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Effect of heat treatment on the Nb distribution and corrosion resistance of Zr-Sn-Nb-Fe zirconium alloy

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Abstract

After being treated in different ways, Zr-Sn-Nb-Fe alloy specimens are exposed in 0.01mol/L LiOH aqueous solution at 350°C under 16.8 MPa. The examination of microstructures and second phase particles (SPPs) of these specimens was carried out by high-resolution transmission electron microscopy (HR-TEM). The specimens treated at 800°C before the final cold rolling have a better corrosion resistance than those treated at 680°C, and the specimens treated at 500°C, after the final cold rolling, have a better corrosion resistance than those treated at 560°C. TEM examination shows that the SPPs existing in the 800°C/500°C specimen, which has the best corrosion resistance, contains a lot of Nb element, which results in the reduction of the niobium content in the α-Zr solid solution.

Keywords: zircaloy; heat treatment; corrosion resistance; microstructure; second phase particles

1. Introduction

Zircaloy has been successfully used as fuel cladding in nuclear reactor environments for many years. However, as light water reactors tend to be operated in more severe environments, that is, increased burn-up, high operation temperature, and high pH in the first loop, higher corrosion resistant alloys have been continuously developed as a substitute for zircaloy. Some developments have been made by modifying the chemical composition of zircaloy.

Several new zirconium alloys such as ZIRLO (Zr-1.0Nb-1.0Sn-0.1Fe) [1], M5 (Zr-1Nb-O) [2], E635 (Zr-1.0Nb-1.0Sn-0.4Fe) [3], and N18 (Zr-0.3Nb-1.0Sn-0.3Fe-0.1Cr) [4] have been developed and are being tested in-reactor. In this manner, most new zirconium alloys that are being developed contain Nb element. However, it is reported that the corrosion behavior of the Nb-containing Zr alloy is very sensitive to the microstructures that can be changed by heat treatment. Therefore, the establishment of an appropriate thermal process is necessary, for the optimum corrosion resistance of the alloys containing Nb.

Thorvaldsson *et al.* [5] proposed that the corrosion resistance of Zircaloy-4 could be related to the accumulated annealing parameters (ΣA), which is an index of the total number of heat treatments received in the α-region after β-quenching. The parameters combine the annealing time (t) in h and temperature (T) in K for each heat treatment. The accumulated annealing parameters (ΣA) can be described as follows:

$$\sum A = \sum_i t_i \exp[-Q / RT_i],$$

where Q is the activation energy and R is the gas constant. The weight gain of Zircaloy-4 decreases with an increase in the accumulated annealing parameter [6-7]. However, Zhou *et al.* [8] have proposed that the solid solution contents of Fe and Cr in α-Zr, which result from a different heat treatment, are essential factors affecting the corrosion behavior of Zircaloy-4.

Baek [9] and Isobe [10] studied the corrosion resistance of Nb-containing zirconium alloys in relation to accumulated annealing parameters, and found that weight gain increased with an accumulated annealing parameter. This result was contrary to that of Zircaloy-4.

The previous work by the authors [11-12], on Nb-containing zirconium alloys, revealed that a uniform distribution of fine β-Nb (containing iron) particles are important factors for improving the corrosion resistance. In this study, the corrosion resistance of Zr-Sn-Nb-Fe alloys containing 1.16 wt.% Nb in relation to heat treatment and microstructure was investigated.

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2. Experimental

2.1. Specimens

The vacuum consumable arc remelting method was employed for producing a 5 kg ingot of Zr-Sn-Nb-Fe zirconium alloy. The chemical composition of the alloys is shown in Table 1. The β-quenching treatment was conducted to homogenize the composition within the ingot after being hot forged. Then the ingot was made into plates of about 0.5 mm in thickness through various rolling and intermediate annealing processes. The heat treatments before the final cold rolling were carried out at two different temperatures, 680°C for 5 h and 800°C for 1 h. The final heat treatments were also carried out at two different temperatures, 500°C for 30 h and 560°C for 10 h. The above-mentioned different heat treatment processes gave four kinds of specimens, expressed as 680°C/500°C, 680°C/560°C, 800°C/500°C, and 800°C/560°C. The microstructure of the heat-treated specimens was investigated by transmission electron microscopy (TEM) (JEM-2010F) along with energy dispersive spectroscopy (EDS). The TEM specimens were prepared by mechanical grinding (up to 60 μm) and twin-jet polishing in a solution of ethanol (80 vol.%) and perchloric acid (20 vol.%) at 25°C (the applied voltage and current are 20 V and 30 mA, respectively). The composition analyses on the precipitates in the heat-treated samples were conducted with energy dispersive spectroscopy (EDS). More than 20 precipitates from each kind of specimen were analyzed, to minimize the detection error.

Table 1. Chemical composition of Zr-Nb-Sn-Fe-Cr alloy and Zircaloy-4

Alloy	Sn /wt.%	Nb /wt.%	Fe /wt.%	Cr /wt.%	O /10^{-6}	Zr
Zr-Nb-Sn-Fe alloy	1.02	1.16	0.29	—	1200	Bal.
Zircaloy-4	1.2	—	0.21	0.10	1100	Bal.

2.2. Corrosion tests

The corrosion test specimens were prepared after the final heat treatment. Rectangular-shaped specimens, 20 mm × 25 mm in size, were chemically polished using a pickling solution (a mixture of 10 vol.% HF, 30 vol.% HNO_3, 30 vol.% H_2SO_4 and 30 vol.% H_2O) in the final step. The out-pile corrosion test was conducted in 0.01 mol/L LiOH aqueous solution at 350°C under a pressure of 16.8 MPa, and in 400°C superheated steam under a pressure of 10.3 MPa. The corrosion resistance of the specimens was evaluated by measuring their weight gains per unit surface area in relation to the exposure time. The corrosion tests of Zircaloy-4 specimens were also conducted as a reference.

3. Results and discussion

3.1. Effect of heat treatment on the corrosion behavior

The effect of heat treatment on the corrosion behavior of Zr-Sn-Nb-Fe alloy specimens tested in different media is shown in Fig. 1. There was a weight gain in four kinds of specimens, which increased with the order of 800°C/500°C,

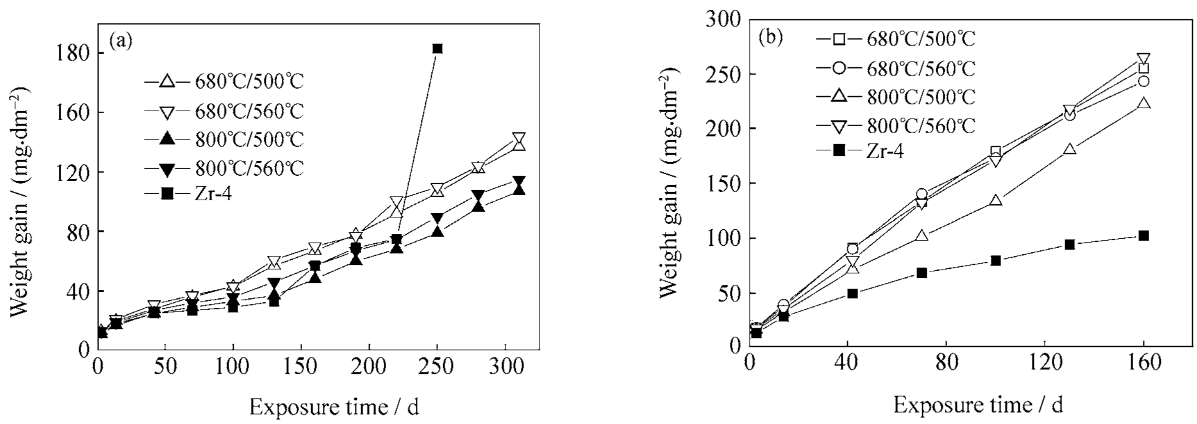

Fig. 1. Weight gain against exposed time of Zr-Sn-Nb-Fe specimens tested in different media: (a) LiOH solution at 350°C; (b) 400°C superheated steam.

800°C/560°C, 680°C/500°C, and 680°C/560°C when corrosion tests were carried out in 0.01mol/L LiOH aqueous solution (Fig. 1(a)). The weight gains in four kinds of specimens, in 400°C superheated steam, for 160 days, increased with the order of 800°C/500°C, 680°C/560°C, 680°C/500°C, and 800°C/560°C (Fig. 1(b)). The accumulated annealing pa-