Cr effect on the corrosion behavior in Zr alloy

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1. Introduction

For more than 50 years, zirconium alloys have been used for light water reactor core material and have shown good in reactor corrosion performance. Under extended exposure conditions, their corrosion performance is regarded as one of the important factors that may restrict the reactor operation.

Many studies have been done to improve their corrosion resistance [1-4]. Effects of heat treatment and chemical composition on the corrosion resistance have been investigated; some of the results were actually applied for improved corrosion resistant core material [1-4]. They have reported that the corrosion resistance of Zr alloy were affected by the alloying element, so many researchers have studied to establish the ideal composition [5,6].

In this work, autoclave corrosion tests in water and microstructural observations were performed on the Zr base alloys to investigate the effects of Cr, one of major alloying element.

2. Experimental procedure

The chemical composition of experimental alloy is given in Table I. The materials used in this study were melted into about 300g button ingots by nonconsumable arc melting. As input materials, sponge zirconium (nuclear grade), and Chromium (99.99%) grain were used. Several melting cycles were performed in order to ensure chemical homogeneity. Subsequently, 1mm thick sheet specimens were produced from these small ingots by hot rolling, cold rolling and annealing (Table II).

Table I. Chemical composition of experimental alloy

Sample	А	В	Cr	Zr
	Composition, wt%			
1	0.4	0.3	0.05	Bal.
2	0.4	0.3	0.1	Bal.
3	0.4	0.3	0.15	Bal.

Table II. Manufacturing process of test specimen

Process	Conditions		
Melting	Arc Melting (300g)		
Heat Treatment	$1050^{\circ}C \rightarrow W. Q.$		
	Preheat : 640°C 20m		
Hot Kolling	Reduction : 60%		
Annealing	Vacuum anneal : 580°C 3h		
Cold Rolling	Reduction : 50%		
Annealing	Vacuum anneal : 580°C 2h		
Cold Rolling	Reduction : 50%		
Annealing	Vacuum anneal : 580°C 2h		
Cold Rolling	Reduction : 55%		
Final Annealing	Vacuum anneal : 580°C 8h		

The microstructural analysis for the precipitates was performed by using the polarized Optical Microscopy (OM) and Transmission Electron Microscopy (TEM). The observation of optical microstructure was performed for the perpendicular section to the rolling direction of specimens.

The precipitates characteristics were analyzed by using TEM equipped with Energy Dispersive Spectroscopy (EDS). Specimens for the TEM observation were prepared by a twin-jet polishing with a solution of ethanol (90 vol.%) and perchloric acid(10 vol.%) after a mechanical thinning to about 50 µm.

The corrosion test was performed in a static autoclave of 360°C water. Corrosion specimens of 15mm x 15mm x1 mm in size were cut from the annealed sheets and mechanically polished with SiC paper. For comparison of the corrosion properties with commercial Zr alloys, R alloy and Zry-4 strips were used. The polished specimens for corrosion test were pickled in a solution of H₂O (45 vol.%), HNO₃ (45 vol.%), and HF (10 vol.%). The corrosion resistance was evaluated by measuring the weight of the corroded samples after suspending the corrosion test at a periodic term.

3. Results

The corrosion behavior of the experimental alloys, R alloy, and Zry-4 was investigated in 360°C water for 187 days. The periods of the corrosions test were 6, 13, 32, 50, 91, 126, 152 and 187 days. Fig. 1 shows the weight gain of all alloys. The Zr–0.4A–0.3B–0.1Cr alloy which showed a good corrosion resistance. All experimental alloys showed better corrosion resistance than R alloy and Zry-4 strips.



Fig. 1 Corrosion behavior of experimental alloys.

From the optical microstructure of the final annealed alloys shown in Fig. 2, the equiaxed grains were observed. The chemical composition for the precipitate revealed the microstructure consisted of α -Zr, β -Nb, and Zr(A,B,Cr)₂ precipitates.



Fig. 2 Microstructure of experimental alloys.

4. Conclusions

The corrosion behaviors of Zr-base experimental alloys including Zircaloy-4 and R alloy have been investigated. The weight gains of the experimental alloys were much lower than those of the Zirclaoy-4 and R alloy in the 360°C water, and the corrosion resistance of Zr-0.1wt%Cr was better than Zr-0.05wt%Cr and Zr-0.15wt%Cr.

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