DESIGN AND MANUFACTURING TITANIUM JEWELLERY THROUGH ADDITIVE AND CONVERSION TECHNOLOGIES

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Abstract: Nowadays there are an enormous variety of titanium (Ti) jewellery artefacts. These products have a high specific strength, are corrosion resistant, induce a warm feeling to the human touch and are easily surface modified by temperature or anodization to acquire a sophisticated aesthetic colour. Ti is more durable than gold or platinum, has a lower price and presently is a fashion material due to the successful use in challengeable applications. This paper presents the work that has been developed in our research laboratory to cast Ti to produce parts to automotive industry. Using the knowledge obtained, the authors explored the possibilities to design and manufacture Ti jewellery. This paper describes the whole process to produce jewellery titanium artefacts. Combining 3D modelling, stereolithography, conversion technologies with silicone and low melting point metallic moulds and precision casting in ceramic shells moulds in controlled atmosphere, we were able to manufacture complex shapes with shiny thin sections, that after an adequate heat treatment exhibit a variety of attractive colours that are more difficult and expensive to obtain with existing technology for manufacturing jewellery products (metal forming and machining).

Keywords: jewellery, titanium, conversion technologies, additive manufacturing.

1. Introduction

High specific strength (tensile strength/density), corrosion resistance and biocompatibility are the titanium main attributes. Space vehicles, satellites and airplanes use it due to the high specific strength. The creep resistance (till 550°C) and specific strength makes it attractive for airplanes reactors. In oil rigs for Deep Ocean can be seen in the extraction tubes, due to the fatigue resistance (induced by the ocean waves), high specific strength and corrosion resistance to the salt water, debris and carried fluids. The medicine sector currently employs it in distinctive medical applications, due to the biocompatibility (is hypoallergenic) and corrosion resistant to body fluids, and, when compared with other potential materials, has the closest elasticity modulus to the human bone. It is also used in components to process chemical products due to the good corrosion resistance (Lutejering et al. 2005).

With contributions in important human goods, parts for penetration in the Deep Ocean and our galaxy and push the medicine, science and industry to new high levels of the human knowledge, Ti assumes itself as a metal with a great impact on the recent humanity history.
1.1 Titanium in jewellery

Jewellery is the art of producing jewels that in reality are artefacts with ornamental characteristics, having as a tenuous frontier the human body.

Ti manufacturing as a meaningful industrial product only started after the second half of the XX century. Its use in jewellery rapidly took place and the same happened with the world dissemination that was under deep changes in teaching methodologies of decorative arts.

Until this moment, gold and silver, materials under continuous development through the years, were the base materials for the manufacturing of jewellery artefacts. These two noble materials were easily processed by goldsmiths, artists or simple technicians due to the lower melting point, simple foundry procedures, easy welding, and much more important, its excellent cold malleability. For Ti, the simple change of a ring size, it is almost impossible. If, for any reason, gold and silver need to be cut, a simple plier can do it, whether Ti demands specific and expensive cutting equipment.

Seen from this perspective, Ti is in fact a non-functional material in terms of jewellery, but ably occupies a place among the “precious” metals. Besides the well-known mechanical properties, its durability is eternal (no erosion problems over time), is considered inert, does not react with water or with the human body fluids and is hypoallergenic (skin reactions do not occur). Its resistance to corrosion is such that its colour and brightness last long periods of time without change. On the other hand is synonymous of modernity, which, although expensive is cheaper than the gold or platinum. Presents in natural state a silver colour, very bright and has a high capacity for surface oxidation (perhaps the more relevant property in jewellery), allowing a surface with an endless range of colours (Pietro 1999).

The first artistic approaches in Ti were done in England in the 60s (The Art of Reflection and Refraction 2009) by a group of researchers led by J.B Cotton from the corrosion section of the Department of research and development of the Imperial Metal Industries, which presented several corrosion studies in new materials, pioneering the development of different anodization methodologies for Ti. In 1967, with Hayfield, the group presented the publication entitled "Decorative Finishes on Titanium" (Hayfield 1998). This document was prepared with the intent of revealing and captivating at the same time decorative arts teachers and students to the beauty of colours that could be obtained using certain surface oxidation techniques, where each colour was function of the oxide layer thickness produced on its surface

In 1967, Ann Marie Shillito, in the School of Jewellery of the Institute of Arts and Design of Birmingham, designed the oldest Ti jewellery piece (fig. 1), a buckle, machined from a Ti bar coloured anodized, for a belt (The Art of Reflection and Refraction 2009).

In 1976 took place the "Electrum Gallery", the first exhibition dedicated to Ti. This event had three young artists, Ed de Largie, Kevin Coates and James Brent Ward, with already extensive work in Ti, all of them from the Royal College of Arts (London) and with high knowledge of how to work the Ti (Vads 2009).

Modernity in jewellery proclaims that all materials must have the same weight, but in reality this does not happened with Ti. Until 1975 it was seen as a very special material being skilfully used by designers to perform single memorable artefacts or small usually limited series. Only in the second part of the 70’s, beginning of the 80’s, Ti pieces began to appear, at common prices, in the jewellery sections of the big jewellery stores. Nowadays, there are many artists to intensively using Ti in their creations and diverse websites are selling Ti artefacts.

2. Manufacturing prototypes for Ti jewellery artefacts

What is necessary for the physical materialization of a dream? Using Additive Manufacturing (AM), the idea arises, the object quickly takes shape and the machine makes it. AM is the term to describe the physical and fast manufacturing of objects directly obtained from 3D CAD files. This manufacturing technology was established to quickly provide, in the developing phase
(product development), a better design communication (Warfel 2009). There is a wide range of AM equipment’s dedicated to the world of jewellery, with some machine manufacturers considering this a priority market. The jewellery, as an industry, is an economic sustainable activity in continuous growth.

There are two different ways that can be used to produce final metallic prototypes using AM. The first way uses dedicated equipment that works with Ti powders that are deposited, layer by layer, until the prototype is obtained in accordance with a .STL file generated from a 3D CAD program. The second one is employing the AM or any other manufacturing process to produce a non-metallic prototype that is used to directly or indirectly convert it in the final metallic model(s) (Alves et al. 2001, Vasconcelos et al. 2006a,b).

2.1 Direct conversion

In the direct conversion, a model, usually obtained by an AM process, is directly converted into the final metallic part. Processes such as Stereolithography (quick cast), Solidscape, SLS, or others, produce a model that is lost during the conversion process. This way, a metallic prototype can rapidly be obtained. This procedure is very interesting, but only allows the production of a single part because the model is lost, which means that does not tolerate errors during all the conversion stages (Alves et al. 2001). Of course that several parts can be obtained if the same number of prototypes is made.

2.2 Indirect conversion

In the indirect conversion, the prototype, obtained by any traditional or AM process, is used to produce a mould to cast a wax for investment casting. This way, single or pre-series of parts can easily be obtained, although, with a longer deliver time.

Another possibility is the direct production of the mould where different parts could be injected. 3D Systems developed an epoxy resin that has superior mechanical properties to the common thermosets resins. If necessary, metallic frames can be used to reinforce the mould to withstand the high mechanical loads produced during the injection process. With these moulds short series of lost models in thermoplastic waxes with complex and accurate shapes can be obtained. Although this seems very interesting, due to the low thermal conductivity of these moulds, only few models can be injected during a working day, and so it has only interest when speed is the goal.

In terms of jewellery, this process is very expeditious for wax injection for production of small series of models to be used in foundry by investment casting (Alves et al. 2001).

2.2.1 Silicone moulds

Any model can be used as mother model to produce silicon rubber moulds, normally processed at room temperature using vacuum systems.

This method allows the manufacturing of short series of parts in rigid or flexible polymers. In the case of jewellery, thermoplastic waxes are used to work as lost models for the investment casting process.

There are two different silicon families for rapid moulds manufacturing. Addition silicones have the particularity of having a room temperature post-cure null shrinkage, while condensation silicones are characterized by their lower price and higher volume changes.

Usually, this is a manual process, although in the last years several vacuum chambers were introduced in the market with automatic mixing and casting in controlled environment. The main stages of the process are described in figures 2 and 3.

Figure 2: Casting of the silicone over the model, placed in a box with the associated gating system (entrance of material, gas escaping channels and raisers)

Figure 3: Cut the silicon mould along the parting plane to remove the model
2.2.2 **Resin moulds**

With this indirect process, short prototypes series can be obtained with excellent dimensional and geometrical reproducibility. These types of moulds are usually made with polyurethane or epoxy based resins filled with metallic charges to promote better rigidity and thermal conductivity. They are already similar to the traditional metallic ones for thermoplastics injection.

The objective of these moulds is to inject thermoplastics waxes to produce lost models for investment casting. They follow the same principle for rubber moulds, with the exception of some particularities related with the materials employed (processability) (Vasconcelos et al. 2006a,b) and parting plane definition due to negative drafts. The main process stages can be seen on figures 4 to 6.

![Figure 4: Place the mother mould with gating system and guides over the parting plane](image)

![Figure 5: Casting the resin](image)

![Figure 6: Casting the resin over the first half mould](image)

The mother model, usually obtained by AM, is usually divided as a function of the previously selected parting plane. Place the mother model (with the associated gating system considering the parting plane(s) and guiding system) over the parting plane. Apply the demoulding film over the previous mount and cast the filled resin. After the resin cure, remove the parting plane to place the remaining mother model, gating system (and demoulding agent). Cast the resin and after curing, demould. Clean and post-cure in accordance to the resin technical specifications.

The mould is now ready to receive the injection of the thermoplastic waxes.

2.2.3 **Metallic moulds**

The objective of these moulds is to quickly inject a large number of thermoplastic waxes parts for investment casting. With this indirect process, large series of parts with excellent dimensional and geometrical reproducibility can be obtained.

These moulds are made in low melting point alloys (see table 1), usually cast under vacuum in a metallic frame that allows more rigidity of the assembly and facilitates the connection to the structure of the injection machine.

Table 1: Chemical composition and density of some low melting point alloys (ASM International, 1998).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melting point °C</th>
<th>Chemical compos. (wt. %)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bi</td>
<td>Pb</td>
</tr>
<tr>
<td>A</td>
<td>70</td>
<td>50,00</td>
<td>26,70</td>
</tr>
<tr>
<td>B</td>
<td>95</td>
<td>52,50</td>
<td>32,00</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>46,00</td>
<td>20,00</td>
</tr>
</tbody>
</table>

These alloys should have melting points between 70°C and 120°C, because the wax injection temperatures are around 65-75°C, and the AM materials for prototypes have working temperatures lower than 120°C. Higher temperatures can irreversibly damage these masters.
The main manufacturing stages for these moulds are similar to the ones indicated for resin moulds.

The mother models are usually obtained by AM (frequently with paints containing metallic pigments). The model, with gating and the guidance system is placed on a surface containing the parting plane. The demoulding film is applied over the previous mount and the low melting point alloy is cast under vacuum, and rapidly cooled. The procedure for the other half mould is then repeated (see figures 7 and 8).

In a previous paper (Paiva et al. 2011) we presented the results of the first trials to produce bracelets, necklaces and rings (see figures 9-11). Considering the experience and scientific knowledge obtained we challenged a jewellery designer to create some artefacts considering the limitations of the process, and using the city of Porto as an inspiration thematic.

3. Experimental part

The following experimental part describes the methodology employed to manufacture jewellery artefacts, using an AM process associated with indirect conversion technologies, to produce lost models for the investment casting of titanium. The final Ti parts were submitted to different surface finishing.

Wrought iron is present in the architecture of the city of Porto, in railings, balconies and gates, is part of a cultural heritage. Defined the concept, the idea is to transpose into personal ornaments city grids.

The field research is important to realize what kinds of shapes are widely used and most characteristic
repeated patterns to be used in this new context (see figure 12).

This was the first model designed, but when the group starts to analyse the manufacturing process restrictions, some limitations emerged in terms of dimensions (avoid thicknesses less than 1.5 mm) and some sharp angles that would be impossible to reach by the lost wax process, which is the process that will be used in production.

The next step was to fix the template but always bearing in mind the original design so as not to change the concept. Figure 15 shows the original drawing and the final one, where one can see the changes introduced.

To have a clearer idea of what it will be the artefact when finished, it is usual to make renders that give the idea of the product by assigning materials and textures to a virtual image. Figure 16 shows the images obtained with the software Key Shot 2.

Figure 12: Pictures of wrought iron ornaments of the houses of the city of Porto

After the collection of images, the next step is to define the drawing (figure 13).

Figure 13: Sketches of the parts to be produced

After the renderings it is imperative to move to a 3D CAD program, in this case Rhinoceros was used to initiate the process of prototyping (figure 14).

Figure 14: First drawing of the model to be produced

Figure 15: Initial concept (left) and final drawing (right).

Figure 16: Renders of the pin.
After all this stages, and approval by the product development team, the model goes to the prototyping phase.

### 3.1 Prototypes
3D CAD files were converted into .STL files of 0.1mm layer resolution to produce the prototypes by AM, using the stereolithography (SL) apparatus Viper Si from 3D Systems (USA), with the RenShape SL 7810 resin (Huntsman). The pin obtained is presented in figure 17.

![Figure 17: Prototype in SL of the pin.](image)

### 3.2 Moulds for indirect conversion
A two component polyurethane resin, filled with aluminium powder (1 part resin to 2.7 parts Al powder, in weight), was mixed for 3-5 minutes and cast in a box containing the SL pin. After hardening at room temperature for 24h, the SL model was removed from the model (during this task the model was broken due to it intricate shape). The slenderness of the model demanded ejector pins for the demoulding of the injected wax models.

Figure 18 shows the resin mould and the wax parts injected on it.

![Figure 18: Resin mould and wax parts.](image)

### 3.3 Casting and assembly the waxes
The waxes used in this study are identical to those referenced in the traditional jewellery (Castaldo waxes, reference Aqua marine).

The wax was heated at 67°C and injected into the mould at 2.5 bar. The lost wax models were then welded to the gating system (figure 19).

![Figure 19: Assembly of the wax models to the gating system.](image)

### 3.4 Manufacture of the ceramic shells
The first two ceramic layers were obtained with a slip based on an aqueous solution of colloidal silica (in a reduced %) mixed with yttria flour, while the remaining layers were made with water based colloidal silica mixed with alumina flour. The sand for the first two layers was yttria while for the other layers was alumina. Figure 20 shows some stages of the shells manufacturing process; washing, slurry for the first layer, sand shower and drying.

![Figure 20: Manufacturing stages of the ceramic shells](image)
A total of nine layers were made (Duarte et al. 2007, gives more details about this process). The shells were then placed in an oven at 900°C for 2h for dewaxing (thermal shock and calcination), followed by a presintering at 1200°C for 1h to improve the mechanical properties of the shell.

3.5 Cast titanium
The Ti alloy used in this study was the Ti6Al4V, ASTM B 348-06a. To facilitate and enable a good casting, the shells were pre-heated (to mitigate thermal shock with the ceramic shell walls), covered with a glass fibre blanket at 1000°C. Ti was cast at 1700°C and cooled under an inert atmosphere of argon, with a cooling time around 30 minutes (figure 21).

After this phase, a chemical cleaning with an aqueous solution of nitric (7%) and hydrofluoric acid (15%) was applied to remove any eventual tiny debris still existent.

The final surface finish obtained is enough to perform the staining by heat. If a polished finishing is demanded, it is necessary to perform a series of sequentially-sanding grinding operation with SiC papers, followed with abrasive pastes for metal.

3.7 Colouring
In these parts we did not explore the colours that can be obtained by the heating process. After chemical cleaning (solution of hydrofluoric and nitric acid), the parts have to be cleaned with acetone and placed in an oven at 700°C. The golden colour appeared after 7 min and heterogeneous colour after 14 min (see figure 9).

Staining by heat is the most widely used method by jewellers because of the ease with which it is held. For this, is necessary an oven with a temperature controller, normal cleaning agents and ordinary sandpaper for the surface preparation to colour. The anodization process is more complex and needs dedicated equipment; such as electrolytes, chemical compounds and a power source that allows the voltage control and current intensity between an anode and a cathode (electrolytic cell). More details can be obtained in Paiva 2012.

Due to time restrictions, we did not try different colorations. Figure 23 shows one part after rough polishing. The parts should now be submitted to the coloration process (if desired) and brazing the needle. Other parts of this family are under development.
4. Conclusions

This work has shown that current 3D CAD tools enable expeditiously modelling of geometric shapes starting from a simple sketch.

The presented manufacturing methodology allows the manufacturing of prototypes with the necessary quality (shape and dimensional accuracy) for jewellery.

Rigid moulds manufactured for indirect conversion technology allowed obtaining waxes with adequate quality for investment casting.

The ceramic shells manufacturing methodology allowed cast Ti alloys under controlled atmosphere to produce jewellery artefacts with adequate quality and different finishes that can be obtained by colorization by heat, shot peening and polishing.

From CAD file to the final part, using the described methodology, it is possible to obtain jewellery artefacts in 4-5 days.

References


