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Effect of deformation on corrosion behavior of Ti–23Nb–0.7Ta–2Zr–O alloy

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ABSTRACT

The influence of deformation on the corrosion behavior of a newly developed multifunctional beta titanium alloy Ti–23Nb–0.7Ta–2Zr–O (mol%) in Ringer's solution at 310 K was evaluated using an electron backscatter diffraction technique and electrochemical measurements. The results showed that the effect of deformation on the corrosion resistance of the beta titanium alloy is complicated. Small levels of plastic deformation are detrimental to the corrosion resistance, whereas large deformations tend to eliminate this detrimental effect.

1. Introduction

Titanium and its alloys have become preferred metallic materials for orthopaedic applications due to their good mechanical properties and excellent biocompatibility. Hence, the merits and demerits of using titanium and its alloys as implant materials have been well studied [1–4]. The higher elastic modulus than that of human bone is one of the drawbacks for titanium and its alloys, which has kept the researchers in quest of new alloys having a low elastic modulus with high strength. However, none of the alloys developed to date were completely satisfactory. Very recently, a multifunctional β titanium alloy, Ti–23Nb–0.7Ta–2Zr–O (mol%, TNTZO), has been developed by Saito et al.[5,6]. Compared with the most currently used titanium-based biomaterial Ti–6Al–4V, the TNTZO alloy has the advantage of ultra-low elastic modulus and ultra-high strength. It also has the advantage of consisting of nontoxic alloying elements such as niobium, tantalum and zirconium. A very attractive characteristic of the TNTZO alloy is that its elastic modulus drops further when cold working is applied. After 90% cold work, the modulus can drop below 40 GPa, and the strength can simultaneously increase up to 1200 MPa, which fully meets the requirement of low modulus and high strength for application as artificial bone.

Corrosion resistance is vital for materials used for orthopaedic applications. However, the corrosion resistance of materials is affected by many factors, such as crystal defects, metallurgical structure, composition, etc. In general, plastic deformation can change the corrosion resistance of metallic materials. It has been reported that plastic deformation has detrimental effect on the corrosion resistance of stainless steels due to the formation of defective interfaces and of defects in the grains resulted from the accumulation of internal stresses during the deformation process [7,8]. However, plastic deformation has a beneficial effect on the corrosion resistance of high strength cast iron because the change of shape of graphite after deformation results in a surface with a small number of inclusions per unit area [9,10]. As a promising implant material, the as-annealed TNTZO alloy has been determined to have better corrosion resistance than Ti–6Al–4V in Ringer's solution by the authors; details of these determinations will be reported elsewhere. The deformed TNTZO alloy has exhibited better mechanical properties than the as-annealed TNTZO alloy. However, information about the influence of plastic deformation on the corrosion resistance of the TNTZO alloy is rather limited. Hence, the aim of the present work was to examine the corrosion resistance of the TNTZO alloy in Ringer's solution,

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typically when plastic deformation of the material was applied using electron backscatter diffraction (EBSD) and electrochemical measurements.

2. Experimental

The starting material was cylindrical rods of the as-annealed TNTZO alloy. Samples with the dimension of φ4 mm×8 mm were carefully cut out from the rods by a wire-cutting machine, and then uniaxially compressed to 1.6% and 50.4% true strain using a universal testing machine. After deformation, specimens for subsequent testing were sliced transversely in the direction perpendicular to the loading direction. X-ray diffraction (XRD) profiles indicated that none of the samples show the presence of ω phase and α" martensite.

Specimens for crystal orientation measurements were electropolished in a 6% perchloric acid+30% butanol+64% methanol solution at a closed circuit voltage of 25 V, and then tested using EDAX EBSD facilities attached to the JEOL JSM-6460 scanning electron microscope (SEM) operating at 20 kV. A high speed CCD camera (DigiView) for pattern acquisition and TSL OIM analysis software were used. Orientation information was acquired on a hexagonal grid using a step size of 2 μm. For generating orientation and grain boundary maps, a grain tolerance angle of 15° was used, which distinguishes between low angle and high angle grain boundaries. The grain orientations were examined by inverse pole figure maps.

Specimens for electrochemical measurements were connected to a copper wire and embedded in an epoxy cold mounting resin. The surface of the specimens exposed to the electrolyte was mechanically ground to 5 μm silicon carbide paper finish, and then ultrasonically degreased in acetone, cleaned in distilled water and finally dried in air. The electrochemical studies were conducted in a Parstat 2273 Advanced Electrochemical System, with platinum wire and a saturated calomel electrode (SCE) as the auxiliary and reference electrodes, respectively. The electrolyte used was a naturally aerated Ringer's solution, of which composition is 9 g/l NaCl, 0.42 g/l KCl and 0.25 g/l $CaCl_2$. The open circuit potential variation with time was measured in Ringer's solution at 310 K. Potentiodynamic polarization scans were carried out with a scan rate of 1.66 mV/s in the potential range from about 250 mV below the open circuit potential to 2500 mV (SCE).

3. Results and Discussion

The image quality (IQ) maps of the as-annealed and the deformed TNTZO specimens in cross sectional view are shown in Fig. 1. The microstructure of the annealed TNTZO specimen consists of equiaxed grains 10 to 50 μm in size. A similar microstructure is observed in the 1.6% deformed specimen. After deformation to 50.4%, the equiaxed shape of the grains is still retained. The misorientation angle distributions determined in the areas in Fig. 1 are shown in Fig. 2. It is clear that the proportion of low angle boundaries is initially about 12%; however, it increases sharply when the alloy is deformed and increases to near 24% in the 1.6% deformed alloy and to near 40% in the 50.4% deformed alloy. Previous study has revealed that the TNTZO alloy deforms by traditional dislocation glide on slip systems, rather than the dislocation-free deformation mechanism [11,12], so the increase in proportion of low angle boundaries is related to the rise in dislocation density. Assessment of internal strain by EBSD can be made by measurement of the small misorientations associated with sub-boundaries in a deformed specimen. The internal strain can be inferred from the changes in the misorientation, which has an approximately linear relationship in the low angle regime [13]. Therefore, the increasing proportion of low angle boundaries in the TNTZO alloy implies increasing internal strain and resultant degradation of the quality of the IQ map. In Fig. 1, the bright region of the IQ map means low internal strain in that area, and the dark region implies high internal strain. It can be clearly seen in Fig. 1(c) that the distribution of strain is inhomogeneous in the heavily deformed specimen.

Fig. 3 shows the inverse pole figure (IPF) of the as-annealed and deformed TNTZO specimens obtained from EBSD mappings in the areas in Fig. 1. It can be seen that the as-annealed TNTZO specimen is texture-free. However, weak preferred orientations have arisen in the 1.6% deformed specimen. After deformation to a high degree (50.4%), a strong texture component parallel to the longitudinal direction of the bar corresponding to orientation {100} and {111} is apparent in the TNTZO alloy. This indicates that the {100} and {111} planes, which are the medium close-packed planes of the bcc metals, are the dominating orientation parallel to the surface of the specimens.

The open circuit potential vs. time behavior of the TNTZO alloy in Ringer's solution at 310 K is shown in Fig. 4. The as-annealed specimen shows the noblest potential and the 1.6% deformed specimen the least noble. With increasing immersion time, the potentials of the three specimens behave very differently. For the as-annealed and the 1.6% deformed specimens, potentials increase slowly towards positive values until they reach a steady value. For the 50.4% deformed specimen, however, the potential decreases at the first stage, and is followed by an increase. Subsequently, the potential decreases again before reaching a steady value. The variation of open circuit potentials with immersion time reflects the thinning or thickening of the surface oxide film. The increase in potential represents growth of the film, whereas the decrease in potential reflects the dissolution of the passive film. A steady potential indicates that the thickness of the film does not change; i.e. the passive film remains inert and protective. The present results show that all TNTZO specimens form a protective oxide film in Ringer's solution.

Typical potentiodynamic polarization curves for the TNTZO specimens in Ringer's solution at 310 K are presented in Fig. 5. It can be seen that small deformation (1.6%) causes an increase in corrosion current density by up to one order of magnitude. However, as the deformation degree increases from 1.6% to 50.4% the corrosion current density decreases rather than continue to increase. All TNTZO specimens reach their respective stable passive current densities as the potential increases, and exhibit a wide passive region. The partial stabilization of passive current densities implies that a protective passive film has formed. Small oscillations of