Effect of titanium ion implantation on the corrosion behavior of zircaloy-4

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Due to its low thermal neutron capture cross-section, good corrosion resistance, and adequate mechanical properties, zircaloy-4 is often specified for engineering use in the nuclear industry; for instance, it can serve as a fuel cladding and core structure material [1]. With the development of high burn-up fuel, improvements in the performance of zircaloy-4 are increasingly required. It is well known that certain modification methods, such as ion implantation, a type of ion beam surface processing (IBP), can significantly improve the corrosion resistance [2, 3], so there is a growing interest in the effect of ion implantation on the structure and the corrosion property of zirconium alloys in recent years. Some ion implantations, such as Ni [4], Y [5], N [6], La [7], have been reported to improve the aqueous corrosion resistance of zircaloy-4 significantly. However, similar to the same group IVA element zirconium, in the Chemical Periodic Table, little attention was paid to titanium ion implantation up-to-date. In this work we report the results of a study of titanium implantation on the corrosion behavior of zircaloy-4.

The composition of zircaloy-4 is Sn: 1.4 wt.%, Fe: 0.23 wt.%, Cr: 0.1 wt.% with balanced zirconium. The samples were machined to 50 mm × 20 mm × 1.4 mm from a sheet of fully annealed zircaloy-4, and subsequently mechanically polished with 200–800 grade emery paper, degreased in acetone and ethanol, rinsed in natural water at least three times and finally rinsed in de-ionized water.

Zircaloy-4 samples were loaded onto a steel-made sample holder in the target chamber of the MEVVA implanter at a vacuum level of 1.8×10^{-4} Pa. The implanted area had a diameter of 12 cm. The titanium implantation was carried out at an extracted voltage of 40 kV, and the beam current was 2 mA. During implantation, no special cooling was used for the samples and the maximum temperature of the samples was 150°C. The implanted ions were at normal dose range from 5×10^{16} to 4×10^{17} ions/cm^2.

Electrochemical polarization measurement was conducted in a 0.5 M H_2SO_4 water solution using a Zahner Elektrik IM6e potentiostat at room temperature. All electrochemical potential measurements were taken with respect to a saturated calomel electrode (SCE). Immediately after the specimen was immersed in the solution, a scan was performed starting in a cathodic region of approximately −0.5 V SCE and scanned into the anodic region of approximately +2.0 V SCE. From the polarization curves, corrosion potential and passive current density were used to rank corrosion resistance of the implanted zircaloy-4.

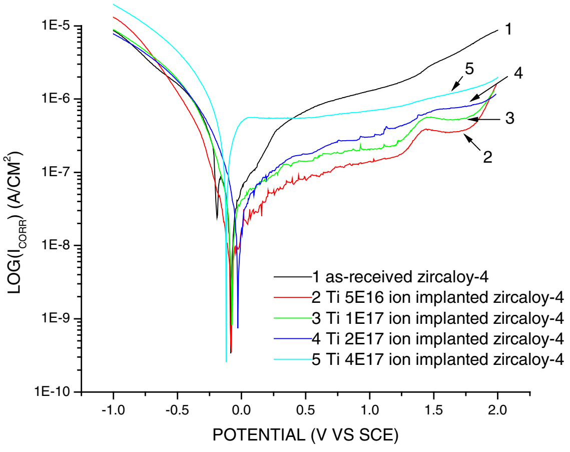

Figure 1 Effect of titanium ion implantation on the electrochemical behavior of zircaloy-4 in a 0.5 M H_2SO_4 water solution at room temperature.

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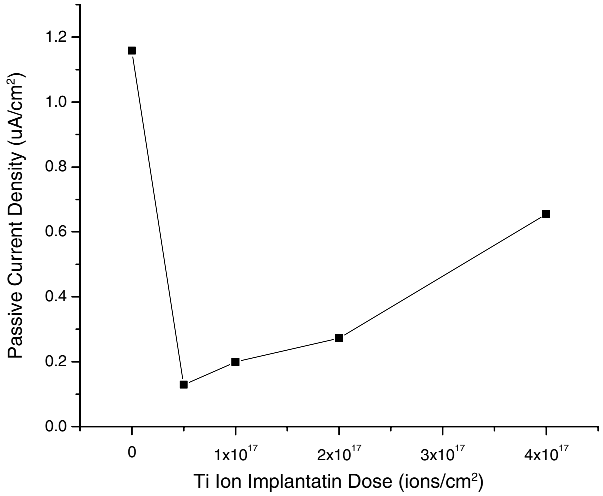

Figure 2 The dependence of passive current density Ip on the Ti implantation doses.

The structural and morphological changes of the post-irradiation zircaloy-4 surface were observed and identified by selected area electron diffraction (SAD) analysis and bright field examination using a JOEL JEM 200CX TEM with the accelerating voltage 200 kV. The camera constant of TEM SAD was calibrated by X-ray diffraction results.

Fig. 1 shows the polarization curves of the as-received zircaloy-4 and zircaloy-4 implanted with titanium at a dose range from 5×10^{16}, 1×10^{17}, 2×10^{17} to 4×10^{17} ions/cm^2. The passive current density was used to rank the corrosion resistance. In order to explore the relationship between the implantation dose and the corrosion property more clearly, the data of the passive current density and the implantation dose was summarized in Table I and plotted in Fig. 2. It is interesting that at lower dose, the passive current density decreased rapidly, at the point of 5×10^{16} ions/cm^2, the passive current density of implanted zircaloy-4 specimen is approximately a order of magnitude lower than that of the as-received zircaloy-

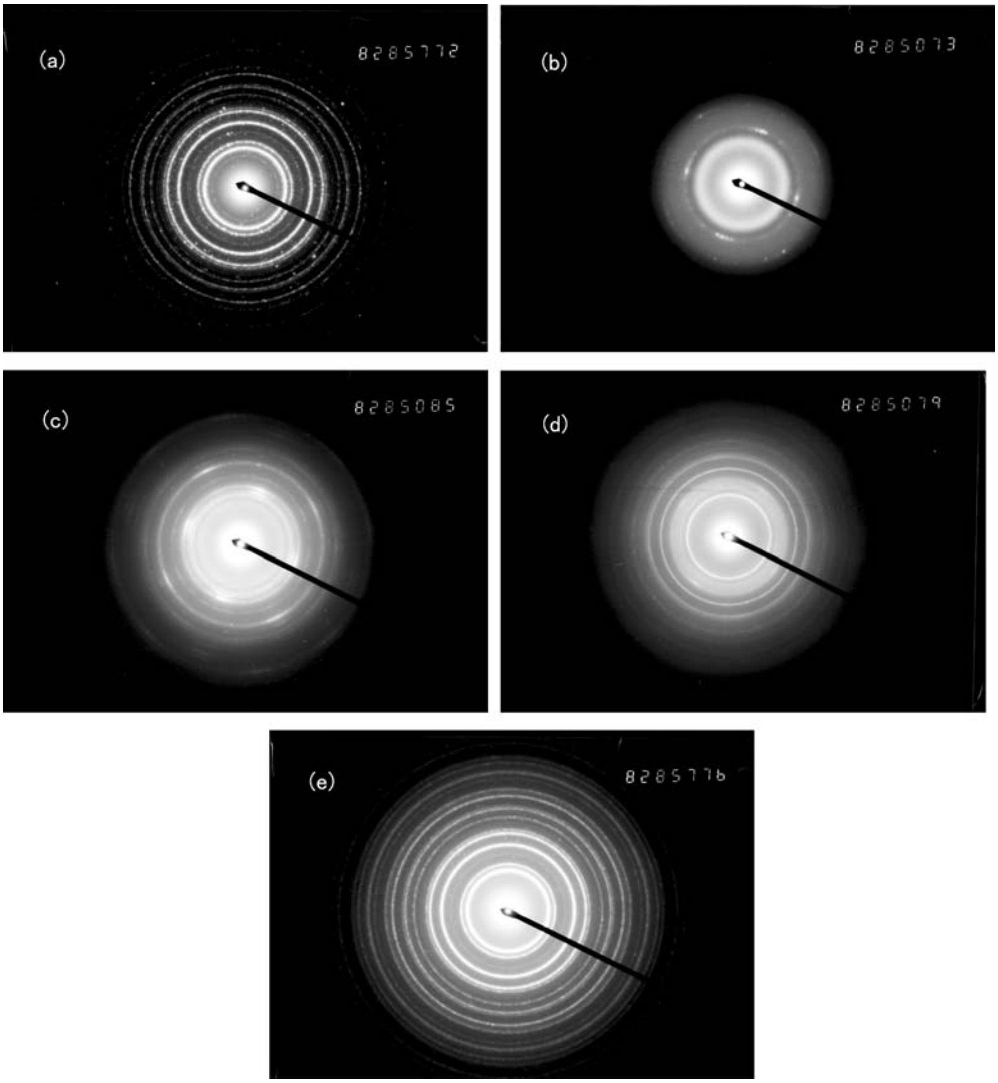

Figure 3 The SAD pattern of TEM observation for the sample of (a) as-received zircaloy-4 and the sample of zircaloy-4 implanted with Ti at the dose of (b) 5×10^{16} ions/cm^2; (c) 1×10^{17} ions/cm^2; (d) 2×10^{17} ions/cm^2; (e) 4×10^{17} ions/cm^2.

TABLE I The data of the passive current density and the Ti ion implantation dose

Irradiation dose (ions/cm^2)	Passive current density (μA/cm^2)
0	1.257
5×10^{16}	0.1292
1×10^{17}	0.1991
2×10^{17}	0.2725
4×10^{17}	0.6549

4 specimen. However, the passive current density keeps rising with the increase of dose ranging from 1×10^{17} to 4×10^{17} ions/cm^2, at the point of 4×10^{17} ions/cm^2, it is approximately five times than the minimum one

SADs for the unimplanted zircaloy-4, and the zircaloy-4 implanted with Ti at a dose range of 5×10^{16}, 1×10^{17}, 2×10^{17}, and 4×10^{17} ions/cm^2 are given in Fig. 3a–e. Fig. 3a shows typical polycrystalline structure obtained for the as-received zircaloy-4. When subjected to the 5×10^{16} ions/cm^2 dose, as shown in Fig. 3b, the diffraction rings became obscure, which indicates that the surface structure is amorphous. With the increase of implantation dose, however, the polycrystalline diffraction rings begin to appear again, and a polycrystalline phase together with an amorphous phase is clear, as shown in Fig. 3c and d. When the dose increases up to 4×10^{17} ions/cm^2, a well-defined polycrystalline structure comes into being as shown in Fig. 3e.

From the results of three-sweep potentiodynamic polarization measurements and TEM analysis, it can be concluded that when zircaloy-4 is subjected to lower dose, the corrosion resistances was improved because of the formation of an amorphous phase on the sample surface. However, with the increase of the implantation dose, deterioration of the electrochemical behavior of implanted specimens can be ascribed to structure change and the recrystallization of the implanted sample surface.

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