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# COLOURING TITANIUM ALLOYS BY ANODIC OXIDATION

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The present study is focused on analyzing the change of colors of anodized titanium and effects of applied electrolytic voltages on chromatics. The titanium specimens were anodize in 20 g/L citric acid and 20 g/L baking soda electrolyte by use of different voltages. The colors of anodize titanium were measured with a spectrophotometer and then evaluated in the CIELAB color space. It is found that different volt produces different colors. Anodizing in the range of 15 V to 150 V produces respectively a wide spectrum of color ranging from brown to fuchsia. It can be concluded that the colors of the anodize titanium are dependent upon the applied voltages.

*Key words:* titanium alloys, anodization, color, oxide, solution

## INTRODUCTION

Titanium is attractive for its low weight, fatigue resistance, corrosion resistance and biocompatibility. Thanks to these properties, titanium is applied in aeronautics, aerospace, bioengineering, sport and jewelry [1] also in substitution of nickel free stainless steel [2-3]. In order to color titanium four different methods are available: thermal-oxidation, chemical-oxidation, anodic oxidation and nitrizing. By either method the color can be well defined by the thickness of the film (mainly $TiO_2$) formed on the Ti substrate surface [4-5].With the anodizing technique, titanium can be both anodized in acid and basic solution and the coloration of the oxide film produced through anodic oxidation is dependent on the anodizing condition [6]. The nature of electrolyte and the oxide layer can be used to confer to the surface a colored appearance. In fact when titanium is suspended in an electrolytic bath as an anode and a current is passed through the bath, oxygen is produced at the anode surface. This oxygen combines with the titanium to form titanium oxide. The interference taking place between the oxide and light results in the appearance of colors on the metal surface and oxides with different thickness generate different colors.

To obtain a desired color on the surface, the feeding voltage applied during the anodizing process can be controlled [7]. The traditional anodizing technique employed a lab DC power supply to apply a constant voltage/current directly and the anodizing processed for a period of time.

G. Napoli, A. Di Schino (andrea.dischino@unipg.it, Università di Perugia, Dipartimento di Ingegneria, Perugia, Italy
M. Paura, T. Vela, Seamthesis, Nera Montoro (Terni), Italy

## MATERIALS AND METHODS

Type II titanium and V titanium was selected as experimental material for this study. Cylindrical sample of 10 mm of diameter were cut from a hot rolled titanium bar. The titanium specimens were cleaned in acetone liquid and dried. The specimens were anodized in 20 g/L citric acid electrolyte bath bath using different voltages in a specially designed electrochemical cell (Figure 1). The DC power supply was TTi EX752M. Titanium specimens were connected to the anode using a titanium grade II wire and the cathode was connected to a stainless plate.

## EXPERIMENTAL

For coloring the titanium samples the voltage was set and the power turned on until the desired color is reached, then the power was shut off and the titanium

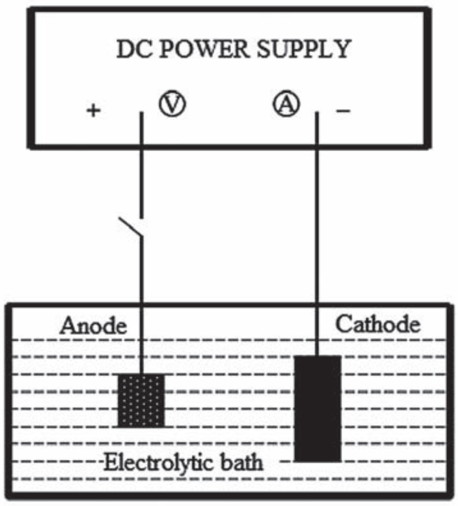


**Figure 1** Schematic electrochemical cell for titanium anodization. [1]

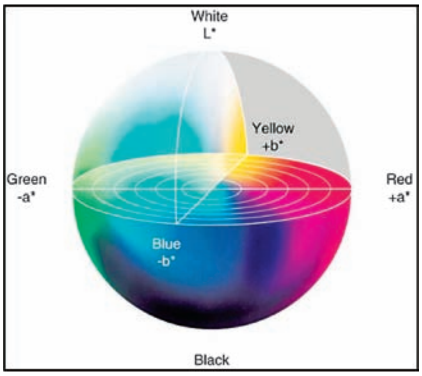


**Figure 2** CIELAB color space.

removed and rinsed thoroughly. Color measurements were carried out by using spectrophotometry techniques (Konica Minolta CM-2600d): the values obtained belong to the colorimetric space CIELAB, which is defined as standard colorimetric space. The three coordinates of CIELAB (Figure 2) represent the lightness of the color (L* = 0 yields black and L* = 100 indicates diffuse white; specular white may be higher), its position between red/magenta and green (a*, negative values indicate green while positive values indicate magenta) and its position between yellow and blue (b*, negative values indicate blue and positive values indicate yellow).

## RESULTS AND DISCUSSION

In this study, the measurements of spectral reflectance of anodized titanium shows that CIE coordinates are distributed extensively in the uniform 3 dimensional color space with the changing of voltages. Results show that anodizing with different voltages ranging from 15 V to 150 V (Table 1 and Table 2) produces a wide gamma of colors, as can be seen in Table 3. At different voltages applied the thickness of titanium oxide film are varied. The higher the voltages applied, are the thicker film. The different thickness of titanium oxide film cause the variations of refractive index and reflective index which produces various colors of anodized titanium (Figure 4 and Figure 5). The values of L* ranges from 40,05 to 70,54, the values for a* ranges from -9,36 to 19,71 meanwhile the values of b* ranges from -36,00 to 42,70. Is clearly show that there are not no remarkable differences between pure titanium (grade II) and Ti 6Al-4V (grade 5), in terms of produced colors, at the same applied voltage and current. The main difference is that titanium grade 5, at high voltages, produces a grey oxide that is not pleasing on the eyes (Figure 3) and is also insulating for the passing current. In fact for the sample 14, that was anodized at 150 V was not possible to evaluate the CIELAB parameters because the spectrophotometer returns non reliable values for the L*, a* and b* components.

Table 1 **List of voltages values and electric current values for the grade II sample anodized in citric acid bath.**

| Sample | Voltages / V | Ampere / A |
|---|---|---|
| 1 | 17 | 0,05 |
| 2 | 30 | 0,10 |
| 3 | 40 | 0,15 |
| 4 | 60 | 0,25 |
| 5 | 80 | 0,37 |
| 6 | 100 | 0,52 |
| 7 | 150 | 1.5 |

Table 2 **List of voltages values and electric current values for the grade V sample anodized in citric acid bath.**

| Sample | Voltages / V | Ampere / A |
|---|---|---|
| 8 | 17 | 0,03 |
| 9 | 30 | 0,04 |
| 10 | 40 | 0,11 |
| 11 | 60 | 0,17 |
| 12 | 80 | 0,25 |
| 13 | 100 | 0,30 |
| 14 | 150 | 1,00 |

Table 3 **List of colors, for titanium grade II and grade V anodized in a citric bath, samples in CIELAB color space.**

| Sample | L* | a* | b* |
|---|---|---|---|
| 1 | 45,23 | 18,26 | 8,25 |
| 2 | 41,03 | 6,57 | -36,00 |
| 3 | 53,17 | -7,53 | -24,76 |
| 4 | 69,31 | -8,35 | -6,57 |
| 5 | 70,54 | -3,00 | 33,27 |
| 6 | 67,47 | -0,96 | 24,68 |
| 7 | 61,91 | 13,05 | 4,59 |
| 8 | 40,05 | 10,93 | 42,70 |
| 9 | 46,79 | -2,16 | -33,50 |
| 10 | 59,10 | -9,36 | -23,01 |
| 11 | 72,35 | -6,47 | 29,86 |
| 12 | 64,13 | 10,89 | 24,36 |
| 13 | 59,33 | 19,71 | -9,29 |
| 14 | n.a | n.a | n.a |

**Figure 3** Photo of the sample 14. Is visible the grey oxide deposited on the specimen surface.

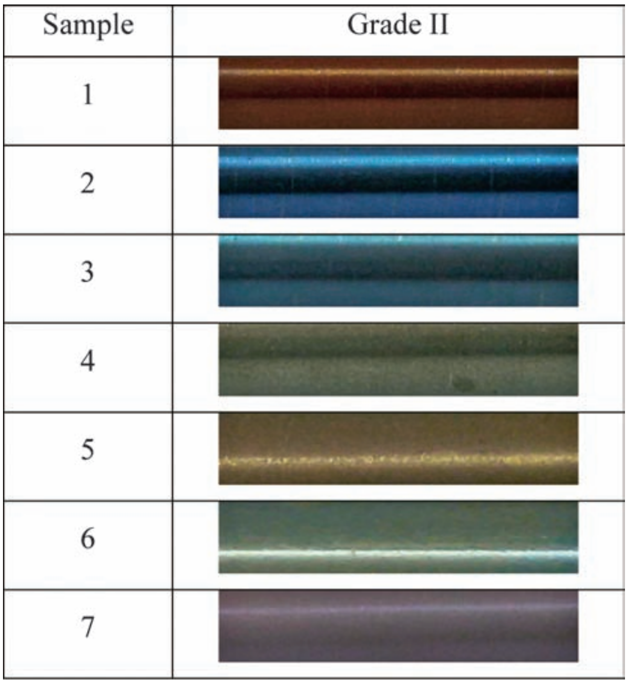


**Figure 4** Photos of titanium grade II anodized in a citric bath.

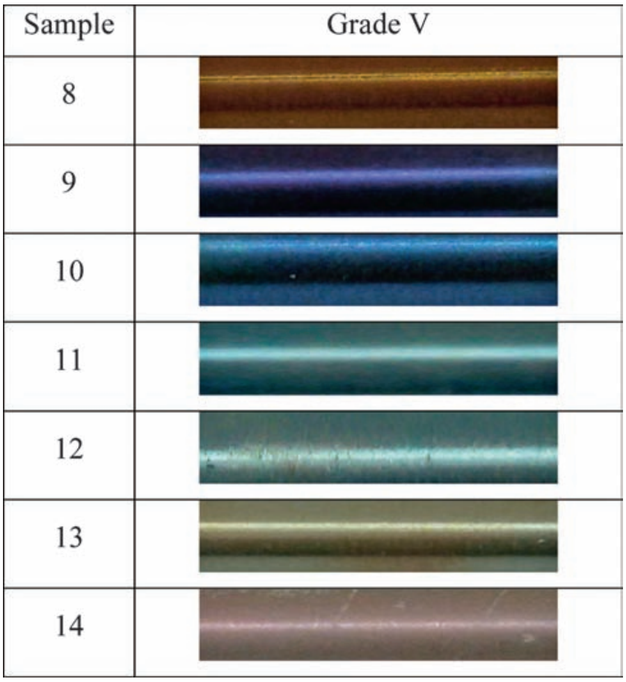


**Figure 5** Photos of titanium grade V anodized in a citric bath.

## CONCLUSIONS

Results shows that:

- Colors of anodized titanium are voltage controlled or voltage dependent. Many vivid colors of titanium can be obtained by means of anodizing through changing voltage applied.
- With growing potential, the chromatic scale that can be achieved consists of the following order of colors: brown/ yellow – blue/light blue – gold – fuchsia/purple.
- There are no differences, in terms of produced colors, between titanium grade II and titanium grade V but the latter at high voltage produces a grey oxide that is not pleasant on eyes and ruin all the specimen surface.
- Titanium grade II and grade V show an excellent uniformity of color from a macroscopic point of view.
- The surface finishing influences the resulting color, as it determines the surface behavior for what concerns light scattering, and therefore the brightness of colors

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**Note:** The responsible for English language is: Elisabetta Petricci, Terni, Italy