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Electrochemical and Tribological Behaviour of Ti6Al4V Subjected to the Duplex SMAT/Plasma Nitriding

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Abstract: In this work, SMAT (surface mechanical attrition treatment) was performed on Ti6Al4V. Plasma nitriding of the SMATed samples was investigated in comparison with coarse-grained samples. The samples were characterized using optic microscope, SEM, TEM and Vickers microhardness tester. The results showed that a significantly thicker compound layer with higher hardness was obtained for the SMATed samples when compared with un-SMATed samples after nitriding. Corrosion resistance of Ti6Al4V in a Ringer's solution was studied by electrochemical techniques including open circuit potential measurement, potentiodynamic polarization and EIS (electrochemical impedance spectroscopy). Overall, our results identified the beneficial impacts of the duplex SMAT/nitriding treatment on corrosion behaviour of Ti6Al4V. Wear tests were also performed on a ball-on-disc tribometer where the treated samples were rubbed against a 6 mm diameter alumina ball under a normal load of 5 N using Ringer's solution as lubricant media. The friction coefficient of the SMATed and nitrided samples was reduced compared to the untreated samples. Wear rates demonstrated that SMAT combined with nitriding improved wear resistance of Ti6Al4V alloy.

Key words: Surface mechanical attrition treatment, plasma nitriding, corrosion, wear, Ti6Al4V.

1. Introduction

Ti6Al4V alloy has been widely used as a suitable material for several applications in various sectors such as aerospace, marine and biomedical. In addition, Ti6Al4V represents at least 45% of total titanium application [1]. Although this alloy presents excellent properties and good corrosion resistance, its mechanical applications are limited because of the poor wear resistance property due to its relatively low surface hardness [2-4]. Hence, to solve this issue, various surface treatments were used to improve the properties of Ti6Al4V and enhance its behaviour.

Over the past years, researchers have studied many different types of surface techniques in order to improve surface properties. Several treatments are currently used including plasma nitriding [5, 6], shot peening [7-9], surface nanocrystallization [10] and SMAT (surface mechanical attrition treatment) [11, 12].

It has been mentioned in the literature that most of materials damage such as corrosion, wear and fretting fatigue occur on the surface. Therefore, it is necessary to optimize the microstructure and the properties of materials by means of techniques mentioned above in order to improve their global behaviour and increase their lifetime [13-15].

SMAT is a promising method which can generate a nanocrystalline surface layer. Actually, SMAT induces localized plastic deformation that results a formation of nanocrystalline layer without modifying significantly the chemical composition of the material [16, 17]. Moreover, this method leads to getting materials with excellent properties, in which the coarse-grained matrix provides the ductility while nanocrystalline layer furnish good surface properties. The SMAT process has already been applied to

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several metallic materials such as titanium [18, 19], aluminum [20, 21], iron [22, 23], stainless steel [24, 25], carbon steels [26], etc.

The nitriding is a surface treatment that can improve wear, corrosion resistance and mechanical behaviour of metallic materials [27-32]. In plasma environment, nitrogen is transferred to the metal, and then penetrates into the surface by diffusion which leads to the formation of a modified layer [33]. The diffusion of nitrogen is accelerated by an increase of the number of grain boundaries and of the dislocation density. Thus, the activation energy for the diffusion of nitrogen will be significantly reduced due to the grain boundaries in nanocrystalline materials; that will contribute to an amelioration of the nitriding kinetics [34].

Recently, duplex treatment (SMAT/nitriding) has become an innovative technique to improve the surface characteristics of various materials [35]. The diffusion in nanostructured materials has become an attractive topic able to ameliorate surface properties of materials. The scientific interests were focused not only on reducing the treatment temperature and/or time [35, 36] but also to improve the kinetics of nitrogen diffusion [37, 38]. However, few studies have been carried out on the duplex treatment SMAT/nitriding of titanium alloys.

The SMAT process was developed to generate a nanostructured surface layer on metallic materials [39-44] by grain refinement mechanism. Furthermore, it was reported that SMAT can shorten the gas nitriding temperature and/or decrease nitriding duration [42, 45-47]. The defects induced by SMAT (dislocations, twins) could accelerate the atomic diffusions promoting the dynamic process of chemical reaction.

In this study, the Ti6Al4V alloy was first treated by SMAT and then plasma nitrided. We investigated the effects of the duplex treatment SMAT/nitriding on the corrosion and wear behaviour of Ti6Al4V. The objectives of the present work were to investigate the possibility of using the duplex SMAT/nitriding process to improve the wear and corrosion resistance of Ti6Al4V. The microstructures of the SMAT nitrided samples were investigated.

2. Experimental Details

2.1 Material and Surface Treatments

A titanium alloy Ti6Al4V with the chemical composition of (wt%): 5.5 Al, 3.5 V, 0.3 Fe, 0.08 C, 0.2 O, 0.05 N and Ti balance was used. The samples were cut to 20 mm × 10 mm × 5 mm plates. The substrate presented a microhardness of about 350 $HV_{0.2}$. The Ti6Al4V plates were prepared for SMAT in order to generate a nanostructure layer. The SMAT technique has been described in our earlier paper [48].

SMAT of Ti6Al4V was performed using 2 and 3 mm balls for 15 and 20 min. About 20 mm separate the sample and the balls. The optimized parameters used for SMAT treatment of the Ti6Al4V alloy were as following: (1) SMAT1: Amplitude = ± 100%; Time = 15 min; Diameter of beads = 2 mm and (2) SMAT2: Amplitude = ± 100%; Time = 20 min; Diameter of beads = 3 mm.

The samples (SMATed and coarse-grained) were cleaned carefully with acetone then immediately subjected to plasma nitriding. A DC-pulsed plasma nitriding furnace was employed (Applied voltage = 0-1,000 V, the pulse frequency = 40 kHz). Then, plasma nitriding was carried out in a 20% N2+80% H2 gas mixture at a pressure of 500 Pa [49]. Nitriding of SMATed and coarse grained samples was carried out at 580 °C for 20 h. After nitriding during the required time, the samples were cooled to a constant 25 °C.

2.2 Samples Characterization

The microstructure of the cross-section of the treated samples was examined using an optical microscopic, SEM and TEM. Before characterization, the samples surfaces were polished by a solution (50 vol.% HCl + 25% HNO3 + 25% H2O) and finally

dried in order to reveal the nitrided layer. Moreover, microhardness profiles were measured by a Vickers microhardness tester using a 20 g load. Five indentations were carried out and averaged for each point.

Electrochemical experiments were carried out using Gamry electrochemical workstation at 37 °C, and a Ringer's solution (NaCl 8.6 g/L, $CaCl_2$ 0.322 g/L and KCl 0.3 g/L) was used as the corrosive medium. A conventional three electrode system, with a platinum plate as counter electrode and SCE (saturated calomel electrode) as reference, was used. Using a suitable software approximation, Tafel extrapolation was employed in order to determine the electrochemical parameters.

Wear tests were performed on a CSM tribometer in Ringer's solution at 37 °C by using a ball-on-disc contact configuration. The tribological tests were carried out on samples having dimensions of 20 mm × 10 mm × 5 mm. For reference, fretting wear tests were also performed on untreated samples. Tests were conducted against an alumina ball at a frequency of 1 Hz and a normal load of 5 N; the sliding time was 1 hour. The properties of alumina balls are: Vickers hardness = 1950, elastic modulus = 382 GPa, Poisson's ratio = 0.24. The wear properties were characterized by measuring the friction coefficient and the volume loss.

3. Results and Discussion

3.1 Microstructural Characterization

Fig. 1 shows the thickness of the nitrided layer of Ti6Al4V samples observed using an optical microscope. The observations for three samples after nitriding show that SMAT modifies the thickness of the nitrided layer. Also, we observe that for both samples (nitrided SMAT1 and nitrided SMAT2), the thickness of the nitrided layer increased after SMAT. Actually, the depths of the nitrided layer are about 12±2 μm and 15±2 μm for the nitrided SMAT1 and the nitrided SMAT2, respectively. However, for the nitrided sample (without SMAT), the thickness of the nitrided layer is about 9±2 μm. Furthermore, it can be clearly seen that the thickness of the nitrided layer is not uniform, indicating preferential diffusion of nitrogen into the material along grain boundaries and dislocations [46].

Fig. 2 presents SEM and TEM micrographs of the transversal view of Ti6Al4V sample after SMAT/nitriding. These observations clearly show an important density of twins. TEM micrographs of the top surface of SMATed and nitrided Ti6Al4V sample show nano-grains with size between 50 nm and 100 nm.

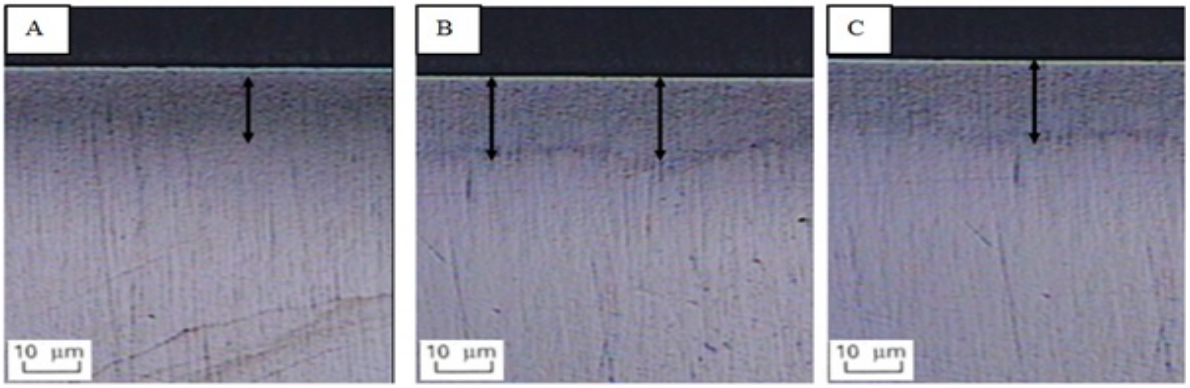

Fig. 1 Cross sectional optical microscopy of Ti6Al4V. (A) Nitrided coarse-grained; (B) Nitrided SMAT1; (C) Nitrided SMAT2 samples.

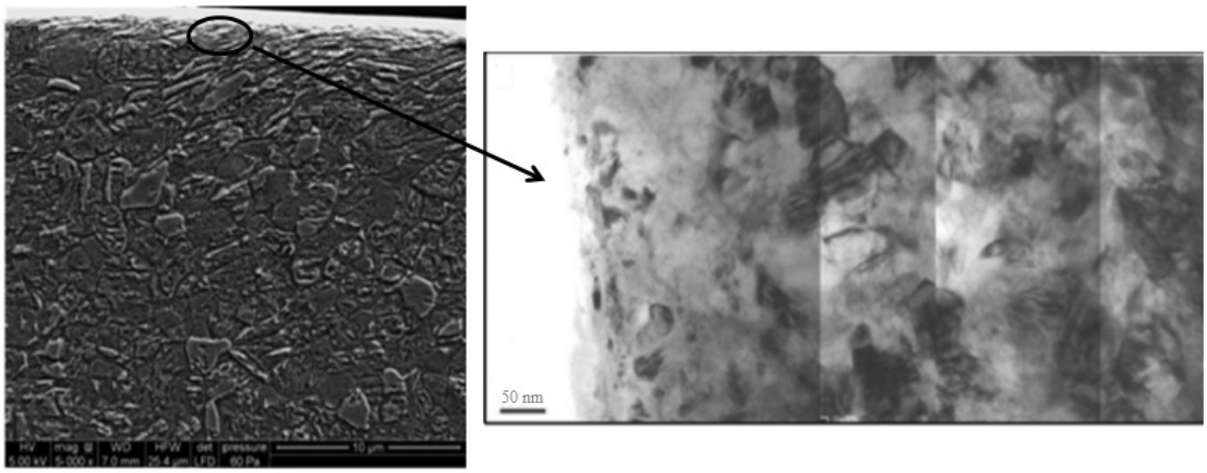

Fig. 2 Cross-sectional SEM (left) and TEM (right) micrographs of Ti6Al4V sample after SMAT2/nitriding.

3.2 Microhardness Measurements

In order to gain information regarding the effect of SMAT/nitriding on the hardness, vickers micro-hardness measurements were carried out through the cross-sections of the samples.

The average micro-hardness value measured on the topmost surface of the SMATed nitrided sample was 1,050 $Hv_{0.2}$. A remarkable increase of micro-hardness value was found for the SMAT nitrided samples in comparison with untreated sample. This increase can be attributed to the dispersed and refined nitride particles and the solid solution of nitrogen in α-Ti exerting the hardening effects [50].

It has been noted, in recent studies, that nanomaterials tend to have better mechanical, physical and chemical properties than traditional coarse-grained polycrystalline materials. This is can be explained by the Hall-Petch relation [51]. In the SMAT-nitrided sample, the grain size of the top surface layer varied between 10 and 50 nm [52] and the improvement of hardness value may be attributed to the formation of the nano-scale nitrides at lower temperature [53, 54].

3.3 Corrosion Behaviour

3.3.1 Open Circuit Potential

The current vs. time plots of the nitrided sample and those subjected to SMAT/nitriding is shown in Fig. 4. The potential monitoring was performed during 24h in Ringer's solution.

Initially, the OCP (open circuit potential) was approximately -0.4 V/SCE for the coarse-grained nitrided sample. For both treated samples (SMATed and nitrided), the OCP increases in the noble direction indicating the formation of a passive film on the metal surface and the growth of an oxide film which became compact with time [55, 56]. Sun et al. [52] have also observed a similar trend for a titanium layer of a Ti/Al clad sheet composite.

The figure shows that the potential values of the SMATed and nitrided specimens increase and stabilize at values close to -0.12 V/SCE. Thus, for the titanium alloy a significant influence of the SMAT/nitriding treatment can be noticed on the evolution of the open circuit potential.

3.3.2 Polarizations Curves

Fig. 6 shows typical polarization curves of the coarse-grained and SMAT nitrided samples in Ringer's solution. The scanning voltage ranges between -500 mV and 1,500 mV at a rate of 1 mV/s. In addition, values of current density corrosion (I_{corr}), corrosion potential (E_{corr}) for the three Ti6Al4V samples are shown in Table 1. Generally, the corrosion current density is considered as an important parameter for the assessment of the corrosion rate [57].

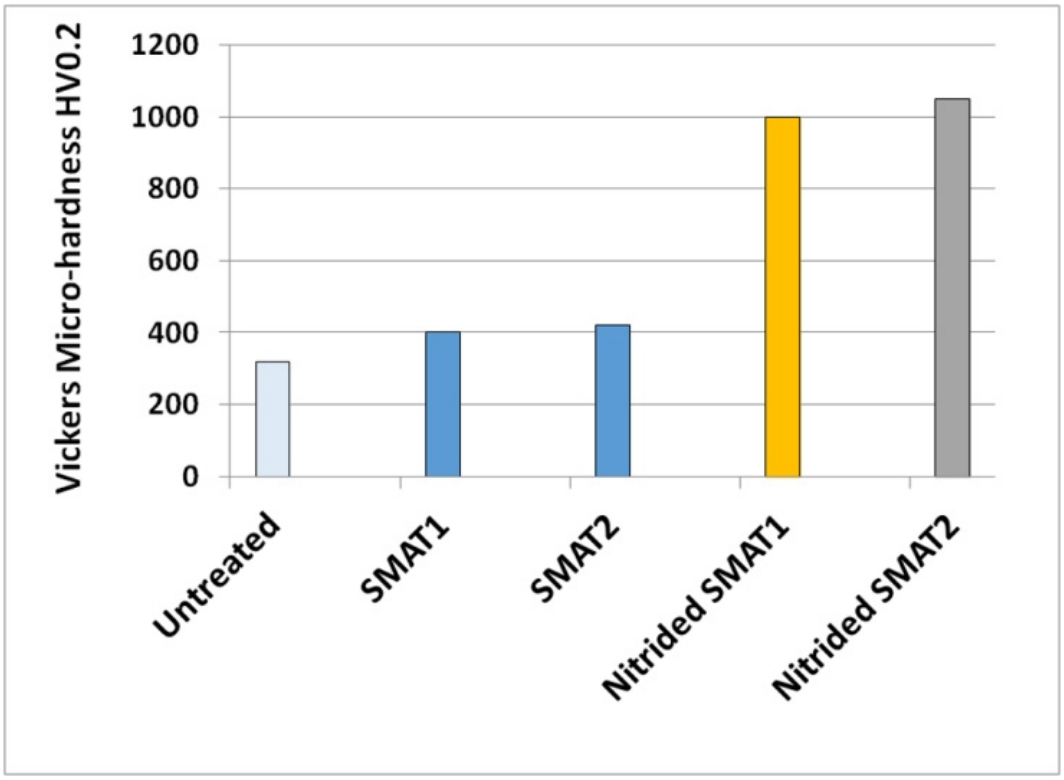

Fig. 3 Surface hardness of Ti6Al4V samples before and after SMAT nitriding.

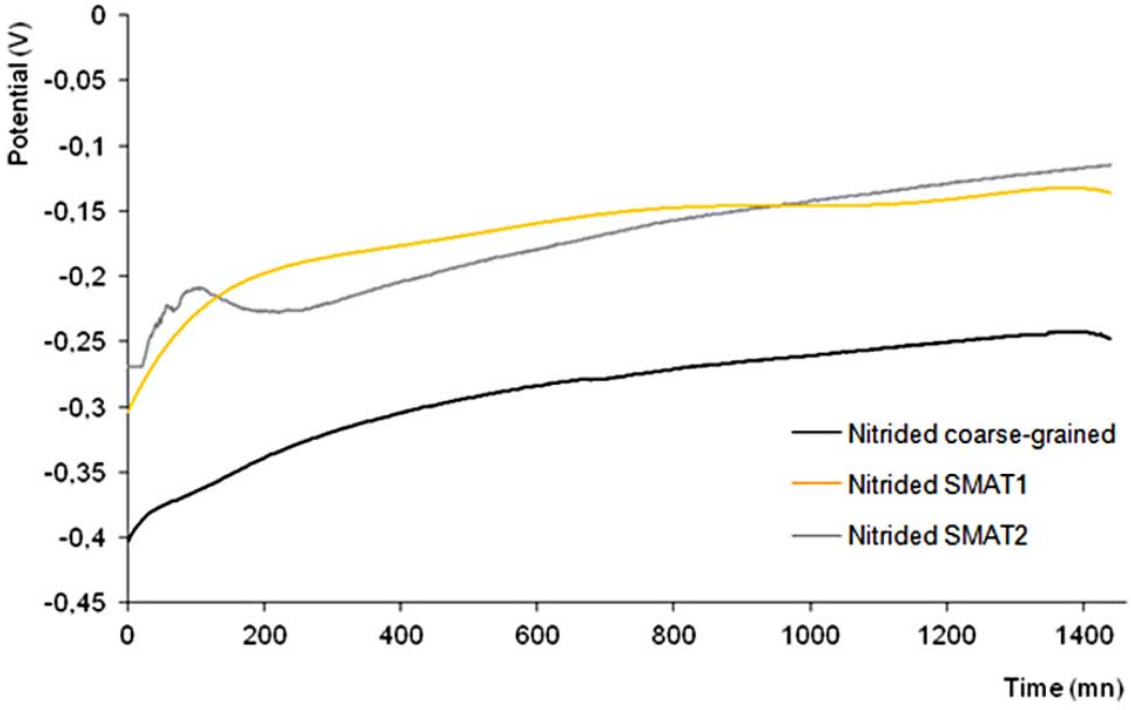

Fig. 4 Evolution of the OCP of Ti6Al4V samples immersed in Ringer's solution.

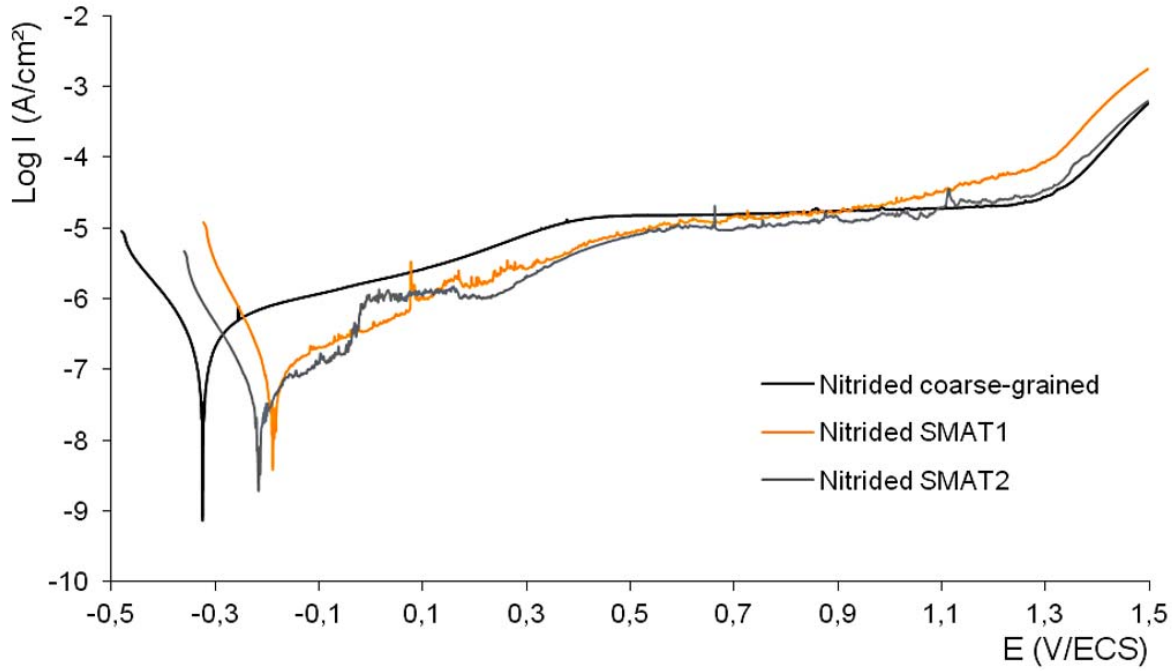

Fig. 5 The potentiodynamic polarization curves of Ti6Al4V samples before and after SMAT/nitriding.

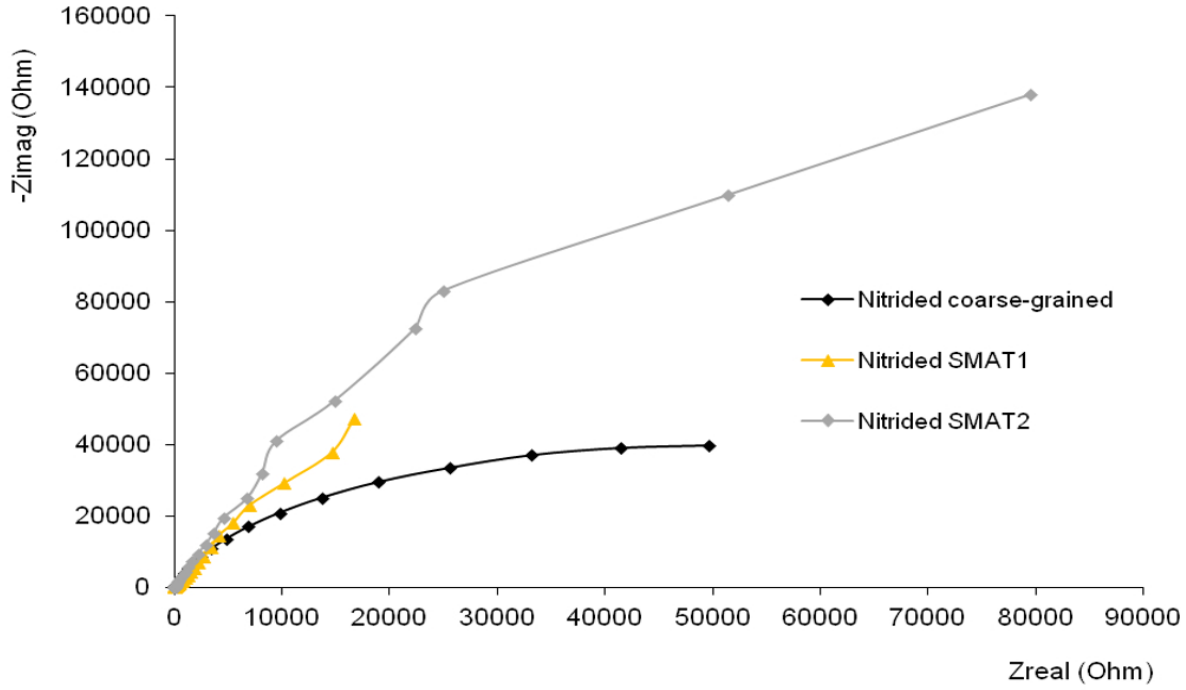

Fig. 6 Nyquist diagramm of Ti6Al4V samples in Ringer's solution.

Table 1 Corrosion parameters from polarization plots.

Nitrided sample	Without SMAT	SMAT1	SMAT2
E_{corr} (mV)	-320	-193	-216
I_{corr} (nA/cm^2)	72	31	18

According to the polarization curves, the Ti6Al4V samples present a typical active-passive transition in the Ringer's solution. Following the anodic active region, a very wide steady passive zone with low current density extending to about 1.3 V is always obtained, indicating perfect passivity. Nevertheless, at higher potential values, oxygen reactions and transpassive dissolution lead to an increase of the anodic current [58].

Compared to the coarse-grained nitrided sample (E_{corr} = -320 mV/SCE and I_{corr} = 72 nA/cm^2), the SMAT nitrided samples present high values of corrosion potential (about -193 mV/SCE for the SMAT1-nitrided sample), and low values of the current density (18 nA/cm^2 for the SMAT2-nitrided sample). This nobler corrosion behaviour may be attributed to the nitrided layer formed on the surface. It is obvious that the nitrided layer provides an excellent corrosion resistance due to the presence of N atoms.

In the present work, the ameliorated corrosion resistance of the SMAT nitrided samples compared to that of the coarse-grained nitrided sample can be explained not only by the significantly thicker nitrided layer formed on the surface but also by the reduced grain size induced by SMAT [50]. In conclusion, the duplex SMAT/nitriding treatment has a beneficial effect on corrosion behaviour of Ti6Al4V.

3.3.3 Electrode Impedance spectroscopy tests

The EIS measurements were carried out using the 10 kHz to 10 mHz frequency range by applying a sinusoidal potential signal of ±5 mV. The obtained impedance spectra were analyzed using Gamry EIS300. Nyquist graphics of the impedance measurements are presented in Fig. 6; the real impedance is plotted vs. the imaginary impedance at each frequency for Ti6Al4V samples. According to impedance test results, the best result is observed for the SMAT2 nitrided specimen. Actually, the diameter of the capacitive semicircle in the Nyquist plot increases for the SMAT2 nitrided sample compared to the coarse-grained nitrided sample. It can be deduced that the corrosion resistance of Ti6Al4V can be increased by the SMAT/nitriding treatment under specific conditions (SMAT and nitriding parameters).

The equivalent circuit in Fig. 7 is proposed to fit the experimental data in order to determine the electrochemical parameters. In this equivalent circuit, Rs (Ω.cm^{-2}), Rtc (Ω.cm^{-2}) and CPE (constant phase element) represent the electrolyte resistance, the charge transfer resistance and the capacitance behaviour of the passive oxide layer, respectively.

Bode plots for the three Ti6Al4V samples are shown in Fig. 8. At low and medium frequencies, a

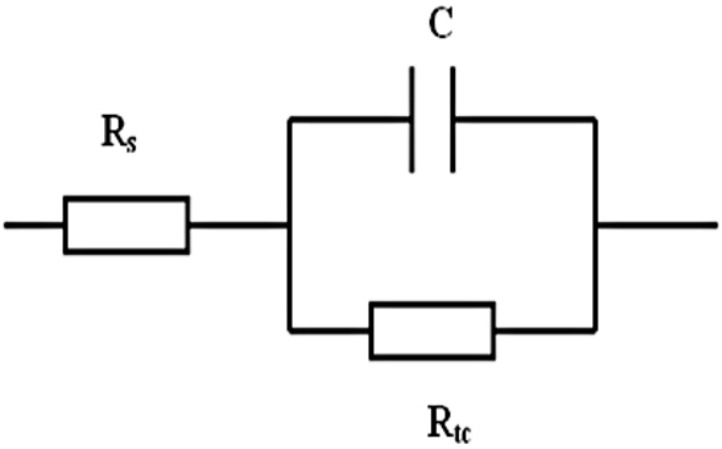

Fig. 7 Equivalent circuit used to fit EIS spectra.

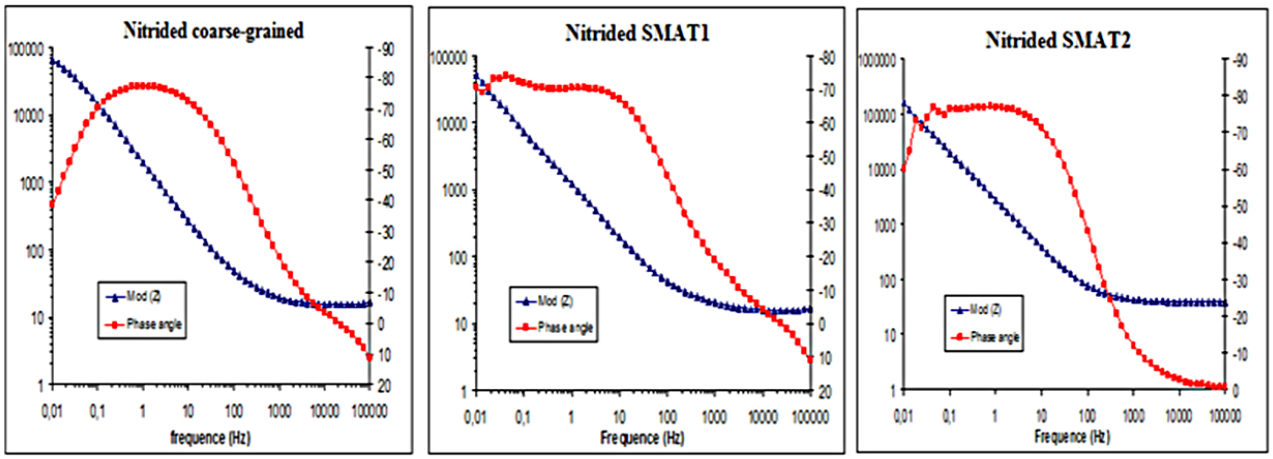

Fig. 8 Bode diagrams of Ti6Al4V samples in Ringer's solution.

Table 2 EIS data simulation for Ti6Al4V before and after SMAT/nitriding.

Nitrided sample	R_S (Ω)	$R_{tc} \times 10^3$(Ω)	C_{dl} (μF)
Without SMAT	16.94	58.93	82.83
SMAT1	17.55	66.16	78.2
SMAT2	41.55	220	66.4

high impedance value of the order of 10^4-10^5 Ω/cm^2 was obtained, which could be explained by a good corrosion resistance for the SMAT nitrided samples.

The fitting quality of the equivalent circuit (CPE) can be estimated by the error distribution between the experimental and simulated data. Several trails were made in order to establish which CPE fits better the experimental impedance data. The simulated values obtained are shown in Table 2.

R_{tc} values increase after SMAT/nitriding treatments and reach a maximum value of 220 kΩ for the SMAT2-nitrided sample. This increase is associated with the formation of a passive layer in Ringer's solution on the surface of sample leading to an improvement of the corrosion properties of Ti6Al4V.

The EIS results obviously indicate that there is significant effect of the duplex SMAT/nitriding process on corrosion behaviour of Ti6Al4V.

3.4 Wear Behaviour

3.4.1 Friction Coefficient

Fig. 9 shows the values of the friction coefficients of treated samples of titanium alloy against the alumina contact. As shown in the figure, the untreated sample exhibits an average friction coefficient of 0.38. This friction is greatly reduced in the presence of SMAT treatment. Indeed, for an applied load of 5 N, the friction coefficient of the treated samples (SMAT1 and SMAT2) is about 0.27. This decrease in friction coefficient can be attributed to the increase of surface hardness after SMAT (Fig. 3). It has also been cited that the refined grain size of nanocrystalline alloys leads to lower friction coefficient [59]. The SMAT/nitriding treatment seems to have little effect on values of friction coefficients of the two SMATed nitrided samples which have a coefficient of friction of 0.26.

3.4.2 Volume Loss

Fig. 10 shows the volume loss after the wear test for the samples before and after SMAT/nitriding. It is clear that the wear loss volume of the two samples (SMAT1 and SMAT2) is less than that of untreated sample, indicating that the wear resistance of the two samples was improved by SMAT. Actually, the value of wear loss of the coarse-grained (without SMAT) sample is 0.47 mm^3, this value has decreased after SMAT to reach 0.41 mm^3 for both SMATed samples. This can be explained mainly by the formation of

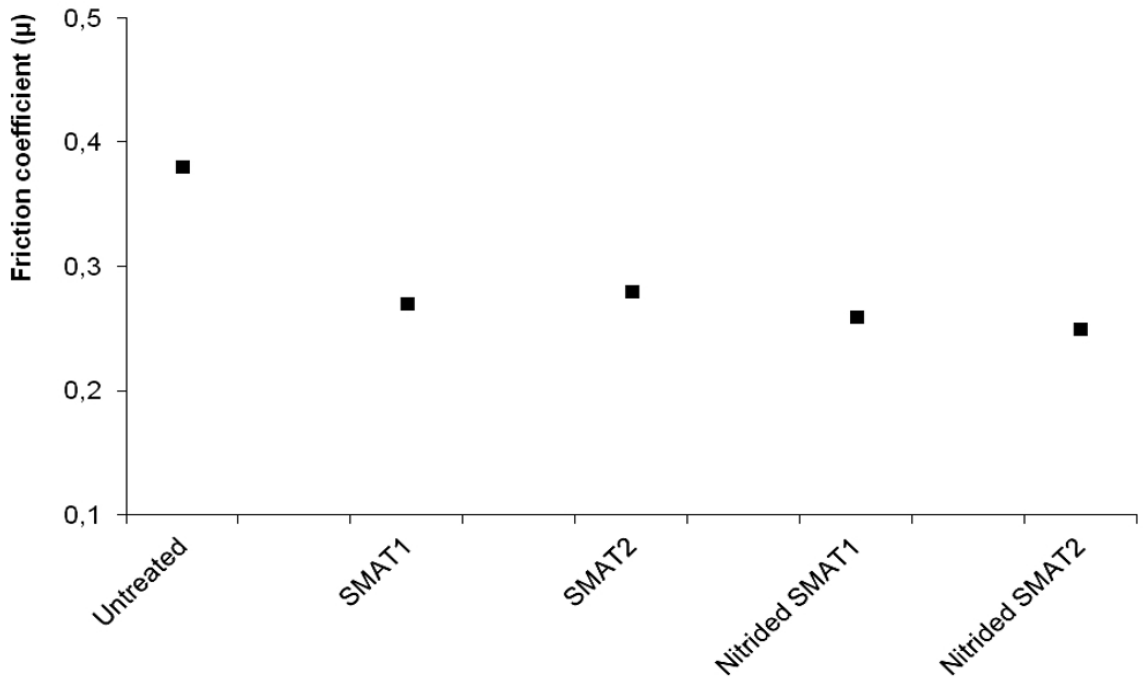

Fig. 9 Friction coefficient of untreated sample and SMATed and/or nitrided samples.

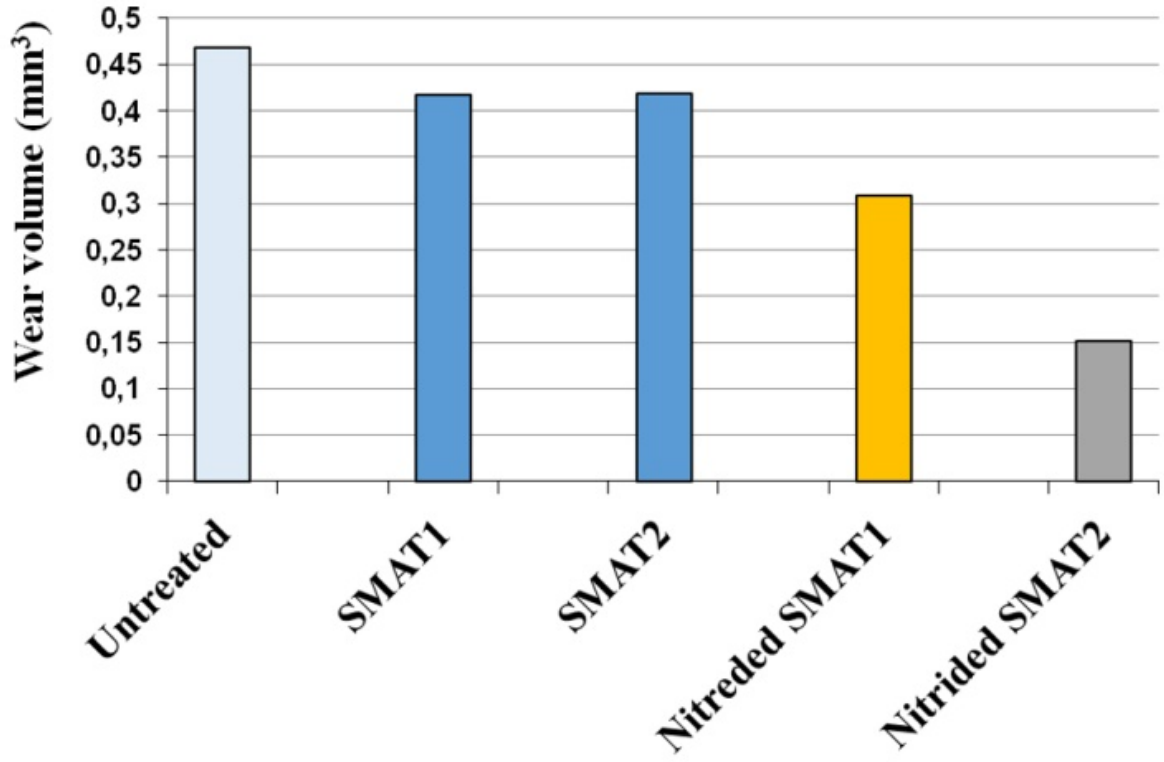

Fig. 10 Comparison of wear loss obtained from weight loss method between the untreated and treated samples in Ringer's solution.

nanocrystalline layer and higher surface hardness; the volume loss decreases when the surface hardness increases. In addition, the reduction in the friction coefficient and wear loss of treated samples can be attributed to the small contact area between the test samples and alumina ball counterpart [60].

The wear volume losses of the SMAT nitrided samples decrease significantly compared to those of the untreated sample. The duplex treatment SMAT/nitriding significantly improves wear resistance of the titanium alloy; the SMAT2-nitrided sample has a wear volume of 0.15 mm^3 wear corresponding to a decrease of 32 mm^3 compared to the untreated case.

All these observations are consistent with the surface micro-hardness values: the values of the volume loss are inversely related to the hardness of samples, because in the harder sample, the indentation depth in the sample is smaller, so that the force needed in the plastic deformation is diminished.

Above experimental results indicated that the SMAT/nitrdiding treatment leads to the improvement of wear resistance of Ti6Al4V. These findings might be of high interest for biomedical applications.

4. Conclusion

The objective of the present work was to improve the corrosion resistance and triboligical properties of titanium alloy Ti6Al4V by the duplex SMAT/nitriding process.

Electrochemical corrosion tests indicated that the coarse grain nitrided sample showed lower impedance, and higher corrosion current density, as compared to the SMAT nitrided samples. The above results indicated that SMAT/nitriding could help in preventing release of metal ions from the biomaterial in physiological environment. In addition, results have revealed a better stability of the passive film in Ringer's solution with a net increase of free potential of samples treated with the duplex SMAT/nitriding process.

The surface hardness of the SMAT-nitrided samples was much higher than those of the SMATed samples without nitriding. The average friction coefficients obtained on the different samples did not show a noticeable difference between the SMATed samples before and after nitriding. However, the wear and corrosion resistance was remarkably enhanced in the case of SMATed nitrided samples.

The SMAT/nitriding treatment could be an effective method for modifying properties of current materials to reach a new generation of materials used for biomedical applications.

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