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Formation of Ti-O Biomedical Film on Ti6Al4V Alloy by DC Glow Plasma Oxidizing

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Abstract

Ti-O film is a kind of biocompatible surface materials. In this paper, a new method, glow discharge plasma oxidizing, has been used in synthesizing Ti-O gradient films on Ti6Al4V substrates. The effects of ion bombardment and process parameters on the structures of titanium oxide layers have been investigated. The results demonstrate that DC glow plasma oxidizing is more efficient in preparation of dense, hard, and high adhesive Ti-O biomedical films on titanium and its alloys. Samples treated by this method show higher hardness values than by others. Especially, in the condition of hollow cathode discharge, the ion bombardment enhances ionization of oxygen, promotes the oxygen permeation and facilitates the formation of the oxide of low valence states of titanium.

1. Introduction

Ti-O film has been utilized in many biomedical aspects, such as dentureclasps, artificial dental roots, hip joints, intraluminal metallic stents and artificial heart valves etc[1-4], as Ti-O film has good tissue and blood biocompatibility. In comparison with titanium and its alloy, Ti-O film is hard, wear-resistant and will reduce the adverse reaction in response to the wear particles due to the friction. On the other hand, Ti-O film has an anti-coagulation role in preventing thrombus formation while being used in blood-contacting occasion. The measurements of dynamic clotting time and hemolysis rate has demonstrated that Ti-O film has blood compatibility better than those of 316L stainless steel, NiTi alloy and low temperature isotropic pyrolytic carbo.

Up to now, Ti-O film can be fabricated by various methods, including ion-beam-assisted deposition (IBAD) [3], plasma-immersion-ion implantation (PIII) [5], magnetron sputtering [6,7], reactive sputtering [8,9], electrolytic oxidation [10,11] etc. In the present paper, a new method for fabricating Ti-O film is introduced, which is DC glow plasma oxidizing technique. In comparison with other methods, this method is very efficient in preparing thick, hard, and high adhesive Ti-O films, which may be even more suitable for biomedical applications. Besides the structures of Ti-O films, the effect of technology parameters including bombardment energy, temperature and oxygen partial pressure on characteristics of Ti-O films such as thickness and hardness will be discussed.

2. Experimental

The test equipment was a change of original metalizing furnace [12,13]. The discharge pattern of the DC glow plasma oxidizing equipment can include that of single glow or hollow cathode glow as shown in Fig. 1.

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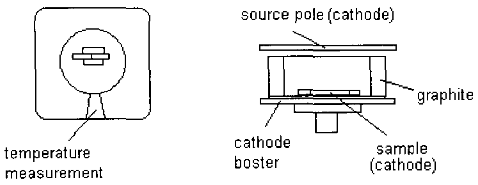

Fig. 1. Schematic sketch of DC glow-discharge plasma oxidization.

Ti6Al4V alloys were used as source electrode and samples (substrates), which were exerted equal bias voltage. The test processes were as below. Ti6Al4V samples were cut into 15mm × 10mm × 2 mm, ground down to 1000-SiC paper, polished, ultrasonically cleaned in ethanol, and dried before they were placed in treatment furnace. Prior to oxidizing, the chamber was evacuated to a base pressure of 10-4 Pa. Then Ar and oxygen gas were induced into the chamber, partial pressure of which was controlled respectively by each flowmeter. The working pressure was maintained at 20 ~ 60 Pa. The working temperature was maintained at 973K ~ 1273K, and the treatment period was 2~4 hr. The source electrode and samples were applied by an equal DC bias voltage of 600 ~ 1300 V, and the hollow-cathode glow discharge was produced. It is believed that oxygen gas was ionized in plasma, permeated into the surface layers of Ti6Al4V specimens and oxidized to form the Ti-O films. Among them, process parameters including cathode bias voltage, treatment temperature and oxygen partial pressure affect the film structures.

The chemical composition of the surface layer and microstructures were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The phase structure identification was conducted using X-ray diffraction (XRD). Microhardness measurements (Knoop indenter, 25 gf; Vickers indenter, 50 and 100 gf) were carried out on the modified layers and on the matrix.

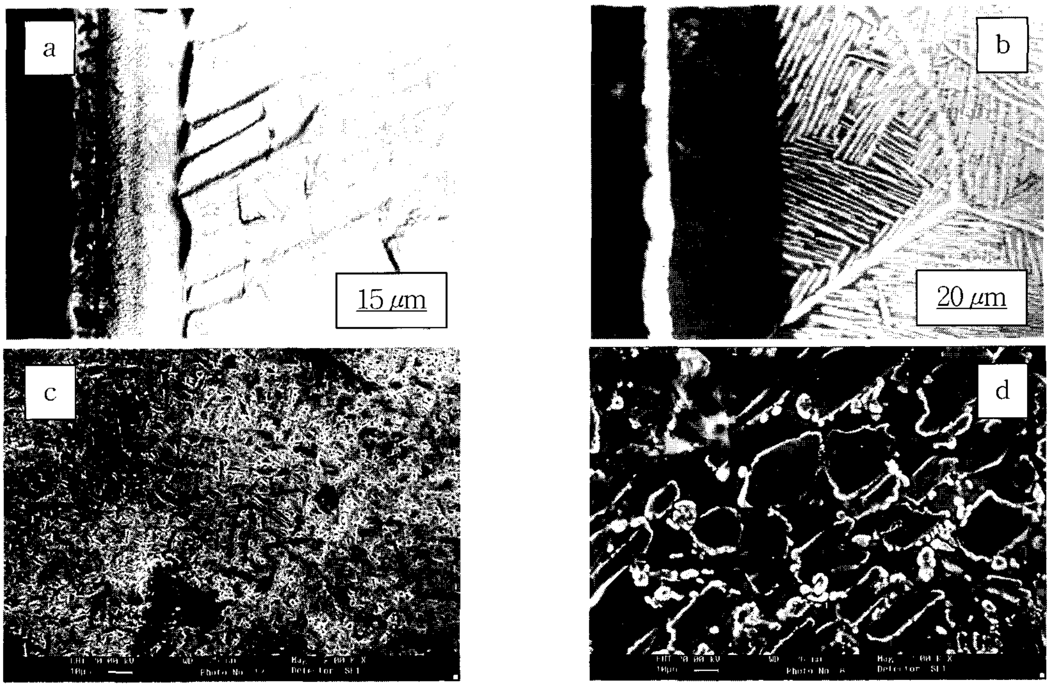

Fig. 2. (a) and (c): cross-section fracrograph and surface morphology of Ti-O films formed under conditions of high oxygen pressure and low bombardment. (b): cross-section fracrograph of Ni-doping Ti-O films formed under conditions of low oxygen pressure and high bombardment. (d): surface morphology of Ti-O films formed under conditions of low oxygen pressure and high bombardment.

3 Results and discussion

3.1 Micrographs and bombardment

In previous work [13], the structural characteristics of Ti-O films under bombardment condition have been discussed. Figure 2 shows the cross-section fractograph and surface morphology of the obtained Ti-O films on Ti6Al4V substrates.

The structures of obtained films are different under different conditions. XRD and EDAX analysis results indicated that all phases existed in Ti-O films were *rutile* TiO_2, TiO_{1+X}, TiO, α-Ti(O) and other unobvious phases (P) [13] as shown in Fig. 3. Figure 3 shows structural characteristic of Ti-O film formed on Ti6Al4V using dc glow plasma oxidizing technique. The Ti-O film can be divided into two parts. The first part is the outer layer consisting of TiO_2 and TiO_{1+X} in which the thickness is denoted as δ_E, and the second part is the inner layer consisting of TiO, α-Ti(O) solid solution and other unobvious phases in which the thickness is denoted as δ_P. The total thickness of Ti-O film can be marked with $\delta = \delta_E + \delta_P$.

It is well known that oxygen possesses a great solubility in titanium at elevated temperature. Going beyond the solubility, all the titanium oxides with different valence states will appear. However, in comparison with the oxidation method by heat treatment, the bombardment action makes the structures of Ti-O films changed to some extent. Under conditions of high oxygen pressure and low bombardment, the Ti-O films consist of more titanium oxide (compound) with high valence states of titanium as shown in Fig. 2(a) and (c), and the δ_E/δ value is greater. On the contrary, under conditions of low oxygen pressure and high bombardment, the Ti-O films consist of more titanium oxide with low valence states of titanium and diffusion phase (α-Ti crystals rich in oxygen interstitial atoms) as shown in Fig.2 (b) and (d), and the δ_P/δ value is greater. Especially, in the condition of hollow-cathode discharge, the ion bombardment enhances ionization of oxygen, promotes the oxygen permeation and facilitates the formation of the oxide of low valence states of titanium. However, the ion bombardment strength can be judged with sputtering yield. Sputtering yield can be expressed by the following equation [14]:

$$y_1 \fallingdotseq 4.24\times10^{-8} nR^2 E_0 \frac{m_1 m_2}{(m_1+m_2)^2} \exp(-10.4 \frac{\sqrt{m_1}}{m_1+M_2} E) \quad (1)$$

where y_l is the sputtering yield, R is the collision radius, and E is the sputtering enegy. While the values of other parameters are fixed, the sputtering strength decreases as R decreases in accordance with a parabolic law.

Oxygen atom is a small-radius interstitial one. The back-sputtering of oxygen is much weaker while oxidizing. Meanwhile, the ion bombardment make the oxygen ionization intense, results in a high oxygen potential, and enable a lot of oxygen atoms to be adsorbed at the active surfaces of titanium and subsequently diffuse inner to form a wide gradient Ti-O diffusion coatings. Initial titanium oxide compounds are formed at grain boundaries, for the grain boundaries are the shortcuts for oxygen diffusion, where the oxygen concentration is quite high. Nevertheless, the high-valence oxides are liable to be

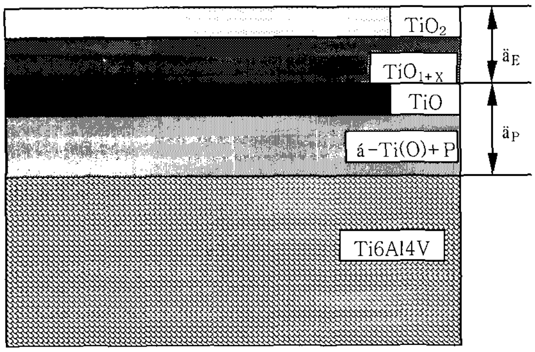

Fig. 3. Structural sketch map of Ti-O film formed on Ti6Al4V using dc glow plasma oxidizing technique.

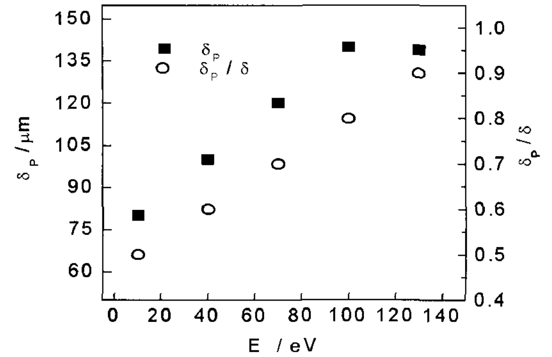

Fig. 4. Effect of bombardment energy on absolute and relative value of the thickness of the oxidizing films.

removed by bombardment of energy-carrying particles. The poor adhesion of the oxide is usually ascribed to the tensile stresses which occur at the titanium oxide interface as a consequence of the high Pilling Bedworth ratio of rutile and titanium [15]. Thus, the relative quantity of oxide existed remain little, and the width of oxygenizing layer consisting of solid solution is correspondingly greater. Figure 4 shows the Effect of bombardment energy on absolute and relative value of the thickness of the oxidizing films.

The existence of TiO may be related to the following changes:

$$TiO_2 \rightarrow TiO + O, \quad Ti^{4+} + 2e^- \rightarrow Ti^{2+} \qquad (2)$$

Ti-O bonding in *rutile* TiO_2 is much weaker than that in *NaCl* TiO [16]. In the action of cathode sputtering, TiO increases at the expense of decrease in the quantity of TiO_2.

3.2 Affecting factors

The factors affecting the characters of Ti-O film include oxygen partial pressure, working temperature and treatment time. Figure 5(a) shows the plasma-oxygenizing kinetics of Ti6Al4V specimens. It is seen that the curve of relationship between film thickness and treatment time is a parabola. It implies that oxygenizing is a diffusion process, which is controlled by diffusing factors. It is known that vacancy cluster or defect cluster in the surface layer of specimens, resulting from ion bombardment, is beneficial to the diffusion of displacing-solution elements [17]. However, it has a little influence upon the diffusion of interstitial elements. The reasons why the Ti-O films are thicker synthesized using dc glow plasma oxidizing are that ion bombardment enhances oxygen ionization, and absorptivity, driving effort for diffusion increases as the oxygen partial pressure increases [Fig. 5(b)]. The role of temperature is similar to that of oxygen partial pressure [Fig. 5.(b)].

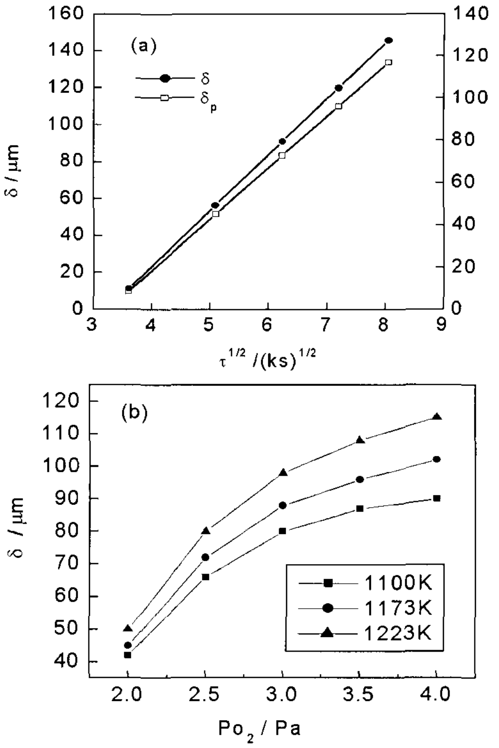

Fig. 5. (a)plasma-oxygenizing kinetics, and (b)effect of temperature and oxygen partial pressure on thickness of Ti-O film.

3.3 Microhardness

The hardness of oxygenizing layer is relative to O/Ti ratio as shown in Fig. 6.

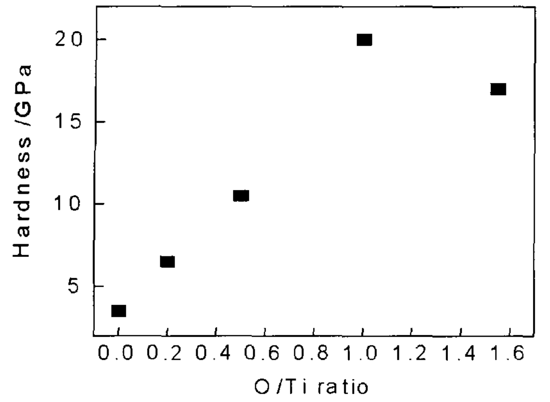

Fig. 6. Relationship between hardness of Ti-O film and O/Ti ratio.

The hardness of TiO_{1+X} decreases as x increases. It is reported that TiO possesses a very high hardness value. *NaCl* TiO possesses a same hardness as *NaCl* TiN does, which is 20 Gpa [16]. The reason is that the Ti-O bonding is much strong in *NaCl* TiO. Moreover, the hardness of diffusion layer increases with oxygen solution. Low hardness of titanium is owing to its hexagonal-close-packed structure with low c_0/a_0 ratio [18]. While oxygen solutions in titanium, oxygen atoms occupy the octahedral interstice and cause the crystal cell to expand in c direction. In accordance with XRD data, it is calculated the lattice parameters of α-Ti solid solution with the presence of oxygen interstitial atoms. The results are as below: $a_0 = 0.2954$ nm, $c_0 = 0.4821$ nm, $c_0/a_0 \approx 1.632$. In comparison with the data from ASTM card: $a_0 = 0.2950$ nm, $c_0 = 0.4585$ nm, $c_0/a_0 \approx 1.554$, it can be seen that the c_0/a_0 ratio of α-Ti solid solution with the presence of oxygen interstitial atoms has increased. The increase of the c_0/a_0 ratio leads to an increase of hardness. Titanium deforms by prismatic and pyramidal slip systems, characterized by a fairly large number of slip planes; by increasing the c_0/a_0 ratio, the number of slip planes is restricted developing a hardness increase [15].

4. Conclusions

There exists a obvious relationship between the structures of Ti-O films and process parameters including bombardment energy, oxygen partial pressure, temperature and time. Ion bombardment enhances oxygen ionization, promotes oxygenizing, and facilitates the formation of the oxide of low valence states of titanium and diffusion layer consisting of solid solution. The samples treated by using dc glow plasma oxidizing show thicker hardened layers, having higher hardness values. It can be said that the dc glow plasma oxidizing is more efficient in preparation of dens, hard, and high adhesive Ti-O biomedical films on titanium and its alloys.

References

[1] M. P. Casaletto, G. M. Ingo, S. Kaciulis, G. Mattogno, L. Pandolfi, and G. Scavia, App. Surf. Sci. **172**, 167 (2001).

[2] E. Czarnowska, T. Wierzchon, and A. Maranda-Niedbala, J. Mat. Proc. Tech. **92-93**, 190 (1999).

[3] F. Zhang, X. Liu, Y. Mao, N. Huang, Y. Chen, Z. Zheng, Z. Zhou, A. Chen, and Z. Jiang, Surf. Coat. Techn. **103-104**, 146 (1998).

[4] Y. X. Leng, J. Y. Chen, Z. M. Zeng, X. B. Tian, P. Yang, N. Huang, Z. R. Zhou, and P. K. Chu, Thin Solid Films **377-378**, 573 (2000).

[5] M. Rinner, J. Gerlach, and W. Ensinger, Surf. Coat. Techn. **132**, 111 (2000).

[6] T. Sonoda_, A. Watazu, J. Zhu, A. Kamiya, T. Nonami, T. Kameyama, K. Naganuma, and M. Kato, Thin Solid Films **386**, 227 (2001).

[7] O. Banakh, P. E. Schmid, R. Sanjines, and F. Levy, Surf. Coat. Techn. **151-152**, 272 (2002).

[8] T. Sonoda and M. Kato, Surf. Sci. **402-404**, 241 (1998).

[9] F. Lapostolle, A. Billard, and J. von Stebut, Surf. Coat. Techn. **135**, 1 (2000).

[10] Y.-T. Sul, C. B. Johansson, Y. Jeong, and T. Albrektsson, Med. Eng. Phys. **23**, 329 (2001).

[11] Y. Han, S.-H. Hong, and K. W. Xu, Surf. Coat. Techn. **154**, 314 (2002).

[12] Z. Xu, US Patent, 47332539.

[13] C. L. Zheng, Z. Xu, X. S. Xie, and Z. Y. He, J. Univ. Sci. Techn. Beijing (in Chinese) **24**, 44 (2002).

[14] B. H. Gao and S. Y. Cui, Vac. Phys.(in Chinese), (Science Press, Beijing, 1983)

[15] F. Borgioli, E. Galvanetto, F.P. Galliano, and T. Bacci, Surf. Coat. Techn. **141**, 103 (2001).

[16] A. Bally and P. Hones, Surf. Coat. Techn **108-109**, 166 (1998)

[17] C. J. Li and Z. Xu, Surf. Eng. **3**, 310 (1987).

[18] K. E. Budinski, Wear **151**, 203 (1991).