TITANIUM THE MAGICAL METAL

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ABSTRACT

Titanium has been widely used in jewellery from the second half of the twentieth century. Mainly appreciated for its colour potential, recent decades have seen its increasing use as a lightweight metal in fine jewellery for setting diamonds. However it is not so widely known that it was in the UK that titanium was first used for designed jewellery and that its use was supported by the Goldsmiths' Company.

This paper outlines the early history of titanium use and its introduction as a jewellery metal, highlighting some of the different techniques that were used; being part of a PhD research project at Central Saint Martins titled **Variability in coloured titanium surfaces for jewellery** completed in 2010. The research, presented in brief here, used scientific analytical techniques to explore in detail the surfaces of titanium before and after colouring, explaining in part why the process can be variable. The outcomes of the research suggest process parameters that will aid jewellers in the workshop.

The paper presents continuing research into the practical use of titanium, with a link to an online video, sponsored by Goldsmiths in 2017 exploring different ways of producing designs on the metal. Techniques such as machine engraving, guilloche engraving and recent investigations into the use of a laser cutter are outlined. Finally the paper presents some recent examples of titanium set diamond pieces and contemporary usage of the metal.

INTRODUCTION

The jeweller's art has historically 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 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, relatively unresponsive metal that is difficult to shape and slow to work. It cannot be soldered in the workshop or annealed or reworked and is a poor conductor of heat.

However the colour palette of the precious metals is limited to white, yellow and red. Designs for polychrome jewellery have 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.

TITANIUM DEVELOPMENT

Titanium may be truly called a space age metal for had not its unique combination of properties, light weight and high strength been needed by the USA aerospace programme in the 1950s, it may have remained an interesting curiosity for metallurgists.
Although the existence of this new element was established in the late 18th century[1] it was not isolated as a pure metal until the early 20th Century.
The commercial production of titanium started in the 1950s based on the Kroll process and developed rapidly[2].
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.'*[3]
As can be seen, Table 1, titanium fills a space between aluminium and iron in terms of weight but has a higher melting point and is as strong as steel [2].

Metal	**Specific Gravity**	**Melting Point ^{0}C**	**Thermal Conductivity W/m-K**
Aluminium (Al)	2.7	660	200
Titanium (Ti)	4.5	1668	<20
Iron (Fe)	8	1535	55-80
Silver (Ag)	10.5	960	400
Gold (Au)	19.3	1062	300

Table 1**:** Comparison of properties of titanium with other metals.

However, as the USA space programme provided the impetus for the growth of titanium production, so the radical change in policy and consequent drop in demand caused a crisis, and, in 1958 the price of the metal dropped significantly[4]. This put titanium within reach of other applications and its corrosion resistance proved particularly useful in the chemical process industries.
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 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. Much effort has been expended to develop a continuous process and the recently introduced powder process has reduced costs.

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[1] Barksdale, Jelks, *Titanium, Its Occurrence, Chemistry and Technology*, 2nd Edition, Ronald Press Co., New York 1966
[2] McQuillan, A D, McQuillan, M K, *Metallurgy of the Rarer Metals, No. 4, Titanium*, Butterworths, London 1956
[3] Cook, Maurice, *Titanium The New Metal with Big Possibilities*, The ICI Magazine, 32, 207, January 1954, p2.
[4] Lippert, T W, *1st International Conference on Titanium 1968*, Jaffee, RI and Promisel, NE, (ed), *Pergamon* Press, London, p.6, 1970.

There is much anecdotal evidence to suggest that simple pins and earrings had been fabricated by workers in titanium plants from the early days of its manufacture. An example, perhaps in a more sophisticated setting, is the silver pendant by Malcolm Green, hallmarked 1963, set with titanium sponge, which is now in the collection of the Worshipful Company of Goldsmiths'. Figure 1.

Figure 1: Titanium sponge set in silver by Malcolm Green 1963.

INTRODUCTION TO JEWELLERS

Titanium 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 search for new outlets.

The promotion of the use of titanium for decorative purposes was initiated by Joe Cotton[5] while he was a senior researcher at Imperial Metal Industries (IMI), the metals division of ICI. In 1964 when based at the IMI laboratories in Witton, Cotton approached one of the tutors at the nearby School of Jewellery in Birmingham, Gerald Whiles, with the idea that titanium would be a worthwhile new material for students to use. With guidance and support from industry, the early users of titanium for jewellery set out to explore the new design possibilities that were created by virtue of the coloured metal surfaces that could be obtained. With titanium the colours appear as if by magic when the metal is oxidised, either electrochemically or by heat.

The workshop methods initially suggested by IMI, with minor variations, continue to be used today and examples of the basic steps can be viewed in the videos produced by Goldsmiths.[6] In brief anodising gives greater control to the energy input and produces more evenly coloured surfaces while the poor thermal conductivity of titanium means that heating produces variable effects. Studio jewellers have used both methods of oxidising titanium to create a wide variety of decorative effects. Fabrication techniques, suitable for gold and silver, had to be adapted and the sequence of production steps had to be amended so that all the forming of a piece was completed before colouring took place.

One of the pioneer jewellers who first used titanium at Birmingham (1965-1968) was Ann Marie Shillito and this belt buckle, Figure 2 is the first identifiable piece of designed titanium

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

[6] www.youtube.com/channel/UCFCLQTrLJvK4_dksXcXGipQ

jewellery. She continued working in titanium during her time at the Royal College of Art (RCA) from 1968-71.

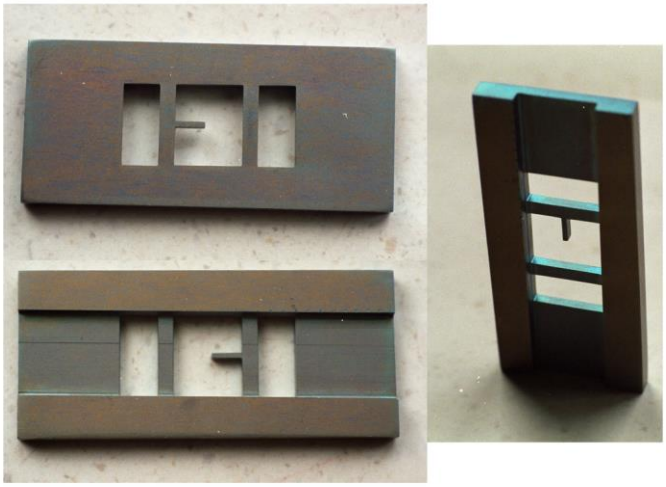

Figure 2: Machined and anodised titanium belt buckle by Ann Marie Shillito 1967.

Another artist of note in the early decorative use of titanium was Pietro Pedeferri, Figure 3. A University researcher in the field of electrochemistry in Milan, he was inspired by the colour possibilities of the metal to produce wonderful compositions on titanium. His artistic experiments started in 1968 and he has published several books on the subject of titanium art as well as many scientific papers.[7]

Figure 3: Pietro Pedeferri with his titanium artwork 2006.

The virtual exhibition of historic titanium jewellery is on line[8] and the following examples show just some of the effects that can be achieved: Figures 4-7.

[7] Pedeferri, Pietro, *Drawings on Titanium*, clup, Milan 1981.
[8] www.reflectionandrefraction.co.uk

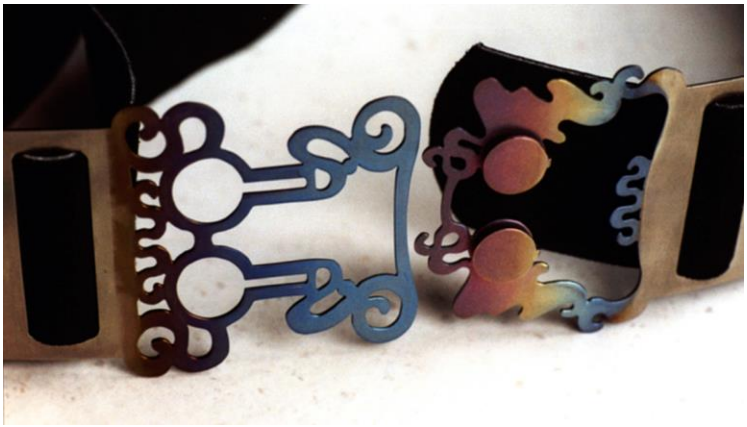

Figure 4: Dip-anodised belt buckle Ann Marie Shillito 1970.

Figure 5: Titanium bowl, pressed, hammered, polished and anodised James Brent Ward ca 1978, image courtesy of James Brent Ward.

Figure 6: Cloudscape brooch, optical illusion titanium set in a silver frame by Ed de Large 1978, image courtesy of Ed de Large.

Figure 7: Brooch by Kevin Coates using mixed metals featuring 'star-studded' titanium 1983.

Word of mouth spread of the use of titanium through the 'close-knit' jewellery school network in the late 1960s as tutors and students saw pieces incorporating the new metal in degree shows. By the early 1970s titanium had become a regular product used in Jewellery courses and in 1976, the second year of the LOOT exhibitions, eleven of the three hundred and thirty exhibitors showed work incorporating titanium. In the catalogue, Graham Hughes, the Art Director at Goldsmiths' Hall, noted[9] the use of '*a new metal and new colour'* in the pieces exhibited.

While at the RCA James Brent Ward became interested in the technical aspects of the metal and its processing. With sponsorship from the Goldsmiths' Company, he published a report in 1978 that became the standard guide for jewellers on working with refractory metals[10].

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 limited edition pieces.

The LOOT exhibition in Minneapolis in 1978 featured a significant number of titanium pieces and subsequent workshops given in the USA by UK jewellers carried the use of titanium for designed jewellery across the Atlantic

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 to appear in the windows of the High Street Jewellers. 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.

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.

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[9] Hughes, Graham, *Introduction to Loot Exhibition Catalogue,* Goldsmiths' Hall, London 1976.

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

RESEARCH PROJECT

My research was undertaken in order to document the early history of the use of titanium in jewellery, including the basic techniques used, and to investigate the problem area of colour variability. The methods of analytical science were used to explore the mechanism responsible for the appearance of colour on titanium and examine the factors that influence colour development. Briefly the project examined and tested systems for measuring the colour appearance of oxidised titanium, the effects of surface structure on colour development, the nature and composition of the oxide layer and a theoretical method for calculating the oxide layer thickness.[11]

COLOUR

The development of the appearance of colour on the surface of titanium is due to an optical phenomenon called thin film interference. Colour is observed when reflected light waves are out of phase such as when light is reflected and refracted by a thin transparent film. The transparent 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. The wavelength that is extinguished varies as the film thickens.

Thin film interference was first described by Robert Hook in 1665 in Micrographia[12], where he proposed a theory to explain the 'fantastical colours' seen on soap bubbles. Newton[13] noted that bands of colour, which he called '*chromatic scales'*, appeared in repeating sequences as a film thickened, which he called first, second and third order tints, Figure 8.

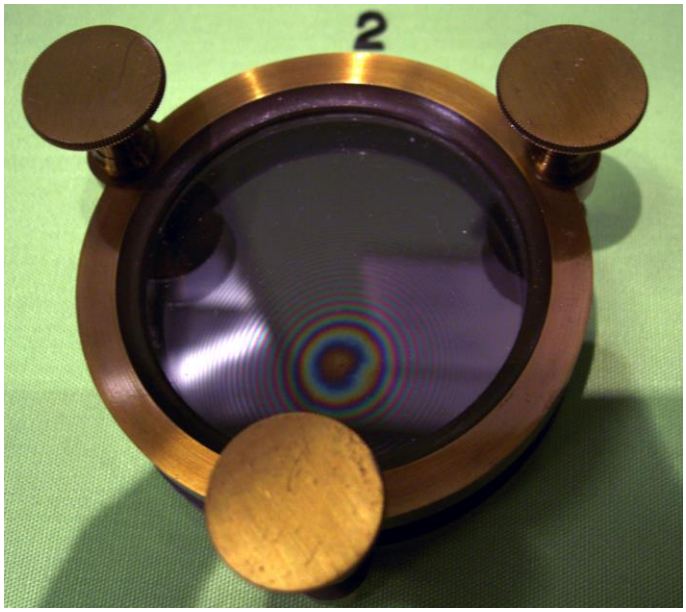

Figure 8: Apparatus formerly on display in the Science Museum showing Newton's rings.

[11] Bartlett, L, *Variability in coloured titanium surfaces for jewellery*, PhD Thesis, Central Saint Martins College of Art and Design, London, December 2009.

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

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

Almost a century later in 1801 Thomas Young[14] used interference to confirm the wave theory of light.
The diagram, Figure 9, adapted from the table by Evans,[15] illustrates how the interference colour of a thin film changes as the film thickens and the absorption bands of the first, second and third orders travel across the spectrum.

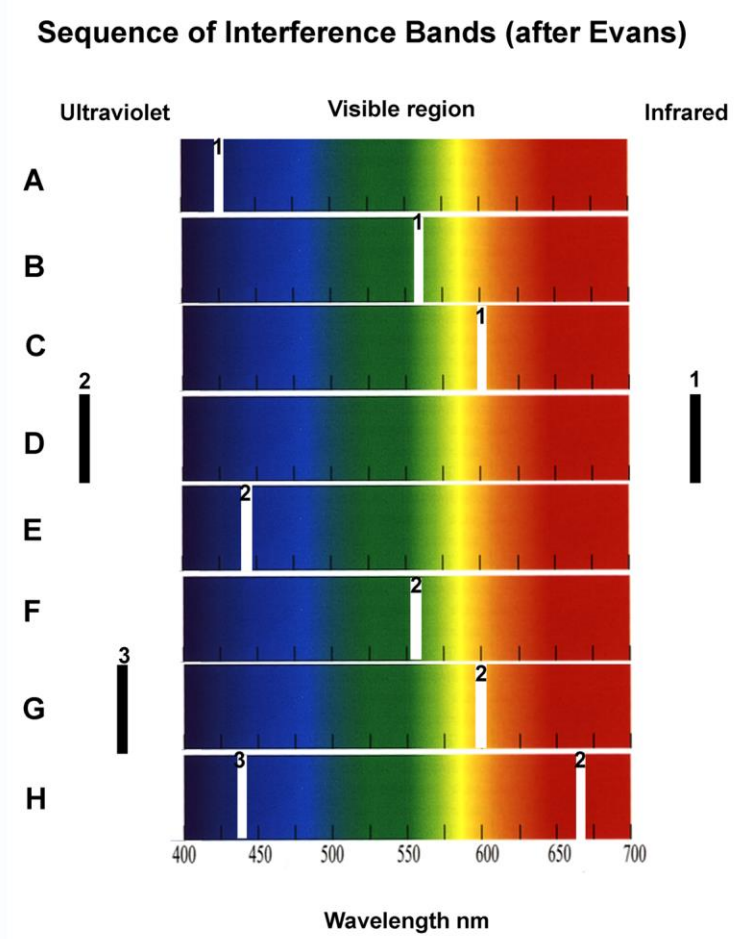

Figure 9: Diagram after Evans showing colour sequencing of interference bands, e.g. in cases B and C the band travels through the green and yellow parts of the spectrum giving purple and blue colours respectively.

The mechanics of interference colour on the surface of titanium are similar to those for any system that exhibits this form of colour. 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. The colours produced depend solely on the thickness of the layer of oxide and the refractive index of the oxide.
Under normal conditions titanium has a very thin layer or air-formed film of oxide on its surface but this can be thickened by further reaction with oxygen under the application of energy in the form of heat or electricity, i.e. anodising. The natural oxide layer is usually

[14] Peacock, George, ed. *Miscellaneous Works of the late Thomas Young,* John Murray, London, 1855, p.141.
[15] Evans, U R, *The Corrosion and Oxidation of Metals-Second Supplementary Volume*, Arnold, London, 1976, p.378

in the range 0.5 - 7 nanometres (nm) thick. Thickened films that produce interference colours are in the range 40 - 120 nm. Thicker layers, up to 500 nm do not show this phenomenon.
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. 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 and data obtained from colour measuring may be used to characterise each of the colours produced in terms of the wavelength at which maximum absorbance occurs.
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 the titanium surface is opaque and not self-luminous, the most appropriate system for the measurement of the colour appearance of oxidised titanium was deemed to be CIElab[16], which is most often used in the print, paint and textile industries. This was confirmed experimentally and allowed the derivation of a simple method for communicating the results by feeding the numerical values obtained from the measurements into a computer graphics programme, such as Photoshop. The colour can be thus be reproduced at any location worldwide within the consistency of the displays used, Figure 10.

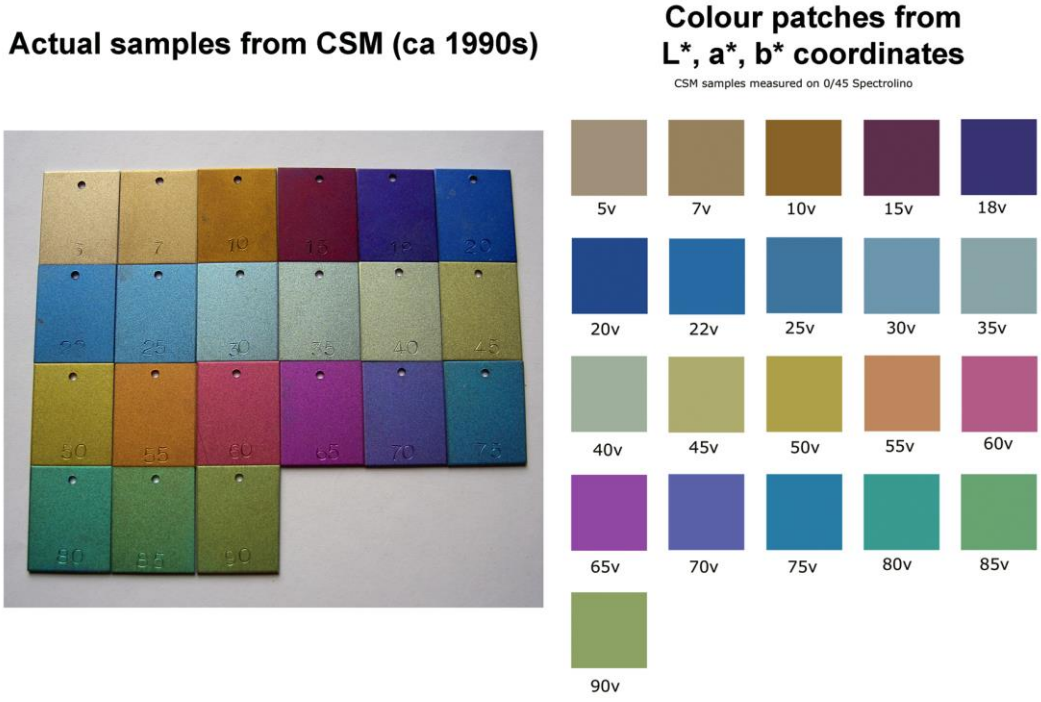

Figure 10: Comparison of photo of actual samples (etched and anodised) with Photoshop created patches.

SURFACES
The titanium metal surface on which the oxide grows is one of the most likely sources of colour variability. The scientific literature[17] noted that the speed at which an oxide layer grows on titanium when it is anodised is influenced by the surface roughness of the metal.

[16] Malacara, Daniel, *Color Vision and Colorimetry,* Spie Press, Washington, USA 2002, p 32.
[17] Hass, G, *Vacuum*, 2, 331, 1952.

As part of the project different surface finishes, from highly polished to matt, were examined. The results demonstrated that substantially different voltages were required to produce similarly coloured anodised surfaces on the different titanium surfaces.
No correlation between the degree of roughness of the surface and the speed at which the colour developed was established. The use of scanning electron microscopy (SEM) and White Light Interferometry (WLI) showed that the surface structure of the oxide layer was largely determined by the original metal surface but that in all cases oxidation slightly increased the roughness of the surface, Figure 11.

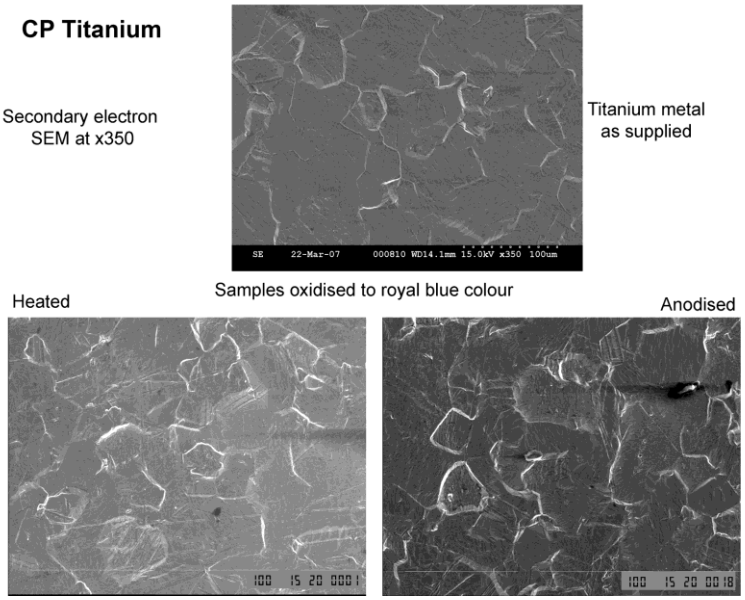

Figure 11: SEM images of uncoloured and coloured titanium sheet.

Exceptions were observed for the thicker oxide layers which show porous structures and are not very colourful and for the phenomena, named 'Flower' oxides, Figure 12, in honour of the late Prof Harvey Flower[18]. The sculpture created in honour of Prof. Flower is now in the Microscopy suite of the Materials Dept at Imperial College, London.

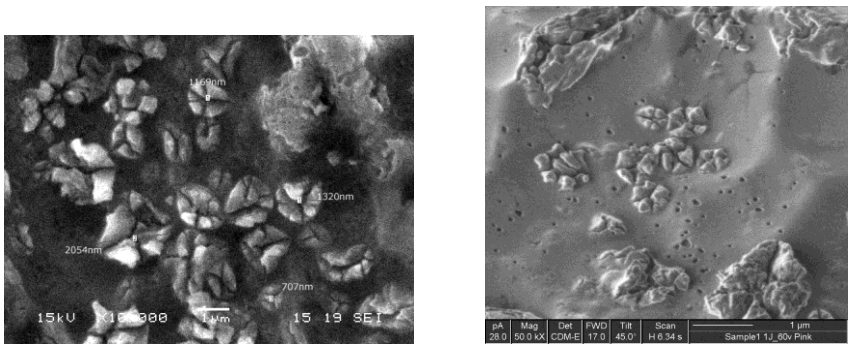

Figure 12: SEM and Crossbeam images of anodised scrap CP Titanium sheet showing 'Flower' oxides.

OXIDES

Although it is generally accepted[19] that the composition of the oxide layer is mainly titanium dioxide, its crystalline form may vary from anatase to rutile, which have different refractive

[18] Bartlett, L, *Optics and Laser Technology*, 38, 440, 2006.
[19] Aladjem, A, *Journal of Materials Science*, 8, 1973, p688

indices. The likely impact of such variation was calculated by using the interference formula to estimate the thickness limits for an oxide layer that produces a specific colour.
For example a theoretical difference in layer thickness of 12 nm could be attributable to the presence of all anatase or all rutile for a pink colour with maximum absorbance at 500 nm. However such a difference may be within the error of the metric and therefore not of major significance in colour variability.

LAYER THICKNESS

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.
To confirm this fine cross-sections of similarly coloured oxide layers were prepared and examined by Transmission Electron Microscopy (TEM). Thus the structures of the oxide layers could be clearly observed and accurate measurements of the layer thicknesses made. Although some difference in structure between the two layers had been expected the actual result was astonishing.

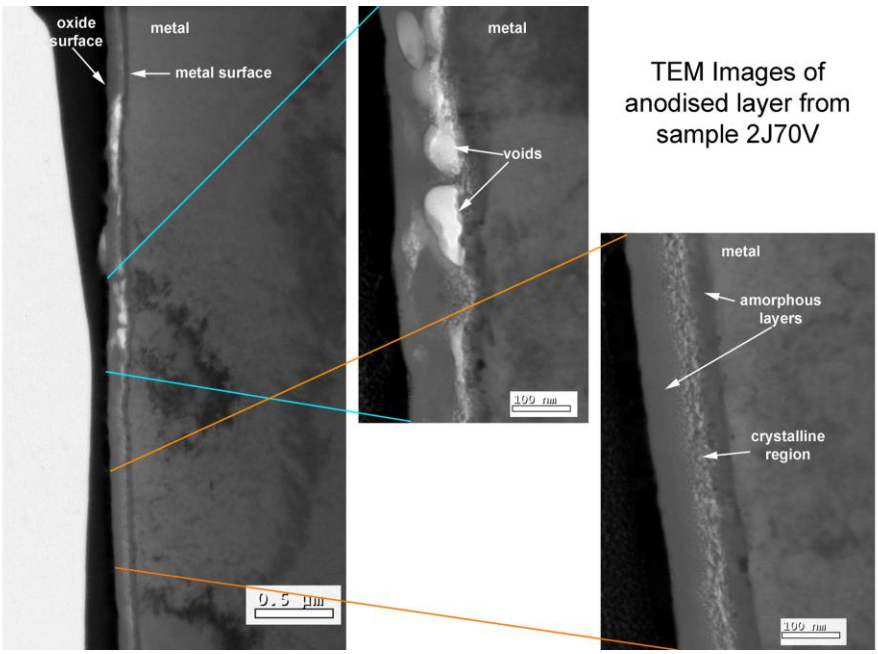

Figure 13: TEM images at different magnifications of titanium sheet anodised to a gold colour.

The anodised layer, Figure 13 is mostly a sandwich structure of relatively uniform thickness (139 nm +/-4 nm) along its length but showing the presence of random voids within the oxide layer. Diffraction measurements confirm that both the region of the layer attached to the metal surface and the region that had been in contact with the electrolyte were amorphous. At higher magnification it can be seen that the middle crystalline section is slightly less than half the thickness of the total layer. 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 are not present, the thickness of the anodised oxide layer is uniform and consistent with interference theory.
In complete contrast to the anodised layer, the oxide layer created by heat, Figure 14, is entirely crystalline. 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 is completely crystalline with variable thickness increasing along the length of the sample from 135 nm to 255 nm, which could be the effect of unevenness in heating. At the higher

magnification 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 it is not possible to fully resolve the possible distinct regions within the overall oxide layer.

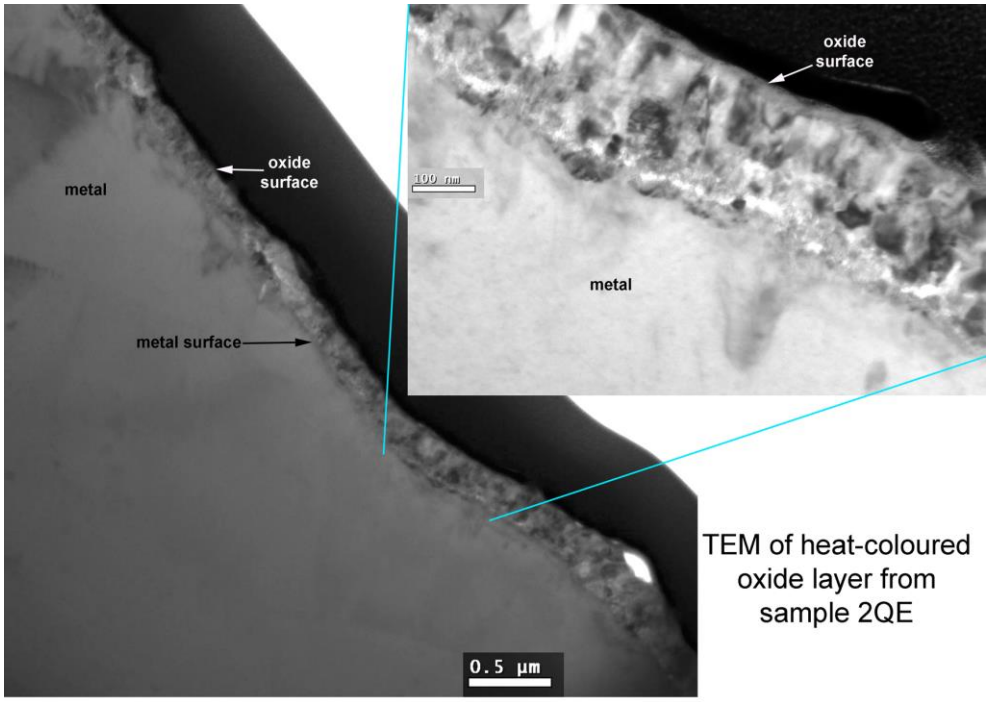

Figure 14: TEM images at different magnifications of titanium sheet heated to a gold colour.

These images show for the first time, on workshop-generated samples of oxidised commercially produced titanium sheet, the very different oxide layer structures that are created by anodising and by heating the metal.
The conclusion is that the presence of apparently random voids within the anodised oxide layer is likely to be the major cause of the observed colour variation. The differential structures also gave a strong indication that the heat created oxide had a more durable structure.
OUTCOMES
By defining the colour appearance of oxidised titanium it has been possible to produce titanium ‘spectrum’ showing the sequence of colours that may be achieved, Figure 15.

Figure 15: Interference ‘spectrum’ for oxidised titanium.

The comparison of the wavelength of maximum absorption, which defines the colour, with the anodising voltage, presented in graphical form, Figure 16, 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.

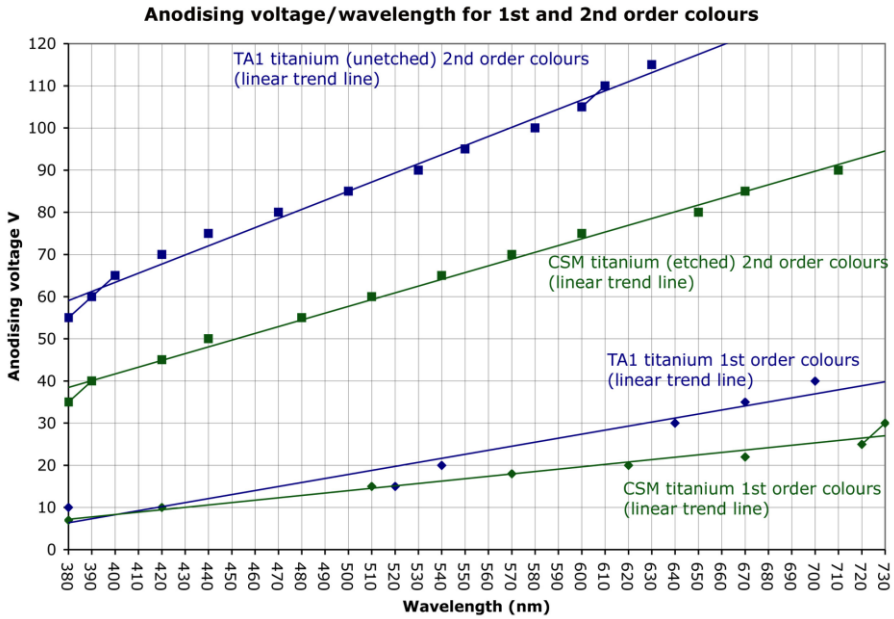

Figure 16: Graph of anodising voltage against wavelength for first and second order interference colours for etched and unetched titanium surfaces.

This graph can be used to determine the anodising voltage required to achieve specific colours. 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. Historically the titanium surface was prepared using a hydrofluoric acid etch but this is now largely confined to industrial production. For the workshop jeweller alternative methods must be used to homogenise the surface. The most reliable is abrasion but great care needs to be taken to thoroughly clean the surface after each grade of grit so that contamination is minimised. The use of freshly prepared titanium, supplied protected with a polymer film, also minimises contamination when compared to the factory off cuts which were used in the past. The experimental confirmation that different surfaces colour at different rates gives the jeweller many possibilities for both controlled and spontaneous pattern making. Anodising at a specific voltage will give different colours on the same piece of metal for differently prepared surfaces. This effect is also applicable for heat colouring. Therefore it is possible to create pattern by manipulating the surface finish either by simple filing or mechanically. The relative rate of colouring can also be influenced by using photocopy images as resists or simply drawing on the metal with permanent felt-tipped pens, Figure 17.

Figure 17: Simple heat-coloured brooches using different methods to alter the titanium surface, Lynne Bartlett.

Other methods of surface manipulation include machine engraving with a programmed design. The titanium can be anodised to one colour, engraved and then re-anodised to a different voltage, producing a wide range of decorative possibilities. Designs can be developed from simple black and white scanned images or by use of programmes such as Illustrator, Figure 18. It should be noted here that a major misconception has arisen in practice when carrying out multiple anodising steps. 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. In practice there is some thickening of the oxide layer across the entire exposed, immersed surface which 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.

Figure 18: Anodised and machine engraved cuffs, Lynne Bartlett.

Titanium cuts well on guilloche machines, Figure 19. The most striking effects can be obtained when the metal has been coloured, engraved and coloured further.

Figure 19: Examples of titanium engine turning experiments.

The combination of anodising with subsequent heating, preferably in a kiln, permits a more evenly coloured surface to develop the greater durability of a heat-coloured one.
Laser cutting of titanium has been used for jewellery since the 1980s and in the early 2000s both Sarah O'Hana and Ann-Marie Carey explored the decorative potential of the use of lasers to create coloured pattern on titanium. The interesting and subtle effects produced are shown in Figure 20. In development at the moment is the possibility of using relatively low powered lasers to cut through and thin the oxide layer to reveal a different colour. This procedure for creating pattern on titanium shows interesting potential and needs further development, Figure 21.

Figure 20: Laser patterned titanium bangle, Sara O'Hana 2004, image courtesy of Sara O'Hana.

Figure 21: Experiments using a laser cutter to cut through a previously created anodised titanium surface.

CONCLUSION

In recent years uncoloured titanium has been widely used for its the strength and light weight, particularly in sports equipment and spectacles. The popularity of body piercing and the biocompatibility of titanium have been combined to produce a range of mass-produced titanium body jewellery. 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 being successfully marketed to men.

Since the 1990s more and more use has been made of titanium in fine jewellery areas. There is evidence that both piercing and casting have been used to create mounts for pave-set diamonds and other gemstones. In the following examples the light weight of the titanium creates a more comfortably wearable large piece of jewellery, Figures 22-24.

Figure 22: Diamond set titanium brooch with conch pearl.

Figure 23: Articulated ring with tsavorites and diamonds set in titanium and white gold by G (Glenn Spiro) 2014

Figure 24: Cast and anodised titanium gem set brooch by Stephen Webster 2008, image courtesy of Stephen Webster.

At the same time contemporary jewellers such as Dorothea Prohl and David Bielander use titanium, both natural and coloured in their work. It has also been combined with ‘found objects in experimental pieces, Figure 25.

Figure 25: Patinated metal necklace with coloured titanium links, Giles Last 2018.

Thus it is possible to say that titanium over fifty years since it was introduced as a jewellery metal is just one of the materials in the jewellers’ repertoire, albeit for some a special metal.