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Durability of titanium adhesive bonds with surface pretreatments based on alkaline anodisation

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ABSTRACT

The most recent works suggest that the alkaline anodizing process (NaTESi) based in a bath of sodium hydroxide may be an attractive alternative to chromic acid anodizing (CAA) for surface pretreatment of titanium alloys for preparing hybrid adhesive bonds Ti6Al4V/Carbon Fiber Reinforced Composite (CFRC). This work compares several anodizing processes used for surface preparation, such as CAA, NaTESi and two modified NaTESi processes. The surface morphology, roughness, surface free energy and, especially, the initial strength adherence and durability under the wedge crack tests have been characterized. Wedge crack tests were performed in three different ageing media that may be representative of the environment that adhesive joints based upon Ti6Al4V/CFRC have to withstand during aircraft service life environments: hot/wet conditions; CTB3 + TS test, that combines wet-dry cycles with exposure to a corrosive environment (CTB3) and thermal shocking (TS); and immersion tests in a Lap Joint Simulant Solution (LJSS). The results indicate that despite the morphological differences of the oxide grown by CAA and NaTESi, the initial adhesive strength with an epoxy adhesive and the durability of the bond are similar for both anodizing processes. Conversely, higher initial adhesive forces are exhibited for both modified NaTESi anodizing processes.

1. Introduction

The progressive substitution of metallic materials by carbon fiber reinforced composites (CFRC) in commercial aircraft structures [1,2] also leads to the need to redesign the hybrid metal/CFRC structures. Since the early 50s, titanium and titanium alloys have been widely used in structural elements for aircraft due to properties such as low density, good mechanical properties and high resistance to elevated temperatures and corrosion [3]. The use of titanium alloys for metal/CFRC structures is particularly emphasized because in addition to their mechanical properties, such alloys are compatible with CFRCs from a galvanic corrosion resistance standpoint [4].

Today the main joining process for hybrid structures, – metal/CFRC – continues to be mechanical riveting. However, it is known that adhesive bonds have many advantages over mechanical joints [5–7]. Composites, in particular, show a high sensitivity to notches and all kinds of mechanical stress concentrators [8]. Nevertheless, the adhesion process is very complex and depends greatly on the surface preparation of the adherents [9]. Numerous papers have considered the factors that influence the strength and durability of the adhesive/adherent bonds and laboratory tests used for their evaluation [9–18]. The basic requirements that must be followed for an effective surface treatment are those that make it possible to achieve a surface with high chemical reactivity with the adhesive and mechanical interlocking of the adhesive on the substrate surface. In other words, achieve a surface roughness which provides an increase in the available area for chemical bonding, as well as the creation of topographies where the adhesive can penetrate [19]. Additionally, an adhesive bond always requires good adsorption and good contact between the adhesive and adherent, provided by a suitable surface energy and effective wettability [20]. The main parameters which determine surface energy of the adherent are the chemical composition and surface roughness [21,22], being not just the average roughness, but also the topography at the nanoscale. Although, roughness is a parameter that has always been taken into account when developing adhesive bonds [23], an important prerequisite that must be fulfilled is to have a surface free of contaminants that might produce secondary reactions and weakening of the substrate/adhesive interface [24]. Literature contains a large variety of surface treatments (physical [8,25], chemical [7,26], and electrochemical [14,27] among others) for titanium and Ti alloys that modify the

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strength of the bond by changing the substrate in various ways: surface energy, roughness and surface composition. Particularly interesting are the reviews by Baldan [8], Critchlow and Brewis [28], Molitor, Barron et al. [29], and Venables [30], which gather information about surface pretreatments for titanium adhesive bonds and the various adhesion mechanisms which have been proposed to explain the effects observed.

Anodizing processes for titanium alloys stand out from other treatment types because it makes possible to tailor the microstructure, thickness and chemical composition of the oxide layer. At an industrial scale, chromic acid anodizing (CAA) has been used extensively as it achieves the best results in terms of both adhesion and durability of titanium adhesive bonds [30,31]. Nevertheless, the toxicity and carcinogenicity of Cr (VI) do not make it sustainable and oblige a search for less harmful alternatives.

NaTESi anodizing is a potential alternative to chromic acid anodizing for titanium and its alloys due to the advantageous characteristics of the titanium oxide produced and the fact that the oxide is grown in an alkaline bath that prevents titanium from hydrogen embrittlement [32]. This fact is highlighted in the works most recently published [4,33–41], suggesting that the development and research on the NaTESi anodizing process is of great interest. For example, the recent study by He et al. [36] concluded that the surface morphology obtained in this alkaline anodizing process was mainly governed by the temperature balanced electrochemical reactions in the electrolyte/oxide and oxide/metal interface. The oxide dissolution process is due to the presence of tartrate ions ($(C_4H_4O_6)^{2-}$) to form titanium tartrate complexes ($[Ti(C_4H_4O_6)_y]^{4-2y}$), and temperature, which has a strong influence on the ionic mobility. These authors also studied the apparent shear strength and fracture behavior of anodized Ti6Al4V bonded with epoxy. T. Mertens et al. [4] compared the NaTESi anodizing process with plasma treatment for structural bonding of titanium and, evaluated the adhesion properties by means of a wedge test in hot/wet conditions. A similar study was carried out by A. Kurtovic et al. [34], but in this work the authors compared the adhesion properties of the NaTESi anodizing process with laser treated titanium surfaces, evaluated by means of the floating roller peeling test (in hot/wet and room temperature conditions) in addition to wedge test (in hot/wet conditions). Another studies performed an in-depth characterization of the TiO_2 layers grown on NaTESi electrolyte with [35] or without additives [33].

Recently, work based on NaTESi processes for titanium and its alloys, in addition to characterizing the anodic oxide layer, also studied adhesion properties through varying experimental parameters such as the use of different anodisation voltages [39] and/or different titanium alloys like near-alpha, near-beta and alpha–beta [40]. A most recent investigation made by L. Pan et al. [41], showed the improvements on titanium adhesion by combining NaTESi process with electrografting process.

The present work shows a comparative study among several anodizing processes: CAA, NaTESi, and two modifications of the latter, characterizing the morphology, surface energy and roughness of the surfaces and, the adhesion and durability of adhesive bonds for each pretreatment. The strength and durability of the adhesive bonds were evaluated via wedge crack tests, in three different exposure conditions: conventional hot/wet conditions in humidity chamber; wet-dry cycles with exposure to a corrosive environment combined with thermal shock (CTB3+TS); and immersion in the Lap Joint Simulant Solution (LJSS). The latter was used for a better understanding of the behavior of titanium bonded joints on in-service aircraft since the composition of this solution was based on measurements performed by capillary electrophoreses of residue extracted from lap joints from in-service aircraft.

Literature is scarce studying the durability of titanium bonded joints with different surface pretreatments in more realistic conditions beyond constant high humidity. The novelty of this work is precisely the study performed using the wedge crack tests in the CTB3+TS conditions and in LJSS solution immersion.

2. Material and methods

The titanium samples used were Ti6Al4V alloy (Grade 5). The main alloying elements are the α-phase-stabilizer aluminum and the β-phase-stabilizer vanadium. The samples were firstly degreased with methyl-ethyl-ketone (MEK), followed by immersion in a commercial chromate-free alkaline cleaner (TURCO 4215 NCLT®), 50 g/L, at 50 °C for 10 min. The specimens were then etched with a commercial alkaline product, TURCO 5578®, using a solution with a concentration of 400 g/l, at 97 °C for 30 min. The samples were then deoxidized in a 7 M HNO_3 solution at room temperature to remove metal impurities deposited on the surface which are insoluble in alkaline baths. Finally, before the anodizing process, the natural passive oxide layer was removed by immersion in an aqueous solution mixture of 40 v% HNO_3 and 2 v% HF for 45 s, at room temperature, with gentle manual shaking. After each of the steps, the samples were rinsed with deionized water at room temperature for 5 min.

After surface preparation the samples were anodized using four different baths and conditions. Detailed description of the anodizing processes are listed in Table 1. The last two anodizing processes are modifications of the NaTESi anodizing process, developed by Matz [32] for structural bonding of titanium: a

Table 1
Setup of the anodizing processes.

Anodizing process	Parameters				
	Bath composition	Potential (V)	Voltage ramp (V/min)	Temperature (°C)	Time (min)
NaTESi	NaOH 7, 5 M Na-tartrate 0, 33 M EDTA 0, 067 M Na_2SO_3 0, 02 M	10	–	30	15
M1NaTESi	NaOH 7, 5 M Na-tartrate 0, 33 M EDTA 0, 067 M Na_2SO_3 0, 02 M	10	–	40	15
M2NaTESi	NaOH 7, 5 M Na-tartrate 1 M EDTA 0, 067 M Na_2SO_3 0, 02 M	10	–	40	15
CAA	H_2CrO_4 5% NH_4HF_2 0, 1%	10	2	RT	20