voltage.

The experimental verification of theoretical thickness/voltage relationship within experimental uncertainty.

7.4. Areas for Further Work

Areas for further exploration arise both from the possible search for solutions to the identified cause of colour variation in oxidised titanium and from those avenues of exploration that were not followed within the project because they led away from the main thrust of the investigations.

The project has demonstrated that the most likely cause of colour variability in oxidised titanium is the presence of randomly distributed voids within the anodised oxide layer and further work needs to address this identified problem area. The programme of experimental workshop colouring procedures and investigations[25], arising from information gathered during the preliminary research, suggested useful avenues of future exploration for the development of workshop practice and scientific examination. Three possible avenues of exploration for dealing with the problem of voids are suggested:

- techniques that prevent the formation of the voids.
- techniques that remove the voids after they are formed.
- techniques that ensure an even size and distribution of voids within the oxide layer.

As the literature reported that some titanium alloys colour more readily than others, a future project could be an investigation to determine whether the use of alloyed material instead of Commercial Purity (CP) metal would prevent the formation of voids during the anodising process.

Another area of exploration for the prevention of void formation, suggested from the project, is the modification of the workshop anodising procedure. Examination of the samples prepared by the pre-treatment anodising processes would establish if the modified processes could prevent the build-up of voids in the anodised oxide layer. The absence of voids in the commercially produced sample of anodised titanium[26] suggests that precise control of the voltage during anodising may prevent the formation of voids but details of the exact process used are not disclosed.

The improved control over the colouring process demonstrated by the combination of anodising and heat[27] may be attributable to removal of voids, formed in the anodised layer, by the subsequent heating. This proposition needs to be investigated by analysis of the structure of the oxide layer of a sample prepared in this way, before and after the heat treatment step in order for changes in the oxide structure to be observed.

An unexpected outcome of the project was the discovery of 'Flower' oxides[28] during the SEM investigations of surface morphology. A substantial project for further study would be the further investigation of the phenomenon in order to elucidate their genesis and structure and how they might be exploited.

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[25] Chapter 6, p204.
[26] Chapter 5, p168.
[27] Chapter 6, p206.
[28] Chapter 4, p123.

Lynne Bartlett FGA DGA

Jeweller and Gemmologist

12 Mossbury Road
London SW11 2PB
Tel/Fax 0207 228 6254

2002

Dear,

Titanium Jewellery PhD Project

As your titanium jewellery was one of the reasons that I first became interested in the metal, it would be very helpful if you would participate in my research project.
I am undertaking a PhD at Central St Martins entitled:
'An investigation into the scientific, technical and design issues involved in the colouration of titanium and other refractory metals in jewellery and related decorative areas.'
This project allows me to amalgamate my early chemical training with my recent experience as a jeweller in a study that combines art and science.
The object of the research is to apply modern surface analytical techniques, such as Transmission Electron Microscopy, to decorated titanium pieces in order to understand the exact nature, both chemical and physical, of the oxide film.
At the same time I plan to record the history of the use of refractory metals in jewellery and allied fields in the UK.
I would be very grateful if you would complete the enclosed questionnaire to assist in the project.
The questionnaire has two purposes. The first is to enquire into the early use of titanium and the other refractory metals as jewellery materials by yourself and others and the second is to obtain details of the many possible processes that have been used to colour these metals. This information will be used, under strictly confidential terms, to create test samples for detailed scientific examination of the surface of the oxidised metal.
A stamped, addressed envelope is enclosed for your reply. Alternatively, if you would prefer to respond by e-mail please let me know at l.bartlett1@csm.linst.ac.uk.
Many thanks for your co-operation and time.

Yours Sincerely,

Lynne Bartlett

Titanium: The scientific, technical and design issues.

Questionnaire for Artists/Makers

Name of Artist/Maker:

Address: **Date of completion:**

Thank you for participating in **t**his questionnaire..

Please give any information on your experience with titanium and other refractory metals in any manner that suits you should you find that the questions do not fit in with your way of working.

A) Awareness of the material:

1.   At about what date did you personally first hear about titanium/and other refractory metals?
     Year

2.   Where was this?   (e.g. college, workshop, exhibition, publication, other (please specify))

3.   When did you first see or handle any titanium?

4.   Under what circumstances did this occur?

5.   Around what date did you first *consider* using titanium in your own work?

6.   Why was this?

7.   Where was this?

B) Early usage of the metal:

1.   When did you first *actually* use titanium?

2.   What did you consider that the use of titanium brought to your design options?

3.   From where did you obtain a supply of the metal and, if known, what grade did you use?

4.   What pieces did you make with titanium?

5.   What techniques did you use to fabricate the piece?

     Cutting

     Bending/forming

     Riveting

     Finishing

     Other (please specify)

6.   Did you use other metals/materials with titanium and if so what?
     Silver

     Gold

     Plastics

Other (please specify)

7. Did you colour the titanium and if so how?

8. What did you think of titanium as a material for jewellery?

9. What were the good and bad points about the metal in terms of jewellery design and manufacture?

C) Regular production of jewellery using refractory metals:

1. Please give the approximate dates when you used titanium in your work?

2. What grades or alloys of titanium did you use, if known?

3. Who was your trade supplier?

4. Was the cost economically viable?

5. Were the supplies reliable?

6. Did you continue to use the same techniques as with your early use of titanium?

7. Did your work with titanium develop through; experimentation,

                                   trade/customer demand,

                                   design decisions?

8. What were the problems you encountered in using titanium?

9. Which was the most difficult?

10. Did you develop new ways of processing the material for yourself?

11. Do you still use titanium in your work?

12. Is this on a regular basis or just occasionally?

D) Discontinued use of some or all of the refractory metals:

1. At about what date did you stop using titanium?

2. What were the main reasons for this?

E) Technical details of colouration:

1. Would you be prepared, providing it is made under a confidential disclosure agreement, to give precise details of your decorative techniques so that they could be reproduced solely for the production of test 'coupons' for detailed scientific analysis?

2. If your answers to this questionnaire prove particularly valuable, would it be possible to arrange a follow-up visit to your workshop?

Lynne Bartlett   11th September 2002

College/Year	63/4	64/5	65/6	66/7	67/8	68/9	69/70	70/1	71/2	72/3	73/4	74/5	75/6	76/7	77/8	78/9	79/80	80/1
Birmingham	Arthur Griffiths	Arthur Griffiths	Arthur Griffiths															
Birmingham		Hamish Bowie	Hamish Bowie	Hamish Bowie														
Birmingham			Ann Marie Shillito	Ann Marie Shillito	Ann Marie Shillito													
Birmingham					Graham Crimmins	Graham Crimmins	Graham Crimmins	Graham Crimmins										
Birmingham					Scilla Speet	Scilla Speet	Scilla Speet											
Birmingham									Judy Keeling	Judy Keeling	Judy Keeling							
Birmingham										Chris Howes	Chris Howes	Chris Howes						
Birmingham											Brian Podschies	Brian Podschies	Brian Podschies	Brian Podschies				
Birmingham												Gaynor Andrews	Gaynor Andrews	Gaynor Andrews				
Birmingham																		Mark Walker
Central				Eric Spiller	Eric Spiller	Eric Spiller												
Central				Terry Hunt	Terry Hunt	Terry Hunt												
Central					Alan Wright	Alan Wright	Alan Wright											
Central								James Brent Ward	James Brent Ward	James Brent Ward	James Brent Ward							
Central								Kevin Coates	Kevin Coates	Kevin Coates								
Central											Reema Pachachi	Reema Pachachi	Reema Pachachi					
Central											Brian Eburah	Brian Eburah	Brian Eburah					
Central												Jane Townsend	Jane Townsend	Jane Townsend				
Central														Barry & Sally Milburn	Barry & Sally Milburn	Barry & Sally Milburn		
RCA					Dorothy Hogg	Dorothy Hogg	Dorothy Hogg											
RCA						Ann Marie Shillito	Ann Marie Shillito	Ann Marie Shillito										
RCA						Eric Spiller	Eric Spiller	Eric Spiller	Eric Spiller									
RCA								Scilla Speet	Scilla Speet	Scilla Speet								
RCA										Ed de Large	Ed de Large	Ed de Large						
RCA										Lexi Dick	Lexi Dick	Lexi Dick						
RCA										Kevin Coates	Kevin Coates	Kevin Coates	Kevin Coates					
RCA												James Brent Ward	James Brent Ward	James Brent Ward				
RCA														Reema Pachachi	Reema Pachachi	Reema Pachachi	Reema Pachachi	
RCA																	Clarissa Mitchell	Clarissa Mitchell

Table 2.1A: Timeline of jewellers in the UK using titanium at colleges.

Titanium samples used throughout the project

Designation	Material Source	Form	thickness	Size (cm)	Colouring method	Number of samples	Preparation	Prepared for:	Also used individual samples for:	Reference in Chapter:
1	**Scrap**	**sheet**	**0.5mm**						WLI/SEM at LCC	4
1A	"	"	"	3 X 1	heat	one	half polished	SEM		4
1B	"	"	"	3 X 1	heat	one	half polished	SEM		4
1C	"	"	"	3 X 1	anodise	one	half polished	SEM		4
1D	"	"	"	3 X 1	anodise	one	half polished	SEM		4
1E	"	"	"	3 X 1	anodise	one	half polished	SEM		4
1F	"	"	"	3 X 1	anodise	one	half polished	SEM	SEM at LCC/87V	4
1G	"	"	"	3 X 1	anodise	one	half polished	SEM		4
1H	"	"	"	3 X 1	heat	one	half polished	SEM		4
1I	"	"	"	3 X 1	heat	one	half polished	SEM		4
1J	"	"	"	3 X 1	anodise	twelve	unpolished	SEM	Colour/WLI/FIB/60V	4, 5
1K	"	"	"	1.5 X 1.5	anodise	two	half polished	trials	SEM/xsect/110V	4
1L	"	"	"	3 X 1	anodise	four	half polished	trials		6
1M	"	"	"	2.5 X 1.5	anodise	three	unpolished	trials		n/a
1N	"	"	"	3 X 1	anodise	four	unpolished	trials		n/a
1O	"	"	"	3 X 1	anodise	one	unpolished	trials		n/a
1P	"	"	"	3 X 1	heat	one	unpolished	trials		n/a
2	**RMS**	**sheet**	**0.406mm**						WLI/SEM at LCC	4
2A	"	"	"	2.3 X 1	heat	one	half polished	SEM		4
2B	"	"	"	2.3 X 1	heat	one	half polished	SEM		4
2C	"	"	"	2.3 X 1	anodise	one	half polished	SEM		4
2D	"	"	"	2.3 X 1	anodise	one	half polished	SEM		4
2F	"	"	"	2.3 X 1	anodise	one	half polished	SEM	WLI/89V	4
2G	"	"	"	2.3 X 1	anodise	one	half polished	SEM	SEM at LCC/112V	4
2H	"	"	"	2.3 X 1	heat	one	half polished	SEM	WLI/2H	4
2I	"	"	"	2.3 X 1	heat	one	half polished	SEM		4
2J	"	"	"	1.5 X 1.5	anodise	nineteen	unpolished	Colour	WLI/FIB/Crossbeam/TEM/70V/90V	3, 4, 5
2K	"	"	"	1.5 X 1.5	anodise	ten	unpolished	Colour		3
2L	"	"	"	1.5 X 1.5	anodise+heat	2Xfive	unpolished	XRD	xsect/120V	5
2M	"	"	"	1.5 X 1.5	heat	two	unpolished	XRD		5
2N	"	"	"	1.5 X 1.5	anodise	2xtwo	polished	TEM?	mislaid	n/a
2O	"	"	"	1.5 X 1.5	heat	two	polished	TEM?	mislaid	n/a
2P	"	"	"	1.5 X 1.5	anodise	four	polished/acid	trials	SEM	n/a
2Q	"	"	"	1.5 X 1.5	heat	six	unpolished	replace 2O	FIB/Crossbeam/TEM/2QE	5
2R	"	"	"	1.5 X 1.5	anodise	one	unpolished	trials		n/a
2S	"	"	"	1.5 X 1.5	anodise	one	unpolished	demo		n/a
2T	"	"	"	1.5 X 1.5	anodise	fourteen	unpolished	trials		6
3	**Advent**	**foil**	**0.125mm**						WLI/SEM at LCC	4
3A	"	"	"	2.3 X 0.6	heat	one	as supplied	SEM		4
3B	"	"	"	2.3 X 0.6	heat	one	as supplied	SEM		4
3C	"	"	"	2.3 X 0.6	anodise	one	as supplied	SEM		4
3D	"	"	"	2.3 X 0.6	anodise	one	as supplied	SEM		4
3E	"	"	"	2.3 X 0.6	anodise	one	as supplied	SEM		4
3H	"	"	"	2.5 X 1	heat	one	as supplied	SEM		4
3I	"	"	"	2.5 X 1	heat	one	as supplied	SEM		4
3J	"	"	"	1.5 X 1.5	anodise	nine	as supplied	Colour	WLI/80V	3, 4
3K	"	"	"	3 X 3	anodise	thirteen	as supplied	Colour		3
TA	**Timet**	**sheet**	**0.7mm**							
TA1	"	"	"	5 X 5	anodise	twenty-three	as supplied	Colour		3
TA2	"	"	"	5 X 5	anodise	twenty-four	as supplied	Colour		3
TA3	"	"	"	5 X 5	anodise	eight	as supplied	trials		6
TA4	"	"	"	5 X 5	anodise	thirteen	as supplied	trials		6
TA5	"	"	"	5 X 5	anodise	six	as supplied	trials		6
TA5	"	"	"	5 X 5	heat	three	as supplied	trials		6
TB	**Timet**	**sheet**	**0.5mm**							
TB1	"	"	"	5 X 5	anodise	twelve	as supplied	Colour		3
CSM set	Anodised sample set from CSM	**sheet**	0.9mm	3.5 X 2	anodise	eighteen	acid etch	Colour	WLI/FIB/Leo/5V/60V	3, 4, 5
H -samples Commercial	Horie	sheet	0.25mm	2.7 x 2.7	metal				WLI/SEM at LCC	4
	"	"	"	2.7 x 2.7	anodise	twenty-three	as supplied	Colour	WLI/SEM at LCC/FIB/66V	3, 4, 5

Table 2.3A: Detailed list of samples used throughout the project

Comparison of Initial Test Samples Measured at LCC and Westminster

Samples (2J)

Measurements of metals for Lynne Bartlett at LCC

CIE Lab -0/45 (mean of 2 sides)

Voltage	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115
L*	28.82	31.085	36.795	43.88	50.385	52.365	54.595	55.725	54.905	54.115	52.11	50	45.935	43.81	40.975	40.845	41.69	42.67	45.12
a*	7.32	3.205	-3.395	-6.425	-6.32	-5.595	-4.59	-3.87	-3.02	-1.34	1.705	7.335	10.44	10.585	10.155	6.14	2.025	-0.79	0.52
b*	-8.185	-13.81	-16.09	-10.445	-5.13	-1.485	3.44	10.485	16.345	23.915	25.305	22.34	8.95	1.145	-5.24	-7.35	-7.245	-5.17	-3.195

CIE Lab - Spectraflash 600 - spec. inc

Voltage	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115
L*	40.29	43.96	52.26	62.05	71.8	76.06	78.13	78.66	78.3	76.72	74.22	69.19	60.86	55.72	51.86	51.45	52.26	54.09	53.2
a*	10.65	3.73	-6.55	-10.43	-10.07	-8.99	-7.44	-6.04	-4.59	-1.72	2.9	12.94	20.13	19.97	17.21	2.97	-6.77	-9.03	-1.26
b*	-14.75	-21.59	-21.7	-14.06	-5.52	0.7	7.34	18.62	28.62	39.07	42.64	34.88	10.87	-3.79	-14.26	-13.36	-9.95	-3.94	-0.92

Trial Samples (2K)

Measurements of metals for Lynne Bartlett at Westminster

The given values represent averages from 3 measurements taken for each sample, using the HunterLab UltraScan Spectrocolorimeter.

Settings: view area - small, port size - 6.4mm

source - D65 (for colorimetry), observer - 2 deg. (for colorimetry)

Voltage	20	30	40	50	60	70	80	90	100	110
L*	26.07	35.05	57.83	66.58	69.1	67.22	61.37	48.11	45.32	48.13
a*	23.01	6.69	-7.22	-6.9	-6.07	-4.79	8.28	22.61	2.41	-0.69
b*	-16.17	-22.65	-14.02	-2.15	14.8	36.06	33.13	-4.72	-12.92	-4.3

Table 3.1A: *Lab values for titanium sample sets 2J and 2K.*

CIELab values for TA1 Series

Anodising Voltage	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120
Integrating sphere spectrophotometer -Spectraflash without specular light included																							
L*	38.74	38.73	37.44	38.74	43.8	48.8	58.3	63.39	68.89	72.63	72.13	74.12	71.04	69.72	62.32	55.16	50.71	47.7	48.32	50.67	51.64	51.66	51.72
a*	10.99	11.03	10.95	3.52	-3.74	-7.18	-10.56	-9.69	-8.11	-7.35	-4.88	-5.08	-1.33	1.67	12.94	23.32	21.79	14.95	0.01	-7.88	-9.19	-3.69	-1.54
b*	-7.43	-7.42	-12.81	-22.95	-25.97	-24.92	-15.01	-5.75	0.96	5.09	16.89	21.74	31.48	40.91	25.26	4.84	-9.84	-18.47	-17.06	-9.83	-7.29	-2.86	-1.36
Integrating sphere spectrophotometer -Spectraflash with specular light included																							
L*	60.5	39.97	38.91	40.42	45.53	51.08	61.1	66.52	72.15	76.55	74.83	77.68	74.52	72.66	65.04	57.29	52.66	49.37	50.1	52.43	53.46	53.69	53.18
a*	4.29	11.26	11.62	9.92	-3.91	-7.56	-11	-10.12	-8.4	-7.58	-4.68	-5.1	-1.15	2.01	14.13	25.25	23.69	15.96	-0.64	-8.89	-10.43	-4.58	-1.7
b*	29.3	-7.99	-13.15	-13.23	-26.71	-25.99	-14.95	-5.6	1.55	5.81	18.06	23.44	33.84	43.53	26.98	4.9	-10.9	-19.75	-17.9	-10.21	-7.39	-1.69	-0.83
0/45 spectrophotometer -Spectrolino																							
L*	52.35	36.66	35.3	36.25	40.25	45.12	53.37	58.53	63.06	67.63	65.45	69.01	65.56	65.06	58.43	51.5	47.93	45.36	45.54	47.49	48.97	49.06	49.51
a*	4.59	11.97	8.87	9.1	-2.55	-5.85	-8.7	-8.06	-6.43	-6.01	-2.83	-4.07	-0.45	1.78	12.39	20.73	20.1	14.36	2.09	-4.45	-6.33	-2.27	-0.37
b*	25.51	-1.13	-12.74	-11.89	-24.03	-22.8	-14.34	-5.13	0.4	4.27	14.79	19.38	27.98	36.35	22.69	4.76	-8.58	-15.62	-15.26	-9.84	-7.54	-3.84	-2.7

Table 3.2A: *Comparison of Lab values for different instruments and modes for the same sample set TA1.*

CIELab values from measurements on Spectraflash 600 - spec. inc

Anodising Voltage

	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120
TA1 Series																								
L*		60.5	39.97	38.91	40.42	45.53	51.08	61.1	66.52	72.15	76.55	74.83	77.68	74.52	72.66	65.04	57.29	52.66	49.37	50.1	52.43	53.46	53.69	53.18
a*		4.29	11.26	11.62	9.92	-3.91	-7.56	-11	-10.12	-8.4	-7.58	-4.68	-5.1	-1.15	2.01	14.13	25.25	23.69	15.96	-0.64	-8.89	-10.43	-4.58	-1.7
b*		29.3	-7.99	-13.15	-13.23	-26.71	-25.99	-14.95	-5.6	1.55	5.81	18.06	23.44	33.84	43.53	26.98	4.9	-10.9	-19.75	-17.9	-10.21	-7.39	-1.69	-0.83
TA2 Series																								
L*	69.78	51.35	44.84	41.24	43.29	48.39	59.21	65.29	69.26	71.8	75.96	75.69	74.97	70.45	70.03	63.29	54.99	50.38	49.91	49.58	50.82	52.9	53.24	52.87
a*	1.25	10.29	3.4	4.9	3.48	-4.2	-10.25	-10.86	-9.04	-5.7	-5.67	-3.92	-2.06	3.87	7.19	17.22	24.04	19.25	6.92	3.02	-3.06	-8.09	-2.16	-0.57
b*	14.11	36.58	-14.13	-25.71	-19.61	-24.45	-14.85	-11.3	0.55	10.28	12.66	19.99	30.71	29.89	37.88	21.65	-3.03	-16.6	-17.18	-17.15	-15.35	-7.74	-0.84	-0.84
Differences		13.14	11.1	14.43	9.509	3.657	14.05	5.559	6.819	9.145	7.136	2.245	8.333	7.574	8.104	6.405	8.345	7.576	9.414	3.772	7.937	2.431	2.604	1.172

Table 3.3A: Comparison of two sample sets of the same material anodised at different times.

COMPARISONS OF REFLECTANCE
Data from first measurements of 2J series at LCC
Measurements on Spectrolino - 0/45

In each voltage column the rows **L***, **a***, **b*** are CIE Lab values; the wavelength rows (380–730) are Spectrum (relative reflectance) values.

Anodising Voltage	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115
L*	28.94	30.53	37.03	44.07	50.28	52.9	54.51	55.49	54.97	53.83	52.42	49.7	45.87	43.5	41.01	40.76	41.9	42.47	45
a*	7.77	3.85	-3.41	-6.55	-6.27	-5.5	-4.44	-3.75	-2.71	-1.36	1.54	7.21	10.86	10.04	10.67	5.59	1.87	-0.84	0.62
b*	-6.79	-13.78	-16.48	-10.66	-5.13	-1.13	4.53	10.88	16.69	24.37	25.41	21.78	10.19	1.23	-5.07	-7.42	-6.9	-5.37	-3.16
Wavelength																			
380	0.1354	0.1532	0.1774	0.1577	0.1486	0.1182	0.094	0.0866	0.1245	0.1558	0.1747	0.1857	0.1591	0.1508	0.1313	0.1357	0.141	0.148	0.1633
390	0.1296	0.1553	0.186	0.1724	0.1702	0.1439	0.1042	0.0785	0.098	0.137	0.1625	0.1919	0.1725	0.1654	0.1405	0.1405	0.1462	0.15	0.1708
400	0.119	0.1483	0.1845	0.1797	0.1819	0.1631	0.1216	0.0825	0.0823	0.1078	0.1363	0.1783	0.1723	0.1646	0.147	0.142	0.1424	0.1453	0.1707
410	0.1112	0.1416	0.1801	0.1879	0.194	0.1801	0.1419	0.0981	0.0803	0.0862	0.1121	0.1596	0.1672	0.1646	0.1532	0.1464	0.1453	0.1458	0.1685
420	0.101	0.1324	0.1754	0.1901	0.2015	0.1922	0.1594	0.1174	0.0882	0.0736	0.0916	0.1366	0.1553	0.1602	0.155	0.1493	0.1475	0.1454	0.166
430	0.0921	0.1242	0.1693	0.1916	0.2077	0.2022	0.1744	0.1375	0.1028	0.072	0.0801	0.1141	0.1413	0.1529	0.1547	0.1518	0.1508	0.1473	0.1633
440	0.0841	0.1162	0.1631	0.1914	0.2118	0.2097	0.1874	0.1556	0.1204	0.0795	0.0774	0.0958	0.1263	0.1441	0.1512	0.1522	0.1534	0.1495	0.1617
450	0.0774	0.1084	0.1562	0.1906	0.2151	0.2163	0.1984	0.1724	0.1383	0.0936	0.0826	0.0845	0.1121	0.1343	0.1459	0.1516	0.1557	0.1512	0.1601
460	0.0711	0.1009	0.149	0.1883	0.2163	0.2204	0.2073	0.1862	0.1547	0.1109	0.0925	0.0799	0.1009	0.1249	0.1382	0.1488	0.1557	0.1521	0.1586
470	0.0656	0.0936	0.1418	0.1846	0.2165	0.2232	0.2142	0.1976	0.1691	0.1289	0.1061	0.0821	0.0935	0.1166	0.1299	0.1443	0.154	0.1519	0.157
480	0.0611	0.0872	0.1345	0.1807	0.2155	0.2249	0.2193	0.2074	0.182	0.1462	0.1212	0.0894	0.0907	0.1109	0.1213	0.1384	0.151	0.1506	0.155
490	0.0577	0.0814	0.1275	0.1765	0.2142	0.226	0.2236	0.2157	0.1935	0.1619	0.1364	0.1004	0.0927	0.108	0.1139	0.1322	0.1469	0.1486	0.1533
500	0.0551	0.0762	0.1209	0.1717	0.2117	0.2258	0.2268	0.2221	0.203	0.1758	0.1509	0.1132	0.098	0.1073	0.1078	0.1258	0.1415	0.1455	0.1513
510	0.0535	0.072	0.1146	0.1668	0.2092	0.225	0.2291	0.2277	0.2115	0.188	0.1646	0.1271	0.1056	0.1088	0.1038	0.12	0.1363	0.1421	0.1496
520	0.0525	0.0686	0.1085	0.1618	0.2063	0.224	0.2307	0.2322	0.2188	0.1987	0.177	0.1413	0.1147	0.1118	0.1021	0.1154	0.1313	0.1384	0.1481
530	0.0522	0.0656	0.1085	0.1563	0.2025	0.2219	0.2312	0.2352	0.2245	0.2074	0.1878	0.1546	0.1244	0.1157	0.102	0.1117	0.1262	0.1341	0.1465
540	0.0525	0.0632	0.1027	0.1506	0.1984	0.2195	0.2311	0.2374	0.2292	0.2148	0.1973	0.1669	0.1341	0.1202	0.1035	0.1094	0.1219	0.13	0.1451
550	0.0534	0.0616	0.0976	0.1453	0.1945	0.2172	0.231	0.2395	0.2335	0.2217	0.2066	0.1787	0.144	0.1258	0.1068	0.1086	0.1189	0.1266	0.1442
560	0.0546	0.0604	0.0925	0.1394	0.1895	0.2137	0.2296	0.2401	0.2361	0.2267	0.2138	0.1887	0.1531	0.1312	0.1108	0.1087	0.1165	0.1232	0.1431
570	0.0566	0.06	0.0882	0.1342	0.1852	0.2108	0.2288	0.2414	0.2392	0.232	0.2208	0.1987	0.1624	0.1377	0.1164	0.1105	0.116	0.1213	0.143
580	0.0585	0.0595	0.0838	0.128	0.1794	0.206	0.226	0.2403	0.24	0.2346	0.2258	0.2064	0.1704	0.1435	0.1219	0.1126	0.1157	0.1194	0.1423
590	0.0608	0.0599	0.08	0.1222	0.1736	0.2011	0.2231	0.2391	0.2403	0.2369	0.23	0.2134	0.1782	0.1499	0.1281	0.1159	0.1169	0.1187	0.1424
600	0.0632	0.0603	0.0765	0.1162	0.1674	0.1957	0.2193	0.237	0.2399	0.2382	0.233	0.2193	0.1852	0.1563	0.1346	0.1197	0.1192	0.1188	0.1428
610	0.0659	0.0611	0.0736	0.1107	0.1611	0.1902	0.2154	0.2348	0.2391	0.239	0.2354	0.2243	0.192	0.1629	0.1414	0.1243	0.1223	0.12	0.1436
620	0.0686	0.0623	0.0711	0.1052	0.1545	0.1842	0.2109	0.2317	0.2377	0.2388	0.2368	0.2285	0.198	0.1692	0.1481	0.1292	0.1262	0.1218	0.1445
630	0.0714	0.0635	0.0689	0.0998	0.148	0.1777	0.2059	0.228	0.2355	0.2381	0.2376	0.2316	0.2033	0.1752	0.1546	0.1343	0.1305	0.1243	0.1456
640	0.0743	0.065	0.0673	0.0948	0.1412	0.1714	0.2007	0.2241	0.233	0.2368	0.2378	0.2341	0.208	0.1812	0.161	0.1397	0.1352	0.1273	0.147
650	0.0774	0.067	0.0662	0.0905	0.1351	0.1652	0.1956	0.2202	0.2305	0.2355	0.2375	0.236	0.2126	0.1869	0.1674	0.1455	0.1403	0.1311	0.1487
660	0.0805	0.0691	0.0657	0.0865	0.1292	0.1591	0.1904	0.2162	0.228	0.2342	0.2375	0.238	0.2168	0.1927	0.1737	0.151	0.146	0.135	0.1505
670	0.0839	0.0714	0.0654	0.0829	0.1235	0.1531	0.1853	0.2122	0.2251	0.2326	0.237	0.2393	0.2206	0.1981	0.1797	0.1571	0.1519	0.1394	0.1528
680	0.0873	0.0738	0.0656	0.08	0.1183	0.1471	0.1804	0.2083	0.2223	0.2313	0.2364	0.2407	0.2243	0.2032	0.1857	0.163	0.1578	0.1444	0.1552
690	0.0907	0.0764	0.0662	0.0771	0.1129	0.1414	0.1748	0.2037	0.2156	0.2291	0.2352	0.2415	0.2271	0.2076	0.1909	0.1687	0.1631	0.1491	0.1577
700	0.094	0.0791	0.0672	0.075	0.108	0.1359	0.1697	0.1996	0.2124	0.2272	0.2342	0.2418	0.2299	0.2119	0.1965	0.174	0.1688	0.1541	0.1602
710	0.0975	0.0819	0.068	0.0731	0.1032	0.1301	0.1646	0.1951	0.2086	0.2251	0.2327	0.242	0.2323	0.2158	0.2011	0.1794	0.1742	0.1591	0.1626
720	0.1011	0.0847	0.0694	0.071	0.0992	0.1249	0.1593	0.1906	0.2057	0.223	0.2314	0.2417	0.2344	0.2194	0.2057	0.1844	0.18	0.1638	0.1649
730	0.1046	0.0874	0.0712	0.0699	0.0953	0.1197	0.1546	0.1865		0.221	0.23	0.2418	0.2365	0.2228	0.2104	0.1897	0.1852	0.1693	0.1681

Table 3.4A: *Relative reflectance data for sample set 2J measured with 0/45 spectrophotometer*

COMPARISONS OF REFLECTANCE
Data from first measurements of 2J series at LCC
Measurements on Spectraflash 600 - spec. inc

Anodising Voltage	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115
	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab	CIE Lab
L*	40.29	43.96	52.26	62.05	71.8	76.06	78.13	78.66	78.3	76.72	74.22	69.19	60.86	55.72	51.86	51.45	52.26	54.09	53.2
a*	10.65	3.73	-6.55	-10.43	-10.07	-8.99	-7.44	-6.04	-4.59	-1.72	2.9	12.94	20.13	19.97	17.21	2.97	-6.77	-9.03	-1.26
b*	-14.75	-21.59	-21.7	-14.06	-5.52	0.7	7.34	18.62	28.62	39.07	42.64	34.88	10.87	-3.79	-14.26	-13.36	-9.95	-3.94	-0.92

Wavelength	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115
	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum	Spectrum
380	33.49	37.32	38.36	34.99	31.19	24.86	14.64	15.91	27.48	36.98	41.55	43.2	31.28	26.46	21.91	22.42	24.43	25.26	23.16
390	31.35	36.41	39.37	37.69	35.98	30.19	19.29	11.91	18.9	29.73	37.36	43.77	33.54	29.09	23.21	21.16	22.44	23.14	23.1
400	29.19	35.1	39.78	39.93	39.77	35.14	25.39	12.58	13.43	22.14	31.42	41.49	34.61	30.98	25.48	21.65	21.4	21.62	22.93
410	26.74	33.3	39.43	41.11	42.57	39.07	31.07	16.56	11.81	16.1	24.63	37.14	34.02	31.8	27.6	22.98	21.27	20.94	22.5
420	24.4	31.45	38.65	41.91	44.86	42.47	35.96	21.72	13.51	12.8	18.65	31.57	32.53	32.06	29.37	24.6	22.07	20.97	22.09
430	22.21	29.43	37.64	42.32	46.6	45.19	39.96	27.12	17.52	12.33	14.53	25.41	29.93	31.46	30.53	26.16	23.38	21.74	21.92
440	20.07	27.39	36.3	42.11	47.7	47.32	43.21	32.02	22.3	14.23	12.8	19.61	26.55	29.98	30.81	27.4	24.73	22.72	21.71
450	18.25	25.53	35.08	41.89	48.58	49.2	45.88	36.32	27.41	17.7	13.33	15.19	23.18	27.95	30.48	28.31	26.11	23.9	21.68
460	16.5	23.68	33.64	41.41	49.15	50.56	48.16	40.02	32.08	22.01	15.63	12.66	20.2	25.38	29.28	28.52	27.11	24.96	21.65
470	15.08	21.98	32.25	40.74	49.47	51.63	49.98	43.12	36.08	26.38	18.96	12.13	18.04	22.81	27.57	28.29	27.76	25.82	21.66
480	13.75	20.34	30.7	39.85	49.31	52.37	51.47	45.83	39.8	30.9	23.02	13.4	16.72	20.38	25.36	27.5	27.92	26.4	21.62
490	12.72	18.9	29.27	39.07	49.32	52.99	52.71	48.21	43.1	35.06	27.25	16.01	16.42	18.62	23.13	26.4	27.66	26.73	21.7
500	11.85	17.56	27.78	38.05	49	53.22	53.59	50.1	45.77	38.67	31.24	19.42	16.83	17.55	20.95	24.93	26.99	26.67	21.66
510	11.18	16.39	26.34	36.97	48.54	53.3	54.26	51.69	48.07	41.95	34.98	23.34	17.87	17.13	19.02	23.31	25.97	26.35	21.66
520	10.68	15.35	24.92	35.8	47.89	53.16	54.65	52.99	50.14	44.81	38.43	27.39	19.41	17.29	17.59	21.72	24.67	25.71	21.54
530	10.39	14.45	23.58	34.65	47.26	52.87	55	54.06	51.9	47.39	41.62	31.37	21.28	17.92	16.61	20.23	23.22	24.91	21.49
540	10.25	13.74	22.25	33.38	46.32	52.52	55.09	54.9	53.42	49.66	44.43	35.06	23.43	18.96	16.17	18.99	21.74	23.94	21.39
550	10.23	13.17	20.96	32.06	45.35	51.9	55	55.51	54.59	51.55	46.93	38.46	25.73	20.28	16.24	17.96	20.31	22.83	21.23
560	10.36	12.7	19.76	30.71	44.23	51.1	54.74	55.89	55.5	53.16	49.09	41.48	28.13	21.72	16.75	17.25	18.96	21.75	21.13
570	10.62	12.39	18.63	29.33	43.04	50.26	54.39	56.16	56.31	54.54	51.13	44.2	30.64	23.44	17.7	16.89	17.89	20.69	20.98
580	11.03	12.25	17.63	27.94	41.75	49.3	53.82	56.26	56.91	55.76	52.83	46.7	33.21	25.36	19.1	16.97	17.11	19.82	20.95
590	11.5	12.17	16.69	26.55	40.4	48.21	53.16	56.2	57.33	56.68	54.29	48.87	35.74	27.34	20.79	17.38	16.64	19.09	20.91
600	12.07	12.22	15.83	25.16	38.95	46.99	52.36	55.93	57.48	57.39	55.53	50.83	38.25	29.45	22.75	18.09	16.47	18.56	20.9
610	12.7	12.38	15.08	23.78	37.4	45.6	51.4	55.48	57.46	57.79	56.43	52.31	40.57	31.58	24.82	19.08	16.63	18.2	20.86
620	13.37	12.64	14.49	22.5	35.85	44.26	50.38	55.02	57.44	58.22	57.3	53.82	42.86	33.83	27.11	20.35	17.15	18.18	21
630	14.13	12.99	13.98	21.25	34.31	42.84	49.36	54.43	57.25	58.45	57.99	55.06	45.03	36.04	29.49	21.85	17.95	18.35	21.16
640	14.94	13.44	13.64	20.13	32.78	41.35	48.18	53.74	56.97	58.58	58.49	56.16	47.04	38.24	31.87	23.46	19.01	18.76	21.34
650	15.74	13.95	13.42	19.09	31.26	39.91	47.04	53.1	56.63	58.59	58.91	57.14	48.9	40.4	34.23	25.2	20.29	19.34	21.6
660	16.62	14.49	13.25	18.12	29.69	38.34	45.74	52.16	56.08	58.44	59.14	57.84	50.55	42.45	36.56	27.04	21.75	20.12	21.81
670	17.5	15.14	13.21	17.17	28.19	36.71	44.41	51.23	55.48	58.13	59.22	58.37	51.98	44.36	38.7	28.89	23.29	21.02	22.08

Table 3.5A: *Relative reflectance data for sample set 2J measured using the Spectraflash 600 with specular included.*

Wavelength (nm)	Anodising voltage																						
	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120
380	3.36	31.81	32.57	32.54	39.42	43.55	35.56	29.52	24.89	16.19	18.59	20.03	32.98	38.75	38.65	29.5	24.53	21.36	21.45	23.58	24.52	23.73	22.69
390	3.59	28.61	30.03	30.42	39.24	43.82	37.8	31.56	28.49	21.04	16.29	14.24	25.64	33.85	38.49	32.67	27.62	22.81	20.45	21.69	22.43	23.31	22.69
400	4.56	25.72	27.39	28.17	38.48	43.59	39.5	33.6	31.69	26.65	16.96	12.52	19.19	27.59	36.45	34.35	30.22	25.1	21.04	20.91	21.27	22.82	22.67
410	5.87	22.93	24.83	25.72	37.26	42.73	40.76	35.57	34.49	31.7	19.24	14.12	14.73	20.95	32.8	34.44	31.99	27.42	22.69	21.15	21.09	22.38	22.32
420	7.36	20.42	22.45	23.51	35.83	41.61	41.45	37.42	36.85	36.1	22.31	17.54	13.25	15.41	28.38	33.3	32.92	29.52	24.79	22.09	21.79	22.13	22.01
430	8.96	18.22	20.26	21.28	34.17	40.19	41.74	38.82	39	39.67	25.64	21.91	13.99	11.91	23.56	30.86	32.88	30.87	26.76	23.53	22.91	22.02	21.8
440	10.59	16.23	18.1	19.3	32.41	38.61	41.65	39.95	40.71	42.55	28.77	26.51	16.32	10.77	19.4	27.55	31.73	31.51	28.49	25.03	24.23	22.11	21.61
450	12.26	14.61	16.3	17.51	30.56	36.92	41.26	40.69	42.25	44.92	31.8	30.84	19.59	11.84	16.2	23.93	29.64	31.32	29.68	26.37	25.5	22.38	21.56
460	13.9	13.25	14.65	15.91	28.78	35.2	40.73	41.16	43.52	46.93	34.44	34.81	23.24	14.43	14.47	20.4	26.94	30.3	30.27	27.47	26.6	22.68	21.57
470	15.51	12.2	13.34	14.61	27.03	33.46	40.03	41.4	44.46	48.48	36.87	38.27	26.83	17.81	14.12	17.56	24.06	28.75	30.27	28.15	27.39	22.94	21.58
480	17.19	11.29	12.15	13.42	25.3	31.65	39.25	41.46	45.36	49.82	39.24	41.45	30.44	21.92	14.91	15.37	21.11	26.54	29.61	28.49	27.9	23.2	21.66
490	18.83	10.63	11.24	12.5	23.62	29.92	38.3	41.38	45.91	50.82	41.34	44.19	33.74	25.98	16.54	14.12	18.69	24.11	28.46	28.32	28.02	23.39	21.7
500	20.41	10.15	10.5	11.75	22.02	28.17	37.3	41.08	46.44	51.56	43.21	46.47	36.75	29.82	18.64	13.69	16.82	21.63	26.85	27.75	27.76	23.5	21.71
510	21.98	9.84	9.92	11.14	20.43	26.44	36.19	40.73	46.44	52.07	44.79	48.47	39.46	33.39	21.13	13.98	15.57	19.31	24.85	26.73	27.15	23.42	21.67
520	23.48	9.67	9.56	10.71	18.95	24.71	34.94	40.1	46.45	52.39	46.1	50.12	41.88	36.72	23.77	14.99	14.97	17.26	22.71	25.42	26.17	23.21	21.59
530	24.97	9.68	9.37	10.46	17.52	23.11	33.69	39.5	46.24	52.53	47.27	51.54	44.08	39.66	26.52	16.53	14.95	15.69	20.58	23.93	25.04	22.92	21.54
540	26.44	9.82	9.29	10.39	16.24	21.51	32.34	38.65	45.96	52.47	48.2	52.68	46.03	42.32	29.3	18.62	15.49	14.64	18.62	22.34	23.66	22.55	21.41
550	27.83	10.08	9.38	10.42	15.06	20.02	31.01	37.77	45.57	52.33	49	53.64	47.79	44.72	32.05	21.01	16.49	14.14	16.95	20.81	22.25	22.15	21.33
560	29.16	10.43	9.64	10.57	14	18.59	29.6	36.77	44.96	51.96	49.51	54.41	49.29	46.78	34.68	23.69	17.9	14.18	15.64	19.31	20.86	21.68	21.17
570	30.4	10.84	9.95	10.83	13.01	17.22	28.13	35.65	44.21	51.52	49.86	54.84	50.51	48.51	37.2	26.48	19.63	14.73	14.78	18.02	19.53	21.21	21.01
580	31.62	11.4	10.39	11.19	12.19	16.02	26.72	34.5	43.46	50.95	50.06	55.25	51.64	50.11	39.62	29.37	21.69	15.8	14.43	17.04	18.43	20.81	20.92
590	32.72	11.99	10.94	11.66	11.5	14.94	25.28	33.28	42.53	50.22	50.1	55.4	52.49	51.38	41.81	32.2	23.98	17.29	14.54	16.37	17.56	20.45	20.87
600	33.75	12.64	11.55	12.18	10.9	13.96	23.85	31.98	41.52	49.37	49.97	55.41	53.24	52.47	43.88	34.94	26.4	19.1	15.08	16.03	16.95	20.16	20.79
610	34.79	13.37	12.24	12.78	10.5	13.15	22.44	30.69	40.4	48.46	49.75	55.29	53.72	53.34	45.7	37.6	28.89	21.21	16.06	16.03	16.72	19.97	20.78
620	35.66	14.1	12.93	13.42	10.18	12.46	21.11	29.33	39.22	47.42	49.38	54.99	54.04	54	47.32	40	31.37	23.43	17.31	16.38	16.73	19.88	20.79
630	36.45	14.84	13.68	14.1	9.97	11.85	19.82	27.92	37.94	46.25	48.82	54.58	54.21	54.51	48.8	42.22	33.8	25.78	18.87	16.98	16.98	19.87	20.83
640	37.26	15.64	14.48	14.8	9.89	11.43	18.61	26.55	36.63	45.08	48.23	54.05	54.28	54.82	50.08	44.23	36.16	28.17	20.61	17.84	17.53	19.98	20.92
650	38.04	16.46	15.32	15.58	9.97	11.14	17.56	25.26	35.34	43.88	47.59	53.53	54.28	55.16	51.24	46.1	38.46	30.54	22.5	18.98	18.31	20.19	21.08
660	38.68	17.3	16.16	16.33	10.1	10.94	16.5	23.92	33.94	42.51	46.78	52.84	54.08	55.28	52.16	47.71	40.59	32.89	24.52	20.25	19.26	20.46	21.22
670	39.38	18.18	17.03	17.2	10.39	10.91	15.64	22.67	32.6	41.18	45.93	52.08	53.8	55.27	52.92	49.14	42.52	35.17	26.54	21.68	20.39	20.85	21.41
680	39.98	19.09	17.98	18.06	10.72	10.97	14.83	21.48	31.21	39.83	45.1	51.28	53.45	55.18	53.57	50.37	44.36	37.33	28.63	23.23	21.66	21.34	21.65
690	40.49	20	18.89	18.93	11.2	11.19	14.18	20.33	29.87	38.43	44.15	50.42	52.93	54.96	53.98	51.32	45.92	39.22	30.6	24.78	22.93	21.86	21.9
700	40.93	21.12	20.04	20.01	11.93	11.71	13.79	19.38	28.5	37.02	43.24	49.55	52.54	54.67	54.29	52.1	47.36	41.18	32.73	26.54	24.49	22.56	22.25
L*	60.5	39.97	38.91	40.42	45.53	51.08	61.1	66.52	72.15	76.55	74.83	77.68	74.52	72.66	65.04	57.29	52.66	49.37	50.1	52.43	53.46	53.69	53.18
a*	4.29	11.26	11.62	9.92	-3.91	-7.56	-11	-10.12	-8.4	-7.58	-4.68	-5.1	-1.15	2.01	14.13	25.25	23.69	15.96	-0.64	-8.89	-10.43	-4.58	-1.7
b*	29.3	-7.99	-13.15	-13.23	-26.71	-25.99	-14.95	-5.6	1.55	5.81	18.06	23.44	33.84	43.53	26.98	4.9	-10.9	-19.75	-17.9	-10.21	-7.39	-1.69	-0.83

Table 3.6A: Actual measured data for TA1 sample set using Spectraflash with specular included.

Averages for measurements made for CSM samples on Spectrolino at LCC 6/02/06

D50

Sample	CSM5v	CSM7v	CSM10v	CSM15v	CSM18v	CSM20v	CSM22v	CSM25v	CSM30v	CSM35v	CSM40v	CSM45v	CSM50v	CSM55v	CSM60v	CSM65v	CSM70v	CSM75v	CSM80v	CSM85v	CSM90v
CIE Lab																					
L*	66.85	61.80	51.95	33.85	32.10	39.19	49.61	54.05	65.99	70.88	74.97	74.03	71.20	66.79	57.78	51.00	50.65	55.15	62.80	66.60	69.15
a*	2.54	3.92	9.99	25.25	15.20	0.32	-10.97	-12.12	-11.07	-8.48	-7.53	-6.32	-2.51	16.22	35.80	38.29	9.08	-19.01	-31.66	-25.65	-13.86
b*	13.04	21.49	40.72	-8.81	-36.41	-39.67	-35.43	-26.43	-14.68	-3.76	7.23	28.71	43.99	28.62	-6.55	-32.43	-36.00	-28.35	-4.89	16.75	26.78
Spectrum R																					
380	0.1551	0.0522	0.0976	0.3539	0.4176	0.4739	0.5153	0.4361	0.3735	0.1445	0.0937	0.3206	0.4269	0.4703	0.4045	0.2009	0.1742	0.2977	0.3938	0.3874	0.2601
390	0.1785	0.0669	0.0674	0.3249	0.4073	0.4730	0.5274	0.4578	0.4263	0.2284	0.0761	0.2431	0.3882	0.4891	0.4649	0.3285	0.1438	0.2040	0.3583	0.4192	0.3710
400	0.1967	0.0841	0.0438	0.2821	0.3802	0.4546	0.5204	0.4602	0.4546	0.3020	0.1273	0.1518	0.3155	0.4734	0.4832	0.4162	0.2307	0.1437	0.2692	0.3946	0.4072
410	0.2146	0.1026	0.0310	0.2419	0.3519	0.4341	0.5098	0.4588	0.4741	0.3590	0.2051	0.0922	0.2313	0.4406	0.4822	0.4625	0.3353	0.1933	0.1751	0.3359	0.4015
420	0.2291	0.1203	0.0264	0.2028	0.3200	0.4080	0.4925	0.4501	0.4826	0.3969	0.2769	0.0816	0.1511	0.3898	0.4632	0.4792	0.4027	0.2921	0.1389	0.2485	0.3640
430	0.2426	0.1373	0.0277	0.1682	0.2889	0.3817	0.4735	0.4401	0.4873	0.4245	0.3360	0.1125	0.0946	0.3273	0.4345	0.4805	0.4403	0.3752	0.1864	0.1637	0.3027
440	0.2550	0.1535	0.0333	0.1373	0.2582	0.3541	0.4523	0.4274	0.4875	0.4437	0.3818	0.1655	0.0741	0.2551	0.3943	0.4691	0.4569	0.4275	0.2715	0.1317	0.2242
450	0.2668	0.1693	0.0424	0.1114	0.2287	0.3264	0.4304	0.4137	0.4850	0.4570	0.4170	0.2235	0.0891	0.1836	0.3449	0.4479	0.4598	0.4559	0.3461	0.1717	0.1539
460	0.2779	0.1840	0.0538	0.0899	0.2008	0.2986	0.4065	0.3982	0.4798	0.4654	0.4436	0.2770	0.1279	0.1240	0.2874	0.4174	0.4523	0.4676	0.3979	0.2448	0.1278
470	0.2880	0.1980	0.0667	0.0727	0.1747	0.2711	0.3816	0.3813	0.4721	0.4695	0.4628	0.3226	0.1772	0.0879	0.2258	0.3783	0.4363	0.4674	0.4291	0.3127	0.1597
480	0.2975	0.2113	0.0806	0.0599	0.1508	0.2444	0.3562	0.3636	0.4627	0.4706	0.4765	0.3599	0.2273	0.0814	0.1670	0.3321	0.4133	0.4584	0.4454	0.3625	0.2244
490	0.3072	0.2245	0.0954	0.0511	0.1298	0.2195	0.3315	0.3460	0.4528	0.4703	0.4870	0.3908	0.2738	0.1018	0.1192	0.2811	0.3849	0.4432	0.4521	0.3958	0.2910
500	0.3163	0.2369	0.1106	0.0457	0.1112	0.1957	0.3064	0.3276	0.4413	0.4676	0.4938	0.4152	0.3139	0.1407	0.0898	0.2275	0.3502	0.4215	0.4501	0.4153	0.3444
510	0.3255	0.2493	0.1262	0.0436	0.0955	0.1738	0.2822	0.3094	0.4294	0.4640	0.4985	0.4351	0.3484	0.1884	0.0832	0.1767	0.3111	0.3951	0.4425	0.4258	0.3837
520	0.3349	0.2617	0.1422	0.0444	0.0825	0.1538	0.2588	0.2915	0.4176	0.4599	0.5019	0.4519	0.3779	0.2379	0.0980	0.1343	0.2686	0.3642	0.4303	0.4298	0.4113
530	0.3433	0.2732	0.1579	0.0475	0.0718	0.1351	0.2355	0.2726	0.4037	0.4534	0.5021	0.4641	0.4015	0.2843	0.1287	0.1053	0.2237	0.3275	0.4124	0.4271	0.4280
540	0.3515	0.2842	0.1734	0.0528	0.0636	0.1184	0.2127	0.2539	0.3891	0.4459	0.5006	0.4733	0.4209	0.3258	0.1688	0.0940	0.1803	0.2868	0.3900	0.4198	0.4371
550	0.3603	0.2956	0.1892	0.0601	0.0580	0.1040	0.1915	0.2359	0.3749	0.4385	0.4989	0.4815	0.4376	0.3627	0.2128	0.1009	0.1430	0.2444	0.3642	0.4093	0.4411
560	0.3672	0.3054	0.2038	0.0685	0.0545	0.0914	0.1707	0.2172	0.3583	0.4283	0.4938	0.4853	0.4490	0.3926	0.2551	0.1228	0.1151	0.2007	0.3327	0.3932	0.4380
570	0.3759	0.3164	0.2192	0.0786	0.0532	0.0812	0.1521	0.2000	0.3432	0.4196	0.4903	0.4899	0.4602	0.4200	0.2959	0.1560	0.1013	0.1610	0.2995	0.3757	0.4329
580	0.3820	0.3251	0.2328	0.0892	0.0537	0.0726	0.1340	0.1822	0.3254	0.4075	0.4826	0.4901	0.4664	0.4405	0.3309	0.1941	0.1016	0.1271	0.2617	0.3524	0.4211
590	0.3885	0.3339	0.2462	0.1005	0.0561	0.0663	0.1179	0.1654	0.3080	0.3955	0.4749	0.4896	0.4712	0.4581	0.3618	0.2340	0.1161	0.1041	0.2237	0.3264	0.4064
600	0.3942	0.3416	0.2586	0.1122	0.0597	0.0620	0.1034	0.1494	0.2899	0.3822	0.4655	0.4873	0.4738	0.4719	0.3878	0.2727	0.1412	0.0941	0.1868	0.2973	0.3875
610	0.3999	0.3492	0.2706	0.1241	0.0647	0.0596	0.0910	0.1346	0.2723	0.3689	0.4558	0.4843	0.4753	0.4834	0.4102	0.3089	0.1732	0.0981	0.1545	0.2663	0.3655
620	0.4044	0.3559	0.2815	0.1359	0.0707	0.0589	0.0804	0.1209	0.2542	0.3546	0.4446	0.4794	0.4747	0.4917	0.4283	0.3410	0.2083	0.1144	0.1291	0.2341	0.3398
630	0.4081	0.3614	0.2914	0.1476	0.0776	0.0597	0.0718	0.1083	0.2362	0.3394	0.4322	0.4731	0.4721	0.4972	0.4426	0.3688	0.2432	0.1398	0.1137	0.2025	0.3109
640	0.4112	0.3663	0.3003	0.1588	0.0850	0.0620	0.0651	0.0973	0.2184	0.3238	0.4188	0.4654	0.4679	0.5004	0.4535	0.3925	0.2764	0.1710	0.1092	0.1737	0.2797
650	0.4146	0.3713	0.3091	0.1700	0.0929	0.0655	0.0605	0.0879	0.2018	0.3085	0.4057	0.4578	0.4634	0.5027	0.4627	0.4134	0.3075	0.2049	0.1160	0.1504	0.2479
660	0.4183	0.3765	0.3179	0.1812	0.1015	0.0701	0.0576	0.0800	0.1860	0.2938	0.3929	0.4502	0.4586	0.5043	0.4706	0.4317	0.3360	0.2397	0.1325	0.1342	0.2165
670	0.4221	0.3814	0.3263	0.1923	0.1105	0.0757	0.0564	0.0735	0.1711	0.2791	0.3796	0.4422	0.4529	0.5047	0.4768	0.4476	0.3613	0.2730	0.1561	0.1267	0.1865
680	0.4260	0.3867	0.3347	0.2033	0.1198	0.0822	0.0566	0.0685	0.1572	0.2649	0.3665	0.4340	0.4469	0.5047	0.4819	0.4613	0.3840	0.3046	0.1846	0.1283	0.1603
690	0.4289	0.3910	0.3421	0.2137	0.1290	0.0892	0.0582	0.0648	0.1441	0.2500	0.3525	0.4245	0.4394	0.5025	0.4846	0.4722	0.4033	0.3329	0.2151	0.1382	0.1387
700	0.4320	0.3957	0.3498	0.2241	0.1383	0.0967	0.0610	0.0623	0.1319	0.2359	0.3388	0.4153	0.4324	0.5005	0.4868	0.4819	0.4205	0.3589	0.2466	0.1551	0.1242
710	0.4347	0.3994	0.3565	0.2339	0.1476	0.1046	0.0648	0.0610	0.1207	0.2218	0.3245	0.4052	0.4241	0.4969	0.4875	0.4891	0.4349	0.3813	0.2765	0.1772	0.1171
720	0.4372	0.4031	0.3630	0.2433	0.1568	0.1128	0.0695	0.0607	0.1108	0.2081	0.3103	0.3946	0.4154	0.4932	0.4873	0.4953	0.4474	0.4013	0.3050	0.2026	0.1180
730	0.4403	0.4075	0.3698	0.2529	0.1663	0.1214	0.0751	0.0615	0.1017	0.1949	0.2963	0.3846	0.4073	0.4895	0.4873	0.5010	0.4587	0.4194	0.3323	0.2303	0.1263

Table 3.7A:
Measured relative reflectance and L, a* and b*data for CSM sample set using a 0/45 geometry spectrophotometer.*

Hone samples(av. of three) — Spectrolino-0/45

	1-000a	2-050a	3-100	4-120	5-140	6-160	7-180	8-200	9-250	10-300	11-400	12-450	13-500	14-550	15-570	16-600	17-660	18-700	19-760	20-800	21-900	22-940	23-1000	24-1100
L*	23.14	16.88	14.99	11.24	7.13	4.73	3.36	3.41	10.92	21.65	22.27	21.13	19.86	15.92	14.95	15.96	6.10	9.72	8.68	10.95	19.37	21.66	15.77	18.46
a*	-0.26	0.32	2.35	4.34	7.46	6.78	6.27	2.92	-4.56	-6.54	-4.73	-3.73	-1.45	5.55	8.89	13.11	17.97	17.92	-6.18	-15.23	-17.55	-12.41	-0.79	14.28
b*	0.80	4.80	13.78	13.87	6.36	-3.42	-10.58	-14.38	-15.63	-9.53	4.12	13.95	22.00	16.09	11.05	5.07	-14.85	-22.04	-16.66	-9.88	9.71	15.75	8.78	-3.99
	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum F	Spectrum R
380	0.0308	0.0098	0.0035	0.0094	0.0177	0.0238	0.0267	0.0246	0.0334	0.0389	0.0053	0.0176	0.0297	0.0271	0.0270	0.0347	0.0109	0.0087	0.0098	0.0172	0.0300	0.0285	0.0072	0.0175
390	0.0345	0.0108	0.0026	0.0070	0.0157	0.0233	0.0261	0.0252	0.0370	0.0459	0.0030	0.0131	0.0269	0.0301	0.0315	0.0399	0.0175	0.0189	0.0045	0.0117	0.0340	0.0370	0.0153	0.0084
400	0.0352	0.0121	0.0022	0.0045	0.0123	0.0200	0.0243	0.0248	0.0374	0.0501	0.0052	0.0062	0.0210	0.0284	0.0307	0.0411	0.0222	0.0295	0.0058	0.0046	0.0302	0.0385	0.0226	0.0097
410	0.0358	0.0135	0.0027	0.0032	0.0097	0.0171	0.0217	0.0228	0.0372	0.0524	0.0106	0.0029	0.0140	0.0253	0.0285	0.0394	0.0248	0.0368	0.0109	0.0043	0.0218	0.0349	0.0255	0.0227
420	0.0360	0.0145	0.0034	0.0026	0.0073	0.0142	0.0186	0.0208	0.0359	0.0530	0.0161	0.0026	0.0076	0.0203	0.0245	0.0355	0.0253	0.0405	0.0174	0.0084	0.0120	0.0271	0.0251	0.0333
430	0.0362	0.0153	0.0045	0.0022	0.0055	0.0115	0.0159	0.0185	0.0343	0.0531	0.0210	0.0051	0.0035	0.0147	0.0193	0.0302	0.0245	0.0418	0.0223	0.0141	0.0053	0.0173	0.0222	0.0389
440	0.0364	0.0161	0.0055	0.0027	0.0043	0.0094	0.0135	0.0166	0.0329	0.0532	0.0253	0.0088	0.0023	0.0096	0.0142	0.0241	0.0234	0.0421	0.0256	0.0192	0.0051	0.0088	0.0181	0.0406
450	0.0370	0.0171	0.0068	0.0032	0.0035	0.0078	0.0115	0.0150	0.0317	0.0531	0.0292	0.0131	0.0035	0.0056	0.0094	0.0178	0.0218	0.0413	0.0281	0.0234	0.0100	0.0058	0.0127	0.0396
460	0.0372	0.0178	0.0080	0.0040	0.0029	0.0062	0.0095	0.0130	0.0298	0.0523	0.0320	0.0172	0.0061	0.0031	0.0054	0.0116	0.0191	0.0387	0.0288	0.0258	0.0169	0.0082	0.0074	0.0355
470	0.0374	0.0185	0.0092	0.0048	0.0026	0.0051	0.0079	0.0113	0.0278	0.0510	0.0341	0.0209	0.0095	0.0024	0.0030	0.0066	0.0158	0.0350	0.0286	0.0270	0.0237	0.0143	0.0044	0.0290
480	0.0377	0.0191	0.0105	0.0058	0.0026	0.0044	0.0065	0.0097	0.0259	0.0498	0.0358	0.0242	0.0134	0.0032	0.0023	0.0035	0.0124	0.0307	0.0278	0.0274	0.0293	0.0215	0.0044	0.0212
490	0.0379	0.0199	0.0117	0.0058	0.0029	0.0038	0.0053	0.0083	0.0241	0.0484	0.0371	0.0269	0.0172	0.0050	0.0030	0.0025	0.0090	0.0257	0.0263	0.0272	0.0333	0.0282	0.0068	0.0134
500	0.0380	0.0204	0.0129	0.0068	0.0032	0.0034	0.0044	0.0070	0.0221	0.0467	0.0377	0.0291	0.0205	0.0075	0.0047	0.0033	0.0059	0.0202	0.0240	0.0261	0.0358	0.0333	0.0103	0.0077
510	0.0381	0.0209	0.0141	0.0078	0.0038	0.0034	0.0036	0.0059	0.0201	0.0448	0.0382	0.0307	0.0233	0.0104	0.0072	0.0054	0.0035	0.0149	0.0211	0.0244	0.0370	0.0369	0.0142	0.0061
520	0.0383	0.0214	0.0153	0.0089	0.0044	0.0034	0.0032	0.0050	0.0183	0.0429	0.0385	0.0321	0.0259	0.0134	0.0099	0.0085	0.0022	0.0102	0.0182	0.0224	0.0374	0.0393	0.0177	0.0083
530	0.0383	0.0218	0.0164	0.0100	0.0051	0.0036	0.0028	0.0042	0.0164	0.0408	0.0383	0.0330	0.0279	0.0161	0.0129	0.0120	0.0017	0.0066	0.0150	0.0200	0.0369	0.0405	0.0205	0.0128
540	0.0384	0.0222	0.0174	0.0111	0.0060	0.0038	0.0026	0.0036	0.0147	0.0387	0.0379	0.0336	0.0294	0.0186	0.0156	0.0156	0.0020	0.0043	0.0117	0.0172	0.0357	0.0407	0.0222	0.0185
550	0.0384	0.0227	0.0184	0.0122	0.0068	0.0042	0.0026	0.0032	0.0132	0.0366	0.0376	0.0341	0.0307	0.0208	0.0183	0.0191	0.0029	0.0035	0.0086	0.0143	0.0342	0.0403	0.0235	0.0242
560	0.0385	0.0230	0.0195	0.0132	0.0077	0.0048	0.0028	0.0029	0.0117	0.0344	0.0370	0.0344	0.0317	0.0227	0.0206	0.0224	0.0043	0.0039	0.0060	0.0113	0.0321	0.0393	0.0241	0.0291
570	0.0388	0.0235	0.0205	0.0143	0.0086	0.0052	0.0030	0.0026	0.0103	0.0324	0.0366	0.0347	0.0326	0.0245	0.0227	0.0253	0.0060	0.0054	0.0040	0.0086	0.0296	0.0379	0.0245	0.0332
580	0.0388	0.0238	0.0214	0.0152	0.0095	0.0058	0.0033	0.0025	0.0090	0.0302	0.0359	0.0347	0.0331	0.0258	0.0244	0.0279	0.0078	0.0077	0.0028	0.0062	0.0265	0.0357	0.0243	0.0361
590	0.0389	0.0241	0.0222	0.0161	0.0104	0.0064	0.0038	0.0024	0.0079	0.0280	0.0350	0.0345	0.0334	0.0269	0.0258	0.0300	0.0096	0.0106	0.0023	0.0043	0.0232	0.0330	0.0237	0.0380
600	0.0386	0.0243	0.0229	0.0169	0.0113	0.0070	0.0042	0.0025	0.0068	0.0257	0.0339	0.0340	0.0334	0.0276	0.0269	0.0315	0.0113	0.0137	0.0024	0.0029	0.0195	0.0297	0.0227	0.0389
610	0.0385	0.0243	0.0235	0.0176	0.0121	0.0075	0.0047	0.0026	0.0059	0.0235	0.0327	0.0333	0.0331	0.0279	0.0276	0.0327	0.0128	0.0168	0.0031	0.0022	0.0158	0.0262	0.0212	0.0390
620	0.0382	0.0244	0.0240	0.0183	0.0128	0.0081	0.0052	0.0028	0.0052	0.0214	0.0314	0.0325	0.0328	0.0282	0.0281	0.0335	0.0140	0.0198	0.0042	0.0022	0.0123	0.0225	0.0197	0.0385
630	0.0380	0.0244	0.0244	0.0189	0.0135	0.0087	0.0057	0.0030	0.0046	0.0194	0.0301	0.0317	0.0324	0.0283	0.0284	0.0342	0.0151	0.0225	0.0057	0.0026	0.0092	0.0188	0.0181	0.0377
640	0.0378	0.0245	0.0249	0.0195	0.0143	0.0092	0.0064	0.0033	0.0041	0.0176	0.0290	0.0310	0.0320	0.0284	0.0287	0.0347	0.0161	0.0250	0.0073	0.0035	0.0067	0.0153	0.0164	0.0366
650	0.0377	0.0246	0.0252	0.0200	0.0149	0.0097	0.0069	0.0035	0.0037	0.0159	0.0279	0.0303	0.0317	0.0286	0.0289	0.0350	0.0170	0.0273	0.0089	0.0046	0.0049	0.0121	0.0146	0.0351
660	0.0375	0.0247	0.0257	0.0205	0.0156	0.0103	0.0075	0.0039	0.0034	0.0144	0.0267	0.0296	0.0313	0.0285	0.0290	0.0353	0.0177	0.0293	0.0106	0.0059	0.0036	0.0092	0.0127	0.0334
670	0.0374	0.0247	0.0260	0.0210	0.0163	0.0109	0.0081	0.0042	0.0032	0.0129	0.0255	0.0287	0.0307	0.0283	0.0290	0.0354	0.0183	0.0310	0.0123	0.0073	0.0032	0.0069	0.0108	0.0314
680	0.0372	0.0248	0.0263	0.0214	0.0169	0.0114	0.0087	0.0046	0.0031	0.0117	0.0243	0.0278	0.0301	0.0280	0.0288	0.0353	0.0186	0.0324	0.0138	0.0088	0.0033	0.0051	0.0089	0.0291
690	0.0371	0.0248	0.0266	0.0218	0.0175	0.0118	0.0094	0.0050	0.0031	0.0105	0.0230	0.0269	0.0294	0.0277	0.0286	0.0350	0.0189	0.0335	0.0152	0.0103	0.0041	0.0041	0.0073	0.0267
700	0.0370	0.0247	0.0270	0.0221	0.0180	0.0123	0.0099	0.0053	0.0032	0.0094	0.0218	0.0260	0.0287	0.0274	0.0284	0.0349	0.0192	0.0347	0.0165	0.0118	0.0053	0.0039	0.0058	0.0241
710	0.0369	0.0249	0.0272	0.0225	0.0187	0.0128	0.0105	0.0058	0.0033	0.0085	0.0208	0.0252	0.0281	0.0271	0.0282	0.0348	0.0195	0.0355	0.0176	0.0131	0.0067	0.0041	0.0044	0.0216
720	0.0370	0.0251	0.0276	0.0231	0.0192	0.0134	0.0111	0.0062	0.0035	0.0078	0.0199	0.0245	0.0277	0.0270	0.0281	0.0347	0.0199	0.0363	0.0187	0.0145	0.0086	0.0049	0.0036	0.0189
730	0.0371	0.0254	0.0282	0.0235	0.0199	0.0139	0.0119	0.0068	0.0036	0.0072	0.0189	0.0239	0.0271	0.0268	0.0280	0.0345	0.0203	0.0372	0.0198	0.0158	0.0106	0.0062	0.0029	0.0164

Table 3.8A:
Measured relative reflectance and L, a* and b* data for sample set **H** using a 0/45 geometry spectrophotometer.*

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