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Anodizing of Ti6Al4V alloy for aeronautical applications

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Abstract. The anodizing of Ti6Al4V alloy to improve adhesive bonding for aeronautical applications was investigated. Two electrolytes containing a) hydrogen peroxide (H₂O₂) and sodium hydroxide (NaOH) and b) chromium trioxide (CrO₃) and ammonium biflouride (NH₄F₂) were used. Anodizing was carried out at 10 V and 303 K for different times. Scanning electron microscopy, confocal microscopy and contact angle measurements with the sessile drop method were used to study morphology, roughness and wettability of the anodic films. The morphology of the anodic layers revealed the presence of randomly distributed pores on the surface whose diameters depend on the anodizing solution, being greater than 150 nm for the basic anodizing solution and less than 100 nm, when the anodizing is carried out in acid anodizing solution. Two key aspects that Ti6Al4V alloy surface must has to favor its adhesive bond to other materials are wettability and roughness. According to the results obtained, the anodic layers formed with acid solution for 30 min have the best wettability conditions and the greater surface roughness, compared with the anodic layers formed by other study conditions. These anodic layers will favor the application of epoxy adhesives normally used for adhesive bonding of Ti6Al4V alloy to polymeric materials.

1. Introduction

Titanium and its alloys are widely used in the aerospace industry due to its properties; among them the excellent resistance to corrosion and the good resistance/weight ratio are highlighted [1-3]. About 15% by weight of an aircraft is made of titanium alloys. Of this amount more than 80% is Ti6Al4V alloy [4].

Currently, composite materials also stand out in the new generation of aircraft, since they provide greater structural efficiency and performance [5]. The Ti6Al4V alloy joins to composite materials through mechanical joints. However, there is a need for new and flexible aircraft designs, and for joints with greater durability and better resistance to fatigue. This can be achieved by adhesive bonding and appropriate surface preparation [6]. Several methods have been used to modify the surface condition, maintaining its good macroscopic properties; among them is anodizing [7-8]. Anodizing is an electrochemical process that promotes the formation of a thin layer of oxide (anodic layer) on the surface of the metal, which helps protect the material from atmospheric agents or their environment in general [9]. Recently, research has been directed to the search for a surface with properties that allow a better adhesion between titanium and composite materials [10-13].
The present work studied the effect of the chemical composition of the anodizing solution on the formation on anodic film on the Ti6Al4V alloy with the purpose to obtain surfaces with adequate roughness and wettability that favor its adhesive bonding to compositied materials [10-12].

2. Experimental
2.1. Materials and surface treatment
Samples of Ti6Al4V alloy of 13.5 mm diameter and 4 mm thick were grounded by 180, 120, 180, 220, 320, 400, 600 and 1200 grid SiC paper and cleaned using an ultrasonic agitation in ethanol. Before the anodizing process, the natural passive oxide layer was removed by immersion of the samples in a HNO₃ (65% p/p) and HF (40% p/p) solution for 20 s, at room temperature. Then, they were rinsed in deionized water and dried in warm air. The anodized treatment was carried out using a voltage controlled DC power supply (Kepco BHK 500-0.4 MG) in two different solutions: a) 1 M hydrogen peroxide (H₂O₂) and 0.5 M sodium hydroxide (NaOH), known as AHP and b) 0.5 M chromium trioxide (CrO₃) and 0.018 M ammonium difluoride (NH₄F₂), known as CAA. Ti6Al4V alloy samples connected to the positive output of the power supply, served as anode and a stainless steel sheet as a cathode. The process was carried out at 10 V for 900 and 1800 s at 303 K. The anodized samples were washed with deionized water and dried with cold air.

2.2. Coatings characterization
Surface morphology of the anodized samples was investigated using a Quanta 650 FEG (Field Emission Gun) scanning electron microscopy (SEM) operated at 20kV. The surface roughness was characterized by 3D Hirox 7700 confocal electronic microscope using 560 magnifications to take the topographies. Contact angles were measured using a Dataphysics Model OCA 15 EC by sessile drop method with de-ionized water as liquid. The dosing volume and the dosing rate of water were chosen as 0.5 µl and 1 µl/s, respectively. The average contact angle values were obtained by measuring the contact angle at five different locations on the same sample.

3. Results and discussion
3.1. Anodic layers morphology
The surface of anodic layers reveals the presence of porous with different size and shape. The morphology of porous structure strongly depends on the anodizing solution rather than on the anodizing time (figure 1 (a), (c)). A porous sponge-like structure was observed on anodic layers formed in AHP solution at 900 and 1800 s. No long-range ordering was observed on the porous layer, and the average diameter of the pores ranges between 200 and 300 nm. On the other hand, an ordered porous/nanotubular structure with porous diameter of about 43 nm with preferential dissolution of the oxide formed on β-phase grains of Ti6Al4V alloy was obtained for the samples anodized in CAA solution for 900 s (figure 1 (c)). This morphology is characteristic for samples anodized in solutions that contain fluoride ions [14]. However, when the anodizing time increases to 1800 s (figure 1 (d)) the porous/nanotubular structure is no longer evident, probably due to its chemical dissolution.

It is important to mention that the different porous morphologies obtained on the anodic layers, showed an increase in the surface area with respect to the untreated surface. This would favor adhesion between the Ti6Al4V alloy and other aeronautical and aerospace materials [8-12].

3.2. Surface roughness
The surface roughness results for the different anodizing conditions used and for the pristine condition are shown in table 1 and figure 2. The pristine average surface roughness was 2.75 µm. For the samples anodized in AHP solution, the average roughness decreases as the anodizing time increases from 3.62 to 2.73 µm. On the opposite, for the samples anodized in CAA solution the roughness increases as the anodizing time increases.
One of the bonding mechanisms of adhesive joints of titanium alloys to other materials in aeronautical applications is mechanical cross-linking [7]. Higher surface roughness represents an increase in the area available for mechanical bonding, and in some cases chemical. The roughness represents topographic features in which the adhesive can penetrate and provide greater durability and bond strength [3]. Based on the above, anodizing conditions that allow rough surfaces favor adhesive bonding performance, because they provide a better anchor profile. In the present results, the best conditions are obtained for the anodic layers formed in CAA solution for 1800 s with a value of 3.92 μm followed by the anodic layers formed in AHP solution for 900 s with 3.62 μm. The later one solution offers an additional advantage that is the fact that it is environmentally friendly.

![Scanning electron micrographs of anodic layers formed on Ti6Al4V alloy at 303 K in different solutions. (a) AHP for 900 s, (b) AHP for 1800 s, (c) CAA for 900 s and (d) CAA for 1800 s.](image)

**Table 1.** Surface roughness of anodic layers formed on Ti6Al4V alloy.

| Anodized solution | Anodizing time (s) | Average surface roughness (μm) |
|-------------------|-------------------|-------------------------------|
| Pristine          | -                 | 2.75                          |
| AHP               | 900               | 3.62                          |
|                   | 1800              | 2.73                          |
| CAA               | 900               | 2.95                          |
|                   | 1800              | 3.92                          |
3.3. Contact angles measurements

All anodic layers formed on Ti6Al4V alloy exhibited a hydrophobic character irrespective of the solution and the anodizing time used (figure 3 (b) - (e)). However, longer anodizing times showed a slight decrease in the value of the contact angle (table 1). For instance 139° to 133.1° for samples anodized in AHP solution and 136.4° to 112.4° for samples anodized in CAA solution. This result does not necessarily imply poor wettability of surface, since the curing process of the adhesive is carried out simultaneously with mechanical pressure, facilitating the impregnation of the entire surface [11-12]. The hydrophobic character of anodized surfaces could be explained considering that the contact of the probed drop seems to be affected by the air trapped inside the pores of the anodic layer [15].

Table 2. Contact angles values measured by sessile drop method with de-ionized water as liquid for Ti6Al4V alloy anodized in AHP and CAA solutions at 303 K.

| Surface condition | Anodizing time (s) | Measure 1 | Measure 2 | Measure 3 | Measure 4 | Measure 5 | Average |
|-------------------|--------------------|-----------|-----------|-----------|-----------|-----------|---------|
| Pristine          | ------             | 36,7      | 35        | 36,9      | 36,4      | 38,1      | 36,6    |
| AHP               | 900                | 139,4     | 139,2     | 139,1     | 138,7     | 138,7     | 139,0   |
|                   | 1800               | 132,9     | 134,3     | 133,5     | 132,1     | 132,8     | 133,1   |
| CAA               | 900                | 136,0     | 135,8     | 137,4     | 136,2     | 136,7     | 136,4   |
|                   | 1800               | 112,8     | 111,1     | 113,3     | 112,8     | 112,1     | 112,4   |
(a)

(b)

(c)

(d)

(e)

**Figure 3.** Contact angles measured by sessile drop method with de-ionized water as liquid for anodic layers formed on Ti6Al4V alloy at 303 K in (a) AHP for 900 s, (b) AHP for 1800 s, (c) CAA for 900 s and (d) CAA for 1800 s.

4. **Conclusions**

Porous anodic layers were obtained on Ti6Al4V alloy by anodizing in two different solutions for different times. Two pore morphologies were formed: one sponge-like structure with pore diameters close to 300 nm for the samples anodized in AHP solution and a nanotubular/ordered-like structure with pore diameters not greater than 100 nm for anodizing in CAA solution. The ordered porous structure can be attributed to the presence of fluoride ions in the solution. Different roughness profiles and wettability were obtained, however, the layers obtained by anodizing in AHP solution stood out. Its morphology and roughness showed great variation between crests and valleys offering an anchor profile capable of providing greater durability for the adhesive bond. This anodizing solution could be considered as a replacement for CAA solution, which due to its toxic effects has not been able to continue being used.
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