Effects of Annealing on the Microstructure and Corrosion Behavior of Extruded Zr-1Nb Alloy

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1. Introduction

Zr-Nb alloys have been developed as nuclear fuel cladding materials in PWR due to their superior corrosion resistance [1-3]. As one of them, Zr-1Nb 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-1Nb 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 deformation. The annealing conditions thus became a subject of main concern [5]. However, there has been little indication that the annealing reveals any significant effects on the microstructure and corrosion behavior of Zr-1Nb clad materials. This study was performed in order to evaluate the effects of annealing on the microstructure 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 melting and sintering processes. 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 core and Zr-1Nb alloy can, were prepared by an electron-beam welding process in high-vacuum conditions. They were then extruded at high temperatures. The extruded rods were annealed at 580°C for up to 32 hours. The microstructures of as-extruded and annealed Zr-Nb alloys were observed by TEM/EDS. The preoxidation treatments of the annealed rods in a high-temperature water were done. The corrosion tests were performed at 360°C in ammonia aqueous solution for 150 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-Nb 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 extrusion. Two kinds of Nb-containing precipitates, β-Zr and enriched β (1.0-5.0 wt.% Nb) were observed. Most of precipitates were β-Zr with Nb-concentration of less than 0.5 wt.%.

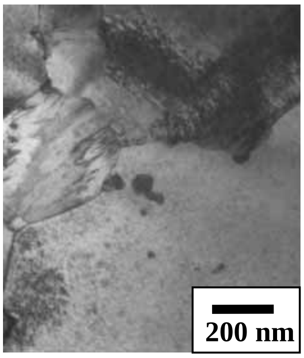
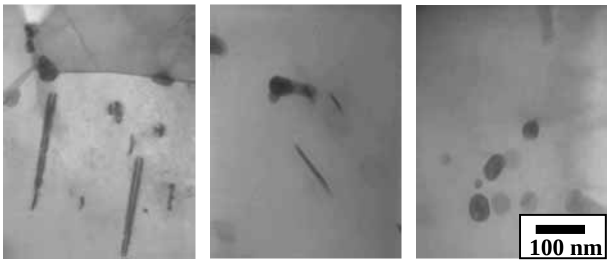


Figure 1. Bright field TEM image of extruded Zr-Nb alloy.

2.3 Effects of annealing on the microstructure

Figure 2 shows the microstructures of Zr-Nb alloy after annealing at 580°C for 3, 16 and 32 hours. The annealing treatments induced the continuous reduction in the amount of dislocations. In addition, the annealing provided the change in the morphology of precipitates from lath-type to spherical-type, resulting in the reduction in the size of precipitates. The results of TEM/EDS on the precipitates indicated that most of lath-type precipitates contained 0.1-0.5 wt.% Nb (β-Zr) while the spherical-type precipitates contained about 20-60 wt.% Nb (enriched β). This observation means that the reaction of phase transformation (β-Zr → α-Zr + enriched β) was occurred during annealing treatments, resulting in the change of morphology from lath-type precipitates to spherical-type ones.



(a) (b) (c)

Figure 2. Bright field TEM images of Zr-Nb alloy after annealing at 580°C for (a) 3, (b) 16 and (c) 32 hours.

2.4 Effects of annealing on the hardness

Figure 3 shows the effects of annealing on the hardness of Zr-Nb alloy. The extrusion induced the increase of hardness due to both the reduction of the grain size and the formation of dislocations (Fig. 1). The annealing for 16 hours led to decrease the hardness. It would be due to the increase of grain size as well as the reduction of dislocation density (Fig. 2). However, no more reduction of the hardness was observed after annealing time of 16 hours. These results coincided well with the variation of grain size (Fig. 3). These results would be useful to determine the annealing time in terms of mechanical properties of extruded rods.

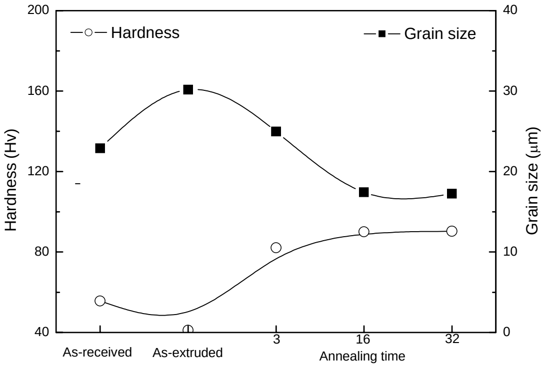


Figure 3. Effects of annealing on the hardness of Zr-Nb alloy.

2.5 Effects of annealing on the corrosion behavior

Figure 4 shows the effects of annealing time on the corrosion behavior of Zr-Nb alloy at 360°C in ammonia aqueous solution. The corrosion behavior exhibited that the corrosion rate was rapid in the initial corrosion period, but decreased greatly after approximately 60 days when the oxide thickness of about 3 μm were formed. This is closely correlated with the increase in the thickness of a protective oxide layer formed in the surface of Zr-Nb alloy. However, it was shown that there were little effects of annealing on the corrosion behavior of the extruded Zr-Nb alloy for up to 150 days. The annealing of extruded alloy at 580°C induced the changes of the materials factors (precipitates, grain size, dislocations 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 effects of annealing time on the corrosion behavior.

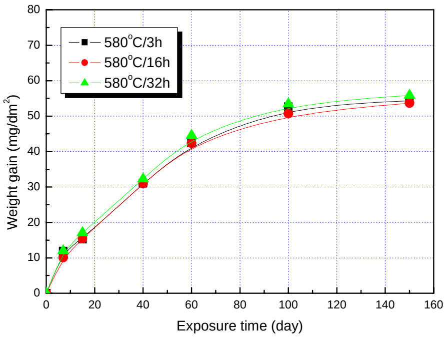


Figure 4. Effects of annealing time on the corrosion behavior of Zr-Nb alloy at 360°C in ammonia aqueous solution.

3. Conclusion

The annealing of extruded Zr-Nb alloys at 580°C led gradually to increase the grain size while the values of hardness decreased. The results of observation on the precipitates of Zr-Nb 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; lath-type β-Zr and spherical-type enriched β. As the annealing time increased, there was a change in the morphology of precipitates from lath-type to spherical-type. However, the effects of annealing on the corrosion behavior of extruded Zr-Nb alloys at 360°C in ammonia aqueous solution for 150 days were not shown yet.

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