Production and Anodic Colouring of Newly-Designed Titanium Jewels

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Summary

Jewels production traditionally implies the use of precious metals; yet in the last decade, non-precious or semi-precious metals have gained much attention. The processing methods applied to these materials often diverge from traditional techniques in order to adjust to the logics of series production: the most applied technologies involve a first forming step by plastic deformation, followed by either mechanical or galvanic surface finishing (in most cases, anodic oxidation). At the same time, laser melting processes have been developed in the last few years in application areas such as mechanics and biomedicine. The use of such technologies has not concerned the typical contexts as yet, such as design products and jeweller's art, though particularly complex shapes can be achieved with extremely high precision. Hence, in this research work, the selective laser melting technology was applied to create titanium jewels prototypes with original design, obtained by computer-aided design modelling; the surface finishing was achieved through anodising processes, which had the aim of generating different colour hues on jewel surfaces through the achievement of interference conditions between light and the so-formed anodic oxide layer.

Introduction

In Italian design history, innovation has always been a crossroad of different cultures, knowledge and skills, which summarise distinct but converging paths to define the creation of objects belonging to a high level manufacturing industry. Jeweller's art represents an area where two essences still coexist, i.e. craft and industry.

Jewels production traditionally implies the use of precious metals, for example gold, silver and platinum, and the processing technologies applied to these metals are strongly traditional, as well as consolidated. A few of the employed technologies have been industrialised, but handcraft production still plays an essential role for a limited series of unique articles. Among the variety of forming technologies in use, a major role is still attributed to processes involving casting; plastic deformation is widely applied, as well. An exceptional importance is attributed to surface finishing processes, which can be divided in two main categories: mechanical finishing, such as polishing or sifter processing, and all other techniques aimed at modifying surface colour, aspect or texture, e.g. enamelling [1–4].

During recent years, large improvements have been made in the fields of jewellery that use either non-precious or semi-precious metals, in particular steel, aluminium and titanium. Processing methods often diverge from the traditional techniques used in jeweller's art, in order to adjust to the logics of series production. The most commonly applied technique consists of a first plastic deformation step followed by either mechanical or galvanic surface finishing (most likely, anodic oxidation); non-precious metals surface treatments represent one of the most interesting fields for the application of surface science in this world, as demonstrated by the countless spin-offs in technologically advanced fields [5–7].

Currently, laser processes are not applied to jewels production, as they are still most often used in mechanical and biomedical fields [8]; however, these techniques have an outstanding potential, since extremely complex shapes can be achieved with extremely high precision. In particular, the combination of selective laser melting (SLM) and stereolithography allows the designer to obtain complex objects by adding metallic powders layer by layer and selectively building the desired shape through a laser beam and a computer-aided design (CAD) three-dimensional model, without any additional equipment [9,10]. This technology does not require the use of moulds; therefore, it seems to be particularly suitable for the creation of unique pieces.

The presented research focuses on the application of SLM to the prototyping of titanium jewels with original design and to the further implementation of the jewels by conferring an iridescent surface colour by anodic oxidation, which consists of creating a thin oxide layer on the metal surface by means of an electrochemical process. This layer not only generates colour appearances on the surface, but also acts as protective barrier towards the metal underneath [11–13]. The need to create a protective film on the surface of certain metals is particularly pressing when these metals are used in the presence of aggressive fluids, such as human perspiration. In fact, good biocompatibility, low ionic release and the maintaining of surface properties are essential requirements for metals application in contact with the human body; surface stability is also needed to avoid aesthetic alterations of the object [14–16].

As already mentioned, the application of anodising agent as a surface modification technique to titanium jewellery is particularly attractive. In fact, the so obtained oxide coatings combine excellent corrosion resistance in most environments, including human perspiration, with an appealing colour produced by the interference of light with the oxide, which is transparent in itself; the same interference effect is the origin of colours of soap bubbles, or butterfly wings [17–19]. Interference colours strictly depend on the thickness of the oxide layer, which can be fine-tuned by choosing the proper anodising parameters, in particular the feeding voltage; colours appear on titanium and their hues change with increasing voltages, up to about 130 V [20–22]. Although obtaining colours on a titanium surface is quite simple, the formation of intense and bright colours requires the application of specific anodising procedures; an exceedingly high feeding voltage can lead to a loss of the interference colour, due to an excessive oxide thickening. Achieving a perfectly uniform colour at a macroscopic and microscopic scale is subject to a careful surface preparation [23].

In the light of these considerations, the work hereby presented concerns the realisation of a series of titanium jewels prototypes, made by SLM and finished by anodising, which was aimed at producing the desired colour with enhanced saturation: a patented anodising procedure was applied [23]. The collection prototypes were designed by Valeria Masconale (Figure 1).

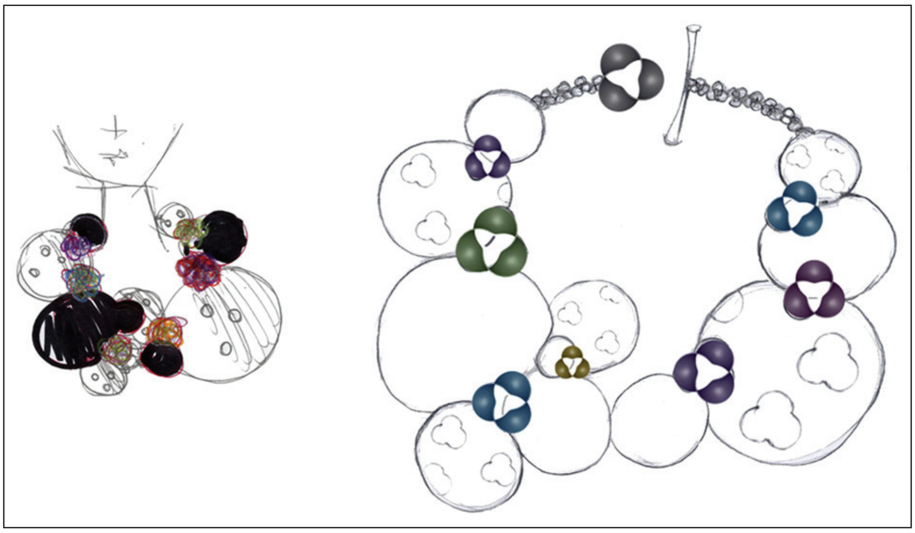

Figure 1 Jewels collection: design inspirations (by Valeria Masconale)

Jewels Design

Selective laser melting

Selective laser melting (SLM) is the rapid prototyping technique applied in this work to create titanium jewels; the equipment is still at the experimental stage. Selective melting by means of a laser beam represents a novel version of the classical selective laser sintering. The addiction of low-melting elements to the treated metal powders is thus avoided, but as a counterpart it requires the use of high-energy laser sources. The advantage assured by SLM is the achievement of high density massive products, preserving the metallurgical properties of objects formed with traditional techniques.

A support is needed during the melting process to maintain the object in the correct position. This is generated by the melting machine itself, so that the obtained support has the same composition of the desired object, the lowest contact area possible is achieved and an easier detachment in the final production stage is attained. The support also allows to create particularly complex geometries, i.e. undercuts, closed links, hollow objects and any desired curvature (Figure 2).

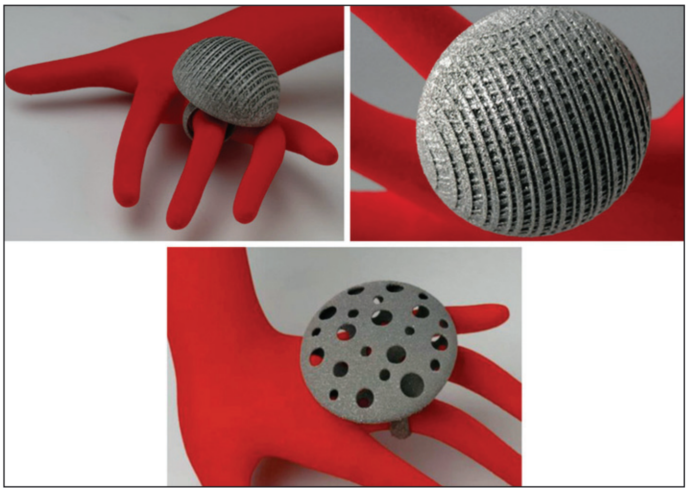

Figure 2 Production of titanium rings: hollow objects, undercuts, textures

Electrochemical colouring

After SLM processing and supports removal, the jewels underwent a finishing procedure, which involved a first electropolishing step intended to increase the surface gloss, followed by electrochemical colouring via anodising. The latter process had already been investigated by the authors, and various anodised titanium jewels and paintings were have been produced by Pedeferri in recent years (Figure 3). Due to the particularly rough surface of these products, a deep analysis of the influence of anodising parameters on the obtained colour was accomplished prior to the final application to these objects.

Figure 3 Paintings on titanium: colours obtained by anodic oxidation (by Pietro Pedeferri)

Anodising can confer interference colours to titanium surfaces thanks to the achievement of interference conditions between the light reflected at the oxide–air interface and the portion of incident light which is refracted by the oxide and then reflected by the metal-oxide interface. The optic path of the latter light beam covers a longer distance with respect to that reflected by the oxide external surface, being the difference between the two paths equal to a double oxide crossing; if the two light beams exiting the surface happen to be in phase, their colour will be strengthened, while in the opposite case the colour will be weakened (Figure 4). The result of this process is the appearance of colours on the anodised surface; the generated hue depends on the spectral components of the incident light that are either weakened or strengthened by interference, and thus on the difference in optic paths, i.e. on the oxide thickness. The interference colour is lost when the oxide thickness exceeds a few hundreds of nanometers.

To obtain interference colours with suitable intensity, a single anodising process is not sufficient. The procedure to be followed was patented by Pedeferri [23], and includes three

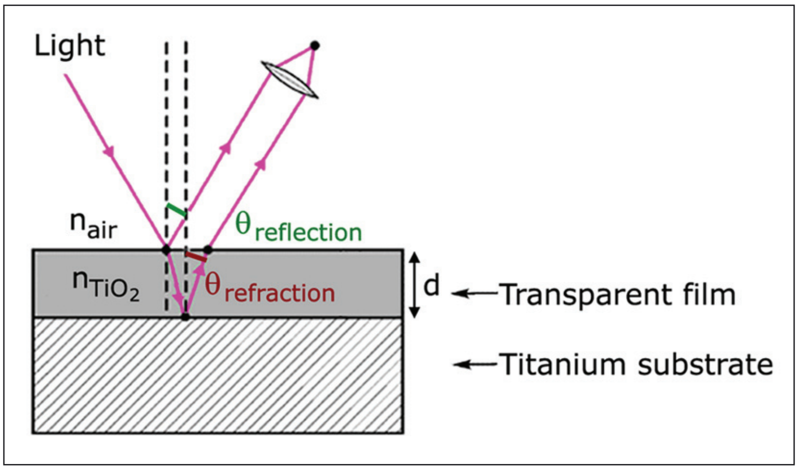

Figure 4 Interference of light with a thin oxide layer on titanium

main steps. The first one, which implies the chemical pickling of the metal surface in a hydrofluoric acid and nitric acid mixture (5% and 20%, respectively), is aimed at preparing a homogeneous surface. Subsequently, a pre-anodising step is performed by immersing titanium in diluted hydrochloric acid and applying a low feeding voltage (4 V).

This step is particularly delicate and its success determines the uniformity of the final colour. The application of the exact feeding voltage is strictly required, since lower or higher pre-anodising voltage causes an irregular oxide growth over the surface, which strongly decreases colour saturation (Figure 5). Finally, the pre-anodised metal is anodised in a diluted phosphoric acid electrolyte. The feeding voltage of this step will define the hue of the interference colour, since it determines the final thickness of the anodic oxide. In Figure 6 the sequence of colours obtainable by anodising at different voltages, i.e. by creating different oxide thicknesses, is shown.

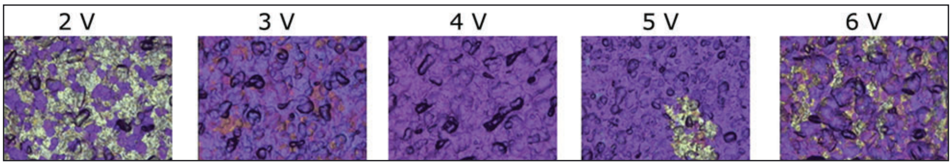

Figure 5 Influence of pre-anodising voltage on final colour homogeneity

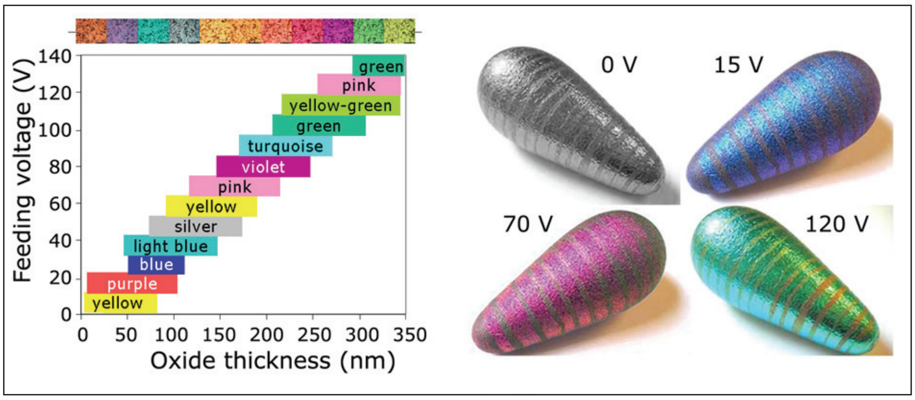

Figure 6 Chromatic scale of interference colours obtainable by increasing feeding voltage during titanium anodising and practical examples

Some remarks should be made about the chemicals involved in the colouring process. Diluted phosphoric acid is not considered to be particularly hazardous to human health, as demonstrated by its applications in the biomedical field (to clean and roughen the surface of teeth where dental appliances or fillings have to be placed) and in the food industry (to acidify foods and beverages, such as colas), though at high concentrations this acid is corrosive. Similarly, hydrochloric acid is also used in commercial cleaning products for household purposes, in which its concentration reaches 12%.

Among the used chemicals, the pickling solution is undoubtedly the most hazardous to the operator's health; nevertheless, most industrial processes requiring the surface cleaning of titanium are based on this pickling solution, whose use can therefore be considered as common practice, though it must be kept in mind that particular attention must be paid to the use of personal protective equipments.

Characterisation

A quantitative analysis of colour attributes was performed on anodised specimens. Colour was measured by means of a spectrophotometer (Konica Minolta CM-2600d; light source, D65) and values were elaborated by applying the CIELab standard system, in which each colour is represented by a point in the colour space, which in turn is identified by three coordinates: a^*, b^* and L^* (hues ranging from green to red, hues ranging from yellow to blue and lightness ranging from black to white, respectively) (Figure 7). The cross section of the diagram is generally used for representations, to better underline the single coordinates; moreover, two additional quantities can be represented on it, i.e. the hue (h_{ab}) and the chroma (c^*_{ab}) [24,25].

Data collected by spectrophotometry are summarised in Figure 7: each point in the a^*–b^* plane represents one interference colour corresponding to a given anodising voltage (Figure 7a). It is also interesting to consider the reflectance spectra of the anodised surfaces, i.e. the percentage ratio between light reflected by the surface and the radiation reflected by a perfectly white surface under identical illumination conditions, as a function of wavelength: the sinusoidal trend of these spectra confirms the origin of the corresponding colours, that is, interference phenomena (Figure 7b). Moreover, it is possible to notice an increase in the number of maxima and minima of the reflectance spectra, as well as a shift of their position towards higher wavelengths, with feeding voltage: the interpretation of these data through interference laws allows to connect these variations in the reflectance curves to a thickening of the oxide that generates the interference effect [13,26].

A key factor in colouring processes is the repeatability of the obtained hue and saturation, especially when serial applications, even for a limited production, are involved. Hence, repeatability tests were performed, to prove the suitability of anodic oxidation in jewellery production. Twenty titanium sheets were anodised by applying identical conditions; their colour (pink hue) was measured by means of a spectrophotometer and values were elaborated by applying the CIELab standard. The evaluation of treatment repeatability was accomplished by considering colour variations among the analysed surfaces: these resulted to be lower than 0.2%, thus proving the excellent reliability of the anodising procedure (Figure 8).

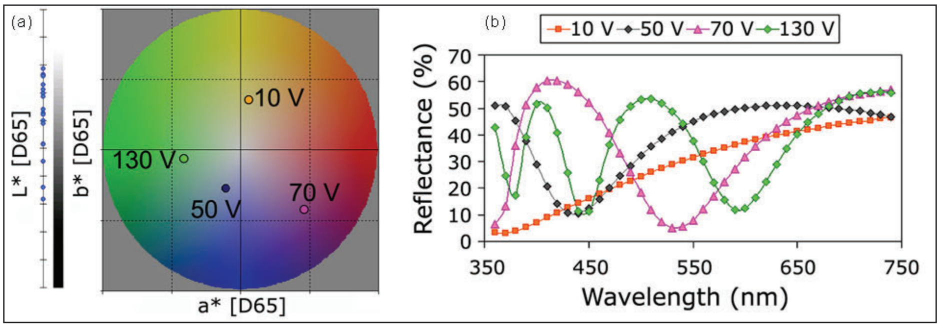

Figure 7 Spectrophotometric measurements of the anodic colours: (a) CIELab representation; (b) examples of reflectance spectra

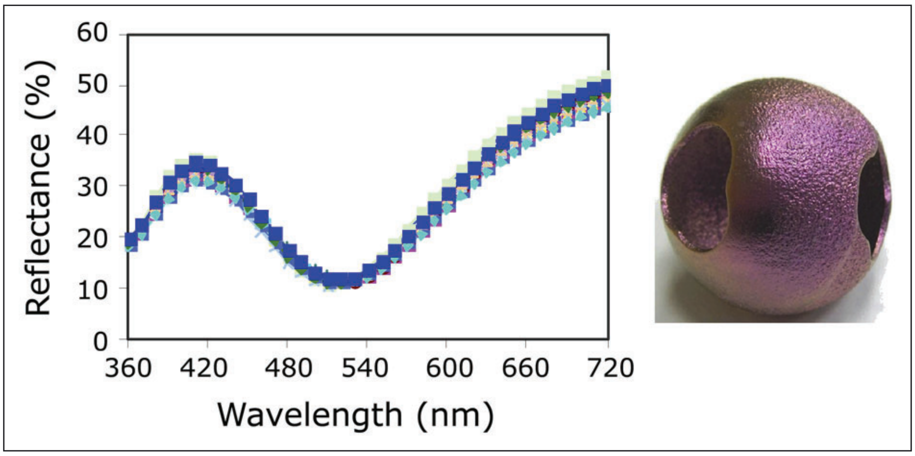

Figure 8 Reliability of anodising treatment: overlapping of reflectance spectra produced by 20 titanium surfaces anodised in identical conditions and corresponding colour product obtained on a titanium module

Realised products

Once an optimal control of both SLM and colouring techniques were achieved, the actual realisation of jewels prototypes could start. CAD designs exhibiting various shapes and curvatures were prepared, transformed into rapid prototyping codes and implemented with the definition of supports; necklaces, bracelets and earrings were designed and produced (Figure 9). In particular, different feeding voltages were supplied to single modules, so as to identify the optimal hue for final product realisation (Figure 10). Tested anodising procedures led to the obtaining of several colours, among which the most appealing ones were the blue, green and yellow hues. In all cases, colour homogeneity was elevated and colour saturation was extremely wide-ranging, depending on the modules surface finishing. In some cases, sandblasting was applied, in other cases electropolishing and hand-polishing were used to obtain a mirror-like surface (Figure 10). Finally, after evaluating the aesthetic effect provided by the different anodic colours, two monochromic hues (i.e. gold and blue) were chosen to produce a bracelet and a necklace; the last jewel here presented underwent electropolishing, after which polychromic colour appearances were conferred to the surface (Figure 11).

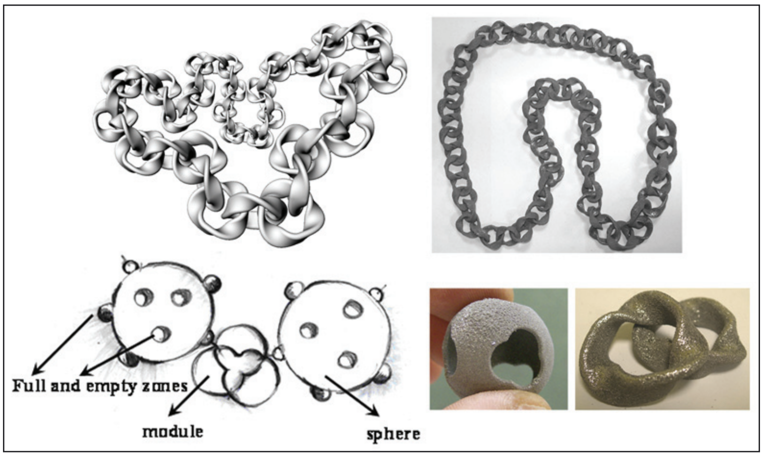

Figure 9 Examples of rapid prototyping design and SLM realisation: closed links necklace design and realised prototype (top); design combining links and spheres and realised single modules (bottom)

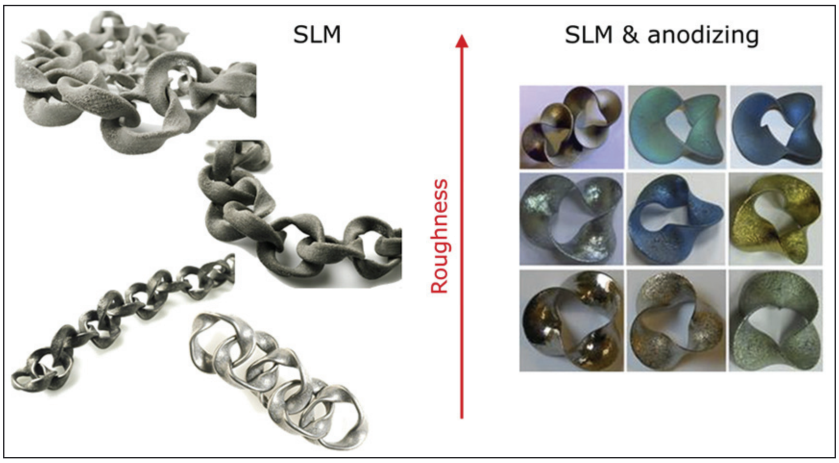

Figure 10 Differently finished chains with SLM alone and SLM + anodising: from top to bottom, sandblasted, pickled, electropolished, hand-polished; influence of surface finishing on the aesthetic appearance of coloured modules with different hues

Figure 11 Examples of finished jewels

Conclusion

The presented work aimed to analyse the possible applications of innovative production and colouring techniques to titanium jewellery. These experimental processes proved to exhibit an attractive potential, since a wide range of shapes, surface finishing and interference colours can be achieved, with no limitations in introducing undercuts and hollow features. After the prototyping step, a future development is foreseen, i.e. the process technological transfer and the final realisation of a complete collection of titanium jewels.

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