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Influence of Ar ion bombardment on the uniform corrosion resistance of laser-surface-melted Zircaloy-4 [1]

Jian Xu *, Xinde Bai, Fei He, Sheguan Wang, Xinzhong He, Yudian Fan

Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

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Abstract

Zircaloy-4 specimens were surface treated by laser surface melting and/or Ar ion bombarding. Corrosion tests were conducted in a 1N H_2SO_4 solution at room temperature and transmission electron microscope (TEM) was employed to analyze the change of microstructures in the surface layer. The potentiodynamic tests showed that the corrosion current density, i_{corr}, was closely related to the surface condition, and it decreased with increasing the fluence of Ar ions. After Ar ion bombardment, a significant improvement was achieved in the uniform corrosion resistance of laser-surface-melted Zircaloy-4 compared with that of the as-received Zircaloy-4. At the end, Gibbs free energy was used to explain why the fine grain structure and the fine dispersion of alloy components always led to the better uniform corrosion resistance. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zirconium-(Zr) base alloys are noted for their low thermal neutron capture cross section, good corrosion resistance, and adequate mechanical properties; and are often specified for engineering use in nuclear industry. Furthermore, it is also known that certain modification methods can significantly improve their corrosion resistance. For example, a heat-treatment such as beta-quenching, can significantly improve the corrosion resistance of Zirconium alloys due to the fine grain size and the fine dispersion of intermetallic precipitates [1,2]. Recent researches have shown that ion beam processing (IBP) [3,4] and laser surface processing (LSP) [5–8] of metal surface can also improve the corrosion resistance.

LSP of metal is a technique where only a small region of material's surface is processed by a laser beam and rapidly quenched by the substrate metal. A quench rate of 10^5–10^8 K/s has been reported in LSP [9,10]. Fine-grain structures and fine dispersions of alloy components can be achieved by rapid quenching [11]. It has been reported that reducing grain size can result in the improvement of corrosion properties of Zr metal and Zircaloy-4 in high-temperature and high-pressure aqueous environments [12].

Ion implantation is not only an interesting technique for modifying materials' properties but also for simulating radiation damage. Some materials' properties under neutron irradiation can be evaluated by instead using heavy ion implantation [13].

In this study, Zircaloy-4 samples' surfaces were modified by laser surface melting. In order to evaluate the influence of radiation on the uniform corrosion resistance of Zircaloy-4 treated by laser surface processing, Ar ion was employed to bombard the as-received and laser-surface-melted (LSM) Zircaloy-4 samples, and then the corrosion characteristics were investigated.

2. Experimental procedure

The composition of Zircaloy-4 used in this study is given in Table 1.

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* Corresponding author. Fax: +86-10 6277 1160; e-mail: zjz-dms@mail.tsinghua.edu.cn.

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Full-annealed Zircaloy-4 sheets of 1.5 mm in thickness were cut into a size of 10.0 mm × 10.0 mm, then all these samples were laser and/or Ar ions processed. Potentiodynamic tests were conducted to investigate the uniform corrosion behavior. Before surface processing, the Zircaloy-4 samples were blasted with 600 grit Al_2O_3 and pickled in the solution of 5% HF + 45% HNO_3 + 50% H_2SO_4 (in volume) at 20°C in order to remove the surface oxide formed during fabrication.

Laser processing was conducted with a 2 kW CO_2 continuous wave (CW) laser and Ar was used as a shielding gas during processing. Laser-processing parameters are listed in Table 2. The sample's surface was melted in overlap to ensure complete surface processing.

Ar ion bombardment was conducted using a 190 kV ion accelerator at room temperature, and the fluence up to 10^{20} ions/m^2 was used. In order to prevent the surface of Zircaloy-4 from being oxidized, samples were treated in 10^{-3} Pa vacuum.

Thin foils for transmission electron microscope (TEM) were prepared by jet-polishing the samples from the unbombarded side using a solution of 10% perchloric acid in ethanol below 243 K. Selected area electron diffraction patterns were observed using a H800 transmission electron microscope to investigate the change in the microstructures.

Potentiodynamic tests were carried out in a 1N H_2SO_4 solution using a JH-2C potentiostat at room temperature. Each of the test samples had a 10^{-4} m^2 area for the working electrode and the scan rate of 2.0 mV/s was used. All electrochemical potential measurements were taken with respect to a saturated calomel electrode (SCE). Immediately after samples were immersed in the solution, an anodic scan was performed starting in a cathodic region of approximately −1.0 V SCE and scanned into the anodic region of approximately +2.0 V SCE. From the polarization curve, i_{corr} was determined.

Feliu et al. [14] gave the method to calculate the corrosion parameters based on the following equation:

$$i = i_{\mathrm{corr}}\left[\exp\frac{2.303(E - E_{\mathrm{corr}})}{\beta a} - \frac{-2.303(E - E_{\mathrm{corr}})}{\beta c}\right],$$

where βa and βc are the anodic and cathodic Tafel slopes, i and E are the experimental polarization data, i_{corr} is the corrosion current density, and E_{corr} is the corrosion potential. A computer program was used to determine the parameters i_{corr}, E_{corr}, βa and βc based on the experimental polarization data, i and E.

Table 1
Zircaloy-4 elemental composition (wt%)

Sn	Fe	Cr	Ni	Zr
1.4	0.23	0.1	0.006	Bal

Table 2
Laser-processing parameters

Power (W)	Beam	Diameter (m)	Feed Rate (m/s)
1400	CW	4×10^{-3}	2.5×10^{-2}

3. Results and discussion

3.1. Ar ion bombardment on Zircaloy-4 samples

The anodic polarization curves of Ar-ion-bombarded Zircaloy-4 samples with various fluences at room temperature are given in Fig. 1. From this figure, it was found that when the fluence was low, such as the fluence of 5×10^{18} Ar/m^2 and 2.5×10^{19} Ar/m^2, its corrosion resistance was always worse than that of the as-received Zircaloy-4 sample, while at the higher fluence the corrosion resistance was better. When the fluence was high enough, such as the fluence of 1×10^{20} Ar/m^2, the corrosion resistance of the Ar-ion-bombarded Zircaloy-4 was better than that of the as-received Zircaloy-4 sample.

As we know, ion beam bombardment always brings all kinds of defects, such as point defects and dislocation loops, to the surface of the materials. The existence of these defects will damage materials and change their properties. Considering the corrosion behavior, the low fluence bombardment can induce many sorts of defects which act as active corrosion points and increase the surface heterogeneity. All these facts accelerate corrosion rate. That is why the low fluence of ion beam bombardment can decrease the corrosion resistance; and the phenomenon is called radiation damage.

Under the condition of Ar ion bombardment, the arrangement of atoms in the surface layer would be disturbed. Fig. 2 displays selected area diffraction patterns obtained from the as-received Zircaloy-4 and the

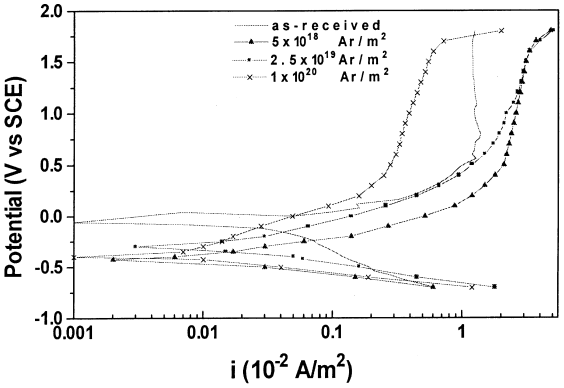

Fig. 1. Anodic polarization curves of Ar ions bombarded Zircaloy-4 at room temperature.

Ar-ion-bombarded Zircaloy-4 with the fluence of 1×10^{20} ions/m^2. From Fig. 2, the diffraction image in (a) and the diffraction rings in (b) suggest that the fine-grain structure was produced during Ar ion bombardment.

Thus, it can be concluded that the surface's microstructure of Zircaloy-4 becomes finer with increasing the fluence of Ar ions, and then the uniform corrosion resistance is improved. This result is corresponding with those of previous experiments [1,2].

3.2. Ar ion bombardment on LSM Zircaloy-4

The anodic polarization curves of the LSM Zircaloy-4 samples bombarded with Ar ions are summarized in Fig. 3. From this figure, it was found that the uniform corrosion resistance of the LSM Zircaloy-4 samples bombarded with Ar ions were much higher than that of the as-received Zircaloy-4 sample, and that the corrosion rate decreased with increasing the fluence of Ar ions. However, the passive region of the LSM Zircaloy-4 bombarded with Ar ions was smaller than that of the as-received Zircaloy-4 sample. Values of i_{corr} with different fluences are given in Table 3.

Now we compare the effect of Ar ion bombardment on the values of i_{corr} of the as-received Zircaloy-4 and those of the LSM Zircaloy-4 in Fig. 4. From this figure, it can be seen that (1) the laser surface melting treatment reduces the corrosion current density, i_{corr}, by approximately one order of magnitude, and (2) the i_{corr} of the as-received Zircaloy-4 decreases with increasing the fluence of Ar ions while no significant changes were observed in the LSM Zircaloy-4 such that the i_{corr} of the Ar ion bombarded as-received Zircaloy-4 was reduced close to that of the LSM Zircaloy-4 at higher Ar ion fluences.

From Fig. 2, it was known that Ar ion bombardment on the as-received Zircaloy-4 can reduce the grain size. Thus, it is easy to understand why the value of i_{corr} drops quickly with increasing Ar ion fluence. However, owing to the very small surface grain size of the LSM samples [6,7], the ability of Ar ion bombardment to reduce the grain size is limited. The bombardment of Ar ions on the LSM Zircaloy-4 can only slightly reduce the grain size and homogenize the distribution of alloy elements in the surface layer. As a result, the corrosion current density drops very slowly.

It is interesting that although the current density of the LSM Zircaloy-4 bombarded by Ar ions decreases, the corrosion potential of the as-received specimen is higher. From Fig. 1, it was seen that the corrosion potentials of the Ar-ion-bombarded Zircaloy-4 were much lower than that of the as-received Zircaloy-4. It is due to the defects induced by Ar ion bombardment in the surface layer, and all these defects would act as active corrosion points in the electrochemical procedure, thus, the as-received Zircaloy-4 is more noble compared to the Ar-ion-bombarded samples. Comparing Figs. 1 and 3, it was found that the corrosion potentials of the LSM Zircaloy-4 bombarded by Ar ions were higher than that of the as-received Zircaloy-4 bombarded by Ar ions. That means, after laser surface melting, the specimens with laser surface treatment are more noble. The reason why the corrosion potentials of the LSM Zircaloy-4 bombarded by Ar ions are still lower than that of the

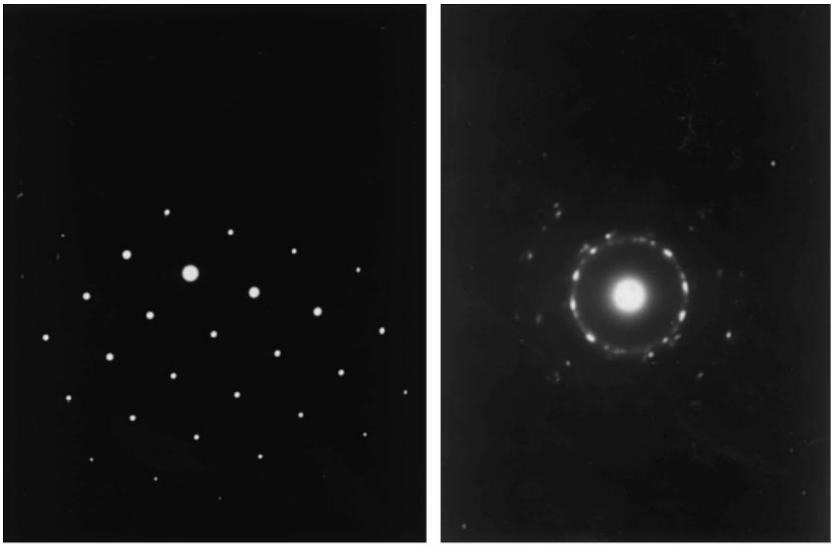
(a) as-received Zircaloy-4 (b)Ar-ion-bombarded Zircaloy-4

Fig. 2. TEM selected area electron diffraction patterns.

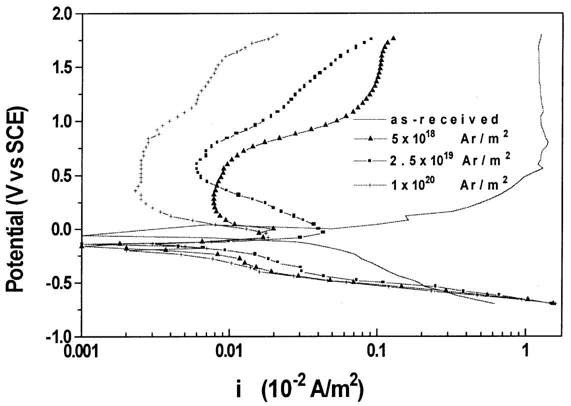

Fig. 3. Anodic polarization curves of Ar ions bombarded LSM Zircaloy-4.

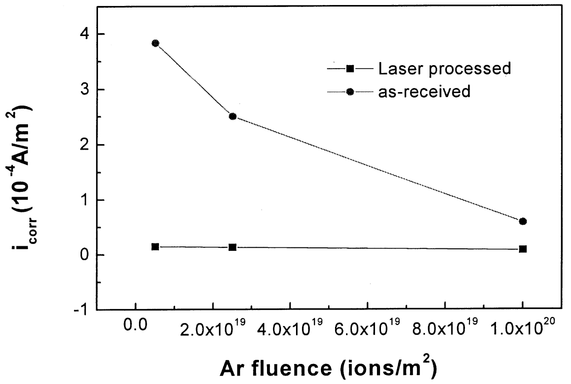

Fig. 4. Effect of laser surface melting treatment on i_{corr} under the condition of Ar ion bombardment.

as-received Zircaloy-4 is also due to the defects induced by Ar ion bombardment in the surface layer.

From Figs. 3 and 4, it can be said that the laser surface melting treatment can significantly improve the uniform corrosion resistance of Zircaloy-4 bombarded by Ar ions. As we know, the finer the gain size and the dispersion of alloy elements are, the better its uniform corrosion resistance is. In fact, the change of corrosion behavior of the surface-treated Zircaloy-4 can be explained using Gibbs free energy. We shall consider that the driving force for the grain size becoming finer is the amount of Gibbs free energy stored in the lattice, and that this excess of free energy is due to the point defect's accumulation and to radiation-induced configurational disorder. With the bombardment of Ar ions, the Gibbs free energy accumulates. Thus, the grain size will become finer and finer, and the precipitates will change from crystalline to amorphous leading to the dispersion of alloy elements. That is why the uniform corrosion resistance of laser and/or Ar ions treated Zircaloy-4 was much better than that of the as-received Zircaloy-4.

Table 3
Corrosion current density of different fluence with or without LSM

Ar fluence (ions/m^2)	5×10^{18}	2.5×10^{19}	1×10^{20}
i_{corr} (as-received) (10^{-4} A/m^2)	3.8	2.5	0.58
i_{corr} (LSM) (10^{-4} A/m^2)	0.146	0.131	0.077

Nowadays, the simulation of neutron irradiation by heavy-ion bombardment is a useful method to preview the corrosion behavior of metals under working condition in nuclear reactor. In this study, the results of corrosion tests of the Ar ions bombardment on the LSM Zircaloy-4 give us a proof that if the LSM Zircaloy-4 were to be irradiated by neutron, its uniform corrosion resistance may be much better than that of an unprocessed one.

4. Conclusions

(1) Laser surface melting and Ar ions bombarding treatment can reduce the grain size and improve the uniform corrosion resistance.

(2) Under the condition of Ar ion bombardment, the corrosion current density, i_{corr}, of the LSM Zircaloy-4 samples is much lower than that of the as-received Zircaloy-4 samples, especially in the low fluence region. When the fluence of Ar ion is high enough, the corrosion current density, i_{corr}, of the LSM Zircaloy-4 samples is very close to that of the as-received Zircaloy-4 samples.

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