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Surface treatment by plasma carbonitriding of Ti-6Al-4V alloy for dental implants

Tratamento de superfície por carbonitretação a plasma de liga de Ti-6Al-4V para implantes dentários

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ABSTRACT

In recent years, intensive development of dentistry stimulates the demand for new titanium implant materials created by surface engineering. Plasma nitriding is proposed as a solution to improve the biocompatibility. This work investigated the influence of plasma carbonitriding on the roughness and contact angle of Ti6Al4V treated in a Ar / N_2 / CH_4 plasma for 3 h and 6 h at 600 °C. The characterization was made by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Theta Lite Optical Tensiometer, and laser confocal microscopy. The XRD results indicated the formation of $Ti_3N_{1.29}$ and Ti_2N phase. It was observed that the surface roughness increases from 0.24 to 0.87 μm after 3 h and from 0.24 to 1.09 μm after 6 h of carbonitriding. The contact angle was 38° and 30° for 3 h and 6 h, respectively.

Keywords: Ti-6Al-4V, Plasma carbonitriding, Dental implants.

RESUMO

Nos últimos anos, o desenvolvimento intensivo de odontologia tem estimulado a demanda por novos materiais de implante de titânio criados por engenharia de superfícies. A nitretação a plasma é proposta como uma solução para melhorar a biocompatibilidade. Este trabalho investigou a influência de carbonitretação por plasma na rugosidade e no ângulo de contato da liga de Ti6Al4V tratado em um plasma Ar / N_2 / CH_4 por 3 h e 6 h a 600 °C. A caracterização foi feita por difração de raios-X (DRX), microscopia eletrônica de varredura por emissão de campo (EC-MEV), tensiometro ótico Theta Lite e microscopia confocal a laser. Os resultados de DRX indicaram a formação das fases $Ti_3N_{1.29}$ e Ti_2N. Foram observados aumentos de rugosidade de superfície de 0,24 para 0,87 μm após 3 h de carbonitretação e de 0,24 para 1,09 μm após 6 h. O ângulo de contato foi de 38° e 30° para 3 h e 6 h, respectivamente.

Palavras-chave: Ti-6Al-4V, Carbonitretação a plasma, Implantes dentários.

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INTRODUCTION

Titanium and its alloys, especially Ti6Al4V, have been widely used in the manufacturing of dental implants because of their superior mechanical property, low density, high corrosion resistance and excellent biocompatibility[1,2]. However, in recent years intensive development of dentistry stimulates the demand for new titanium implant materials created by surface engineering[3].

Properties such as roughness and contact angle are important for cell growth and proliferation, helping to establish the implant. Several studies have shown that increasing in surface micro- and submicron-scale roughness, with feature sizes comparable to cell dimensions, lead to enhanced osteoblast differentiation and local factor production in vitro[4,5], increased bone-to-implant contact in vivo[6,7] and improved clinical rates of wound healing[8,9]. Surface nano-scale roughness, which directly corresponds to the sizes of proteins and cell membrane receptors[10], recently added to the surface of implants to better mimic the hierarchical structure of bone, has also shown promising results in vitro[11], in vivo[12] and in the clinic[13,14], validating the biological relevance of nano-topography for bone formation.

The surface energy of an implant, measured indirectly by the liquid–solid contact angle (CA) and thus related to wettability, is another surface characteristic known to affect the biological response to the implant. Surface wettability can affect four major aspects of the biological system: (i) adhesion of proteins and other macromolecules onto the surface (conditioning); (ii) hard and soft tissue cell interactions with the preconditioned surfaces; (iii) bacterial adhesion and subsequent bio-film formation; and (iv) rate of osseous integration in the clinic (in vivo)[15]. The lower the contact angle, the better wettability of biological fluids on the surfaces of implants.

Plasma surface modification is an effective and economical surface treatment technique for many materials and has aroused growing interests in biomedical engineering[16]. Plasma nitriding has been proposed as a possibility for improving the surface properties[17]. Plasma nitriding of titanium alloys results in a thin composed layer of titanium nitrides, and a nitrogen diffusion zone[18]. Titanium nitride has been successfully used as coating materials due to their tribological properties, biocompatibility and affordable price[19]. In this work, the plasma was generated from the atmosphere $0.49N_2/0.49Ar/0.02CH_4$. Ions of Ar (40 amu) are efficient for sputtering of Ti (47.9 amu) due their similar atomic mass. Therefore, the bombardment of Ar^+ on the Ti surface can produce high surface roughness that is the aim of this work. It is inexorable in plasma nitriding process the presence of residual gas in the vacuum chamber, like O_2 and H_2O, which can oxidize the surface a material to be treated. For minimizing this possible oxidation, we used a low proportion of CH_4 in the plasma atmosphere (associated with the ion bombardment during the plasma nitriding) that contributes to a lower oxidation state of the Ti surface[20].

The aim of this work is to study the surface changes of Ti6Al4V caused by the plasma carbonitriding for biomedical applications, evaluating the behavior of roughness and wettability properties as well as morphology generated by the intense plasma ion bombardment.

MATERIALS AND PROCEDURES

Twenty discs machined from titanium grade 5 (Ti6Al4V) with dimensions of 6 mm × 3 mm (diameter × thickness) were divided into two groups of ten samples. Table 1 shows the treatment parameters used in this work.

The equipment used for the treatment of nitriding consists of: a reactor (discharge chamber) made of stainless steel with 300 mm in diameter and 300 mm in length; an Edwards mechanical vacuum pump with a capacity of 18 m^3/h was connected to the reactor, which is responsible for producing a vacuum of the order of 10^{-3} torr; gas cylinders CH_4, N_2 and Ar; flowmeters for controlling the chemical composition of the gas mixture; a DC power supply; and pressure and temperature gauges.

The crystalline phases were characterized by using a Cu K-a Shimadzu XRD – 600 diffractometer (2 deg. / min, q – 2q) range from 20° to 80°. The surface morphology was evaluated by field emission scanning electron microscopy (FE-SEM) model JSM-6701 F. Samples' contact angle, using water as a probe liquid, were measured using a contact angle detection system (Theta Lite Optical Tensiometer, KSV model CAM 101). The droplet images of de-ionized water (2 µl) on the sample surface were captured within 20 s after supplying water. The roughness parameters Ra and Sa samples were determined using a laser confocal microscope Leica Model DCM3D.

RESULTS AND DISCUSSIONS

XRD results

Figure 1 shows X-ray diffraction spectra recorded for untreated samples (Ti-6Al-4V) and carbonitrided during 3 h (N49_3) and 6 hours (N49_6). The XRD pattern for the as-received material was fitted with the hexagonal a-Ti and the cubic b-Ti phases[21]. The diffraction patterns for samples submitted to 3 h and 6 h of nitriding showed peaks corresponding to $Ti_3N_{1.29}$ and Ti_2N phases, respectively.

Table 1: Treatment carbonitriding parameters.

Samples group	Carbonitriding time (h)	Temperature of treatment (°C)	Plasma Atmosphere	Current of discharge (A)	Cathode Voltage (V)
1	3	600	49% N_2, 49% Ar, 2% CH_4	1.0	700
2	6				

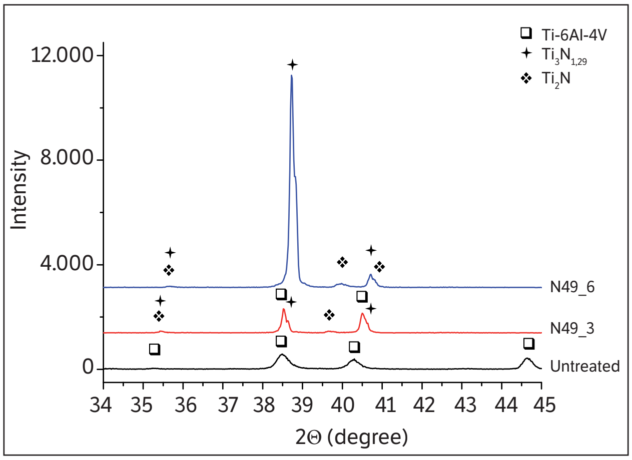

Figure 1: XRD of samples: untreated, N49_3 and N49_6.

Surface morphology

Figure 2 shows the FE-SEM analysis of (untreated) samples, where it is possible to see the scratches and grooves on the surface due to the machining process.

Figure 3 shows the morphologies of the samples submitted to carbonitriding. Figures 3a and 3b show two magnification of a sample treated for 3 h. It is possible to see deep nano-holes associated to high micro-roughness morphology. Figures 3c and 3d show two magnification of a sample treated for 6 h. It is possible to see higher micro-roughness morphology and more deep holes, indicating that the time of treatment is a very important parameter for changing the surface roughness. The morphology of the nitrided surfaces showed rosettes structures, generated by the action of the ion bombardment (mainly due to the argon ions that have the atomic mass closed to the Ti mass). The mixture of micro and nano-topography is excellent for the healing process. The nano-holes promote initial anchor of proteins that form the fibrin network by which cells migrate to the implant surface, while the micro-topography promotes adhesion of osteoblastic cells and stimulates cell differentiation that will result in the production of the new array bone[22].

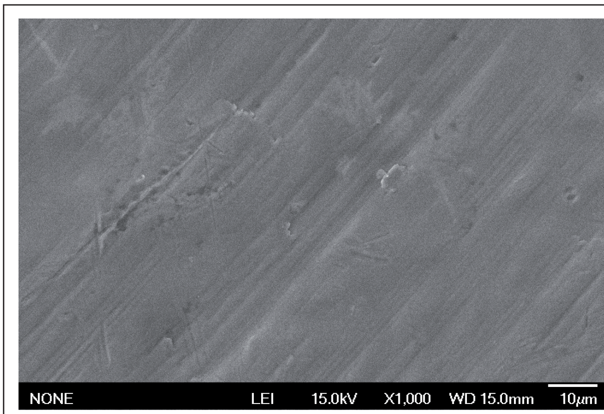

Figure 2: FE-SEM image of machined sample [1000 ×].

Roughness

The roughness of the machined samples showed mean values 0.23 and 0.24 μm of Ra and Sa, respectively. The carbonitriding acted increasing the surface roughness depending on the time of treatment. Samples treated for 3 h showed Ra 0.91 μm and Sa 0.87 μm, while samples treated for 6 h showed Ra 1.09 μm and Sa 1.09 μm. Experimental investigations between 4 weeks and 1 year after implant showed clear evidence that the bone response of moderately rough surfaces (Sa between 1.0 and 1.5 μm) was significantly better than bone responses for smoother surfaces[23,24]. The moderately rough implant surfaces promote the differentiation of osteoblastic cells in vitro and achieve a faster and stronger osseous-integration in vivo[25].

Contact angle

Results showed an important reduction in the contact angle by the action of carbonitriding. The average value of 84° for machined samples was reduced to 38° and 30° for samples treated for 3 h and 6 h, respectively. Figure 4 shows the profile of the water drop on the surface of those samples.

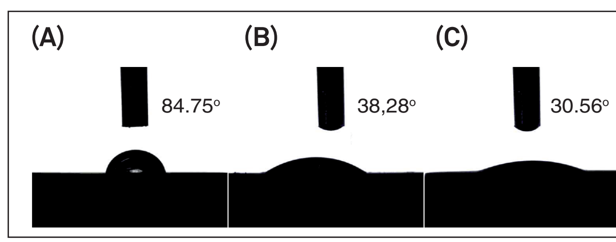

Figure 4: Profile of drop of water on the surface: (A) machined, (B) N49_3, and (C) N49_6.

CONCLUSION

This study evaluated the surface characteristics of Ti6Al4V after plasma carbonitriding. The carbonitrided samples showed on their surfaces TiN_2 and $Ti_3N_{1.29}$ phases; the presence of TiO_2 or TiC phases was not observed. The carbonitriding of Ti6Al4V alloy increases the roughness and decreases the contact angle of

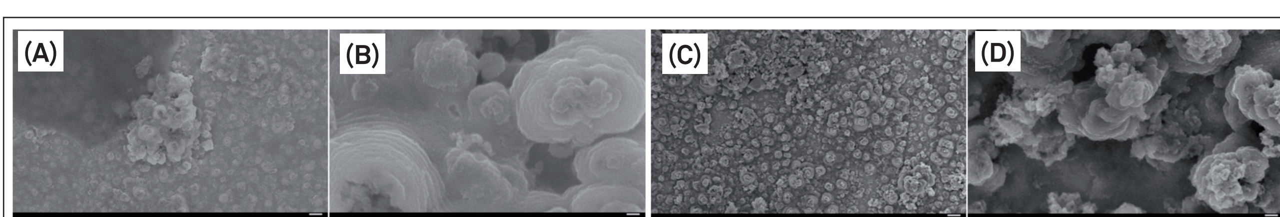

Figure 3: FE-SEM images of nitriding samples: (A) and (B) N49_3 [5000 ×, 50000 ×], (C) and (D) N49_6 [5000 ×, 50000 ×].

de-ionized water drops. The surface morphology was changed by the action of ion bombardment, which produces nano-holes and micro-roughness. These are some properties related to the biological response of the surface. The low contact angle helps in the contact blood clot – implant surface, which will trigger the whole cascade of events (coagulation, formation of fibrin network, etc.) that interfere with the early stages of healing. The nanostructured morphology increases adhesion of proteins responsible for migration and attachment of osteoblastic cells.

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