



Corrosion and tribocorrosion behavior of Ti6Al4V/xTiN composites for biomedical applications

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Abstract: The corrosion and tribocorrosion behavior of Ti6Al4V/xTiN ($x=0, 5, 10$ and 15 , vol.%) composites fabricated by solid-state sintering and their relationship with the microstructure and microhardness were investigated. Simulated body conditions such as a temperature of $37\text{ }^{\circ}\text{C}$ and a simulated body fluid were used. The main results demonstrated a microstructural change caused by the α -Ti stabilization due to solid-solution of nitrogen (N) into the titanium (Ti) lattice, producing a maximum hardening effect up to 109% for the Ti64 matrix by using 15 vol.% TiN. Corrosion potentials of composites changed to more noble values with the TiN particle addition, while corrosion current density of samples increased as an effect of the remaining porosity, decreasing the corrosion resistance of materials. However, changes to a less passive behavior were observed for samples with 15 vol.% TiN. The non-passive behavior of composites resulted in the reduction of the potential drops during rubbing in tribocorrosion tests. Besides, an improvement of up to 88% of the wear rate of composites was seen from the solid-solution hardening. The results allowed to understand the relationship between composition and sintering parameters with the improved tribocorrosion performance of materials.

Key words: Ti64 alloy; composites; powder metallurgy; microstructure; corrosion; tribocorrosion

1 Introduction

The mechanical and chemical properties of Ti alloys are of interest to the biomedical field as a result of their biocompatibility with the human tissue and bones [1], nevertheless, wear resistance

of these alloys has been reported to be one of the main causes of failure [2]. Ti6Al4V (Ti64) alloy is one of the most preferred Ti alloys due to its unique combination of the properties such as excellent corrosion resistance, good toughness, low density, high strength, and relatively low elastic modulus [3,4]. However, its poor wear resistance

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was also reported which contributes to the degradation of the superficial protective oxide layer. This disadvantage limits the applicability of the alloy in different fields and especially, in the biomedical industry [5].

In order to improve the properties of Ti and its alloys, several types of ceramic such as the case of oxides [6], carbides [7–10], borides [11–13], and nitrides [14,15], have been used as reinforcements. They are usually incorporated into the matrix using powder metallurgy (P/M) techniques which involve in situ reactions of the reinforcement with the matrix [16–19]. The addition of reinforcement particles has demonstrated to modify the features of the matrixes in terms of the hardness, density and microstructure, even with small amounts of ceramic particles [20,21]. Those changes usually influence positively the material response against wear and corrosion. For instance, the in-situ formation of TiC and TiB reinforcement due to the addition of B₄C into a Ti64 matrix increases the hardness of composites despite the decrement in density. This hardening effect reduced the wear rate in approximately 35% and, effectively decreased the corrosion current density [22]. Additionally, the load-bearing capacity of the added particles denotes a strengthening mechanism which provides wear protection to the matrix [23]. On the other hand, the processing parameters in the PM process play an important role in the final properties of the composites. For example, the usage of an assisted-pressure system, higher sintering temperature, and long time, facilitate the fabrication of denser and harder materials [24]. In addition, P/M has demonstrated to be a capable method to improve the characteristics expected for biomaterials such as biocompatibility, functionality, wear and corrosion resistance [25].

The principal concern in the use of metallic implants is the generation and release of wear debris and toxic ions as a consequence of the passive film failure [26]. The passive film damage in implants is usually produced by the mechanical contact between the implants components. Tribocorrosion is a degradation resulted from chemical and mechanical interactions between two surfaces during mechanical contact, leading to a synergistic effect of corrosion and wear [27,28]. In a tribocorrosion system, the total material loss results from the contribution of two main

mechanisms: the material removed by the wear and corrosion interaction caused by the sliding on the surface, and the corrosion occurring in the overall exposed surface to the electrolyte [29]. This can be written as follows:

$$V_t = V_{\text{tribocorr}} + V_{\text{corr}} \quad (1)$$

where V_t is the overall volume loss of material, V_{corr} is the volume of material loss by corrosion (inside and outside the wear track), $V_{\text{tribocorr}}$ is the volume loss by the tribocorrosion effect and is determined by the mechanical and chemical contributions according to

$$V_{\text{tribocorr}} = V_{\text{mech}} + V_{\text{wac}} \quad (2)$$

where V_{mech} is the volume removed by mechanical wear, and V_{wac} is the wear-accelerated corrosion. The V_{mech} is the material volume removed from the surface (wear track) while V_{wac} is the cyclic passivation–depassivation contribution caused by the mechanical contact within the wear track [29]. The understanding of those components allows the selection and the design of higher performance materials for each application, i.e., load-bearing or stationary implants. Previous investigations performed on the surface-modified biomedical materials such as AISI 316L steel [30], and CoCrMo alloy [29], provide the complete specific formalism of the analysis method of the tribocorrosion mechanisms occurred in body simulated conditions. On those investigations, treatments such as nitriding and boriding, changed the passive behavior of materials into surfaces with non-passive behaviors. Additionally, the enhancement of the mechanical properties of the surface-treated materials resulted in decreasing the wear contribution to tribocorrosion process. A non-passive behavior was beneficial for materials such as implant biomaterials, which are subjected to tribocorrosion and contrary to passive materials, the formation of passive layer is suppressed and therefore, the risk of material and ion release decreases, improving surfaces and their performance in load-bearing implant application [31].

The tribocorrosion of P/M Ti alloys has been studied and compared with other manufacturing methods such as hot pressing (HP) and laser engineered net shaping (LENS) [32,33]. Results indicated the importance of phase concentration and its relationship to the mechanical and tribocorrosive performance of the alloy, showing that materials

with a higher concentration of α -Ti phase presented a better tribocorrosion performance due to their improved mechanical properties.

In the biomaterials field, a biocompatible matrix with additions of inert particles as reinforcement has been used to fabricate composites for orthopedic applications, and as a bone replacement with improved properties in comparison to monolithic alloys. For example, the reinforcement of Ti64 alloy with hydroxyapatite (HA) particles was studied as a composite biomaterial demonstrating the capability to improve the tribocorrosion resistance. Additionally to the hardening effect, the composite showed better chemical stability by decreasing the corrosion tendency with the increment of reinforcement [33]. Titanium nitride (TiN) presents excellent corrosion and wear resistance with relatively low coefficient of friction (CoF), such attribute promoted its usage as coatings [34–37] or reinforcement [14,15] with the purpose to improve the wear response of many Ti alloys for a vast number of applications including the biomedicine. FALODUN et al [15] demonstrated that small additions of TiN particles (5 vol.%) to a Ti64 matrix could notably increase the hardness of the composite and thus, an improvement on the wear resistance. The increment in hardness is usually attributed to both the microstructural change occurring as an effect of nitrogen diffusion from the TiN particles to the Ti matrix [36], and the load-bearing capacity of the hard TiN particles [37]. Additionally, some studies regarding the sintering behavior of Ti-based composites using TiN particles as reinforcement have been useful to understand the relationship between the sintering parameters and the effects of the TiN particles on the microstructure and properties of Ti matrixes [21,37–39]. The mechanical properties, wear and corrosion performances of spark plasma sintered (SPS) Ti64–TiN composites have been studied [15,40–43]. Nevertheless, the tribocorrosion behavior in biological environments of TiN reinforced Ti64 matrix fabricated by conventional solid-state sintering as a consolidation method has not been investigated. The aim of this work is to investigate the effect of sintering temperature and TiN reinforcing particle content on the microstructural and microhardness characteristics of Ti64/ x TiN composites fabricated by conventional (pressureless)

sintering and their relationship with the tribocorrosion performance in a simulated body fluid (SBF).

2 Experimental

2.1 Materials preparation

Biomedical Ti6Al4V (Ti64) spherical alloy powder with a chemical composition of 5.5%–6.5% Al, 3.5%–4.5% V, 0.25% Fe, 0.08% C, 0.13% O and 0.12% N (Ti balance), AP&C, Inc., with an average particle size of 8 μm was used as the matrix material (Fig. 1(a)), whereas irregular shaped TiN particles with a particle size of <45 μm and composition of 77.6% Ti, 21.2% N, 0.15% C, acquired from Atlantic Equipment Engineers, Inc., served as the reinforcement material (Fig. 1(b)).

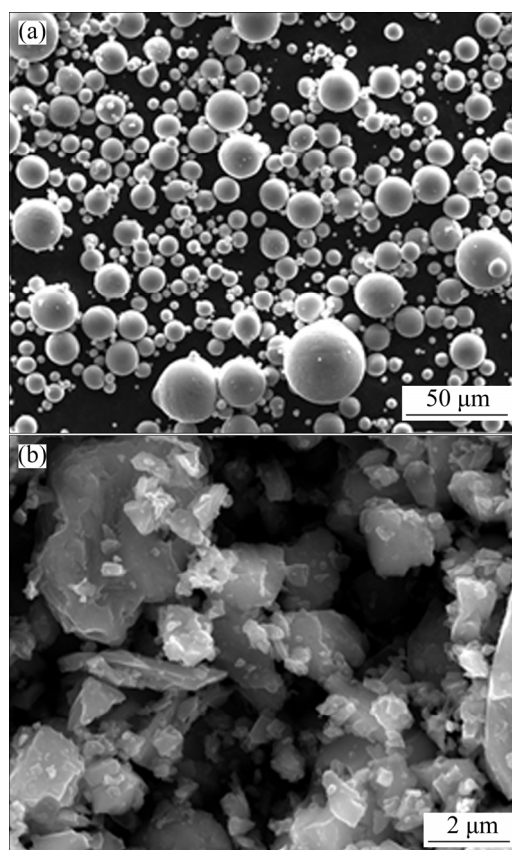


Fig. 1 Ti64 powder used as matrix (a) and TiN reinforcement particles (b)

Ti64/ x TiN composites were produced with three different volume fractions of TiN particles ($x=5, 10$ and 15 , vol.%) using conventional powder metallurgy technique. Samples were named regarding the volume fraction of TiN, e.g., C5 for 5 vol.% of TiN, and so on. Also, Ti64 samples

without reinforcement were prepared for comparison. First, the amount of powder for sample preparation was calculated by considering the rule of mixtures: $\rho_c = \rho_m f_m + \rho_r f_r$, where ρ_c , ρ_m and ρ_r are the mass densities of the composite, the matrix particles, and the reinforcement particles, respectively, and f_m and f_r are the volume fractions of the matrix and reinforcing particle, respectively. Next, Ti64 powders and TiN particles were mixed in a turbula for 30 min. Then, powder mixtures were mixed with 10 wt.% of polyvinyl alcohol (PVA), which was used as binder. Finally, the mixtures were poured into a stainless-steel die of 30 mm in diameter to be pressed under 300 MPa at a speed of 0.5 mm/min to form compacts with about 72% green relative density. The amount of powder was estimated to obtain compacts of 5 mm in height.

The green mold compaction was carried out with a servohydraulic MTS 810 testing machine, which followed the axial displacement of the punch, whilst applying the mentioned pressure. Afterwards, green molds were heated at 450 °C for 30 min in Ar atmosphere to eliminate the binder.

The sintering of the samples was performed in a Carbolite tube furnace at three different temperatures: 1200, 1300 and 1400 °C with a holding time of 60 min for each temperature with heating and cooling rates of 10 and 25 °C/min, respectively, under a high purity Ar atmosphere. More details regarding the sintering behavior, microstructural and microhardness of the Ti64 and Ti64/TiN composites are given elsewhere [21,22]. The sintered samples were metallographically prepared (1200 grid SiC paper for grinding, followed by polishing with an alumina solution with particle size of 3 µm) to obtain a mirror polished surface. Then, the surface of the samples was etched using Kroll's reagent (3 mL HF, 6 mL HNO₃, 100 mL H₂O) to reveal the microstructure.

2.2 Microstructure and microhardness characterization

The microstructure of the samples was observed using a Nikon ECLIPSE MA100 optical microscope, and a TESCAN Mira3 LMU field-emission scanning electron microscope (FE-SEM). With the purpose of assessing the structure identification of samples, X-ray diffraction (XRD) was performed by means of an emperyan

analytical diffractometer using K-alpha copper radiation with an energy of 30 kV and 30 mA, scan rate of 0.2 in a 2θ range of 32°–80°. The Vickers microhardness measurements were cross-sectional measured on the polished surface by means of a Future Tech FM–800 microhardness tester using a load of 3 N and 20 s of dwell time for each indentation. A series of 10 indentations were performed on each sample to obtain the statical microhardness values.

2.3 Electrochemical measurements

Potentiodynamic polarization measurements and Tafel extrapolation were used to evaluate the corrosion resistance of these materials in SBF prepared following the Kokubo procedure [44] with a pH of 7.4 and ion concentrations (mmol/L) of Na⁺ 142.0, K⁺ 5.0, Ca²⁺ 2.5, Mg²⁺ 1.5, Cl[−] 147.8, HCO₃[−] 42.0, HPO₄^{2−} 1.0 and SO₄^{2−} 0.5, which is nearly equal to human blood plasma ion content. Electrolyte was held at 37 °C during tests. Polarization curves were recorded by using a Gamry Reference–600 Potentiostat/Galvanostat and a three-electrode corrosion cell configuration (Fig. 2). In this configuration, a graphite electrode and a saturated calomel electrode (SCE) worked as counter and reference electrodes, respectively, while the sample with an exposed area of 0.25 cm² to the electrolyte functioned as the working electrode. During tests, a scan rate of 0.8 mV/s in a range from −0.5 to 1.5 V was used.

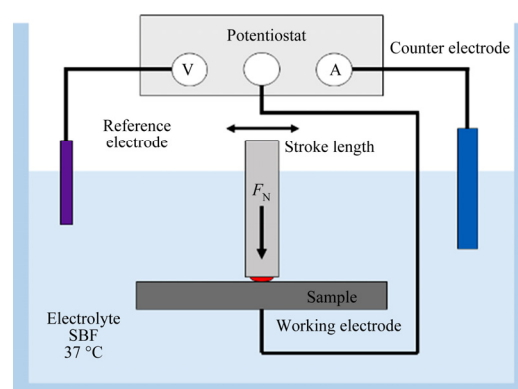


Fig. 2 Schematic of tribocorrosion system

2.4 Tribocorrosion tests

Tribocorrosion tests were performed on both control sample and composites, using a CETR-UMT2 (Campbell, California, USA) microtribometer in a linear ball-on-flat

reciprocating configuration coupled to the corrosion cell used in corrosion experiments, to set the tribocorrosion arrangement shown in Fig. 2. Testing sample immersed in the SBF solution was maintained at 37 °C serving as the working electrode as described above. The surface of the polished samples was rubbed with a non-conductive 10 mm alumina ball acting as a counterpart with a normal load of 2 N, which corresponds to ~208 MPa (Hertzian contact pressure), a stroke length of 7 mm and a frequency of 1 Hz during 1800 s. Experiments consisted of three stages: in the first stage, samples was immersed in the electrolyte during 60 min for the stabilization of the surfaces, followed by a rubbing stage for 30 min, and finally, a recovery stage for 60 min. The OCP was monitored during the whole experiment. Additionally, the CoF was recorded during the wear stage. Each tribocorrosion test was repeated three times to ensure the repeatability of results.

After testing, the volume of the wear tracks was measured by means of an optical profilometer NANOVEA-PS50. Each scan was used to estimate the wear volume and then, the specific wear rate. The morphological characterization of the wear mechanisms, before and after tribocorrosion tests was carried out through a field emission-scanning electron microscopy (Mira3 LMU Tescan FE-SEM).

3 Results and discussion

3.1 Microstructure

SEM images of the monolithic Ti64 samples sintered at 1200, 1300 and 1400 °C are shown in Fig. 3. It is observed that the resultant microstructure after sintering is fully lamellar, and α (dark gray) laths delimited by the β (light gray) phase grouped in colonies. The porosity level and the amount of each phase were estimated by thresholding the optical images of the microstructure of samples employing the ImageJ software, and the α/β ratio is included in Table 1. Additionally, Fig. 4 shows optical micrographs of the microstructures of the Ti64/10TiN composites, which are representative of all reinforced samples, and their microstructural evolution with the sintering temperature. The addition of TiN particles produced an obvious change in the initial microstructure of the Ti64 matrix into α -Ti equiaxed grain shape with some bimodal α/β -Ti grains, as shown elsewhere [21]. Figure 5 shows the XRD patterns of samples sintered at 1300 °C which are representative of the other samples sintered at different temperatures. The XRD analysis (Fig. 5(a)) demonstrated that both the α -Ti and β -Ti which constitute the α/β lamellar microstructure of the

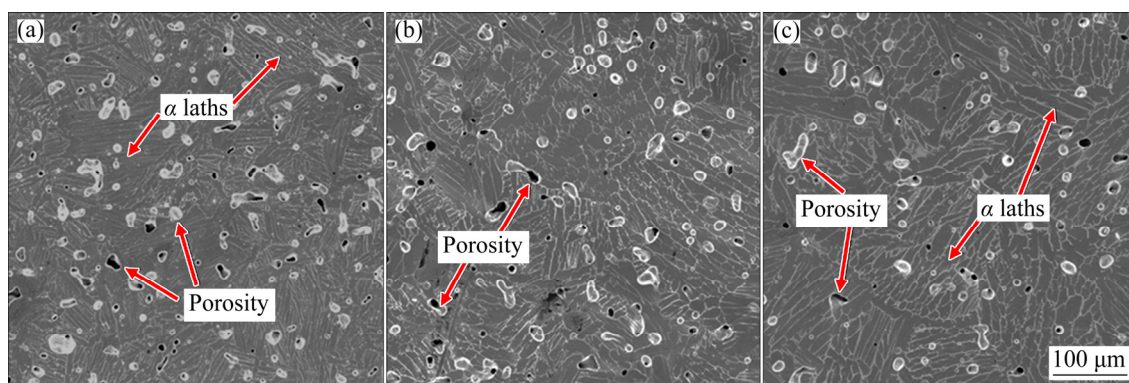


Fig. 3 SEM images of Ti64 samples sintered at 1200 °C (a), 1300 °C (b) and 1400 °C (c)

Table 1 Microstructural characteristics and microhardness values of sintered samples

Sample	1200 °C			1300 °C			1400 °C		
	HV _{0.3}	Porosity/%	α/β	HV _{0.3}	Porosity/%	α/β	HV _{0.3}	Porosity/%	α/β
Ti64	309±33	10.59	1.82	365±51	7.14	1.94	403±53	3.82	1.78
C5	408±59	15.87	1.49	471±68	11.35	1.45	538±62	7.77	1.61
C10	435±73	19.51	2.36	510±77	16.42	2.38	560±46	11.18	1.91
C15	490±82	21.06	2.41	565±90	17.83	2.41	614±59	13.28	2.55

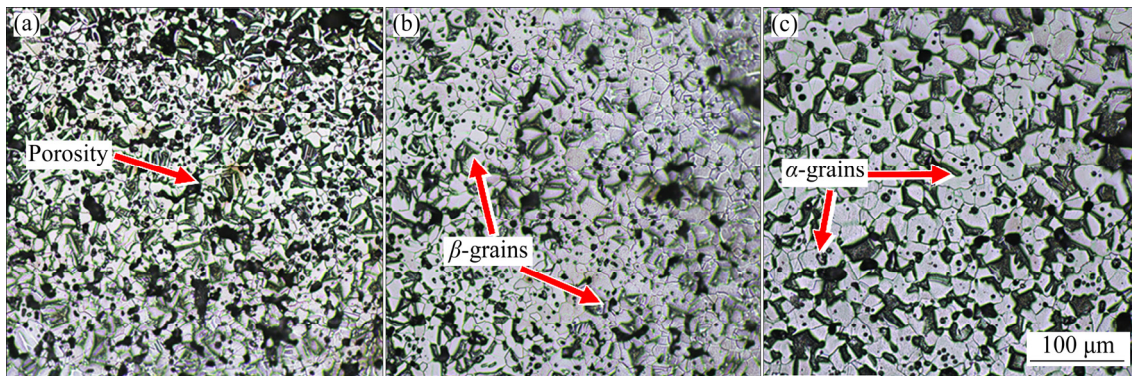


Fig. 4 Optical micrographs of Sample C10 sintered at 1200 °C (a), 1300 °C (b) and 1400 °C (c)

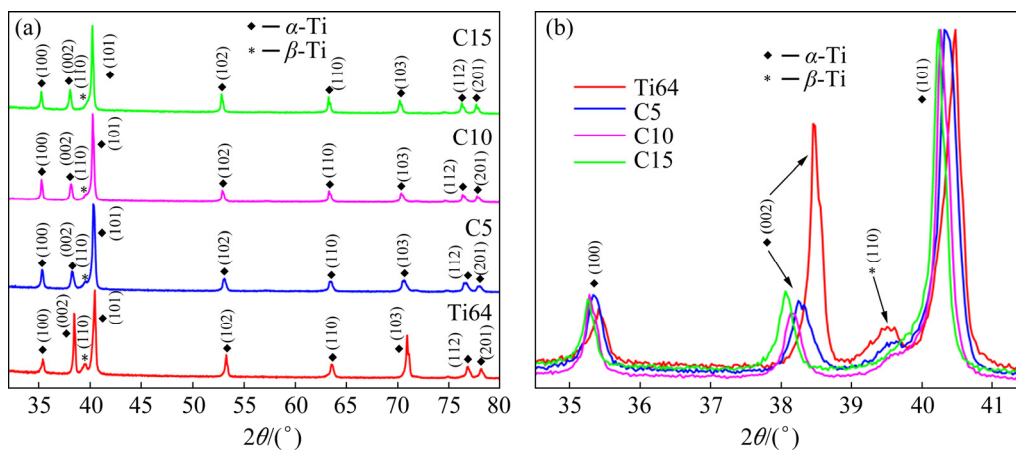


Fig. 5 XRD patterns (a) and main peaks (b) of samples sintered at 1300 °C

unreinforced Ti64 as well as the α -Ti equiaxed microstructure of the reinforced samples corresponded to the HCP structure (JCPDS No. 44-1294) and the BCC structure (JCPDS No. 44-1288), respectively. In addition, as can be observed in Fig. 5(b), the α -Ti phase stabilization caused by the N dissolution into the Ti64 matrix is demonstrated by the fading of the characteristic β -Ti peak at $2\theta=39.5^\circ$, approximately. Furthermore, the solid solution of N into the Ti64 matrix was probed by the peaks shift of the matrix material to lower diffraction angles.

3.2 Porosity and hardness

Table 1 shows the porosity and microhardness for Ti64 and Ti64/TiN samples as a function of the TiN particles content.

As can be noticed in Table 1, the average microhardness for the Ti64 samples increased with the sintering temperature. The microhardness values of the Ti64 samples increased by 65% when the sintering temperature rose from 1200 to 1400 °C. This microhardness increment is attributed to the

increase in the density of the materials, which is caused by the reduction in the final porosity (Fig. 3), as sintering temperature increased. Also, the rise in temperature above the crystallization temperature generated an increment in the grain size of the prior β -grains. Therefore, wider α laths were formed during cooling (lamellar microstructure), preserving the same α/β ratio for all the sintering temperatures. It has already been studied that the α -phase in Ti alloys is stiffer than the β -phase [45]. The microstructural changes that occurred as an effect of the TiN particle addition positively affected the matrix microhardness, as can be seen in Table 1. Hardening of the Ti64 matrix resulted from the nitrogen interstitial dissolution into the α -Ti structure during sintering [36]. Figure 6 shows the microhardness improvement regarding each unreinforced sample sintered at the same temperature. A substantial increase of the microhardness values of composites can be seen regarding the unreinforced samples (up to 109%). Generally, the microhardness improvement of the composites sintered at 1300 °C (dash circle)

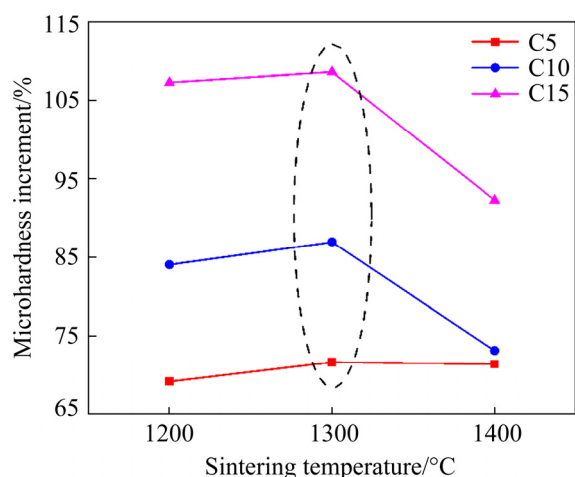


Fig. 6 Microhardness increment resulting from reinforcement of Ti64 matrix

showed higher values in comparison to other sintering temperatures, i.e., 1200 and 1400 °C. Hardness enhancement has been reported as a result of the uniform distribution of Ti_2N hard phase, which can be formed by the reaction between Ti and N, into the Ti64 matrix [15]. However, the N diffusion causing solid solution hardening of the Ti64 matrix is the most likely cause of the microhardness increase of the composites [46]. An additional contribution to the increment in microhardness with the TiN particle addition is given by the decrease in pore size with the sintering temperature, besides the increase in porosity of composites. Additionally, a reduced microhardness increment was achieved for samples with more than 15 vol.% of TiN particles, indicating the beginning of the Ti64 matrix saturation with N from the TiN particles, which is favored with the high sintering temperature. Thus, the microhardness of the composites is maximized at 1300 °C. Further temperatures such as 1400 °C is detrimental to this property.

The densification of the Ti64 and composite samples is equally affected by the sintering temperature. However, the density achieved by the composites is lower than that attained for the Ti64 samples. This decrease in density is because of the decrement in the number of Ti64–Ti64 sinterable contacts caused by the obstruction effect of hard TiN particles and the generation of small pores surrounding the particle cumulus. Similar pore generation resulted in a relative density decrease after TiN particle addition to the Ti64 matrix [15].

3.3 Electrochemical properties

Representative potentiodynamic polarization curves in SBF at 37 °C for both unreinforced and composite samples are shown in Fig. 7. Three different zones can be identified in these curves: (1) the cathodic domain, which is observed at more negative potentials, where the current is determined by the reduction of water and the dissolution of the oxygen, (2) the corrosion potential (ϕ_{corr}), at the

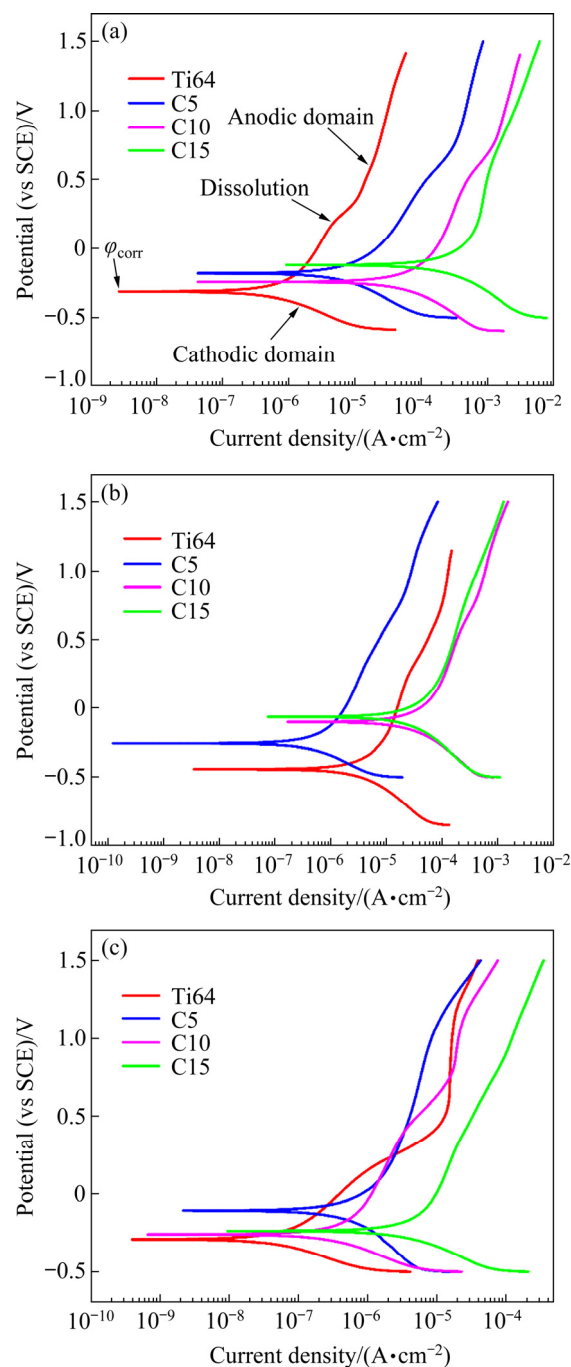


Fig. 7 Potentiodynamic polarization curves recorded in SBF solution at 37 °C of samples as compared with Ti64 samples sintered at 1200 °C (a), 1300 °C (b) and 1400 °C (c)

transition from cathodic to anodic potential, and (3) the anodic domain at high potentials, where passivation behavior is evaluated. The average φ_{corr} values for Ti64 samples at each sintering temperature are very similar in a narrow range between 278 and 297 mV (Table 2). As can be seen in Fig. 7, as the anodic potential increases, the stabilization of the current density indicates the surface passivation by the formation of a TiO_2 film resulted from the exposition to SBF, as confirmed by Raman spectroscopy (not shown here). A dissolution of the passive film indication, which is characterized by a slight increase in current density, is observed starting at approximately 0.2 V for all Ti64 samples. This dissolution is attributed to the degradation of the initial passive film formed by the contact of the surface material with the environment. Further application of anodic potential resulted in repassivation of the surface and stabilization of the current density, indicating the recovery of the passive film. In this regard, the absence of a well-defined passive region in porous materials has been attributed to the inconsistency in the formation of the passive film at the innermost pores caused by the heterogeneities in the overall structure [47].

On the other hand, the φ_{corr} values for Samples C changed to more noble potentials compared to unreinforced samples. The passivation behavior of Samples C were similar to the unreinforced samples. However, the dissolution presented in Samples C becomes imperceptible with the TiN addition, indicating that this damage of the passive layer in SBF at 37 °C is suppressed because of the dissolution of N into the Ti64 matrix. Corrosion studies carried out in different biological electrolytes demonstrated that nitriding treatment increased the corrosion potential and decreased the corrosion density of Ti64 alloys, up to one order of magnitude [48–51]. This behavior was attributed to the formation of TiN/Ti₂N layered coatings on the surfaces of Ti64 and particularly, to the high strength of the chemical bonds of formed titanium nitrides. On the other hand, it was found by POHRELYUK et al [48] that the formation of ε -Ti₂N layer during thermodiffusion nitriding of Ti64 is attained with low concentrations of N (26.77 at.%) at 850 °C, as a result of the solid-solution of N in α -Ti. In that study, the increment in atmospheric N concentration and temperature produced the formation of δ -TiN layer

over the Ti₂N layer, demonstrating that the nitride formation was accomplished. In this work, the high amount of N added to the Ti64 matrix via reinforcing TiN particles is estimated at approximately 26 at.% for composites with addition of 15 vol.% TiN, assuming the complete reaction between reinforcing particles and the matrix material. Hence, following the findings of POHRELYUK et al [48], the formation of a corrosion protective Ti₂N or TiN layer is possible. Nevertheless, in previous work [21], a solid-solution of N into the Ti64 lattice is reported for the Ti64–xTiN system and the formation of secondary phases such as TiN and Ti₂N was not detected. Additionally, the increase in current density with the anodic potential for Samples C is slightly pronounced as compared to that for the unreinforced samples, indicating the loss of passivity caused by the N diffusion into the Ti64 lattice. Moreover, the increase in current density of Samples C10 and C15 sintered at 1300 °C (Fig. 7(b)) and Sample C5 sintered at 1400 °C (Fig. 7(c)), denotes a less passive behavior, being possible to attribute this behavior to the beginning of the formation of the nitride.

Furthermore, the stabilization of the α -Ti phase caused by the diffusion of N into the Ti64 lattice is noticed by the increment in the α/β with the amount of TiN (Table 1). Some considerations related to the microstructure are considered to explain the corrosion potential behavior of Samples C. First, a stabilized α -Ti phase is less susceptible to corrosion than $\alpha+\beta$ microstructure such as microstructure of the sintered Ti64, which contains easy-dissolving vanadium-rich grain boundaries (β -Ti boundaries) [52,53]. Then, as the corrosion process of a lamellar Ti64 alloy occurs at the α/β grain boundaries which act as galvanic couples [54], a decrease in β -Ti grains caused by the α -Ti stabilization reduced the interphases, decreasing the corrosion locations. Thus, the decrease in the corrosion tendency of Samples C can be attributed to the microstructural change and the formation of a noble N-enriched microstructure. Moreover, as can be observed in Table 2, the current densities for Samples C increase with the reinforcement amount. This effect appears to obey the densification of samples. A more evident effect of porosity on the current densities is noticed for the samples sintered at 1200 °C, for which the variation of densities is

homogeneous, while difference in densification behavior of sintered samples becomes narrow at 1400 °C (Table 1). As it has been studied in Ref. [47], a small, sharp and close porosity promotes the trapping of the corrosive electrolyte species. This observation allowed to attribute the behavior of the current density to the effect of the pore size reduction. As corrosion rate is a direct function of the current density, porosity presented in composites surface was able to increase their corrosion rate with TiN addition, as can be seen in Table 2. The Tafel extrapolation potentiodynamic analysis led to the calculation of polarization resistance (R_p) values for Ti64 and Samples C in SBF electrolyte. It can be noticed in Table 2 that the higher R_p values were obtained by Ti64 while

Samples C presented lower R_p values, which decrease with the TiN addition. Samples sintered at 1400 °C presented the higher R_p values, demonstrating the strong effect of the reduced porosity obtained at higher sintering temperatures.

3.4 Evolution of open circuit potential and coefficient of friction in tribocorrosion tests

3.4.1 Ti64 unreinforced samples

Representative curves of the evolution of OCP as a function of time during sliding tests of Ti64 in SBF are shown in Fig. 8(a). In the stabilization period, the OCP reached constant values, demonstrating the existence of a passive film on the sample surfaces. LICAUSI et al [55] showed the influence of the processing route on the passivation

Table 2 Electrochemical parameters from Tafel extrapolation of potentiodynamic polarization curves in SBF solution at 37 °C for Ti64 and Samples C sintered at 1200, 1300 and 1400 °C

Temperature/°C	Sample	$\phi_{\text{corr}}(\text{vs SCE})/\text{mV}$	$J_{\text{corr}}/(\mu\text{A}\cdot\text{cm}^{-2})$	$R_p/(\text{k}\Omega\cdot\text{cm}^2)$	Corrosion rate/ $(\text{mm}\cdot\text{a}^{-1})$
1200	Ti64	-278.05±49.43	0.149±0.03	22.67±4.11	4.44±1.3
	C5	-195.70±20.36	1.333±0.03	2.49±0.06	62.08±50.32
	C10	-164.05±10.99	9.985±0.42	0.33±0.01	95.25±9.723
	C15	-119.80±0.71	42.512±4.44	0.07±0.008	722.8±72.32
1300	Ti64	-308.10±19.06	0.603±0.04	5.53±0.37	10.52±0.78
	C5	-271.80±20.51	0.125±0.04	28.54±10.14	2.61±0.44
	C10	-186.70±93.90	5.463±0.69	0.61±0.07	108.07±16.13
	C15	-128.80±89.30	3.549±0.90	0.73±0.07	97.71±7.88
1400	Ti64	-296.33±8.49	0.015±0.01	194.44±78.56	1.73±2.17
	C5	-124.40±26.87	0.089±0.006	37.38±2.36	1.47±0.42
	C10	-262.80±4.95	0.084±0.02	29.16±5.89	1.97±0.33
	C15	-243.75±10.54	0.826±0.15	4.1±0.78	14.14±3.24

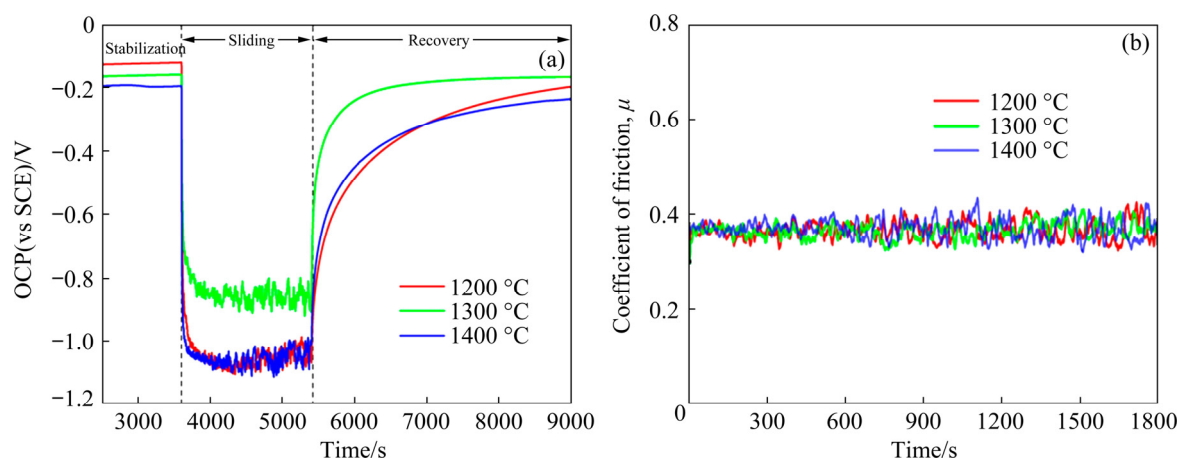


Fig. 8 OCP evolution recorded before, during and after rubbing period of tribocorrosion test in SBF environment (a), and coefficient of friction evolution during sliding (b) of Ti64 samples sintered at 1200, 1300 and 1400 °C

of the samples, i.e., in their comparative, cast Ti64 samples showed more corrosion tendency than those fabricated through PM.

The OCP of the Ti64 in the stabilization period presented a minimum decrement with the sintering temperature, corresponding to the amount and size of porosity. It has been previously studied that the shape and size of porosity affect the corrosion of Ti64 samples, and the results showed a trend to slightly decrease corrosion resistance with the pore size reduction [56,57]. This was attributed to the increment of the surface area beside the trapping of the electrolyte and exhaust restriction of the oxygen supply, which leads to a thinner oxide film in smaller and isolated pores.

During sliding, a sudden potential drop in OCP was recorded corresponding to the removal of the passive film (depassivation) [33,58]. This OCP behavior resulted from the potential difference established between depassivated areas in the wear track (anodic), and the passive areas outside the wear track (cathodic). The OCP values remained low, indicating that a depassivated state prevails during sliding showing oscillation as a result of the local depassivation-repassivation phenomena [55,58]. OCP values during sliding achieve constant values at (0.95 ± 0.03) V, (0.69 ± 0.06) V and (0.88 ± 0.04) V corresponding to Ti64 samples sintered at 1200, 1300 and 1400 °C, respectively. Similar, OCP values were shown by the Ti64 samples sintered at 1200 and 1400 °C after depassivation, despite the difference in the initial OCP decrements, as mentioned before. On the other hand, the Ti64 sample sintered at 1300 °C presented a higher OCP value during rubbing. This result corresponded to the higher J_{corr} value, as denoted in Table 2, which indicates a more anodic corrosion current density, meaning a faster passive film formation on the sample sintered at 1300 °C. In addition, as can be seen in Fig. 7, dissolution of Ti64 samples occurs at approximately 0.2 V; however, the ϕ_{corr} varied slightly. It can be considered a larger difference between ϕ_{corr} and the potential for the beginning of the dissolution as a better stability of the formed passive film since a higher potential is needed to dissolve it from its formation. This difference was similar for samples sintered at 1200 and 1400 °C (0.52 and 0.49 V, respectively) while the difference corresponding to the Ti64 sample sintered at 1300 °C is 0.65 V. On this regard, Ti64 sample

sintered at 1300 °C showed a higher difference than those sintered at 1200 and 1400 °C. Besides, a pronounced slope is observed for this sample, indicating that passivation is achieved rapidly. Thus, a more stable passive film can contribute to decreasing the wear effect during tribocorrosion synergy, decreasing the corrosion tendency of the Ti64 sample sintered at 1300 °C during wear action. The above-described behavior shows a correlation with the α/β ratio for samples (Table 1), for which the higher value is for the sample sintered at 1300 °C. This observation allows attributing the better stabilization behavior to a Ti64 sample with higher amounts of α -Ti phase.

In the model presented by VIEIRA et al [59], two situations are theoretically considered for the galvanic coupling attained during tribocorrosion tests. The first situation refers to a galvanic coupling established between the surface of the completely depassivated wear track and the still passive area surrounding the wear track. A second situation takes place when a short-range galvanic coupling is attained between depassivated and still passive areas within the wear track, which includes the passive area surrounding the wear track. In Fig. 8(a), a continuous decrease in OCP with a quick stabilization is observed for samples sintered at 1200 and 1400 °C. This behavior is consistent with the second consideration of the model described before. For the Ti64 sample sintered at 1300 °C, a more progressive decrease in potential at the onset of rubbing is observed until reaching stable values. This behavior demonstrates a more adherent and resistant passive film, which hinders the galvanic coupling formation. These observations are related to the damage of the passive film suffered during tribocorrosion tests. By comparing Fig. 9(a) with Fig. 9(c), it is possible to observe the differences in wear severity suffered by the Ti64 samples sintered at 1200 and 1400 °C (supported by the areas of the wear track profiles, respectively). Less severity is observed in the wear track of the Ti64 sample sintered at 1200 °C (Fig. 9(a)), while a high wear severity is depicted in Fig. 9(c), when sintered at 1400 °C. This slight difference in severity is reflected in the sharpness of the drop of potentials observed in Fig. 8. The lower wear severity is observed in the wear track of the Ti64 sample sintered at 1300 °C (Fig. 9(b)), corresponding to the OCP attained for this sample.

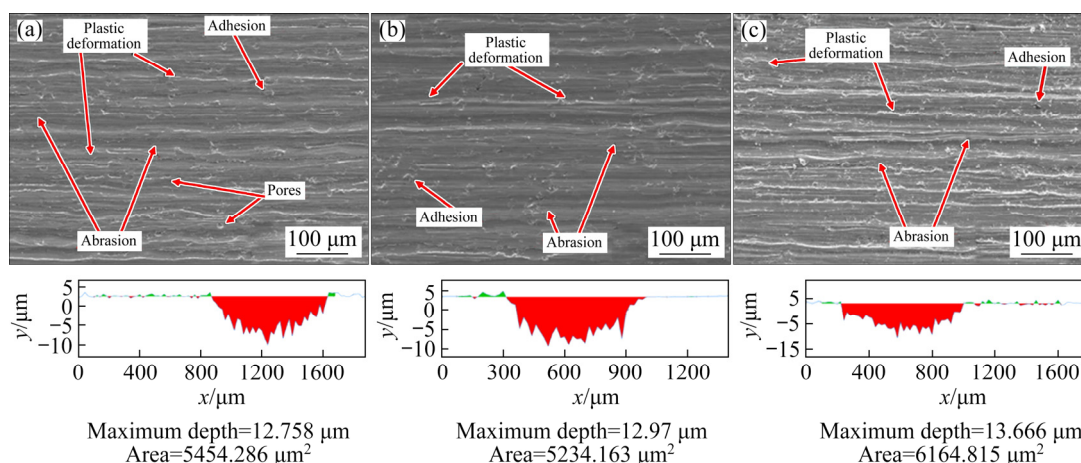


Fig. 9 SEM images and profiles of center of wear tracks produced during tribocorrosion tests of Ti64 samples sintered at 1200 $^{\circ}\text{C}$ (a), 1300 $^{\circ}\text{C}$ (b) and 1400 $^{\circ}\text{C}$ (c)

Figure 8(b) shows the coefficient of friction (CoF) recorded during the reciprocating sliding in the tribocorrosion of Ti64 samples. Despite the differences in the severity of wear shown in Fig. 9, CoF presented similar trends for the three samples with stable value of 0.37 on average regardless of the sintering parameters. This CoF value is similar to those reported for Ti64 sintered samples [32,33] and cast Ti64 [60].

After the sliding period, the OCP increased to passive potentials indicating the repassivation of the active surface (see Fig. 8(a)). The repassivation rate is a relevant characteristic of the tribocorrosion behavior of metals since a quick recuperation of the surface denotes an excellent corrosion resistance, and thus, a good tribocorrosion performance [55]. A comparison of the repassivation rate with the passivation time that has been passed to achieve a certain degree of repassivation could be used as an evaluation of the repassivation speed of material. A shorter repassivation time means a faster repassivation rate [61,62]. For example, in Fig. 8, curves of Ti64 samples sintered at 1200 and 1400 $^{\circ}\text{C}$ show similar repassivation behavior, in which the repassivation time of the designed tests appears to be insufficient to reach a complete recuperation of the passive film on their surface. On the other hand, the sample sintered at 1300 $^{\circ}\text{C}$ showed the fastest repassivation, which was reached after approximately 7500 s, i.e., 35 min after the sliding finished.

3.4.2 Ti64/xTiN composites

The OCP evolution of the composite samples (Ti64/xTiN) as compared to the Ti64 samples

sintered at equal temperature is given in Fig. 10. It can be seen that the OCP values in the passivation period of the tests decrease with the TiN particles addition in most cases. This increment in corrosion tendency is attributed to the amount of porosity present in the sample. Figure 11 shows the edge of the wear tracks after tribocorrosion tests of composite samples. The periphery of the wear tracks shows that the porosity remains similar in size and shape. On the other hand, it is possible to observe that the number of pores increases with TiN particle addition, which decreases the corrosion resistance and relative density as mentioned before.

As seen in Fig. 10, the TiN particle addition seems to prevent the OCP decrement during the sliding period. The Samples C sintered at 1200 $^{\circ}\text{C}$ showed an important improvement in corrosion tendency during rubbing in comparison to the Ti64 sintered sample at the same temperature. The potential drops of reinforced samples are shown in Table 3. The potential drops of Samples C sintered at 1200 $^{\circ}\text{C}$ represent between 2% and 23% approximately, of the decrement of (0.95 ± 0.03) V of the Ti64 sample. In the case of the C10 and C15 samples sintered at 1300 $^{\circ}\text{C}$, OCP drops during rubbing are between 5.7% and 10% approximately, of the decrement of (0.69 ± 0.06) V of the Ti64 sample while the drop of the Sample C5 resulted slightly higher than the unreinforced sample (2.8%). On the other hand, samples sintered at 1400 $^{\circ}\text{C}$ also presented decrement in OCP during the sliding period, representing between 10% and 83% approximately, of the decrement of (0.88 ± 0.04) V of the Ti64 sample.

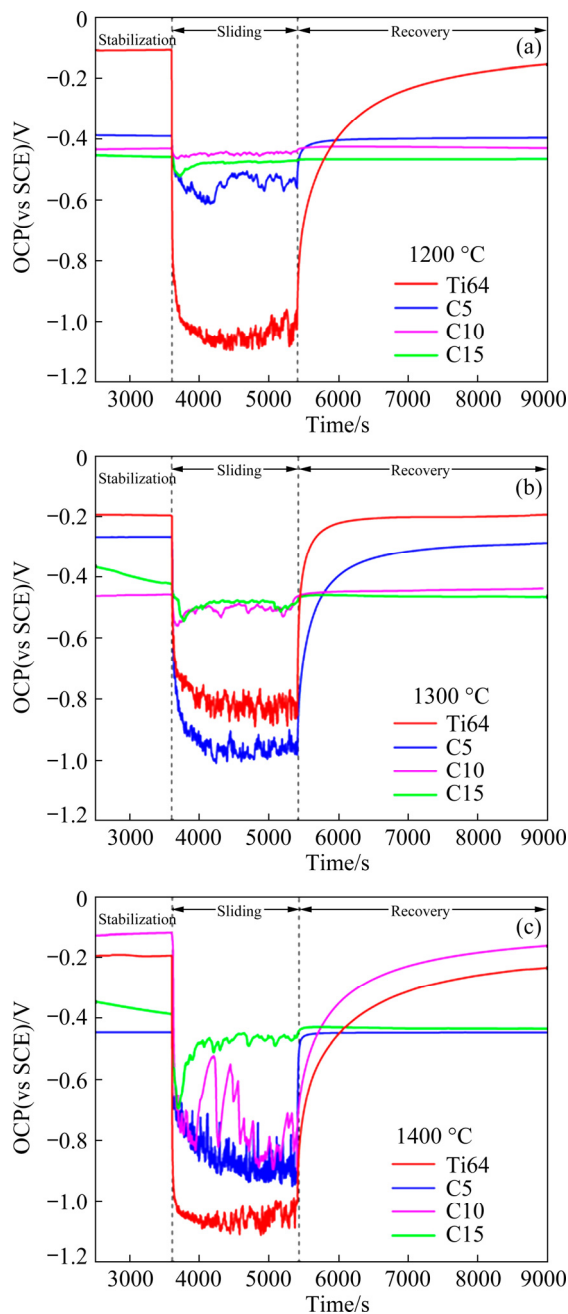


Fig. 10 OCP evolution recorded before, during and after rubbing period of tribocorrosion test in SBF environment of Samples C as compared with Ti64 samples sintered at 1200 °C (a), 1300 °C (b), and 1400 °C (c)

OCP values during rubbing of Samples C follow the passivation behavior described in Section 3.3, in which the addition of TiN particles increased the ϕ_{corr} and accelerated the corrosion by the increase in current density during the potential application. Most of the drops in OCP during rubbing of Samples C were lower as compared to the Ti64 samples, showing the hindering effect of

the TiN addition on the passive film formation on the Samples C. This behavior represents a transition from the condition (2) for the Ti64 samples to the condition (1) for the Samples C with the low additions of TiN, and can be related to the wear severity in each sample shown in Fig. 11. For example, the images of the Sample C5 sintered at 1200 °C showed higher wear severity as compared to the Samples C10 and C15 for which, it is possible to observe that Sample C15 suffered a lower wear severity than the Sample C10. Comparing the images corresponding to samples sintered at 1300 °C, Sample C5 presented the higher wear severity than the other samples, from which, the Sample C15 resulted in lower wear severity. Similar behavior was presented by composites sintered at 1400 °C, in which a less wear severity is shown by Sample C15.

Table 3 Potential drops of composite samples attained in rubbing stage of tribocorrosion tests

Temperature/°C	Sample	Potential drop/V
1200	C5	0.22±0.03
	C10	0.02±0.07
	C15	0.06±0.02
1300	C5	0.71±0.01
	C10	0.04±0.02
	C15	0.07±0.01
1400	C5	0.46±0.08
	C10	0.73±0.04
	C15	0.09±0.09

The diffusion of the higher concentration of TiN particles produced a very low drop of the OCP at the onset of rubbing, which is completely recovered rapidly after rubbing, demonstrating the non-passive nature of materials. ZHAO et al [31] have reported that a nitriding coating is able to increase the OCP in PSB solution of Ti since TiN is a nobler material. Moreover, progressive degradation of layer occurred during corrosion tests because of the non-passive nature of TiN. This corrosion behavior is not beneficial for certain applications, i.e., biomedical implants exposed to biological fluids. However, a good tribocorrosion performance is denoted by nitrided Ti materials since they do not increase their corrosion tendency

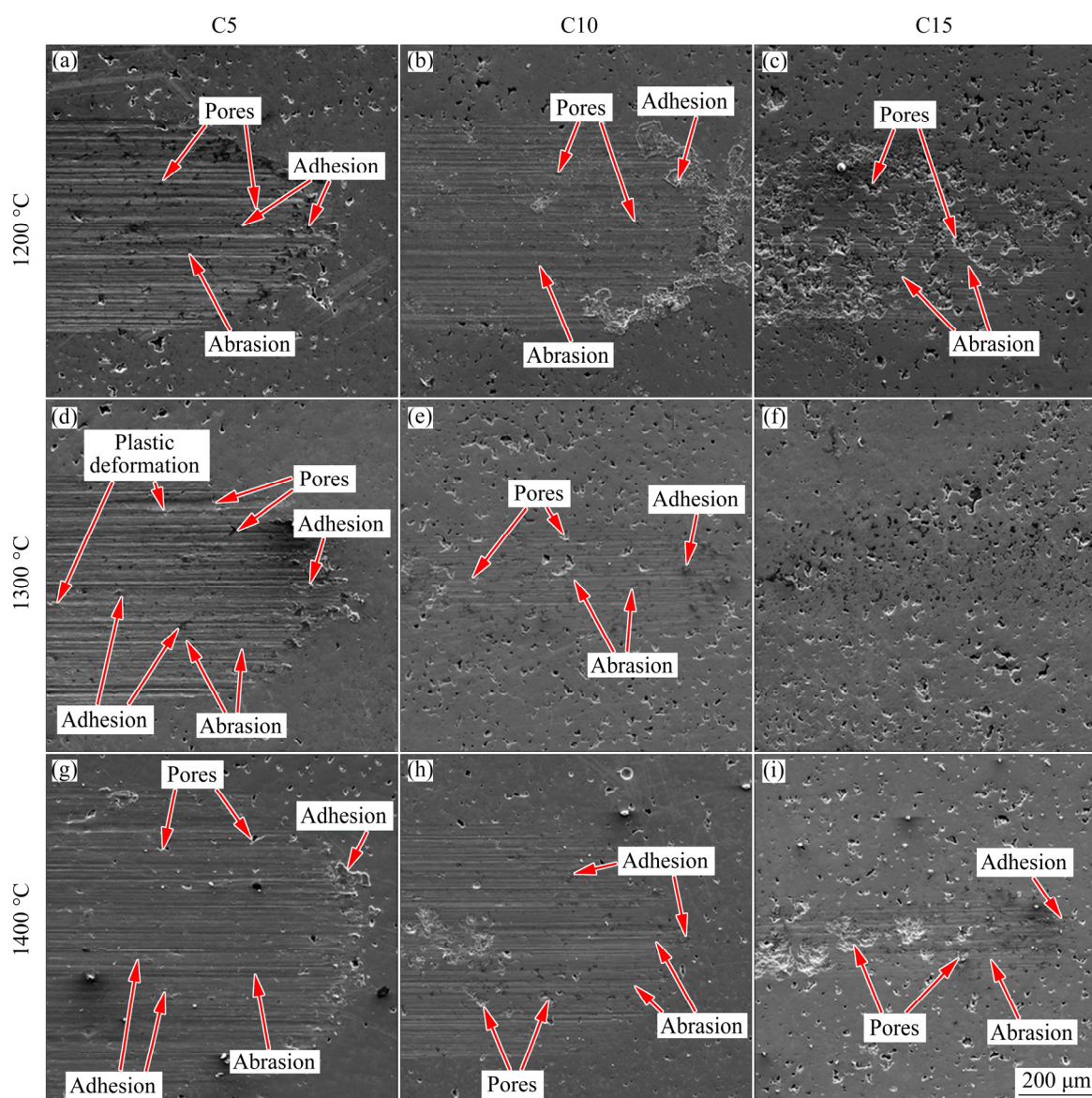


Fig. 11 SEM images of ends of wear tracks produced during tribocorrosion tests of samples sintered at 1200 °C, 1300 °C and 1400 °C

during rubbing, contrary to passive materials which usually lose their corrosion protective film favoring the formation of galvanic coupling. This characteristic is essential for load-bearing implant biomaterials. Nevertheless, the N solid solution in the Ti64 lattice is another reasonable cause of the tribocorrosion behavior improvement of Samples C. N in solid solution has demonstrated to improve the tribocorrosion behavior of CoCrMo alloys [29,62] due to the solution hardening, which decreases the wear-accelerated corrosion.

Figure 12 shows the CoF values of Ti64 and Samples C recorded during tribocorrosion tests. As seen, CoF for Samples C resulted in higher values than those for Ti64 samples. CoF of Samples C

increases abruptly until it reaches constant values, differently to the Ti64 samples, which started with stable CoF values since the beginning of the sliding against the counterpart. This behavior shown by Samples C was previously reported [8,63], attributing the abrupt increase in CoF to the first contact of the counterpart with the reinforcement particles, achieving an adaptation between both surfaces. Contrary to the Ti64 samples, the Samples C recorded CoF behaviors affected by the sintering temperature. The increase in the sintering temperature of the samples slightly decreased the CoF values of Samples C, obtaining more stable values between samples. This is an effect of the increase and the homogenization of the hardness in

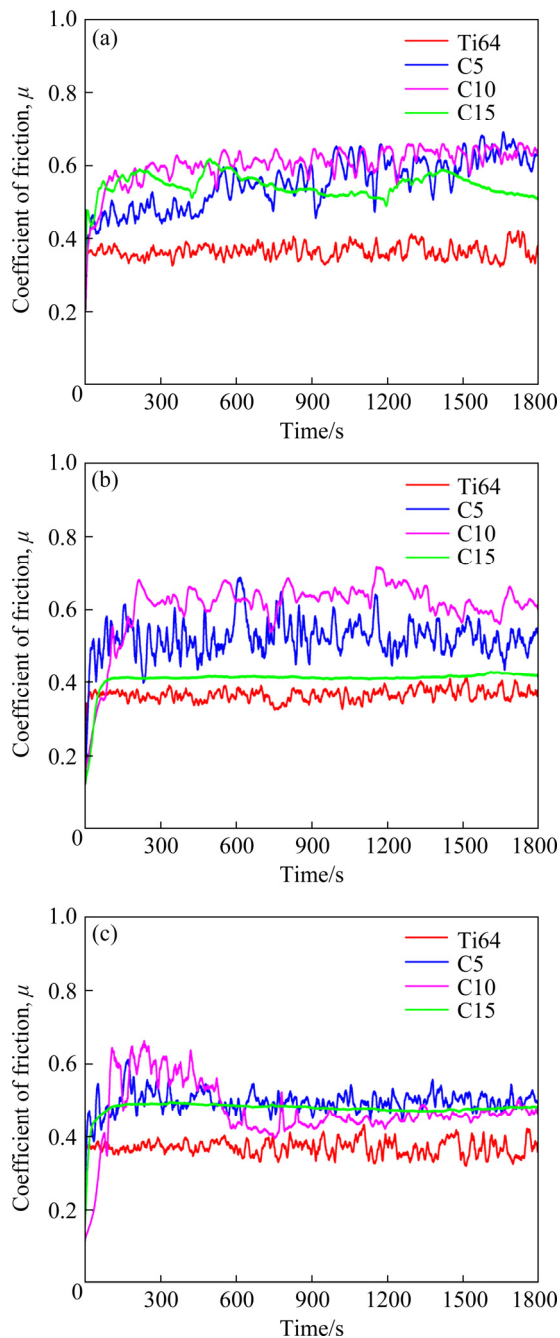


Fig. 12 Coefficient of fraction evolution during rubbing in tribocorrosion test of Samples C sintered at 1200 °C (a), 1300 °C (b) and 1400 °C (c)

Samples C surfaces caused by a higher diffusion between TiN particles and Ti64 matrix. In addition to the higher hardness attained for the Samples C, the differences in the nature of the surfaces with either; higher nitrogen content or diffused in the Ti64 lattice are capable to prevent the “stick-slip” caused mainly by the adhesive characteristics of Ti alloys [64], decreasing the fluctuation level of the CoF values as the N solid-solution increased. However, other factors such as porosity and both

the loose and still attached reinforcing particles should be considered in the fluctuation of the CoF values analysis.

3.5 Specific wear rate and wear mode evaluation

Figure 13 shows the specific wear rate calculated after the tribocorrosion tests of the Ti64 and Samples C regarding the sintering temperature. The bars corresponding to the Ti64 samples show the effect of the sintering parameters on the wear resistance of the samples, which increases with the sintering temperature. This increment is related to the microhardness increment, as explained before. The specific wear rate decreases from $(5.9 \pm 1.3) \times 10^{-4}$ to $(5.6 \pm 2.1) \times 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$ with the sintering temperature (1200 to 1400 °C), obtaining values in the range reported for Ti64 alloy fabricated by MP [33].

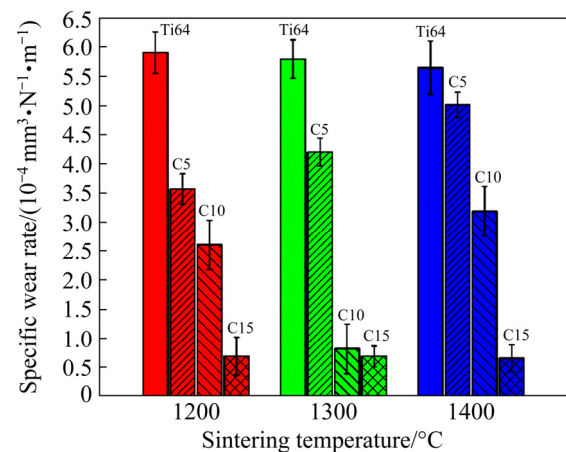


Fig. 13 Specific wear rate of Ti64 and Samples C sintered at 1200 °C, 1300 °C and 1400 °C

With the addition of TiN particles, the wear resistance considerably increases for the Ti64 samples as denoted by the specific wear rate shown in Fig. 13. The samples sintered at the same temperature decreased their wear rate as the TiN amount increased. The reductions (regarding the TiN content: 5, 10 and 15 vol.%) in wear rate were 39.4%, 55.7% and 88.2% for the samples sintered at 1200 °C, 27.4%, 85.7% and 87.9% at 1300 °C, while the reductions for the samples sintered at 1400 °C were 11%, 43.4% and 88.32%. These behaviors of wear rate decrements appear to obey the microhardness of the samples, having a clear tendency corresponding to the microhardness increment shown in Fig. 6. For example, the widest difference or increment in microhardness was

shown by the Samples C sintered at 1200 °C, which corresponds to the widest wear rate decrements as compared to the unreinforced sample. The increment in microhardness of the Samples C sintered at 1400 °C was narrow, corresponding to a narrow decrement in wear rate regarding the unreinforced sample.

In order to analyze the wear mode, detailed SEM images of the center of the wear tracks obtained in tribocorrosion tests of samples sintered at 1300 °C are shown in Fig. 14. These images are representative of the samples sintered at 1200, 1300 and 1400 °C. It is observed in Fig. 14(a) that the surface of the wear track of the Ti64 sample presents a higher roughness than the Samples C tracks (Figs. 14(b, c, and d)), which indicates higher surface damage, corresponding with the specific wear rate values. This is a confirmation of the low wear performance of Ti64 alloy [65]. The wear

grooves and plastic deformation caused by contact and sliding of the counterpart over the sample surface indicate an abrasive wear type which is characteristic of the Ti64 composites subjected to sliding wear [32,33]. Wear grooves observed in Fig. 14 formed by the dragging of wear products are dissipated as the TiN amount increases. This is due to the hardening of the matrix effectively increasing the wear resistance and inhibits the release of material. In addition, some pores resulted from the pulled out TiN particles as observed in Fig. 14(d). Also, plastic deformation decreased considerably with the TiN particle addition. The above observation allowed the determination as the main wear mechanism as a combination of abrasion and adhesion modes caused by the sliding contact of the alumina counterpart against the surface and the material transfer from the surface of the sample to the ball (counterpart).

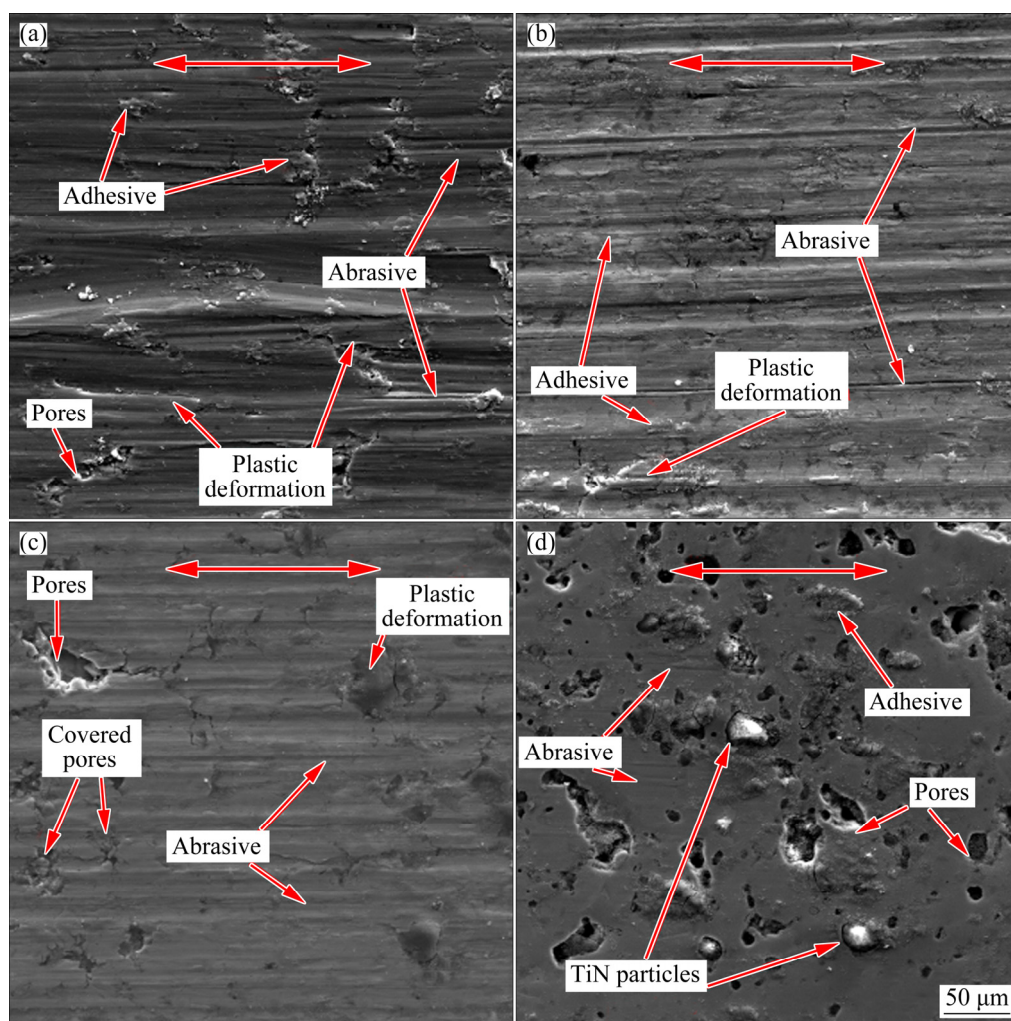


Fig. 14 SEM images from center of tribocorrosion wear track of Samples Ti64 (a), C5 (b), C10 (c), and C15 (d) sintered at 1300 °C

4 Conclusions

(1) Microhardness increased with both the sintering temperature and the TiN particle amount due to the α phase increment and the solution hardening caused by the N diffusion into the Ti lattice, achieving increment up to 109%, by using 15 vol.% of TiN particles at 1300 °C.

(2) Reinforced materials demonstrated more noble corrosion behavior than the Ti64 matrix denoted by the increase in ϕ_{corr} . TiN particle addition decreased the transpassivation behavior and promoted the increase of corrosion current with the applied potential, which indicates rapid corrosion of samples. In addition, the increase in current densities of Samples C regarding the unreinforced samples was observed because of the remaining porosity resulted from the sintering process.

(3) Improved performance in tribocorrosion tests was presented by the Samples C as compared to the Ti64 samples. The increase in the concentration of TiN particles promoted the hindering of passive film formation, producing short potential drops during rubbing. These characteristics, combined with solution hardened materials, result in an excellent combination that promotes the Ti64/TiN materials for the application as load-bearing implant biomaterial rather than in stationary implant applications.

(4) Wear resistance in tribocorrosion tests in SBF of Samples C was improved 88.2% regarding the unreinforced samples. This improvement was attributed to the solution hardening and the load-bearing effects of TiN particles. The main wear mechanism that occurred during the tribocorrosion was a combination of abrasion and adhesion.

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生物医用 Ti6Al4V/xTiN 复合材料的腐蚀与腐蚀磨损行为

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摘 要: 用固相烧结法制备 Ti6Al4V/xTiN ($x=0, 5, 10, 15$, 体积分数, %)复合材料, 研究材料的腐蚀与腐蚀磨损行为及其与显微组织和显微硬度的关系。采用 37 °C 和模拟体液模拟人体环境。结果表明, 当 TiN 含量为 15%时, 氮(N)固溶到钛(Ti)晶格中使 α -Ti 稳定化, 该显微组织的改变使 Ti64 基体的硬化效应达到 58%。随着 TiN 颗粒的加入, 复合材料的腐蚀电位变得更高, 而腐蚀电流密度受残余孔隙率的影响而增大, 使材料的耐腐蚀性降低。然而, 含 15% TiN 样品的钝化行为减弱。复合材料的非钝化行为导致其在腐蚀磨损测试过程中电位降低。此外, 固溶强化使复合材料的磨损率降低 88%。研究结果有利于理解材料的成分和烧结参数与提高腐蚀磨损性能之间的关系。

关键词: Ti64 合金; 复合材料; 粉末冶金; 显微组织; 腐蚀; 腐蚀磨损

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