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Corrosion behavior of Zr alloys with a high Nb content

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Abstract

The corrosion behavior of the Zr alloy with a high Nb content was evaluated in the water loop system containing 2.2 wppm Li and 650 wppm B. The characteristics of the precipitates were analyzed by transmission electron microscopy (TEM) and the oxide was characterized by an X-ray diffraction method using a synchrotron radiation source. On the basis of the results obtained by these measurements, the relationship among the oxidation behavior, the precipitate characteristics and the oxide properties was discussed. It was shown that the Cu addition was of benefit to the corrosion resistance of the Zr alloy with a high Nb content and the corrosion resistance of the Cu-containing alloy (Zr–1.5Nb–0.5Sn–0.2Fe–0.1Cu) was superior to that of the Cr-containing alloy (Zr–1.5Nb–0.5Sn–0.2Fe–0.1Cr). The fine β-Nb precipitates were found more frequently in the Cu-containing alloy than the Cr-containing alloy when heat-treated in the same condition. The fraction of the tetragonal zirconia in the region of the metal/oxide interface was higher in the Cu-containing alloy than the Cr-containing alloy, suggesting that the stabilization of the tetragonal phase in the oxide was promoted more when the smaller precipitates are incorporated into the oxide. It is concluded that the fine distribution of β-Nb is desirable for stabilizing the tetragonal phase in the oxide, thereby increasing the corrosion resistance of the Zr alloy with a high Nb content.

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1. Introduction

A development of more corrosion resistant Zr alloys than Zircaloy-4 has been required by the current more demanding operation conditions and discharge burnups in the pressurized water reactor (PWR) [1]. A number of recent works concentrated on the development of new Zr alloys have shown that Nb would be the most beneficial alloying element to improve the corrosion resistance of Zr alloys [2–6]. Although many studies [2–6] were conducted to evaluate the corrosion behavior of Nb-containing Zr alloys in out-of-pile and in-pile conditions, the optimum Nb content for the corrosion performance was changed according to the chemical compositions and manufacturing processes.

Among the metallurgical parameters which are determined by the manufacturing process, the precipitates are known to play a critical role in influencing the corrosion resistance. The precipitates are incorporated into the oxide film in unoxidized state because the oxidation of the intermetallic precipitates is delayed compared to

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the Zr matrix. The late oxidation of the incorporated precipitates is accompanied by a change of the oxide properties. A number of works revealed that the corrosion resistance of Zr alloys was highly dependent on the particle size distribution of the precipitate [4,6–8]. However, the effect of the precipitate size on the corrosion resistance of Nb-containing Zr alloys [4,6,7] was contrary to that of Zircaloy-4 [8,9]. Therefore, in order to improve the corrosion resistance of Nb-containing Zr alloys, it is essential to examine the effect of the precipitate characteristics on the corrosion behavior of Nb-containing Zr alloys.

In the authors' previous study [10], the Zr alloy with a high Nb content (1.5 wt% Nb) showed an excellent corrosion resistance as compared to the Zr alloy with a low Nb content (0.4 wt% Nb) when properly heat-treated to obtain the metallurgical structure in which the fine precipitates were homogeneously distributed. This result has led to additional studies on the oxidation mechanisms of Zr alloys with a high Nb content in order to better understand the effects of the metallurgical state and the chemical composition on the corrosion mechanisms [11,12]. The preliminary results made it possible to consider the Zr alloy with a high Nb content as one of the most promising alloys as a substitute for Zircaloy-4.

The aim of this study is to investigate the corrosion behavior of Zr alloys with a high Nb content in a condition simulating the water chemistry of PWRs. The characteristics of the precipitates were analyzed by transmission electron microscopy (TEM) and the oxide was characterized by an X-ray diffraction method using synchrotron radiation. On the basis of the results obtained by these measurements, the relationship among the corrosion behavior, the precipitate characteristics and the oxide properties was discussed.

2. Experimental methods

The chemical compositions of the Zr alloys used in this study are shown in Table 1. Button ingots of approximately 200 g were prepared by arc melting under an argon atmosphere and remelted at least five times to promote the homogeneity of the as-cast structure. The arc-melted ingots were β-solution treated at 1020 °C for 30 min in a vacuum furnace, hot-rolled after preheating to 610 °C for 10 min and cold-rolled three times to a final thickness of 1 mm. Between the rolling steps, the cold-rolled sheets were intermediate-annealed at 575 °C for 3 h to obtain the fully-recrystallized structure. Especially, at the annealing step after hot rolling, the variable annealing time ranging from 3 h to 15 h was applied to change the size of the precipitate which is known to play a key roll in controlling the corrosion kinetics of Zr alloys. The final cold-rolled sheets were annealed at 510 °C for 2.5 h to obtain the partially-recrystallized metallurgical form.

Specimens for the corrosion test, 15 by 20 by 1 mm in size, were cut from the partially-recrystallized sheets, mechanically ground by use of 800 grit SiC paper, and then pickled in a solution of 5 vol.% HF, 45 vol.% HNO_3 and 50 vol.% H_2O. The corrosion tests were conducted at 360 °C in the water loop system containing 2.2 wppm Li and 650 wppm B under the pressure of 18.5 MPa in a manner consistent with the ASTM Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys (G2-88). The corrosion behavior of the specimens was evaluated by measuring the weight gain with the exposure time.

The microstructures of the alloys were examined using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscope (EDS). Specimens for TEM observation were prepared by a twin-jet polishing with a solution of 10 vol.% $HClO_3$ and 90 vol.% C_2H_5OH after mechanical thinning to 70 μm. It is well known that the corrosion resistance of Zr alloys depends on the characteristics of the precipitates. The microstructure characterization was concentrated on the variation of the precipitation behavior with the alloying elements and heat treatment conditions. The selected area diffraction patterns (SADP) were obtained and analyzed to determine the crystal structure of the precipitates, and the micro-chemical

Table 1
Chemical compositions and heat treatment conditions of the Zr alloys

Specimen ID	Chemical compositions						Annealing condition after hot rolling
	Nb	Sn	Fe	Cr	Cu	Zr	
A	1.5	0.5	0.2			Bal.	575 °C, 8 h
B	1.5	0.5	0.2	0.1		Bal.	575 °C, 8 h
C	1.5	0.5	0.2		0.1	Bal.	575 °C, 3 h
D	1.5	0.5	0.2		0.1	Bal.	575 °C, 8 h
E	1.5	0.5	0.2		0.1	Bal.	575 °C, 15 h
F	1.5	0.5	0.2	0.05	0.05	Bal.	575 °C, 8 h