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Effects of HA and TiN Coating on the Electrochemical Characteristics of Ti-6Al-4V Alloys for Bone Plates

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Abstract

Effects of HA and TiN coating on the electrochemical characteristics of Ti-6Al-4V alloys for bone plates were investigated using various test methods. Ti-6Al-4V alloys were fabricated by using a vacuum induction furnace and bone plates were made by laser cutting and polishing. HA was made of extracted tooth sintered and then tooth ash was used as HA coating target. The TiN and HA film coating on the surface were carried on using electron-beam physical vapor deposition (EB-PVD) method. The corrosion behaviors of the samples were examined through potentiodynamic method in 0.9% NaCl solutions at 36.5±1°C and corrosion surface was observed using SEM and XPS. The surface roughness of TiN coated bone plates was lower than that of tooth ash coated plates. The structure of TiN coated layer showed the columnar structure and tooth ash coated layer showed equiaxed and anisotrophic structure. The corrosion potential of the TiN coated specimen is comparatively high. The active current density of TiN and tooth ash coated alloy showed the range of about 1.0×10^{-5}A/cm^2, whereas that of the non-coated alloy was 1.0×10^{-4}A/cm^2. The active current densities of HA and TiN coated bone plates were smaller than that of non-coated bone plates in 0.9% NaCl solution. The pitting potential of TiN and HA coated alloy is more drastically increased than that of the non-coated alloy. The pit number and pit size of TiN and HA coated alloy decreased in compared with those of non-coated alloy. For the coated samples, corrosion resistance increased in the order of TiN coated, tooth ash coated, and non-coated alloy.

Keywords : Electrochemical characteristics, Bone plates, Active current density, Pitting potential

1. INTRODUCTION

In order to minimize damage to biological structures, bone plates with high biocompatibility and high corrosion resistance were studied[1]. The good dental bone plates are sufficient osseointegration at interface between an implant fixture and its surrounding bone tissue, and good elasticity and mechanical stability at damaged bone[2].

In this study, in order to fabricate dental and medical bone plates, the effects of hydroxyapatite (HA) made with tooth ash and TiN coating on corrosion resistance and surface phenomena of Ti alloyed bone plates were investigated using various test methods.

2. EXPERIMENTAL

For the aim of minimizing damage to biological structures, HA/TiN multilayer coatings were carried out by using electron-beam deposition method (EB-PVD). Ti-6Al-4V alloys were fabricated by using a vacuum induction furnace and rolled into 12 mm thickness and then homogenized for 24 hr at 1050°C. The bone plates were made by laser cutting and polished for electrochemical test and for HA and TiN coating. HA was made of extracted tooth sintered at 1200°C for 2 hr and then tooth ash crashed to 75~105 μm powder. The compacted tooth ash was used as target for HA coating. The TiN and HA film

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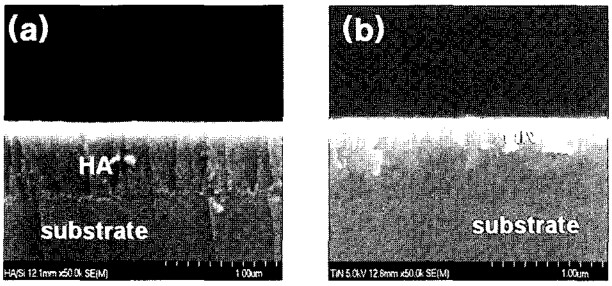

Fig. 1. SEM micrographs of (a) HA and (b) TiN coated layer of bone plate alloy.

coating on the surface were carried on using electron-beam physical vapor deposition (EB-PVD) method. Electrons were accelerated by high voltage of 4.2 kV with 80-120 mA on the deposition materials at 350°C in 2×10^{-6} torr vacuum. The surface morphology of coated layers was analyzed using FE-SEM. Wear resistance of the coating layers were tested by wear tester. Surface roughness was measured by a profilometer. The corrosion behaviors of the samples were examined through potentiodynamic method using potentiostat (EG&G Co. 263A, USA) in 0.9% NaCl solutions at 36.5 ± 1°C. Corrosion surface was observed using SEM, EDS and XPS.

3. RESULTS AND DISCUSSION

Coated films showed fine columnar structure and some defects, as shown in Fig. 1. Fig. 2 shows a little roughness and macro particles resulting from the electron beam instabilities[3] and certain damage of the surface layer in ceramic compound coatings such as HA and TiN[4]. The Ra(μm) of HA and TiN coated sample showed 0.38 μm and 0.07 μm. The XPS analysis, as shown in Fig. 3, confirms that stable phases are formed during TiN and HA film coating by electron beam diffusion. The TiN coated layer is more compact and homogeneous than HA coated layer. These results reveal the influence of the titanium alloy matrix on the structure of the TiN deposit. TiN coated surface showed predominantly

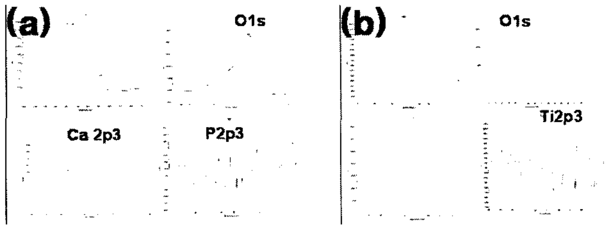

Fig. 3. XPS peaks of (a) HA coated and (b) TiN coated alloy.

TiN(220) and TiN(111) film with fine columnar structure on the surface[5]. The adhesion of TiN layer was higher than that of HA layer from the wear test. The loss of wear volume showed 0.006 g (TiN) and 0.021 g (HA). It is thought that TiN layer on specimen added adhesion force to interface between TiN layer and bone plate surface and TiN layer played a role to prohibit the crack propagation. Therefore TiN layer coated surface showed a good mechanical property. Fig. 2 shows surface morphology of TiN coated bone plate alloy. This surface will give a good biocompatibility to implant surface and it shows clearly different surface in compared with surface of non coated bone plate alloy.

Fig. 4 shows anodic polarization curves for HA, TiN and non coated bone plate alloy in 0.9% NaCl

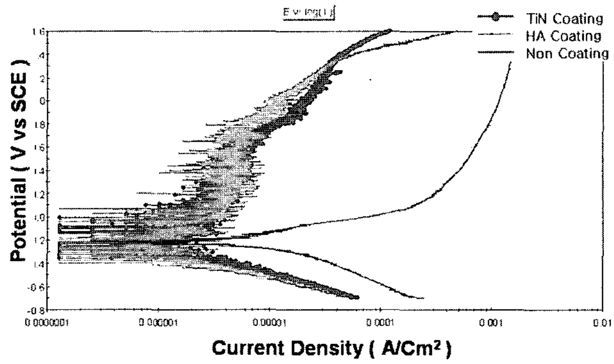

Fig. 4. Anodic polarization curves of HA coated, TiN coated, and non-coated bone plate alloy after potentiodynamic test in 0.9% NaCl solution at 36.5±1°C.

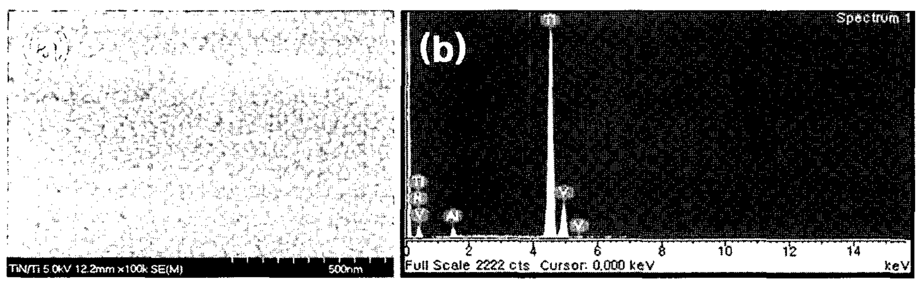

Fig. 2. SEM micrographs of TiN coated bone plate alloy: (a) TiN coated surface and (b) EDS peaks.

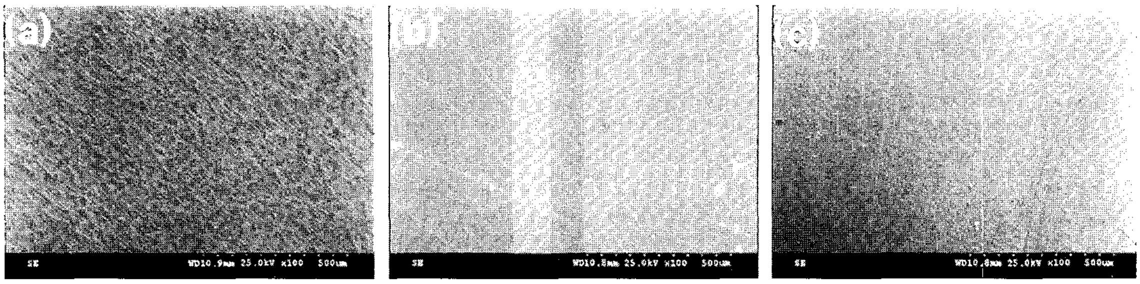

Fig. 5. SEM micrographs of the corroded (a) non-coated (b) TiN coated and (c) HA coated bone plate alloy after potentiodynamic test in 0.9% NaCl solution at 36.5±1°C.

solution at 36.5 ± 1°C. The active current density of TiN and HA coated bone plate alloy showed the range of about 1.0×10^{-5}A/cm^2, whereas that of the non-coated bone plate alloy is 1.0×10^{-4}A/cm^2. The active current densities of layer coating such as TiN and HA are smaller than that of the non coated layer, indicating the good protective effect resulting from more compact and homogeneous layer formation[6,7]. The corrosion potential of HA and TiN coated specimen is comparatively high. The pitting potential of TiN and HA coated bone plate alloy is more drastically increased than that of the non-coated bone plate alloy. In addition, the anodic polarization curves of TiN and HA coated bone plate alloy move to the left and upwards, which causes excellent pitting resistance. TiN and HA coated bone plate alloy has better corrosion resistance than non-coated bone plate alloy as shown in Fig. 4. There is a surface homogeneity and increasing formation of Ti oxide layer from following reaction: $TiN + O_2 \rightarrow TiO_2 + 1/2\ N_2$[7], and secondly, it is thought that protective film formation, such as TiO_2, TiO_2N, and $TiO_2 \cdot H_2O$ on the surface[8,9], play an important role in preventing the ingress of Cl^- and act as a pitting inhibitor against the aggressiveness of Cl^-[10].

Fig. 5 shows SEM photos of non-coated (a), TiN coated (b), and HA coated bone plate alloy (c) after corrosion test. The corrosion morphology shows that micro-pits number and pit size of HA and TiN coated bone plate alloy decrease in compared with those of non-coated bone plate alloy. It can be confirmed that passive film and surface homogeneity act as a pitting inhibitor in chloride solution[11].

4. CONCLUSIONS

It was found that the surface roughness of TiN coated bone plates was more smooth than that of tooth ash coated plates. The structure of TiN coated layer showed the columnar structure and tooth ash coated layer showed equiaxed and anisotrophic structure. The corrosion potential of the TiN coated specimen is comparatively high. The active current density of TiN and tooth ash coated alloy showed the range of about 1.0×10^{-5}A/cm^2, whereas that of the non-coated alloy was 1.0×10^{-4}A/cm^2. The active current densities of TiN coated bone plates were smaller than that of the tooth ash coated bone plates in 0.9% NaCl solution, indicating the good protective effect resulting from more compact and homogeneous layer formation. The pitting potential of TiN coated alloy is more drastically increased than that of the non-coated alloy. In addition, the anodic polarization curves of TiN coated alloy moved to the left and upwards compared with tooth ash coated alloy, which causes excellent pitting resistance. It was found that TiN and HA coated alloy had better corrosion resistance than non-coated alloy. The pit number and pit size of TiN and HA coated alloy decreased in compared with those of non-coated alloy. For the coated samples, corrosion resistance increased in the order of TiN coated, tooth ash coated, and non-coated alloy.

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