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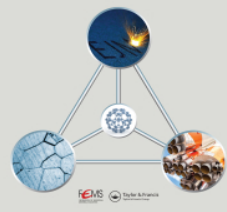
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Surface engineering of titanium alloy TiAl6V4 by multi-interstitial diffusion using plasma processing

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ABSTRACT

Titanium alloy Ti6Al4V possesses a range of highly interesting properties such as excellent corrosion resistance, bio-compatibility and high specific stress but suffers from poor wear resistance. The present work addresses plasma assisted surface treatment using various combinations of nitriding and oxidizing treatments for improving the surface properties of this alloy. The response to the surface treatments is investigated by hardness depth profiling in correlation with the chemical and microstructural evolution. It highlights the advantages of combined nitriding and oxidizing treatments compared to single nitriding for improving surface mechanical properties of titanium alloys.

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Ti6Al4V; surface treatment; micro-hardness

Introduction

Titanium alloys are materials of choice when high specific strength and low weight are required such as in the aeronautic industry. They also present a very good resistance to corrosion in severe chemical environments as for example in the chemical industry or for submarine hulls. Moreover, their biocompatibility makes them very interesting for medical implants. To summarize, titanium alloys could be a sort of universal choice for metallic structures used at moderate temperatures, had they

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not their Achilles heel: poor wear resistance, especially in corrosive aggressive medium. Surface treatments have proved to be an efficient way to remedy this inherent weakness. In this paper, we explore new routes to obtain effective improvements of the surface properties of Ti6Al4V, the most widely used titanium alloy. To this end, sequential plasma enhanced thermo-diffusion of Nitrogen and Oxygen interstitials is applied.

Context

Surface hardening of Ti6Al4V using conventional thermo-chemical processes involving the interstitial elements carbon and/or nitrogen requires relatively high temperatures (well above 900 °C for gaseous nitriding). The high temperature is required to overcome the native oxide layer present at the surface of the material (Christiansen, Jellesen, & Somers, 2018; Zhecheva, Sha, Malinov, & Long, 2005). These high temperatures can significantly alter the mechanical properties of the core material by modifying its microstructure (Christiansen et al., 2018; Takesue, Kikuchi, Akebono, Morita, & Komotori, 2020). A way to overcome or at least minimize this detrimental problem is to use plasma assisted or high energy ionic processes that allow processing at temperatures below 900 °C, i.e. well below the β transus temperature. However, this comes at the cost of a shallower hardened case (Fouquet, Pichon et al., 2004; Oliveira et al., 2018) and results, after a nitriding process, in the formation of a surface zone constituted of very hard layers of TiN and Ti₂N compounds, and a supporting diffusion zone of variable but quite low thickness (Fouquet, Le Bourhis et al., 2004) containing up to 12% of nitrogen.

Counterintuitively, because of a significant interstitial strengthening due to the very high solubility of oxygen in titanium (up to 34%), high temperature oxidizing can be used as a surface treatment. As a consequence of this very high solubility, long range diffusion of oxygen occurs and results in the formation of a thick diffusion zone (Dong et al., 2017; Hertl, Werner, Thull, & Gbureck, 2010; Takamura, 1962; Kim, Konno, Murakami, Narushima, & Ouchi, 2009). The resulting smooth gradient of the mechanical properties is expected to yield a better stability of the surface layers under loading.

To summarize, the two interstitial elements oxygen and nitrogen present different and somehow complementary diffusion behaviours. It appears then promising to combine them in mixed interstitial compounds or solid solutions in titanium and its alloys. In addition, promising improvement of corrosion resistance of Nitro-Oxidized samples has recently been reported (Pohrelyuk et al., 2019). Moreover, according to

Fedirko (Fedirko et al., 2006), the Ti based ternary compounds have higher hardness and wear resistance than any of the corresponding binary compounds. The challenge is to find surface treatment processes that can lead to these very promising compounds without detrimental deterioration of the other properties as for example fatigue life. In this paper, we present the first steps on a route to efficient “low temperature” plasma assisted surface treatment of Ti6Al4V that preserves the mechanical properties of the core material. This study focuses on the mechanical property gradient induced in the supporting diffusion zone, which appears as the key solution to benefit the strong hardening of surface compound layers.

Experiment

Disc samples, 30 mm in diameter and 4 mm in thickness, were cut from a rod of commercial Ti6Al4V (grade 5) titanium alloy, with nominal mass composition of 6 wt% Al, 4 wt% V, Ti balance and mill annealed microstructure: equiaxed alpha grains sheathed in beta phase. Prior to surface treatments, the samples were polished according to the 3 steps Struers® (https://www.struers.com/-/media/Struers-media-library/Materials/Application-reports/Application_Note_Titanium_2015_ENG.pdf) protocol with colloidal silica as final step. A similar procedure was used to prepare the cross sections for micro hardness tests. A custom-built plasma reactor was used for the thermo-chemical treatments (Perriere et al., 1986).

Briefly, the reactor consists of a quartz tube fitted with an external electrode at the gas inlet end of the tube. The treatment temperature is controlled via a tubular furnace surrounding the central zone of the tube. The samples were introduced in the reactor and kept in the “cold” zone during the pre-heating of the furnace to the treatment temperature. For each treatment step, an appropriate gas mixture containing the active gas was introduced in the tube. When necessary, RF power was injected in the system to light up the plasma prior to the transfer of the sample into the working zone of the rig. At the end of the treatment cycle, the sample was taken back into the cold zone and rapidly cooled down to 350 °C, a temperature low enough to prevent any significant additional diffusion. The 10 minutes heating and cooling durations can be neglected compared to the total process time of several hours. The treatment temperature was set at 850 °C (Table 1) that is below the temperature range used for gaseous nitriding, and well below the β -transus temperature of the alpha phase in this alloy (996 °C). Four types of treatment steps have been used: Plasma assisted Nitriding (PN; 60% N₂-40% H₂), Plasma assisted Oxidizing (PO; 100% O₂), Gaseous Oxidizing (GO; 100%

Table 1. Surface treatment sequences used (PN: Plasma Nitriding, PO: Plasma Oxidizing, GO: Gaseous Oxidizing, VD: Vacuum Diffusion)

SAMPLE A	PN (850 °C-8 h)
SAMPLE B	PN (850 °C-32 h)
SAMPLE C	PN (850 °C-8 h) + VD (850 °C-15 h) + PO (850 °C-4 h)
SAMPLE D	PN (850 °C-8 h) + VD (850 °C-15 h) + GO (750 °C-4 h) + VD (850 °C 15 h)

O₂) and Vacuum Diffusion (VD). The total pressure was set to 5 Pa for all steps except VD (10⁻⁴Pa) and the RF power to 700 W for plasma sequences. The different cycles used are summarized in Table 1.

The following protocol was adopted to ensure a significant number of data points in the Vickers hardness profile on the cross-sections: lines of indents, separated by 50 µm, were made along a direction inclined 80 to 85 degrees to the heat-treated surface normal. This results in an actual step size along the normal of 5 to 8 µm. The number of indents made on each of the treated sample depends on the depth of the treated layer and varies from 10 to 30. The load was fixed to 0.245 N and the dwell time to 10 s. The hardness was determined as the mean pressure over the contact surface calculated from the diagonal lengths of the Vickers indent. The chemical compositions and phase identification of both surface compounds and diffusion layers were determined from Glow Discharge Optical Emission Spectroscopy (GDOES) and X-Ray diffraction (XRD) in Θ -2 Θ geometry. Peak identification was made by comparison of the experimental positions to the JCPDS files (00-044-1294; 00-044-1288, 00-017-0386, 00-038-1420 and 00-021-1276 for α -Ti; β -Ti, Ti₂N, TiN and TiO₂ respectively).

Results and discussion

Microstructure

The samples nitrided at 850 °C were only studied as reference for hardness; details about the microstructure can be found in (Fouquet et al., 2004) and will not be discussed in detail here. Briefly, the obtained surface case consists in a shallow δ -TiN layer (100 to 400 nm) followed by a 3 to 4 µm thick ϵ -Ti₂N layer. The supporting diffusion zone, measured on GDOES profiles, reaches 30 to 50 µm.

Figure 1 presents the GDOES composition profiles measured on sample C and Figure 2 the corresponding X-Ray diffraction pattern. The X-Ray pattern is complex and phase identification is not unambiguous. α -Ti phase (red squares) is present together with some tetragonal ϵ -Ti₂N (red triangles). Peaks coming from the sub-oxides TiO, Ti₂O₃, Ti₂O and Ti₃O (blue symbols) are also identified. It is to be emphasized that, even with

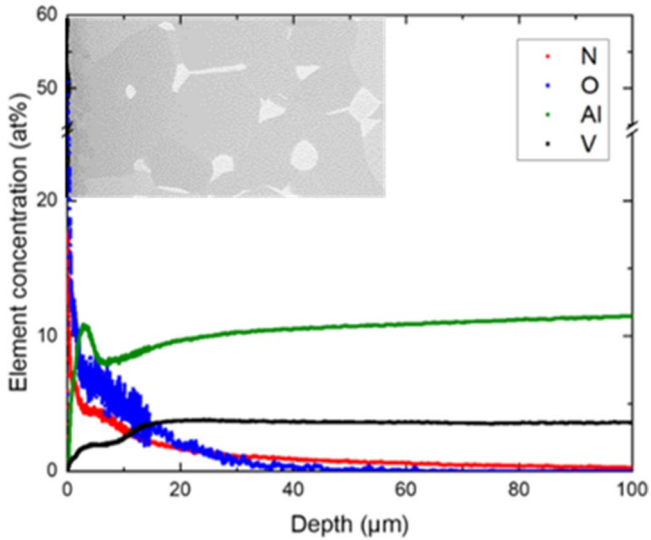


Figure 1. Composition profiles of nitro oxidized sample "SAMPLE C". The surface oxide has spalled off and only a shallow oxygen rich layer is remaining. Notice the high oxygen and nitrogen content in the diffusion tail. Inset: Corresponding SEM cross section at the same scale.

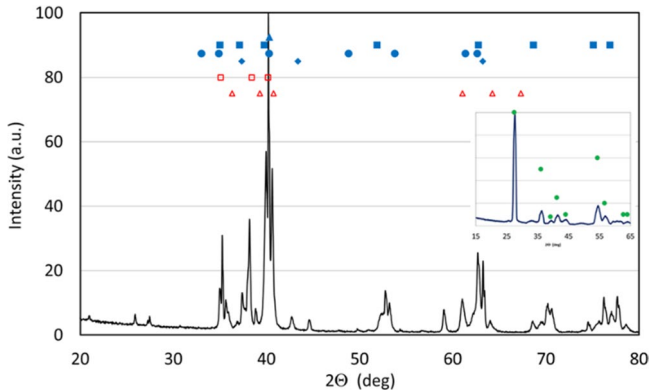


Figure 2. X-Ray diffraction pattern of nitro-oxidized sample "SAMPLE C". α -Ti (red squares) and possibly ϵ -Ti₂N nitride (red triangles) are identified as well as sub oxides Ti₂O₃, Ti₂O and Ti₃O (blue symbols). The tiny peaks are possibly due to the presence of Magnéli phases. In the inset is presented diffraction pattern of the spalled off layer that fits perfectly with the rutile TiO₂ peaks (green dots).

the presence of high superficial oxygen concentration, no TiO₂ oxide could be detected. This is consistent with the absence of O plateau in the composition GDOES profiles in Figure 1. In fact, the surface layer formed during the process spalled off upon cooling of the sample. The

thickness of this spalled of layer, identified using X-Ray diffraction as quasi pure Rutile oxide (see [Figure 2](#) inset), was determined to be 13 μm , based on cross section optical microscopy. Both GDOES and X-Ray diffraction analysis suggest that the major part of the nitride layer formed during the nitriding sequence has been transformed into oxide. Such a transformation has been observed already during titanium nitride thermal oxidation experiments (Desmaison et al., 1979). The diffusion tails, as measured by GDOES, extend to 60 and 100 μm for Oxygen and Nitrogen respectively.

A deep diffusion zone together with a stable hard compound surface layer, i.e. nitride based, is considered optimal when it comes to improving the mechanical properties. This first treatment did achieve a smooth decay of interstitial load and significant diffusion depth but at the cost of a surface layer spall-off. To remedy this problem, a treatment sequence with lower oxidizing potential, i.e. under gaseous oxygen at 750 $^{\circ}\text{C}$, was applied (SAMPLE D).

The spall-off of the surface layer is minimized and at least part of the nitrided layer formed during the nitriding phase of the treatment is preserved giving a peak in the nitrogen profile localized a few microns below the surface ([Figure 3](#)). $\epsilon\text{-Ti}_2\text{N}$ phase is clearly identified in the X-Ray diffraction pattern ([Figure 4](#)). The (002) peak of $\epsilon\text{-Ti}_2\text{N}$ at $2\Theta = 61^{\circ}$ is exalted, indicating a [001] texture of this phase. This texture has

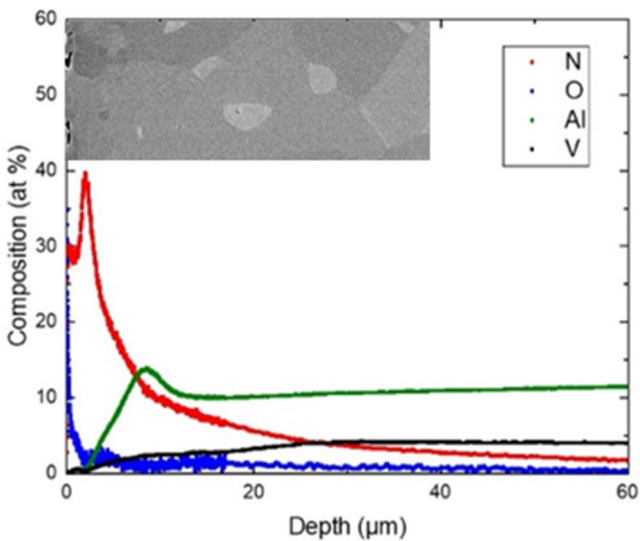


Figure 3. Composition profiles of nitro-oxidized sample "SAMPLE D". A nitrogen rich layer, with a composition close to Ti_2N , is present just below the surface. A very thin oxygen rich layer is also present at the extreme surface. Inset: Corresponding SEM cross section at the same scale.

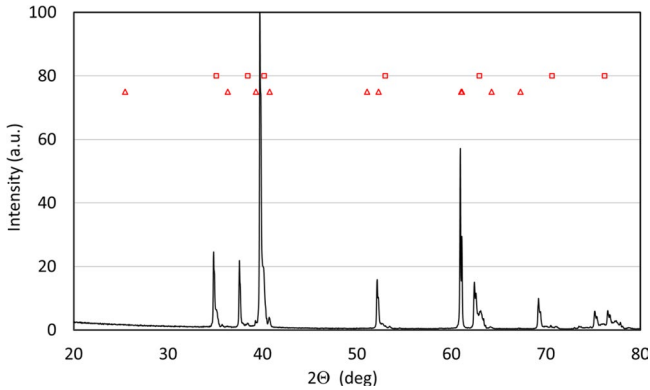


Figure 4. X-Ray diffraction pattern of nitro-oxidized sample "SAMPLE D". α -Ti (red squares) and ϵ - Ti_2N (red triangles) are the dominant phases, no oxide peak is visible. The intensity of the Ti_2N peak at 61° indicates the presence of a [001] texture.

already been observed in pure titanium nitriding experiments (Chen & Jaung, 1997; Drouet, Pichon, Dubois, Bourhis, & Christiansen, 2020). No oxide phase could be identified within the sensitivity of X-ray diffraction.

Hence, for all investigated conditions, surface layers of various thicknesses were formed. It is difficult to determine the exact nature of the surface layers as only the ϵ - Ti_2N compound can be identified unambiguously with the X-Ray diffraction surface analysis. However, the presence of very high nitrogen surface fraction in the GDOES profiles and the quite yellow colour of the treated surface observed for some samples indicate the presence of a very shallow δ -TiN layer. Although titanium oxides are formed during the mixed nitro-oxidizing process, they do not remain on the final sample due to spall off (SAMPLE C) and/or to the dissolution of the oxygen into the matrix during the vacuum diffusion step of the process (sample D).

Mechanical properties

Figure 5 presents the micro-hardness profiles obtained on samples nitrided and oxi-nitrided. The first feature is that the initial bulk hardness, marked by the horizontal grey line, is preserved in the bulk (within the scatter of the measures). The second important point is that for dual oxi-nitriding treatments (filled blue symbols) the hardness increase is more important and the hardening extends deeper in the material when compared to a single nitriding treatment (opened red symbols). If the hardness of the initial condition is considered a cut off value, nitriding for 8 h and 32 h results in an improved zone reaching a depth between

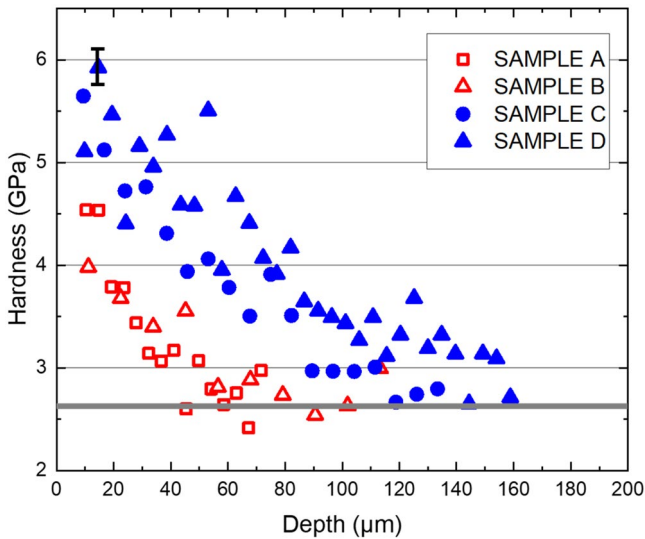


Figure 5. Hardness profiles obtained for the different treatments. In the case of mixed treatments (filled blue symbols), the hardness enhancement extends deeper in the material than for the stand alone nitriding sequences (open red symbols). The grey line indicates the materials hardness before treatment. The black error bar presents the experimental uncertainty of the hardness value measurement. It is not repeated on all points for clarity.

60 and 70 μm , although the exact depths are difficult to determine given the experimental scatter. On the other hand, dual treatments of similar total duration yield a depth of more than 120 μm . These data clearly evidence the advantage of dual treatments to provide a supporting diffusion zone. Noticeably, with a Vickers indent size of several microns, it was not possible to probe the relatively thin compound layers. In the case of pure nitriding, the supporting case, as defined from hardness profiles, under the compound layers remains quite thin. This diffusion zone extends much deeper for mixed treatments but also exhibits higher values of the maximum hardness as measured from the first Vickers indents.

Conclusion

Plasma assisted nitriding and oxidizing thermo-chemical surface treatments at moderate temperature were successfully applied to titanium grade 5 alloy. As a major result of the tested sequences, the use of two interstitial elements, nitrogen and oxygen, is proved to greatly enhance the efficiency of the treatments compared to a stand-alone nitriding. In the resulting supporting diffusion zone, both the diffusion depth and

the maximum hardness value ensure a smooth transition of the mechanical properties between the hardened surface layer and the core material. The hardness profiles extend to depth of very low interstitial concentration of both nitrogen and oxygen. This strongly suggests a very efficient strengthening effect of these two elements at low concentration, in particular for oxygen. Although micro hardness tests did not show any alteration of the core properties, the very long plateau at 850 °C may have non-negligible consequence on the microstructure, as for example grain coarsening, even if the temperature remains below the β transus of the α -Ti grains of this alloy. Complementary mechanical testing, like fatigue and wear behaviour and nano indentation are planned together with further structural characterization.

Disclosure statement

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