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Nuclear Instruments and Methods in Physics Research B 237 (2005) 543–549
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Phase formation in nitrogen ion implanted Ti–Al–Zr alloy and modification of corrosion property

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Received 13 January 2005; received in revised form 6 March 2005
Available online 20 April 2005

Abstract

In the present investigation, surface modification of Ti–Al–Zr alloy with nitrogen ions is considered as a method to improve its performance with respect to corrosion. Nitrogen ions were implanted on Ti–Al–Zr alloy at an energy of 65 keV at different doses between 1×10^{16} and 1×10^{17} ions/cm^2. The valence states of nitrogen, titanium and carbon on the sample surfaces were analyzed by X-ray photoemission spectroscopy (XPS). Glancing angle X-ray diffraction (GAXRD) was employed on the as-implanted and annealed specimens to understand phase formation with increasing doses and annealing temperatures. The implanted samples were subjected to electrochemical study in a solution with pH = 10 in order to determine the optimum dose that can give good corrosion resistance in a simulated nuclear reactor condition. The passive current density and area of the repassivation loop were found to decrease as the doses increased. Nitrogen ions implantation enhanced the passivation and reduced the corrosion kinetics of the alloy surface with increasing tendency for repassivation. The corrosion resistance of as-implanted and annealed samples was better than that of as-implanted samples. Nature of the surface and reason for the variation and improvement in corrosion resistance were discussed in detail.

PACS: 61.66.Dk; 61.14.Qp; 62.20.−x

Keywords: Ti–Al–Zr alloy; Nitrogen ion implantation; Phase formation; Corrosion resistance

1. Introduction

Ti and its alloys offer a unique combination of desirable mechanical properties, low density, high

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0168-583X/$ - see front matter
doi:10.1016/j.nimb.2005.03.008

corrosion resistance and biocompatibility, which make them a more attractive candidate for structural and biomedical applications [1–3]. However, with the working condition becoming severe, a few problems have been encountered with the application of this material such as: poor resistance to abrasion and corrosion, a tendency to seize and gall under loaded contact. Recently, related aspects have been studied widely. One method of improving the resistance of titanium and its alloys to abrasion and corrosion is ion implantation into its surface [3–6]. Schmidt e al. [7] and Leitao et al. [8] found that carbon or nitrogen ion implantation into Ti–6Al–4V leads to a pronounced reduction of oxide particle abrasion during sliding against ultra-high molecular weight polyethylene (HMWPE). A maximum abrasion resistance is achieved by the combination of a high microhardness in the implanted layer and a low oxide film thickness on the surface. Nitrogen ion implantation on Ti–6Al–4V and Ti–6Al–7Nb alloy has been observed to enhance the passivity and reduce the corrosion kinetics of the surface with increasing tendency for repassivation [9–11].

The aim of the present investigation is to understand the surface characteristics and corrosion behaviour of the implanted specimens under equilibrated conditions in a simulated nuclear reactor environment. Ti–Al–Zr alloy specimens were nitrogen ion implanted using 150 keV accelerator at 65 keV and four different doses. XPS and GAXRD were employed to identify the phases produced after implantation and annealing and to correlate them with the corrosion resistance. The corrosion behaviour of the as-implanted and annealed surface was investigated in a solution with pH = 10, and the results were compared with the corrosion behaviour of as-implanted and unimplanted specimens.

2. Experimental work

The material used in this study was an equiaxed hcp α-titanium alloy that contained 2.2 wt.% Al, 2.6 wt.% Zr, 0.03–0.04 wt.% Fe, 0.07 wt.% O and 0.01 wt.% N and had a basal texture. The specimens of 10 mm diameter and 2 mm thick were cut from plates fully annealed after cold rolling, and then mechanically polished with 200–1000 emery paper. Final polishing was done with three steps of alpha alumina1, 0.5, 0.3 and 0.05 μm until the surface became a mirror. The specimens were degreased with trichloroethylene followed by ultrasonic cleaning with deionized water.

The samples were placed onto an aluminum sample holder, the vacuum in the target chamber was 7.0×10^{-4} Pa. The implanted area was of 10 cm diameter. The implantation was carried out with N_2^+ beams at energy of 65 keV using a 150 keV accelerator at different doses ranging from 1×10^{16} to 1×10^{17} ions/cm^2. During the implantation, the beam current density was 2 μA, and the temperature for four doses was below 200 °C, respectively. After nitrogen implantation test, some as-implanted samples were annealed in a sealed capsule at different temperatures in order to understand the influence of annealing temperature on phase formation and corrosion resistance of Ti–Al–Zr alloy.

The valence states of nitrogen, titanium and carbon on the sample implanted were analyzed by X-ray photoemission spectroscopy (XPS). GAXRD was performed on the implanted surface of the specimens by STOE made diffractometer using CuKα radiation with incident angle of 0.3°. The diffraction was recorded for the 2θ range 20–80°.

As soon as the specimens were immersed into the electrolyte the initial potential of the samples was monitored as a function of time up to 60 min, or till the samples reached a stable potential. The aim of the open circuit potential (OCP)-time measurements was to understand the corrosion behaviour of the implanted specimens under equilibrated conditions in a simulated reactor environment.

Electrochemical potentiodynamic polarization of both unimplanted and implanted specimens was carried out in a solution (5.35 g/l NH_4Cl + 70 ml/l ammonia) with pH = 10 and temperature 306 K in order to simulate nuclear reactor environment. Nitrogen gas was continuously purged into the electrolyte throughout the study to eliminate the dissolved oxygen. All the potential measurements were made with reference to a