Influence of Annealing on the Precipitates and Corrosion Behavior of Extruded Zr-1Nb Alloy

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1. Introduction

Zr-alloys have been developed as nuclear fuel cladding materials in PWR due to their superior corrosion resistances and excellent mechanical properties [1-3]. As one of them, Zr-Nb alloys have drawn wide attention as cladding materials of nuclear fuel. In the manufacturing processes of fuel rods, the billets combined with Zr-U alloy for fuel core and Zr-Nb alloy for clad are usually subjected to hot-extrusion at high temperatures [4]. The deformed fuel rods should be annealed to relieve the stress from the hot-deformation. The annealing conditions thus became a subject of main concern [5]. However, there has been little indication that the annealing reveals any significant influence on the precipitates and corrosion behavior of Zr-1Nb clad materials. This study was performed in order to evaluate the influence of annealing on the precipitates and corrosion behavior of extruded Zr-1Nb alloy.

2. Methods and Results

2.1 Preparation of samples and observation

The Zr-U alloys for the core materials of fuel rods were fabricated by the sintering process at high temperatures and in high-vacuum environments. The Zr-1Nb alloy for the clad materials of fuel rods was prepared in extruded and annealed conditions.

The billets, composed of Zr-U alloy inside and Zr-1Nb alloy outside, were prepared. They were then extruded at high temperatures. The extruded rods were annealed at 580^{o}C for up to 32 hours. The microstructures of the as-extruded and annealed Zr-1Nb alloys were observed by TEM/EDS. The corrosion tests were performed at 400^{o}C in steam for 60 days using a static autoclave. The corrosion behavior was determined by the gravimetric method.

2.2 Microstructure of extruded Zr-Nb alloy

Figure 1 shows the microstructure of as-extruded Zr-1Nb alloy. The as-extruded alloy revealed the average grain size of about 0.5 μm along with a high density of dislocations possibly formed during the plastic deformation of extrusion. Two kinds of Nb-containing precipitates, β-Zr and enriched β were observed. Most of precipitates were β-Zr with Nb-concentration of less than 1.0 wt. %.

Figure 1. Bright field TEM image of as-extruded Zr-1Nb alloy.

2.3 Influence of annealing on the precipitates

The results of observation on the precipitates of Zr-1Nb alloy were shown in Table 1. As-received Zr-1Nb alloy contained two kinds of precipitates; enriched β and β-Zr phases. After extrusion, most of precipitates were observed to be a β-Zr. The annealing led to contain two-type precipitates; spherical-type enriched β and lath-type β-Zr. In addition, the annealing provided the change in the morphology of precipitates from lath-type to spherical-type. The results of TEM/EDS study on the precipitates revealed that most of lath-type precipitates contained 0.4-2.8 wt.% Nb (β-Zr) while the spherical-type precipitates contained about 25.7-66.5 wt.% Nb (enriched β). This observation means that the annealing provide the reaction of phase transformation (β-Zr → α-Zr + enriched β), resulting in the change of morphology from lath-type precipitates to spherical-type ones.

Table 1. Precipitates of Zr-1Nb alloys

(Wt %)

		As-extruded	As-extruded	Annealing time (h)		
				3	16	32
β-Zr	Zr	98.7	99.0	98.6	99.6	97.2
	Nb	1.3	0.9	1.4	0.4	2.8
Enriched-β	Zr	68.1	-	74.3	65.1	33.5
	Nb	31.9	-	25.7	34.9	66.5

2.4 influence of annealing on the corrosion behavior

Figure 2 shows the influence of annealing duration on the corrosion behavior of Zr-1Nb alloy at 400^{o}C in steam. The corrosion behavior exhibited that the corrosion rate was rapid in the initial corrosion period, but decreased greatly after approximately 8 days. This is closely correlated with the increase in the thickness of a protective oxide layer formed in the surface of Zr-1Nb alloy. However, it was shown that there was little influence of annealing on corrosion behavior of the extruded Zr-1Nb alloy for 60 days. Then, the final weight gains after corrosion for 60 days appeared to be about 65 mg/dm^2. The annealing of extruded alloy at 580°C induced the changes of the materials factors (precipitates, grain size and so on) which could affect the corrosion behavior. It is thus believed that the corrosion tests for prolonged periods would be necessary to determine the influence of annealing duration on the corrosion behavior.

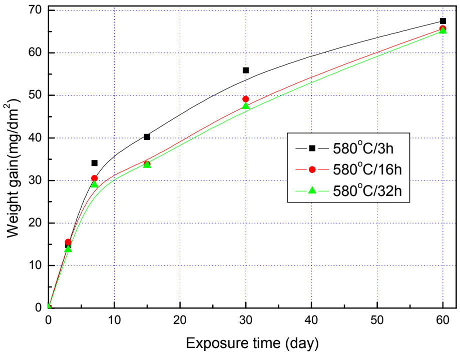

Figure 2. Influence of annealing duration on the corrosion behavior of Zr-1Nb alloy at 400°C in steam.

2.5 Hydrogen absorption

Figure 3 shows the characteristics of hydrogen absorption of Zr-1Nb alloy annealed at 580°C for 3, 16 and 32 hours at 400°C in steam. After corrosion for 60 days, the concentration of hydrogen appeared to be about 8~9 ppm range, showing little influence of annealing duration of the corrosion. With respect to hydrogen pickup fraction, there was little influence of annealing duration. It is believed that these results show a good agreement with the corrosion behavior (figure 2).

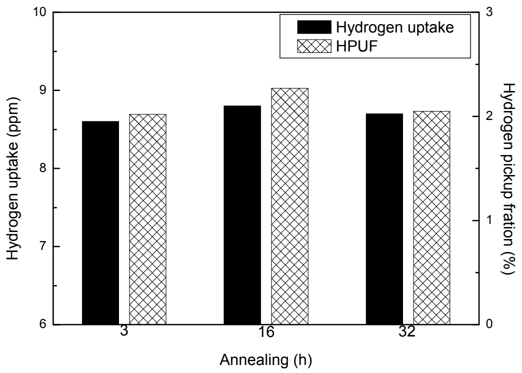

Figure 3. Hydrogen uptake and hydrogen pickup fraction of Zr-1Nb alloys after corrosion for 60 days.

3. Conclusion

The results of observation on the precipitates of Zr-1Nb alloy showed that most of precipitates in the extruded alloy were observed to be a β-Zr. The annealing at 580°C induced to contain two-type precipitates; spherical-type enriched β and lath-type β-Zr. As the annealing time increased, there was a change in the phase from β-Zr to enriched β phase. However, the influence of annealing on the corrosion behavior and hydrogen absorption of extruded Zr-1Nb alloys at 400°C in the steam for 60 days was not shown yet.

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REFERENCES

[1] G.P. Sabol, G.R. Kiop, M.G. Balfour and E. Roberts, Zirconium in the Nuclear Industry, ASTM Spec. Tech. Publ. **1023**, p. 227, 1989.

[2] K. Yamate, A. Oe, M. Hayashi, T. Okamoto, H. Anada, S. Hagi, in: Proceedings of the 1997 International Topical Meeting on LWR Fuel Performance, Portland, OR, 2-6 March, p. 318, 1997.

[3] J.P. Mardon, G. Garner, P. Beslu, D. Charquer, J. Senevat, in: Proceedings of the 1997 International Topical Meeting on LWR Fuel Performance, Portland, OR, 2-6 March, p. 405, 1997.

[4] T.K. Kim, J.H. Park, S.K. Yang, G.S. Joo, J.S. Song, Y.M. Ko, C.T. Lee, D.S. Sohn, "Proceedings of the Korean Nuclear Society Spring Meeting", May 27-28, 2004, Gyeongju, Korea.

[5] T.K. Kim, B.S. Choi, Y.H. Jeong, D.J. Lee, M.H. Chang, J. Nucl. Mater. Vol. **301**, p. 81, 2002.