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Influence of nitrogen ion implantation on the aqueous corrosion behavior of zircaloy-4

Qian Wan[a,*], Xinde Bai[b], Xiaoyang Liu[a]

[a]*Department of Engineering Physics, Tsinghua University, Beijing 100084, China*
[b]*Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

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Abstract

In order to study the effects of nitrogen ion implantation on the corrosion behavior of zircaloy-4, specimens were implanted with nitrogen ions using an accelerator with a dose range from 4×10^{14} to 5×10^{16} ions/cm^2 at about 40 °C. Three-sweep potentiodynamic polarization measurement was employed to evaluate the aqueous corrosion behavior of zircaloy-4 in a 0.5 M H_2SO_4 solution. Scanning electron microscopy (SEM) was used to observe the topographies of nitrogen-implanted zircaloy-4 before and after potentiodynamic polarization curve measurement (POL) measurement the surface graphic character and the change of microstructures were examined by transmission electron microscopy (TEM). It was found that a significant improvement was achieved in the corrosion resistance of zircaloy-4 compared with that of the as-received zircaloy-4. The mechanism of the corrosion behavior of nitrogen-implanted zircaloy-4 was discussed.

Keywords: Zircaloy-4; Corrosion resistance; Ion implantation; Potentiodynamic polarization

1. Introduction

Due to the low thermal neutron capture cross section, good corrosion resistance and adequate mechanical properties, zircaloy-4 is often chosen as a cladding material in nuclear industry [1]. During service in reactors, the cladding was irradiated by neutrons, especially fast neutrons, which results in radiation damage and affects the corrosion behavior [2]. With the concept of high burnup developing, the request to enhance the corrosion resistance of zircaloy-4 became higher. It is well known that certain modification methods, such as ion implantation, a kind of ion beam surface processing (IBP), can result in adherent, defect-free, but thin, surface layers which exhibit exceptional corrosion resistance [3,4]. So there is a growing interest in the effect of ion implantation

*Corresponding author. Tel.: +86 106 277 2856; fax: +86 106 277 2507.
E-mail address: wanqian99@tsinghua.org.cn (Q. Wan).

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on the structure and corrosion property of zirconium alloys in recent years. Some ion implantation, such as Ni [5], Y [6], N [7], La [8] have been reported to enhance the anticorrosion property of zircaloy-4 significantly.

Nitrogen ion implantation is widely employed to be a method of surface modification. Previous work has demonstrated the potential of nitrogen ion implantation of aluminum alloys [9,10], steels [11] and titanium alloys [12–14] to improve their corrosion resistance. However, relatively few papers have reported the effect of nitrogen implantation on the corrosion behavior of zircaloy-4.

In this paper, nitrogen ions were used for implantation into zircaloy-4 specimen surface. Potentiodynamic polarization curve measurement (POL) was adopted to evaluate the effect of damage on the electrochemical behavior. Scanning electron microscopy (SEM) was used to examine the surface topographic character of the nitrogen-implanted zircaloy-4 before and after POL. Transmission electron microscopy (TEM) was employed to examine the surface graphic character and microstructures of the nitrogen-implanted specimens.

2. Experimental procedure

The composition of zircaloy-4 was presented in Table 1. The specimens were machined to 10 mm × 10 mm from a sheet of fully annealed zircaloy-4 with a thickness of 1 mm. Specimen surfaces were prepared by abrasion to a 1000-grit finish followed by chemical polishing with a solution of 10 vol% HF, 30 vol% HNO_3, and 60 vol% H_2O at 20 °C, finally they were rinsed in deionized water.

Electron-transparent TEM thin foil specimens were prepared by means of electron beam deposition on NaCl single-crystal chips at a rate of 0.1–0.2 nm/s. The vacuum remained at better than 1×10^{-4} Pa. The thickness of zircaloy-4 film was real-time monitored by a quartz-crystal oscillator. The total thickness of the films was about 55 nm, in favor of TEM. In order to eliminate the stress induced by electron beam deposition, the thin foil was annealed in a vacuum chamber with better than 1×10^{-4} Pa at 850 °C for 1 h.

Table 1
Composition of zircaloy-4 (wt.%)

Sn	Fe	Cr	Zr
1.4	0.23	0.1	bal

As described above, the manufacturing method of the $10 \times 10\,\text{mm}^2$ samples is different from that of the zircaloy-4 thin films, and as a rule, these different methods may lead to some difference in these two types of samples. However, from the composition of zircaloy-4, it can be concluded that the content of zirconium is more than 98%, almost the same as that of pure zirconium. Besides the manufacturing methods, no difference exists in all other experimental conditions. As a result, the difference between the compositions of these two types of zircaloy-4 samples is slight, and the possible influence of the slight difference on the experimental result can be ignored.

Zircaloy-4 specimens were implanted with nitrogen ion using an energy of 300 keV at about 40 °C. The implantation dose ranged from 4×10^{14} to 5×10^{16} ions/cm^2. During implantation, the beam current density was 0.55 μA/cm^2 and the vacuum pressure was kept better than 1.1×10^{-3} Pa. Subsequently, TEM analysis was performed with a HITACHI H-800 transmission electron microscope to examine the surface graphic character of the zircaoly-4 samples.

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 the cathodic region of approximately −0.5 V SCE and scanned into the anodic region of approximately +2.0 V SCE. From the polarization curves, passive current density was used to rank the corrosion resistance of the implanted zircaloy-4.

The topographic features of nitrogen-implanted zircaloy-4 before and after POL measurement were observed by means of SEM.