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Surface integrity after pickling and anodization of Ti–6Al–4V titanium alloy

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ABSTRACT

The surface integrity of Ti–6Al–4V titanium alloy was studied at different stages of surface treatments, especially pickling and compact anodization, through surface characteristics potentially worsening fatigue resistance.

No significant changes of the equiaxe microstructure were detected between sample core and surface, or after the pickling and anodization steps. Surface hydrogen and oxygen superficial contents were found to remain unchanged. Roughness characteristics (i.e. R_a, R_z but also local K_t factor) similarly showed only slight modifications, although SPM and SEM revealed certain random local surface defaults, i.e. pits about 400 nm in depth. Finally internal stresses, evaluated using X-ray diffraction, highlighted a significant decrease of the compressive internal stresses, potentially detrimental for fatigue resistance.

1. Introduction

Titanium alloys are increasingly used in the aeronautical industry due to their good mechanical properties and their low density. The most commonly used is Ti–6Al–4V because it is a good compromise between titanium's properties. However, additional surface treatment is usually required [1,2] to increase, for instance, superficial mechanical properties (i.e. tribological properties, wear resistance and superficial hardness), as well as to improve its behaviour with respect to corrosion by fluorided acidic solutions. Surface treatments on titanium alloys usually involve three main steps. The first is degreasing step which removes the oil and impurities on the surface, left by previous machining stages. The second is pickling commonly performed by chemically controlled corrosion typically in mixed hydrofluoric-nitric acid bath. The aim of this pre-treatment is to remove the natural passivating layer. Finally, the third stage is the main treatment, i.e. nowadays thermodiffusion treatments (nitriding, carburizing) or shot peening treatments [3–5]. Another simple and cost-effective treatment is anodization, creating either a compact top film or a porous one, including numerous mesopores [6,7]. Porous anodic films are currently being widely studied to prepare innovating photovoltaic cells [8,9] or to enhance osteointegration for bioapplications [10]. In contrast, compact anodic films are used both to colour the titanium surface [11–13] and to improve paint adhesion for aeronautic parts [2,14].

However, previous industrial and academic studies have unfortunately shown, especially for aluminium alloys (AA), that the anodization process causes significant modifications of the AA surface integrity and a subsequent decrease of the fatigue resistance [15–18]. To our knowledge, no research works have previously studied and explained the possible influence of surface treatments, especially pickling or the anodization, on fatigue resistance in titanium alloys. In the case of AA, decreased fatigue resistance after anodization is under investigation and has been mainly attributed to influent surface parameters such as: microstructure [19,20], uptake of embrittling chemical species [20–22], roughness [23,24] and internal stresses [25,26].

Microstructure has an important effect on the fatigue resistance of titanium alloys [19,20]. The main microstructural parameters are α grain size and the percentage and morphology of β phase. For example, a lamellar microstructure does not have the same mechanical properties as equiaxe microstructure [20]. Some surface treatments, such as nitriding or carburizing treatment, can also affect the microstructure and consequently the fatigue resistance.

Hydrogen, carbon, nitrogen and oxygen are the four main potential uptaking and embrittling species. Their respective effects are different but hydrogen embrittlement is well-known to affect mechanical properties of metal parts. This point is particularly critical as Ogawa et al. [27] clearly showed using hydrogen thermal desorption that the amount of absorbed hydrogen in a beta titanium alloy increased with immersion time in fluorided acid solutions.

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The role of roughness on fatigue resistance of metal parts is well known and has been studied for a long time. Roughness can be significantly modified by surface treatments, such as for instance the pickling step. Thus, pickling of AA substrate often modifies the roughness through dissolution of microprecipitates initially included in the multiphase AA matrix [18]. On commercially pure titanium, pickling performed in a concentrated (48%) sulphuric acid bath is similarly used to increase roughness in order to promote osteo-integration [28].

Finally, internal stresses contribute to the average stress applied to the material and consequently its fatigue resistance. Internal stresses may be generated by mechanical treatment (shot peening, ball burnishing), thermal treatment (quenching, annealing) and/or (electro)chemical treatment (nitriding, anodization). For instance, anodization induces compressive or tensile internal stresses, whose intensities depend on the operational parameters of the electrochemical treatment [29–32].

In the present work, the aim was to study the influence of surface treatment (pickling and anodization) on surface integrity of Ti–6Al–4V titanium alloy, widely used for aircraft parts such as for example engine pylons.

Surface integrity was studied through surface characteristics potentially influencing fatigue resistance. Firstly the microstructure of Ti–6Al–4V alloy was carefully studied through two types of substrates, i.e. rolled sheet and forged bar. Secondly, this work only focussed on hydrogen and oxygen uptakes because carbon and nitrogen are not involved, either in pickling treatment or in anodization treatment. Then roughness was studied through R_a and R_z values but also an approach based on the local stress concentration factor (local K_t). Erratic and punctual defaults were observed and characterised to complete the morphological analysis. Finally, internal stresses were measured using XRD methods. These different characteristics were deeply studied at both steps of surface treatment (pickling, anodization) while endurance limit was finally evaluated in order to both clarify the surface changes and predict their potential impact on fatigue resistance.

2. Experimental

2.1. Surface preparation

The substrate material was Ti–6Al–4V titanium alloy. Its chemical composition in weight percent was: 5.5 < Al < 6.5%, 3.5 < V < 4.5%, C ≤ 0.08%, O ≤ 0.20%, N ≤ 0.05%, Fe ≤ 0.30%, H ≤ 0.0125% with Ti accounting for the remainder. Two different substrates were used in this study to finally obtain three different surface states.

The first substrate was Ti–6Al–4V rolled sheet (45 mm × 60 mm × 1 mm). From this substrate, two surfaces were prepared: raw rolled sheet and polished sheet. The polished samples were obtained using 800, 1200, 2400 grade polishing paper discs and 6, 3 then 1 μm diamond paste polishing pads.

The second substrate was Ti–6Al–4V forged bar (length: 105 mm; diameter: 16 mm) turned (feed rate: 0.1 mm/revolution; cutting speed: 25 m/min) to obtain a fatigue specimen (working length: 20 mm; working diameter: 8 mm), that made up a third surface state.

All samples were degreased with ethanol and then acetone. They were then pickled in aqueous 20 w% HNO_3 and 2 w% HF mixed solution at 20 °C for 200 s without stirring.

Finally, the anodization was performed in an electrochemical cell, where the titanium substrate was used as anode and a lead plate as counter-electrode. The anodization was run for 2 min in the direct voltage mode (5–80 V) using a sulfuric acid solution (1 M) thermally regulated at 20 °C. Samples were rinsed with distilled water after each step.

2.2. Characterizations

The thickness of the anodic film was measured using a Bentham PVE300 reflectometer, with a TMc300 monochromator in the 300–900 nm wavelength range. For the anodic film, the refractive index provided by Diamanti et al. [11] was used.

Secondary Ion Mass Spectrometry (SIMS) surface and cross-sectional analysis were performed with a Cameca IMS 4F6 device. The area analysed was 150 μm × 150 μm using a 10 keV Cs^+ primary beam with 10–50 nA current range. It is important to note that this area of analysis was larger than the α and β grain sizes (maximum 40 μm^2).

Prior to microstructural observations, samples were dipped for 10 s in a mixed acid solution (4% HF; 3%HNO_3) at ambient temperature. Sample microstructures were observed with a scanning electron microscope (XL30 ESEM), while α and β grain sizes were estimated by analyzing SEM views with the free software ImageJ [33]. Additional observations of the sample microstructure were carried out using an optical microscope (OM) (Olympus GX 71).

Elementary chemical analyses were performed by energy-dispersive X-ray spectroscopy (Rondec-EDX) coupled with a SEM device, in order to obtain a semi-quantitative analysis of V, Ti, Al contents in both types of grains.

A Mahr perthometer PGK 120 (contact mode in ambient atmosphere, diamond tip with 2 μm radius) was used to access to the amplitude parameters of the roughness, i.e. here the roughness average (R_a) and roughness height (R_z), defined by:

$$R_a = \frac{1}{l}\int_0^l |z(x)|dx \quad (1)$$

with l the length of profile and $z(x)$ the profile height distribution with respect to mean line

$$R_z = \frac{1}{5}\left[\sum_{i=1}^{5}|(z_i)_{max}| + \sum_{j=1}^{5}|(z_j)_{min}|\right] \quad (2)$$

where $(z_i)_{max}$ and $(z_j)_{min}$ are respectively the five higher local maxima and lower local minima of the profile height distribution (z).

The R_a and R_z values shown in this paper were the average values, resulting from 4 to 40 measurements. Corresponding accuracy was low (about 0.01 μm) while the standard deviation was about 0.05 μm for R_a and 0.5 μm for R_z. Only R_a and R_z values were used in this paper but the final conclusion would remain the same with the other roughness indexes.

Unfortunately, roughness indexes do not always provide sufficient information to know the real effect of morphology on fatigue resistance [34,35]. Consequently, Suraratchaï et al. [34] and Shahzad et al. [16] proposed to use the local K_t to determine the morphology impact on the fatigue resistance. The specificity of the K_t parameter is that it takes depth and sharpness of the local defaults into account. Its calculation is based on roughness profile analysis and finite elements simulation [34]. In this method, roughness profile was filtered to extract its "useful" part, the cut length, assimilated to a_0 [23], being here close to 10 μm. Standard deviation for K_t is estimated to be equal to 0.03 for machined samples and 0.5 for laminate samples.

A scanning probe microscope (SPM-Bruker) in contact mode in ambient atmosphere with a 10 nm radius and a 10 μm long cantilever tip was used to characterise erratic local surface defaults at the micro- and nano-levels (50 μm × 50 μm).

The internal stresses were measured by X-ray diffraction (X-pert Philips device) using the well-known "$\sin^2\psi$ method" firstly introduced by Macherauch [36,37]. Measurements were only carried out on unpolished rolled samples because the XRD technique is unsuitable for cylindrical samples (like machined forged bar used