Laser surface colouring of titanium for contemporary jewellery

S. O’Hana*, A. J. Pinkerton1, K. Shoba2, A. W. Gale3 and L. Li1

This paper describes work which emerged through a need to understand more about the potential of laser surface engineering for use in the creative industries. The method of creation of contemporary jewellery pieces and the resultant ‘Ocular’ jewellery series are described from the creative point of view. The work demonstrates how laser controlled oxide growth on Ti–6Al–4V alloy under ambient conditions can be used as an artistic tool by producing precisely defined colours. Use of the method to produce regular areas of even colour and to reproduce freehand drawings on a titanium alloy surface is described. Analysis highlights interference as the main colouring mechanism and suggests a graded surface layer, progressing from an outer layer of TiO2 to lower layers rich in TiO and Ti2O. The model of research by practice presented in this paper offers a contribution to the current debate on partnerships between art and science and engineering.

Keywords: Jewellery, Laser, Titanium oxide, Art

Introduction

The nature of an art jeweller is one of enquiry and investigation. By continually looking for answers to the self-inflicted problems of design and execution, they experiment with and exploit the materials until they yield into place.1 The search continues as outcomes and finished designs often prove unsatisfactory or lead to another dimension, demanding a change of treatment. The accumulated material knowledge is applied together with practical expertise to create three-dimensional artefacts, sometimes with awesome results.2 Not so different is the nature of a (research) engineer or scientist, which is one of seeking to understand and advance. Analysis is one dimension of their work, but the creation of a new process, machine component, building or mathematical model requires engineers and scientists to think beyond pure analysis.

Despite there being clear commonality, art and science are nevertheless often held as different, alien cultures. A language that can be understood by both disciplines helps to encourage hybrid practices that can be extraordinary fruitful.3 Demystifying the technology by bringing inside information out to new audiences is quite often the gateway that opens new territory and applications for emerging technologies. The work of Lynne Murray (Royal College of Art, RCA)4 is a good example of this. Moussi5 described her experience of action research and artistic creation converging and presented a model of action research designed to incorporate artistic creation. The work carried out in this paper encourages this by using high power laser technology to create artefacts that prove the success of the art-engineering and art-science partnerships, partnerships that are only rarely seen.6,7 Polymaths such as artist Thomas Heatherwick and architect Santiago Calatrava have produced work that lies clearly between the boundaries of art and engineering, and though there is also a growing field of digital art in response to this crossover, it is rare to have a reaction emerge as art jewellery. The creation and analysis described in this paper represent a symbiotic relationship in that both art and science are advanced rather than one discipline merely using the other.

The finished series of three-dimensional work described is the Ocular series 1–6, made using Ti–6Al–4V. A spectrum of colours can be achieved on titanium alloy either by applying heat using traditional methods such as gas torches or more commonly by electrolytic oxidation (anodising). The workpiece is immersed in an electrolytic solution as an anode and current is drawn. The oxide thickness created by this method is primarily dependent on other factors such as electrolyte concentration, temperature and anodic surface conditions.11 The oxide thickness created by this method is primarily a function of the applied voltage and there have been a large number of studies on the properties of the oxide films,6–11 which have shown that the composition and microstructure of the anodic oxides are also strongly dependent on other factors such as electrolyte concentration, temperature and anodic surface conditions.11 This means there are a lot of variables to control for an artist. Additionally, masking is difficult, especially when two sided parts are to be created, as in this case.

The surface appearance of the workpiece after heat treating or anodising is due to the formation of a
titanium oxide layer. Interference between light reflecting from the surfaces of the metal and oxide coating can be constructive or destructive at particular wavelengths depending on the oxide film thickness, meaning the frequencies of light reflected become a function of that thickness.\textsuperscript{11} The oxide films grown on reactive metals in general have a higher refractive index than diamond which accounts for the brilliance of the colours seen.

Langdale et al.\textsuperscript{12} treated commercially pure titanium with a pulsed Nd:YAG laser (2–17 kHz frequency, 2–50 mm s\textsuperscript{-1} traverse speed). The authors concluded that layer thickness may have an effect but the different colours they observed corresponded mainly to different titanium oxides. A similar study by Perez del Pino et al.\textsuperscript{13} (Nd:YAG laser, 30 kHz frequency, 56–7 W mean power, 25–300 mm s\textsuperscript{-1} ) confirmed these results; additionally a greater range of oxides was found to form at higher specific energies (defined as laser power/(traverse speed \times beam diameter)). However, a later study by the same authors,\textsuperscript{14} comparing the colours obtained from anodising and laser treating titanium, concluded that light interference phenomenon within an upper TiO\textsubscript{2} surface layer was the mechanism in both cases. The additional oxides created during laser treatment were said to be part of a deeper layer which was not significant for appearance. Carey et al.\textsuperscript{15} drew attention to the potential of lasers in the jewellery industry, but Bartlett noted the unpredictability of the evenness of colours developed in this way, attributing it to ‘flower oxides’.\textsuperscript{16}

The concept for Ocular series 1–6 is grounded in the aesthetic of optical measuring equipment and relates to aspects of vision: ‘seeing the bigger picture’, ‘clouded vision’, ‘blurred vision’, expressions that are linked to the problems of not seeing correctly because of an impediment, be it physical or psychological. Background research was done for this work in the area of optometry and the measuring systems used in the process of eyesight correction. Reclaimed lenses have been used in the process, for the creation of jewellery based on seeing, observing, peering and clarifying vision. The use of lenses within jewellery is not common but a report by Hollarbach\textsuperscript{17} outlines the work of artists making similar claims of aiding discovery, altering perceptions or simply appealing to the wonder of magnification.

The pieces include some unique features including fingerprints, marked by laser as a visual reminder of the manual involvement still present within this predominantly digital environment. The work was shown at the exhibition ‘Walking with scientists’ at The Museum of Manchester, UK in July 2007.\textsuperscript{18}

**Methods**

The base material for the complete jewellery series described in this paper was commercial Ti-6Al-4V alloy plate. It was initially cut into the required shapes for the final pieces using a 35 W Nd:YAG laser (100 ns, 680 mJ pulses at 20 Hz pulse frequency) with argon gas shroud. All cut pieces were prepared using a solution of 1–3 g of ammonium bifluoride dissolved in 10 mL nitric acid and 90 mL deionised water. The workpiece was submerged for 30 s. The shaped and etched pieces were then placed on a honeycombed bed in ambient air and a Universal versal X-660 Laser Platform fitted with a pulsed 60 W CO\textsubscript{2} laser used to treat the surface. This free standing unit comprises the laser, an X–Y beam positioning system with 0.81 x 0.46 m work area, interchangeable focussing optics and computer interface. The laser beam was focused by a 50 mm focal length lens in an enclosed lens cartridge to a spot of diameter 0.15 mm at the workpiece. The pulse frequency was varied in proportion to speed to maintain a constant spatial distribution of pulses on the surface; for this work it was set at 1000 pulses per inch.

To meet the requirements for the series it was necessary to be able to produce defined colours and recreate hand drawn shapes to predefined geometries on both sides of pieces of commercial titanium alloy. Different control methods were used in each case:

(i) where an area of even, predefined colour was required, the laser scanning parameters were preprogrammed with the help of Adobe Illustrator and Corel Draw software packages. A series of parallel beam traces performed in a raster pattern on the required area was then used to form a titanium oxide film on the surface. The relationship between the laser parameters and final colour was obtained through compiling an experimental process map specific to this material and system. Existing literature in the field can provide a guide but many factors are difficult to predict. For example the specific energy parameters used by Perez del Pino et al.\textsuperscript{13,14} and Fedenev et al.\textsuperscript{19} to produce comparable results differed by orders of magnitude because of different surface absorptivity, heat conduction at the workpiece and other effects pointed out by Fedenev et al.

(ii) where rapidly varying colour was required, the same CO\textsubscript{2} laser was driven by a bitmap obtained from a digital graphics package such as Adobe Photoshop or a scanned drawing. The intensity of laser flux delivered to the workpiece surface at each position was based on the bitmap. The resulting marks on the titanium alloy surface replicated the original drawing and appeared to have been applied by hand quite spontaneously. The exact colours obtained were however less predictable than those obtained by the former method.

After completion of a part with areas of even colour, the treated areas were tested by non-destructive methods. The sample was photographed under natural light using a Canon EOS digital camera set to maximum resolution. Images were transferred directly and with no colour correction to microcomputer and treated areas analysed using Adobe Photoshop software for colour balance. This is a considerably simpler method of characterising the surface appearance than the spectrophotometry based techniques used by previous researchers, but as the relationship between visible appearance and TiO\textsubscript{2} layer thickness is now well established.\textsuperscript{14,20} It was not necessary to repeat previous analyses. The surfaces of all samples were examined using a FEI Sirion field emission gun scanning electron microscope (FEGSEM) at magnifications of 100–1600 times and accelerating voltages of 2–20 kV. The surface produced by one set of laser parameters was also tested for phase composition with a Philips X-Pert MPD diffractometer using Cu $K_a$.
radiation ($\lambda=1.54$ A) and measuring using a thin film (grazing incidence) method. The incidence angle was $\sim 0.7^\circ$.

**Results and discussion**

The complete collection of work described in this paper consists of six artefacts, four of which are illustrated. Three of the pieces are directly wearable as pendants using a sterling silver chain and three are designed as objects to look through, in themselves not having any wearable attribute.

Figure 1 shows Ocular nos. 4 and 5 of the jewellery series. As with all the pieces, two Ti–6Al–4V circular plates are surface processed by laser to create a chosen visual effect and mounted on acrylic, trapping a reclaimed lens between them. The markings on each of the plates are different and parameters are chosen specifically for each one. Figure 2 shows a graphical representation of the laser parameters used for Ocular no. 5, drawn in Adobe Illustrator. During the manufacturing process, a representation of the parameters is transferred to Corel Draw software, which subsequently outputs control signals for the Universal X-660 Laser Platform that direct the machine parameters to be used for specific areas.

Figure 3 shows Ocular no. 2 of the jewellery series, containing a square lens. Thumbprints and fingerprints were taken from one of the authors of this paper (Shoba) using indelible ink and then digitally scanned. Various techniques in Adobe Photoshop were used to manipulate the resulting digital images, with text added in layers, and those were sent through to Coral Draw and subsequently the laser for marking in different stages. Different parameters were used to achieve the visual effects shown on the front (Fig. 3a) and back (Fig. 3b) of the piece.

Ocular no. 3 (illustrated in Fig. 4) marks a departure from the previous trend of parameter setting via Coral Draw, in that it relies on original artwork using ink on cartridge paper, shown in Fig. 5a. The subsequent detail taken from this drawing, shown in Fig. 5b is then used for marking the titanium of Ocular no. 3, reverse side. The image was edited in Photoshop and vector drawings that inform the dimension of the object were added in Illustrator. The final image is a combined layer of bitmaps and vectors sent through to Corel Draw for laser processing.

**Visual content/concept**

The Ocular series 1–6 takes some of the inspiration from the original difficulty in communication between art and engineering and builds on the problems encountered on
the way. Before making the final pieces, a number of test samples were created using the CO2 laser and titanium to understand the colour potential. The visual appeal of these samples and the order in which they are carried out, their strictly linear display and formal layout were recreated in Ocular nos. 4 and 5, illustrated in Fig. 1, using different bands of colour within the precut circular shape. The aesthetic is in keeping with the technology itself, a highly controlled, geometric arrangement of oxides, carefully selected for optimum visual impact. The handle shapes interrupting the frame in acrylic allude to the viewer’s holding position and include laser marked words on the edge describing which finger might rest on each handle.

Ocular no. 2 further develops the use of personal fingerprints by offering the obvious position of the thumb and forefinger if the viewer picked up the object. The use of a reclaimed reducing lens confuses the vision although interesting distortions are created by it. The suggestion that Ocular nos. 2, 4 and 5 are made to look through and to hold rather than to wear, places them further into the realm of abstracted monocle than jewellery but continues to encourage the viewer into scrutiny and renewed observation.

Ocular no. 3, illustrated in Fig. 4, shows a difference in the laser marking and was designed to appear more random. This is done by taking an original drawing, shown in Fig. 5a and a detail from it, Fig. 5b, which is then used for laser marking. This piece contributes to the same message as the others in the series: an invitation to look through at another culture, to use the object as an instrument to see differently, maybe to see a clearer picture, perhaps to discover unknown territory though the lens. The size of the lens, unlike that of a normal monocle, forces the viewer to peer, or to squint through, causing a more exaggerated action than that of a normal lens. The struggle to see properly is a parallel drawn between the cultures that find it typically hard to see each other’s point of view. The design is grounded in the aesthetic of optical measuring instruments and employs visual elements taken directly from optometry. These have been observed in situ and recreated by laser using similar materials. Hence the arc measuring 10–80 mm which is cut from opal white acrylic, laser marked and stained with graphite.

Surface spectroscopy and oxide layer thickness

The range of colours created on the titanium surface in piece Ocular no. 5 of the jewellery series was analysed as described in the section on ‘Results and discussion’ and the results of the optical analysis are shown in Table 1.

Surface topography and composition (SEM)

Examination of the samples under FEGSEM in secondary electron (SE) mode showed that the surface topography had been significantly altered by the laser treatment and that the effect was not confined to the deposition of TiO2 layers of 200 or less nanometres indicated in Table 1. Figure 6 shows SE images of the base material and samples treated at 20 mm s$^{-1}$ traverse speed and mean powers of between 6 and 60 W.

There is little change in the original surface geometry seen in sample A, processed at the lowest line energy (defined as mean laser power divided by traverse speed), but this contrasts sharply with the significant change then seen at higher line energies (samples D and H). Sample D shows some surface cracks but these become severe in sample H. Only one occurrence of the ‘flower oxides’ proposed by Bartlett$^{16}$ was seen in this study; this occurred under conditions of high line energy (sample G).

Figure 7 compares SE and back scattered electron (BSE) images of samples produced at the same power (60 W) but two different speeds (20 mm s$^{-1}$ for sample
H and 53.3 mm s\(^{-1}\) for sample J. The greater line energy again produced more cracking. High magnification BSE results indicated some surface segregation of elements, a consequence of the rapid cooling rates due to the self-quenching nature of this process.

From analysis of multiple samples it was possible to derive the process map shown in Fig. 8. Three zones representing parameter combinations leading to an uncracked, partially cracked and severely cracked surface can be seen. The cracks can be attributed to the tension induced by the constraining effect of the underlying layer during surface thermal contraction. Higher line energies and consequent initial expansion at lower traverse speeds and higher laser powers thus lead to more final contraction and damage.

### Surface phase analysis

Figure 9 shows the results obtained from the grazing incidence X-ray diffraction (XRD) analysis of the surface treated at 60 W and 100 mm s\(^{-1}\) and appearing dull green in colour. The four significant phases highlighted were hexagonal α-Ti, cubic TiO, tetragonal rutile TiO\(_2\) and hexagonal Ti\(_2\)O titanium oxides. To show how this complicated diffraction pattern matches each of the identified phases, the reference peak positions of each phase are shown as vertical lines on a separate spectrum. Peaks corresponding to the underlying α-Ti are very strong, evidencing the very thin nature of the surface layer that had developed. They also provide an almost perfect match to the reference angles of diffraction giving good confidence in the accuracy of the identification of phases.

### Table 1 Laser treated titanium surfaces – parameters and effects

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean power, W</th>
<th>Speed, mm s(^{-1})</th>
<th>Colour</th>
<th>R</th>
<th>G</th>
<th>B</th>
<th>TiO(_2) depth, nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6</td>
<td>20</td>
<td>Golden</td>
<td>137</td>
<td>102</td>
<td>64</td>
<td>35</td>
</tr>
<tr>
<td>B</td>
<td>12</td>
<td>20</td>
<td>Deep blue</td>
<td>28</td>
<td>45</td>
<td>71</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td>18</td>
<td>20</td>
<td>Green blue</td>
<td>81</td>
<td>109</td>
<td>110</td>
<td>80</td>
</tr>
<tr>
<td>D</td>
<td>24</td>
<td>20</td>
<td>Pale green</td>
<td>124</td>
<td>130</td>
<td>118</td>
<td>95</td>
</tr>
<tr>
<td>E</td>
<td>30</td>
<td>20</td>
<td>Pink brown</td>
<td>132</td>
<td>119</td>
<td>111</td>
<td>130</td>
</tr>
<tr>
<td>F</td>
<td>36</td>
<td>20</td>
<td>Brown</td>
<td>84</td>
<td>81</td>
<td>72</td>
<td>190</td>
</tr>
<tr>
<td>G</td>
<td>60</td>
<td>6.67</td>
<td>Grey</td>
<td>70</td>
<td>89</td>
<td>96</td>
<td>200+</td>
</tr>
<tr>
<td>H</td>
<td>60</td>
<td>20</td>
<td>Brown grey</td>
<td>62</td>
<td>61</td>
<td>56</td>
<td>190</td>
</tr>
<tr>
<td>I</td>
<td>60</td>
<td>33-33</td>
<td>Dull green red</td>
<td>110</td>
<td>95</td>
<td>88</td>
<td>180</td>
</tr>
<tr>
<td>J</td>
<td>60</td>
<td>53.33</td>
<td>Pink brown</td>
<td>114</td>
<td>116</td>
<td>94</td>
<td>130</td>
</tr>
<tr>
<td>K</td>
<td>60</td>
<td>66.67</td>
<td>Mid green</td>
<td>82</td>
<td>89</td>
<td>81</td>
<td>100</td>
</tr>
<tr>
<td>L</td>
<td>60</td>
<td>100</td>
<td>Blue green</td>
<td>34</td>
<td>52</td>
<td>62</td>
<td>70</td>
</tr>
</tbody>
</table>

*By matching colours to the results of Perez del Pino et al.\(^{14}\) and Goldsmiths\(^{20}\).
measurements. There is evidence for the presence of TiO, although as can be seen from Fig. 9b, the diffraction peaks are smaller than the reference values by increasing amounts on moving from left to right. This indicates a slightly larger lattice parameter than expected which could have been caused by a gradual transition between phases. Indeed, it can be seen that a number of the peaks are quite broad which can indicate a graded phase structure.

Rutile TiO$_2$, which is normally obtained at high temperatures such as 800°C, and held by most authors to be responsible for the interference colours seen on the surfaces, is clearly present. Gyorgy et al. concluded that during pulsed (300 ns) Nd:YAG laser irradiation of Ti under ambient conditions, oxidation proceeds from TiO present in the early stage of the irradiation, through Ti$_2$O$_3$, until the formation of the TiO$_2$ rutile phase at high number of pulses. In this case each part of the surface received only 6 pulses (1000 dpi surface coverage, spot diameter 0.15 mm) so it is likely another mechanism was responsible for this phase. No Ti$_2$O$_3$ or anatase TiO$_2$ was detected in this investigation.

The third oxide found was the hexagonal Ti$_2$O$_3$, which is the same lattice structure as the underlying α-Ti and probably formed lower in the surface layer, partly integrated with it. In all, the XRD results are in agreement with the theory of a graded surface layer progressing from an outer layer of TiO$_2$ to lower layers of more Ti rich oxides.

**Conclusions**

A moderate power (60 W), pulsed CO$_2$ laser, directed via an X–Y beam positioning system within an integrated system and interfaced with commercial graphics software, has been found a very efficient tool for creation of controlled and even areas of colour and designs that appear spontaneous on the surface of commercial purity titanium alloy plate. The parent titanium alloy surface morphology was significantly altered at CO$_2$ laser line energies above a threshold of 0.4–1.1 W mm$^{-1}$, producing a more even surface, but there were also signs of surface cracking at line energies of above 0.75 W mm$^{-1}$. Rutile nitrogen oxide, TiO$_2$, which is usually considered to form an outer surface layer and be responsible for interference colours, plus TiO and Ti$_2$O titanium oxides were detected on the
surface. Results are consistent with the theory of a graded surface layer progressing from an outer layer of TiO$_2$ to lower layers of more Ti rich oxides.

The artefacts shown in this paper, and the exhibition of this work at The Manchester Museum, are an illustration of how the tools and techniques used by researchers in science and engineering can be adopted by the creative industries. This paper is also a demonstration of how science can learn from analysis of art techniques and results. Collaboration between the two has demonstrated how each stands to gain much from the other.

Acknowledgements

The authors would like to thank Manchester Material Science Centre, specifically J. Shackleton and R. Moat, for assistance with XRD and SEM analysis and useful discussions on the results and Dr M. Schmidt and Dr P. Crouse of The Laser Processing Research Centre for assistance with laser cutting and etching of samples. The authors are also grateful for the loan of laser resources at The Virtual Company, City College Manchester.

References