Effects of Plasma Immersion Ion Implantation (PIII) of Nitrogen on Hardness, Composition and Corrosion Resistance of Ti-6Al-4V Alloy

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Ti-6Al-4V samples have been treated by PIII processing at different temperatures (400–800 °C), treatment time (30–150 min) and plasma potential (100 and 420 V). Hardness measurements results showed an enhancement of the hardness for all implanted samples. XRD results detected the Ti2N phase and the best corrosion resistance was found for the samples processed at higher temperature and lower PIII time.

Keywords: Corrosion; Hardness; Plasma immersion ion implantation; Ti-6Al-4V; X-ray diffraction

I. INTRODUCTION

PIII was developed for the beneficial modification of surface-sensitive properties [1]. In analogy to conventional beam-line ion implantation, it uses energetic ions, mostly nitrogen, that are implanted into near-surface region of material. A sample is immersed in plasma and subjected to negative high-voltage pulses. In the electrical field, the ions are accelerated to high energies and incorporated into the sample [2]. This technique circumvents the line-of-sight and retained dose limitation inherent to conventional beam-line ion implantation, and is thus particularly suitable for large components possessing non-planar and complex geometries [3]. Most of the PIII processing was performed at low and moderate temperatures (< 400 °C) [4] and few works investigated the effects of the high temperature plasma immersion ion implantation (PIII) in Ti alloys [5-6]. Pichon et al. [6] carried out PIII treatment of Ti-6Al-4V alloys using R.F. plasma in the range of 200–800 °C. At the highest temperature (800 °C), a 2 μm nitride layer, composed of a mixture of TiN and Ti2N phases, has been attained and nitrogen has diffused to 20-30 μm in the alloy. In another work, Berberich et al. [5] performed PIII implantation of Ti-6Al-4V samples using Electron Cyclotron Resonance Plasma source with temperatures below 200 °C. After that, annealing procedures were accomplished on the samples. Annealing at temperatures above 500 °C, leads to the reduction of TiN phase and the formation of Ti2N deeper in the material. The hardness increases after annealing by a factor of 2.5 compared to the unimplanted state. Consequently, enhancing of the hardness and wear process of the materials due to the N-enriched layer caused by diffusion of N in the sample at high temperature PIII process can be expected. However, in previous studies, the corrosion behaviour of PIII treated Ti-6Al-4V samples at high temperature has not been investigated. So, the objective of this work is to study the effects of N-PIII on surface properties of Ti-6Al-4V alloys.

II. EXPERIMENTAL

The basic components of the PIII processing and their functions were already described elsewhere [7]. The novel parts of this system are the locally heated sample support (SS), and the electrical system to drive the coiled tungsten filament inserted inside the SS, including the high voltage pulse isolator transformer. As described in the previous paper, we used the commercial RUP-4 device to pulse the SS at the high negative voltages (nominal of 30 kV, 100 μs and 1.1 kHz maximum). The filament potential floats with the high voltage pulse while ~110V, ~5 A is used to heat the SS up to 800 °C which remains constant during the PIII treatment. Nitrogen gas was used as plasma source. For all experiments the following parameters were kept constant: pressure= 6x10⁻³ mbar, repetition frequency= 400 Hz, pulse length = 5 μs, plasma potential=400 V and pulse voltage = 5 kV. Three different sets of Ti-6Al-4V samples were PIII processed. The experimental conditions are shown in the table 1 and 2.

Table I. Experimental conditions for N-PIII treatment of Ti-6Al-4V samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Plasma Potential (V)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SET1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>800</td>
<td>30</td>
<td>420</td>
<td>12</td>
</tr>
<tr>
<td>3a</td>
<td>800</td>
<td>60</td>
<td>420</td>
<td>14</td>
</tr>
<tr>
<td>12a</td>
<td>800</td>
<td>90</td>
<td>420</td>
<td>14</td>
</tr>
<tr>
<td>7a</td>
<td>800</td>
<td>120</td>
<td>420</td>
<td>19</td>
</tr>
<tr>
<td>15a</td>
<td>800</td>
<td>150</td>
<td>420</td>
<td>24</td>
</tr>
<tr>
<td>SET2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>60</td>
<td>420</td>
<td>8.5</td>
</tr>
<tr>
<td>8</td>
<td>550</td>
<td>60</td>
<td>420</td>
<td>11.5</td>
</tr>
<tr>
<td>16a</td>
<td>700</td>
<td>60</td>
<td>420</td>
<td>10.5</td>
</tr>
<tr>
<td>3a</td>
<td>800</td>
<td>60</td>
<td>420</td>
<td>14</td>
</tr>
</tbody>
</table>

The reduction of the plasma potential was obtained through the electron shower which allowed the decrease of the plasma potential from 420 V to around 100 V. By actuating this electron shower at different powers, the potential of the plasma can be controlled and it was measured with a Langmuir probe. To characterize the Ti-6Al-4V samples subjected to high temperature PIII we used X-ray diffraction (Philips 3410 diffrac-
Nanohardness measurements were performed on the Ti-6Al-4V samples treated at different experimental conditions as presented in table I. Enhancement of the hardness for all PIII treated samples was observed. The hardness values were higher for the PIII-treated samples at higher temperatures (700-800 °C) than those treated at lower temperatures (400-550 °C) as shown in the table I. The hardness values shown in the table I are associated to the maximum values of the obtained hardness profile. This mechanical behaviour is due to the higher nitrogen diffusion in the PIII treated samples at higher temperatures. There was an enhancement of the hardness from approximately 8.5 GPa up to 14 GPa for the set 2 samples as the PIII process temperatures rises from 400 to 800 °C in 60 minutes of treatment. Therefore, we obtained a hardness improvement of about 2.5 times compared to the untreated specimen. This behaviour is in agreement with Berberich et al. [5] results since they obtained for N-PIII at 200 °C in Ti-6Al-4V alloy an enhancement factor of 2.5 compared to the unimplanted state, after annealing of the samples at 650 °C. At 800 °C, an increase of the hardness (12-24 GPa) was also observed as the PIII process time varied in the range of 30-150 minutes (set 1), respectively. There was an improvement of the hardness of nearly 4 times in comparison with the untreated standard sample, for the case of 150 minutes treatment at 800 °C. The obtained hardness value of 24 GPa is in accordance with the one reported by G.B. Souza et al. [8] in their work about hardness and elastic modulus of ion-nitrided titanium measured by nanoindentation. They showed in the table I are associated to the maximum values of the obtained hardness profile. This mechanical behaviour is due to the higher nitrogen diffusion in the PIII treated samples at higher temperatures. For all samples analyzed, the cathodic branches of the polarization curves exhibit current densities that decrease as the applied potential increases. Cathodic reaction is assumed to be proton and/or oxygen reduction. The anodic branches of the polarization curves of all Ti-6Al-4V samples showed a large passive region (~1.5 V) where the current density was kept constant. This region is associated with the formation of a protective film [9]. Small oscillations of the current density are related to the consecutive formation and repassivation of microsize pits, usually called metastable pits [9].

Figure 2 also shows that, the current density of the passive regions of the set 1 samples increase from 3x10^{-7} up to 3x10^{-6} A cm^{-2} with the N-PIII treatment time increasing from 30 to 150 minutes. The passive current density for PIII-treatment of 30 minutes is approximately the same as for the untreated sample, being about 4 times higher than the one of the untreated specimen (8.5x10^{-6} A cm^{-2}). The corrosion resistance decreases with the PIII-treatment time but the current densities are rather low and a good corrosion resistance is still maintained. This behavior can be explained as increase of the PIII treatment time (30-150 min), resulting in the increase of N penetration (30-150 nm), not sufficient to form a protective nitried layer on the surface.
Figure 3 shows the polarization curves for untreated and treated samples (90 min) obtained at different PIII treatment temperatures (set 2) in 3.5% NaCl. The polarization curves exhibited the same characteristics as detailed in the Fig. 2. As the temperature increases from 400 up to 800 °C, the passive current density decreases from $3 \times 10^{-6}$ A cm$^{-2}$ to $1.5 \times 10^{-6}$ A cm$^{-2}$. This behaviour is coherent because there is more heterogeneity on the sample surface treated in low temperature than the one treated in high temperature. So the corrosion process begins at the surface defects that provoke the discontinuity of the passive film. Besides the passive current density ($1.5 \times 10^{-6}$ A cm$^{-2}$) is about 17 times higher than untreated sample the corrosion resistance is still good.

Some preliminary results from PIII treatment at different plasma potential of 420 V and 100 V are shown in Fig. 4. The same characteristics pointed for the others analyzed polarization curves (Fig. 2 and 3) were observed.

For both curves the first passive region is around $2.3 \times 10^{-7}$ A cm$^{-2}$. A second passive region above 1.6 V was evidenced, however the passive current density for the sample treated at 100 V is about one order of magnitude lower than the one for the sample treated at potential plasma of 420 V. So, this behaviour suggests that the PIII-treated samples at lower plasma potential (100 V) are more corrosion resistant in strong oxidizing media. For all analyzed samples (Fig. 2-4), the polarization curves showed an apparent active/passive region. Ramires et al. [10] inferred that this process is associated with the increase of the oxide layer thickness on the surface, while Marino et al. [11] related it to the formation of the secondary...
FIG. 4: Polarization curves at 550 °C, 600 min: (–) with plasma potential of 100 V, (...) with plasma potential of 420 V.

oxide or a phase transformation induced during the potentiodynamic scan. Anyway, a second passive region above 1.6 V was only evidenced for the PIII-treated samples while for the untreated specimen the corrosion current density increased rapidly above 2.5V.

IV. CONCLUSIONS

Nitrogen PIII in Ti-6Al-4V alloy at high temperature (800 °C) and 150 min treatment time increases the surface hardness by forming crystalline Ti$_2$N phase. However, the best corrosion resistance was found for the samples processed at higher temperature and lower PIII time (30min). PIII treatment with variation of the plasma potential produces more intensive effect on the surface hardness than on the corrosion resistance of the Ti-6Al-4V alloys.

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