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Corrosion behavior of tin ions implanted zirconium in 1N H_2SO_4

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Abstract

In order to study the effect of tin ion implantation on the aqueous corrosion behavior of zirconium, specimens were implanted with tin ions to a fluence ranging from 1×10^{20} to 5×10^{21} ions/m^2, using a metal vapor vacuum arc source (MEVVA) at an extraction voltage of 40 kV. The valence states and depth distributions of elements in the surface layer were analyzed by X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the micro-morphology and microstructure of tin-implanted samples. When the fluence was greater than 1×10^{20} ions/m^2, many small tin balls were produced in the implanted surface. The potentiodynamic polarization technique was employed to evaluate the aqueous corrosion resistance of implanted zirconium in a 1N H_2SO_4 solution. It was found that a significant improvement was achieved in the aqueous corrosion resistance of zirconium implanted with 1×10^{20} ions/m^2. When the fluence is higher than 1×10^{20} ions/m^2, the corrosion resistance of zirconium implanted with tin ions decreased compared with that of the non-implanted zirconium. Finally, the mechanism of the corrosion behavior of the tin-implanted zirconium is discussed.

Keywords: Zirconium; Corrosion resistance; Tin ion implantation; Immersion test; X-ray photoemission spectroscopy (XPS); Auger electron spectroscopy (AES)

1. Introduction

Because of the low thermal neutron capture cross-section, favorable mechanical properties and good corrosion resistance, zirconium alloys are used in the nuclear industry. For example, Zr-alloys can serve as fuel cladding and core structure materials. However, with the concept of high burn-up fuel developing, improvements in the performance of zirconium and its alloys are increasingly required. It is well known that ion beam surface processing (IBP) techniques can significantly improve corrosion resistance [1–4]. Ion implantation offers the possibility to introduce a controlled concentration of an element to a thin surface layer. It was first shown, by Ashworth et al. [5], that chromium implantation could improve the corrosion resistance of iron. Additional studies of palladium implanted into titanium [6] and phosphorus implanted into iron [7] have confirmed that ion implantation with palladium or phosphorus may successfully improve the corrosion behavior.

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It is well known that tin can be a beneficial alloying element for zircaloys. While relatively few papers have reported on the corrosion behavior of tin-implanted zirconium.

In this paper, aqueous corrosion behavior of zirconium after implantation with tin ions was studied. The valence of tin, zirconium, oxygen and absorbed carbon were analyzed by X-ray photoelectron spectroscopy (XPS), the depth distribution of elements in the surface layer was determined by Auger electron spectrometry (AES), and the corrosion resistance of the implanted zirconium was investigated by the potentiodynamic method using a IM6e potentiostat (Zahner Elektrik Company, Germany). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out to observe the morphology and microstructure of the tin-implanted samples. The mechanism of corrosion behavior of tin-implanted zirconium in the aqueous is discussed.

2. Experimental procedure

Zirconium samples were machined to 10 mm × 10 mm from a sheet of zirconium fully annealed after cold rolling. The thickness of the samples was 1.0 mm. The composition of zirconium is Sn: 0.005 wt.%, Fe: 0.15 wt.%, Ni: 0.007 wt.%, Cr: 0.02 wt.%, Al: 0.0075 wt.%, B: 0.00005 wt.%, Cd: 0.00005 wt.%, Co: 0.002 wt.%, Cu: 0.005 wt.%, Hf: 0.01 wt.%, Mg: 0.002 wt.%, Mn: 0.005 wt.%, Mo: 0.005 wt.%, Pb: 0.013 wt.%, Si: 0.012 wt.%, Ti: 0.005 wt.%, U: 0.00035 wt.%, V: 0.005 wt.%, W: 0.01 wt.%, Cl: 0.01 wt.%, C: 0.027 wt.%, N: 0.0065 wt.%, H: 0.0025 wt.%, O: 0.16 wt.%, balanced with zirconium. The zirconium samples were mechanically polished using 200–800 emery paper, subsequently degreased in acetone and ethanol, chemically polished in a solution of 10% HF, 30% HNO_3 and 60% H_2O by volume, and finally rinsed in deionized water.

For implantation the samples were loaded onto a aluminum sample holder having a diameter of 12 cm. The vacuum level of the target chamber of the MEVVA (metal vapor vacuum arc) implantation apparatus was 1.3×10^{-3} Pa. Although the implantation apparatus has no magnet analysis capability, the extracted tin ions were known to consist of 47% Sn^+ and 53% Sn^{2+}. Fluences of 1×10^{20}, 5×10^{20}, 1×10^{21} and 5×10^{21} ions/m^2 were used. The extraction voltage for the tin implantation was 40 kV. Therefore, the implantation energies were 40 and 80 keV for Sn^+ and Sn^{2+}, respectively. There was no additional cooling system during implantation, the beam current density ranged from 8.85 to 35.4 μA/cm^2, therefore the implantation temperature will be changed depending on different beam current densities. Table 1 shows the implantation conditions.

Table 1
Implantation conditions

	Fluence (ions/m^2)			
	1×10^{20}	5×10^{20}	1×10^{21}	5×10^{21}
Beam current density (μA/cm^2)	8.85	22.1	26.5	35.4
Temperature (°C)	100	200	250	310
Implantation time (min)	5	15	20	65

The valence states of tin, zirconium, oxygen and carbon on sample surfaces were analyzed by X-ray photoelectron Spectroscopy (XPS). The surface morphology of implanted samples was studied using a (Hitachi) S-450 scanning electron microscope (SEM). The microstructure of implanted samples was investigated using transmission electron microscope (TEM). Three-sweep potentiodynamic polarization measurements were carried out to investigate the aqueous corrosion resistance of the tin-implanted zirconium. The potentiodynamic tests were performed in a 1N H_2SO_4 solution using IM6e potentiostat at room temperature (25 °C). The tested area was 1 cm^2 and the scan rate was 2 mV/s. All electrochemical potential measurements were taken with respect to a saturated calomel electrode (SCE); measurements were carried out as follows: an anode scan was conducted starting in a cathodic region of approximately -0.4 V with respect to the SCE and scanned into the anodic region of approximately $+2.0$ V with respect to the SCE.

3. Results and discussion

3.1. The valence of the elements in the surface layer

To compensate for a systematic error in XPS measurement, the energy position was first adjusted by comparing the binding energy of the absorbed C 1 s