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Microstructures and properties of zirconium-702 irradiated by high current pulsed electron beam

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ABSTRACT

The microstructure, hardness and corrosion resistance of zirconium-702 before and after high-current pulsed electron beam (HCPEB) irradiation have been investigated. The microstructure evolution and surface morphologies of the samples were characterized by using X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The experimental results indicate that the sample surface was melted after HCPEB irradiation, and martensitic phase transformation occurred. Besides, two kinds of craters as well as ultrafine structures were obtained in the melted layer. TEM observations suggest that high density dislocations and deformation twins were formed after HCPEB irradiation. With the increasing of pulses, microhardness of the irradiated samples was increased from the initial 178 Hv to 254 Hv. The corrosion resistance was tested by using electrode impedance spectroscopy (EIS) and potentiodynamic polarization curves. Electrochemical results show that, after HCPEB irradiation, all the samples had better corrosion resistance in 1 mol HNO_3 solution compared to the initial one, among which the 5-pulsed sample owned the best corrosion resistance. Ultrafine structures, martensitic phase transformation, surface porosities, dislocations and deformation twins are believed to be the dominant reasons for the improvement of the hardness and corrosion resistance.

1. Introduction

Commercially pure zirconium-702 (Zr-702) is composed of 99.2–99.9% zirconium + hafnium. It has been widely used in severely corrosive environments as structural material because of its excellent corrosion resistance, such as columns, reactors, heat exchangers, vaporizers, pumps, piping systems, valves, and agitators et al. [1–3]. However, as zirconium is always used in such harsh conditions, more strict requirements must be put forward to satisfy the growing demand of safety, reliability and economy of structural materials. Therefore, further improving the mechanical properties and corrosion resistance of zirconium to extend the useful life, reduce the maintenance cost, and minimize the downtime has become an important subject, while surface modification technology plays an important role in promoting.

As a powerful tool for surface modification of different materials, high-current pulsed electron beam (HCPEB) is drawing widely attention for its great application potential and advantages of being simple, reliable, effective, and low energy consumption [4–7]. During the irradiation of HCPEB, high energy (10^8–10^9 W/cm^2) can be deposited in the surface layer within a very short time (a few microseconds), and produces extremely fast heating, melting even evaporation, then quick cooling and freezing through the heat conduction of itself. The dynamic stress fields induced by the rapid cooling process lead to intense modifications, which can extend several hundreds of microns in depth in the material. Correspondingly, special modification effects can be achieved. As a result, abundant ultrafine grains, nanostructures, phase transformations and deformation structures et al. are formed within the irradiated surface layer. As a consequence, the mechanical properties, such as microhardness and corrosion resistance can be improved effectively [8–11].

The aim of this work is to determine the modification effects of HCPEB technique on the surface microstructure, hardness and corrosion resistance of Zr-702. The detailed mechanisms for the improvement of microhardness, especially the corrosion resistance after HCPEB irradiation are investigated.

2. Experimental procedures

2.1. Experimental equipment and sample preparation

Our experiments were carried out with Hope -I type HCPEB equipment. It produces an electron beam of low energy (10–40 keV), high peak current (10^2–10^3 A/cm^2), short pulse

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duration (approx. 1 μs), and high efficiency (repeating pulse interval being 10 s). The accelerating voltage, magnetic field intensity and anode-collector distance control the beam energy density [5,7,8].

As-cast state Zr-702 used as the experimental material was cut into square-shaped samples of approximately 10 × 10 × 10 mm. One side was grounded with sandpapers and mirror polished as the initial state. Before HCPEB irradiation, all the samples were ultrasonically cleaned in acetone. Then the polished surfaces of the samples were irradiated by HCPEB source at room temperature with 5, 15 and 30 pulses, respectively. The HCPEB irradiation was carried out under the following conditions: the accelerating voltage 27 keV, the pulse duration 1.5 μs, the energy density about 4 J/cm^2, the off time between each pulse 10 s, and the vacuum 10^{-5} Torr.

2.2. Microstructure characterization

X-ray diffraction (XRD) analysis was carried out with CuKα radiation in a Rigaku D/Max-2500/pc X-ray diffractometer. The microstructures of the surface layer were characterized by using a LEICA DM-2500 M optical microscopy (OM), JEOL JSM-7001F scanning electron microscopy (SEM) and JEM-2100F transmission electron microscopy (TEM). The thin foils for TEM observation were prepared by using mechanical pre-thinning, dimpling, and ion-sputter thinning from the back side until electron transparency occurred. The depth of the near-surface layer that was analyzed was between 0.5 and 1.5 μm.

2.3. Microhardness test

The Microhardness test was carried out using a HV-1000 microhardness measurement device. The applied load was 0.49 N (50 g) with a load time of 15 s. To ensure the accuracy of microhardness test results and minimize measurement error, 7 indentations were tested for each experiment parameter. The maximum and minimum values were removed, and the average value of residual 5 indentations was taken for each experiment parameter.

2.4. Electrochemical measurements and corrosion analysis

Electrochemical measurements were carried out using a Bio-Logic VMP2 electrochemical workstation. In order to ensure the accuracy of the corrosion test results, each experiment parameter was tested with two samples. A conventional three-electrode cell was applied, containing the work electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum sheet as the counter electrode. The geometrically exposed area of the working electrode was 1 cm^2 with other non-working surfaces covered with epoxy resin and the electrolyte solution was 1 mol HNO_3. All measurements were normally conducted by monitoring the open circuit potential for 1 h followed by the electrochemical impedance spectroscopy (EIS) and standard potentiodynamic polarization measurements. The EIS spectra were obtained over the frequency (f) range 10^{-2}–10^5 Hz at the open circuit potential with an AC excitation amplitude of 10 mV. Potentiodynamic polarization tests were performed at a scan rate of 1 mV/s, and the corrosion current densities were Tafel fitted by EC-Lab software. All the experiments were conducted at room temperature (25 ± 1 °C). After rinsing with ion deleted water, the polarized sample surfaces were examined by SEM to characterize the nature of the corrosion damage.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the Zr-702 samples before and after HCPEB irradiation are shown in Fig. 1(a). One can see that all the diffraction peaks corresponded only to the hexagonal phase. As we know, when below 862 °C, zirconium is existing in the form of α-Zr with close-packed hexagonal (hcp) structure (a = 0.323 nm, c/a = 1.593); when above 862 °C, α-Zr will have allotropic transformation into β-Zr in what is known as a body-centered cubic (bcc) structure (a = 0.316 nm) [12]. Meanwhile, martensitic transformation will be induced under the fast cooling condition and achieve the lamellar α' structures. It should be noted that α' phase also has the hcp structure that is similar to α phase, and the difference between them only exists in morphology and formation process. During HCPEB irradiation, extremely fast heating, melting and solidification on the treated surface can be caused coupled with the dynamic stress fields, which can lead to a non-equilibrium transformation. Therefore, it can be deduced that the hexagonal α' martensitic phase was formed under the superfast cooling process, which will be confirmed later by microstructure analysis in the following part.

Seen from Fig. 1(b), compared to the initial sample, the width of peaks became wider after HCPEB irradiation, which resulted from the grain refinement on the surface. Meanwhile, a little shift of diffraction peaks to high degree direction occurred after HCPEB irradiation, as shown in Fig. 1(c). It suggests that there exists residual compressive stress in the subsequent rapid solidification process after electron beams remelting. Zr-702 has lower symmetry and less slipping system because it possesses hcp structure, and therefore it is difficult to meet the requirements of the plastic deformation coordination. Consequently, the stress was hard to release and accumulated on the surface. It is worth noting that the irradiated samples, compared to the initial one, show the change of peak intensity. This is a result of the change of crystallographic texture at the top surface after HCPEB treatment. The texture change may result from the combined effect of following mechanisms. Firstly, the texture can be changed as a result of solidification. Indeed, the new grains of β phase that nucleated from the melt must grow along the thermal gradient direction (i.e. perpendicularly to the irradiated surface) following specific crystallographic directions. Secondly, the subsequent solid state β → α' martensitic transformation may modify the crystallographic distribution of the hexagonal phase by introducing variant selection [13]. Finally, even without solidification texture or phase transformation, it has been established that the deformation induced by the thermal stresses which generated during the fast cooling can also produce texture changes on the surface of the HCPEB irradiated samples [14–16].

3.2. Surface morphologies analysis

Fig. 2 shows the optical microscopy of Zr-702 sample surface prior to irradiation. A chemical etching in 10%HF + 45%HNO_3 + 45%H_2O solution was conducted on the mirror polished surface beforehand. The microstructure is composed of large grains with size ranging from 10 to 50 μm.

Fig. 3 shows the optical morphologies of Zr-702 samples after HCPEB irradiation with different pulses. Because the microstructures on the irradiated surface could be observed directly, the chemical etching process is not needed. Seen from Fig. 3(a)–(c), after being irradiated by HCPEB, the initial mirror surfaces became to be much rougher and volcano-like craters were formed on the surface with the sizes range from tens to even hundred micrometers. According to the previous studies, such typical volcano-like crater morphology is the most common phenomenon, of which the reasonable mechanism can be interpreted by the local sublayer heating and melting that causes eruptions of the sublayer liquid through the outer solid surface [17]. In addition, compared to the 5-pulsed sample, the crater density increased slightly after 15 and 30 pulses. The consequences of abundant volcano-like craters