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Studies on the oxidation behavior of niobium-implanted Zircaloy-4 at 500 °C

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Abstract

The effect of niobium ion implantation on the oxidation behavior of Zircaloy-4 was investigated. It was interesting to find that the oxidation behavior of Zircaloy-4 was deteriorated after niobium ion implantation. Auger electron spectroscopy, X-ray photoemission spectroscopy and glancing angle X-ray diffraction were employed to analyze the depth profile of the element composition, the valence of the oxide scale and the phase of the oxidation products, respectively.

1. Introduction

Zirconium and niobium exhibit good corrosion resistance to organic and inorganic acids and it is possible to improve the properties of zirconium by alloying additions. In fact, the Zr–1%Sn–1%Nb–(0.3–0.5)%Fe alloy designed in Russia more than 20 years ago is superior to either Zircaloy or binary alloys with Nb in its corrosion resistance in different water chemistry coolants [1]. Recently, as a substitute for Zr-4, several kinds of new zirconium alloys such as Zirlo (Zr–0.1Nb–1.0Sn–0.1Fe) [2] and M5 (Zr–1Nb–O) [3] were developed and are being tested in reactor. However, some reports showed that the corrosion behavior of Nb-containing Zr alloy was partly limited by certain factors, such as being very sensitive to the microstructure [4].

Ion implantation has been used in various materials to improve their surface properties and has played an important role in the modifying techniques of materials surface [5,6]. To investigate the oxidation resistance of zirconium alloys and provide a basis for comparing the oxidation behavior of Nb-implanted Zr-based alloys with Zr alloys containing Nb, niobium ion implantation was employed in the present study.

2. Experimental procedure

Zircaloy-4 samples were machined to 10 mm × 10 mm × 0.5 mm from a sheet of recrystallized Zircaloy-4. The composition of Zircaloy-4 is Sn: 1.4 wt%, Fe: 0.23 wt%, Cr: 0.1 wt%, Ni: 60×10^{-6} wt%, the balance zirconium. Subsequently, the samples were mechanically polished with 200–800 grade emery paper, degreased in acetone and ethanol, chemically polished in a solution of 10 vol.% HF, 30 vol.% HNO_3, 60 vol.% H_2O, rinsed in natural water and finally rinsed in deionized water. Finally, the dimensions of the samples were 9.94 mm × 9.94 mm × 0.40 mm.

The samples were loaded onto a steel sample holder in the target chamber of the MEEVA implanter at a vacuum level of 1.8×10^{-3} Pa. The implanted area was 12 cm in diameter. Extracted niobium ions consisted of 1% Nb^{+}, 24% Nb^{2+}, 51% Nb^{3+}, 22% Nb^{4+} and 2% Nb^{5+}, and the average valence of niobium was 3.0. The doses of the implantation ranged from 1×10^{20}, 5×10^{20}, 1×10^{21}, to 2×10^{21} ions/m^2 at the extracted

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voltage of 40 kV and the beam current of 1.5 mA. During implantation, no special cooling was applied to the samples and the maximum temperature of the samples was approximate 135 °C.

The weight gain curves of the samples were obtained on the basis of oxidation experiment in air at 500 °C for 100 min. Auger electron spectroscopy (AES) and X-ray photoemission spectroscopy (XPS) tests were respectively employed to analyze the depth profile of the element composition and the valence of the surface layer of the Zircaloy-4 samples. Glancing angle X-ray diffraction (GAXRD) was also used to examine the occurrence of any phase transformation in the oxide films.

3. Results and discussion

3.1. Weight gain curves of the Zircaloy-4 samples

Five groups of samples, including as-received Zircaloy-4 sample and niobium-implanted Zircaloy-4 samples were oxidized in air at 500 °C for 100 min. Three specimens of each type in a group were oxidized to reduce and even eliminate incidental errors. As a result, a point in an oxidation kinetic curve was determined by an average value from each three specimens. Fig. 1 compares the oxidation curves of Nb-implanted Zircaloy-4 with a dose range from 0 to 2×10^{21} ions/m^2. The curve 1 represents the oxidation weight gain of the as-received sample and curves 2, 3, 4, and 5 represent the weight gains of the implanted specimens with the dose of 1×10^{20}, 5×10^{20} and 1×10^{21}, and 1×10^{21} ions/m^2, respectively. For each curve, the weight gain increases with oxidation time. It is seen that the oxidation behaviors of Nb-implanted samples have been deteriorated compared with that of as-received one. Among the Nb-implanted samples, however, some improvement has been gradually achieved with increase of the dose of the implanted ions. When the dose of the implanted ions is raised to 2×10^{21} ions/m^2, it is indicated that the oxidation weight gain curve of this sample is closest to the curve of as-received sample (curve 1). This observation is not in agreement with the results of many previous reports [7,8]. In those reports, the oxidation behaviors were improved by niobium or yttrium ions implantation.

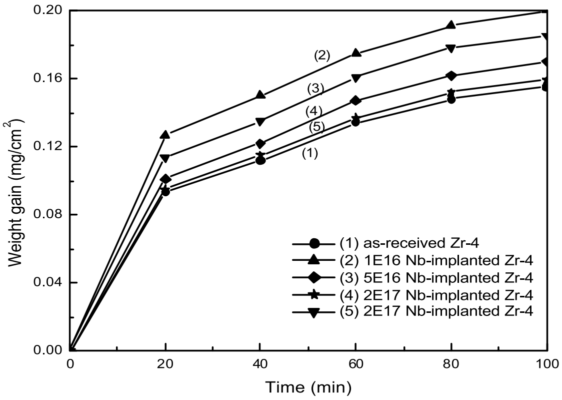

Fig. 1. The oxidation weight gain curves for (1) as-received Zircaloy-4, and for Zircaloy-4 specimens implanted with niobium ions at a dose of (2) 1×10^{20} ions/m^2, (3) 5×10^{20} ions/m^2, (4) 1×10^{21} ions/m^2, and (5) 2×10^{21} ions/m^2 at 500 °C in air.

3.2. Element distribution in the surface layer

AES tests were taken with a PHI-610/SAM spectrometer to analyze the depth and the concentration of the elements in the scale. In the AES measurement, the sputter rate is about 30 nm/min. The AES depth profiles of the specimens implanted with niobium ions are summarized in Fig. 2(a)–(d) respectively. In the Figures, the peak concentrations of niobium for these specimens are correspondingly 8%, 17%, 24%, and 32%, and the depths for the peak concentrations are almost the same value (45 ± 0.75) nm. Because of diffusion of the implanted niobium ions, the depths of niobium ions for these four implanted specimens should be $>45 \pm 0.75$ nm, the depth corresponding to the peak concentration of niobium. Although the oxygen signals fall off after 200–400 s, they remain all through the course of the AES analyses.

3.3. Composition and valance of the oxides

XPS tests employed to analyze the composition and the valence of the surface layer show that the surface energy of the absorbed C on the surface of the specimen is different from the standard binding energy, 284.8 eV. This energy margin is due to the system error and needs to be adjusted by comparing the surface energy of the absorbed C on the surface with that of the standard binding energy. The adjusted XPS spectra of $Nb3d_{5/2}$ and $Zr3d_{5/2}$ are represented in Fig. 3(a) and (b). These figures show that there is no significant change in shape and peak position, but a slight lateral excursion for the curves of different implantation doses. The binding energies coincide well with the standard values of Nb_2O_5 and ZrO_2, that is, 206.9 and 182.1 eV, respectively. Therefore, it can be concluded that the oxides of Nb and Zr in the scale exist in the form of Nb_2O_5 and ZrO_2.

3.4. GAXRD spectra at 0.3° incident angle of Zircaloy-4 samples

Fig. 4 indicates the GAXRD spectra at 0.3° incident angle for Zircaloy-4 samples with and without niobium subsequent to oxidation in air at 500 °C for 100 min.

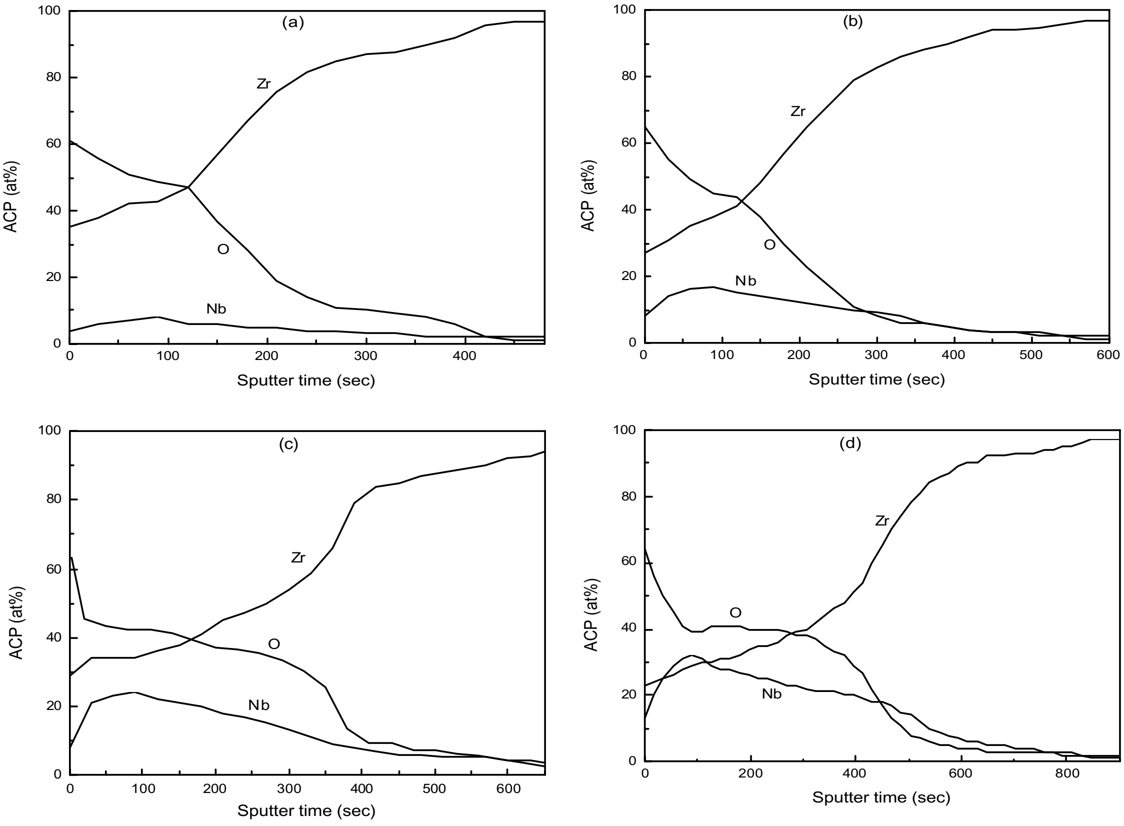

Fig. 2. AES depth profiles of Nb, Zr and O in the surface region of the Zircaloy-4 samples implanted with niobium at (a) 1 × 10^{20} ions/m^2, (b) 5 × 10^{20} ions/m^2, (c) 1 × 10^{21} ions/m^2, and (d) 2 × 10^{21} ions/m^2.

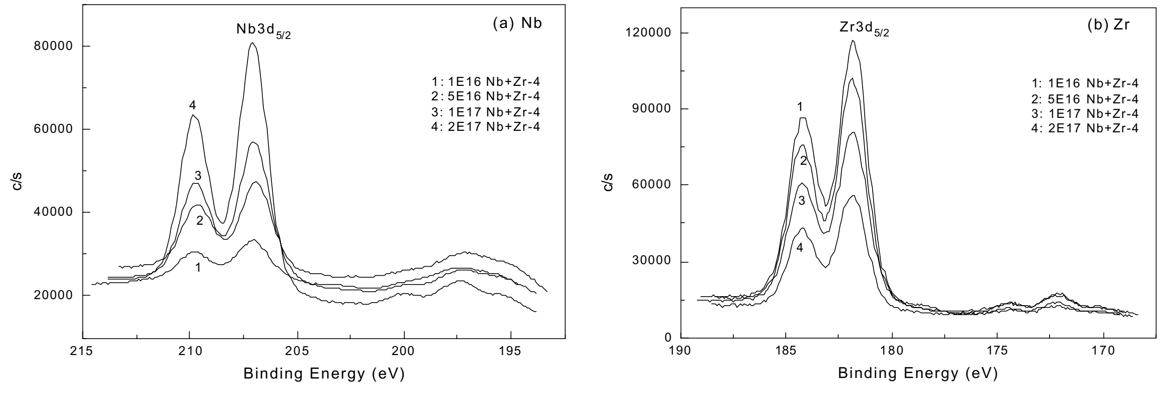

Fig. 3. XPS spectra of (a) $Nb3d_{5/2}$ peak, and (b) $Zr3d_{5/2}$ peak in the scale: (1) air oxidization after 1 × 10^{20} ions/m^2 implantation; (2) air oxidization after 5 × 10^{20} ions/m^2 implantation; (3) air oxidization after 1 × 10^{21} ions/m^2 implantation; (4) air oxidization after 2 × 10^{21} ions/m^2 implantation.

M represents monoclinic zirconia. From the figure, it is clear that all curves for five kinds of samples with and without niobium indicate the same peak positions in the oxide scale. Obviously, the oxide in the scale of every sample is monoclinic zirconia (m-ZrO_2). Not any other phase of the oxide has been found in all these five kinds of samples. As a result, it could be concluded that no phase transformation occurred as a result of niobium ions implantation, no matter how much the dose of implanted niobium ions was.

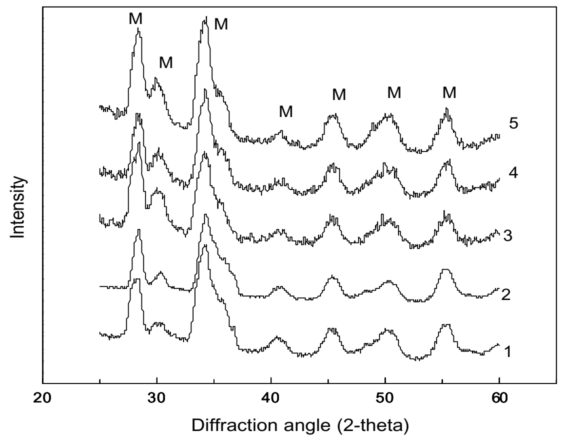

Fig. 4. GAXRD spectra at 0.3° incident angle of Zircaloy-4 implanted with niobium at (1) 0, (2) 1×10^{20} ions/m^2, (3) 5×10^{20} ions/m^2, (4) 1×10^{21} ions/m^2, and (5) 2×10^{21} ions/m^2, and then oxidized in air at 500 °C for 100 min. M represents monoclinic zirconia.

It is well known that when Zircaloy-4 is implanted by yttrium ions, ions of a certain reactive element, the oxide of yttrium in the scale exists in the form of Y_2O_3 and the improvement of oxidation behavior of Zircaloy-4 was achieved. It was found that the structure transformation from monoclinic zirconia to tetragonal zirconia, the chief reason for the significant reduction of oxidation, was attributed to the existence of Y_2O_3. For niobium-implanted Zircaloy-4, however, it has found in this study that the oxide of Nb in the scale exists in the form of Nb_2O_5, and no phase transformation occurs as a result of niobium ions implantation. Therefore, it could be concluded that the existence of Nb_2O_5 played no role in prompting the phase transformation of zirconia, and the deterioration of oxidation behavior for the niobium-implanted Zircaloy-4 should not result from the phase transformation of oxide. It would be worthwhile to further investigate the mechanism why niobium ions implantation led to the deterioration of oxidation behavior.

4. Conclusions

Oxidation behavior of Zircaloy-4 was deteriorated after niobium ions implantation, and the deterioration for the niobium-implanted Zircaloy-4 samples was decreased with increase of the dose of the implanted ions. The oxides of Nb and Zr in the scale of the Nb-implanted Zircaloy-4 existed in the form of Nb_2O_5 and ZrO_2. No phase transformation has been found in the oxide scale of the samples.

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