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Corrosion behavior of the Zr-Nb experimental alloys with final annealing

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1. Introduction

Advanced Zr-alloys with good corrosion resistance and mechanical properties is necessary for more severe operating conditions such as higher burn-up[1]. Recently, Nb-containing zirconium alloys were developed instead of Zry-4 to satisfy the conditions. As the corrosion properties and mechanical strength of the Zr-based alloys with Nb were influenced by microstructure properties. It is considered that microstructure characteristics were affected by the alloying element as well as the heat-treatment conditions [2,3]. Generally, Zr-Nb alloys contain 0.5~1 wt% of Sn to have good mechanical strength. However, it has been reported that the corrosion resistance of zirconium alloys was decreased with increasing of Sn content. X element addition resulted in microstructure refinement and suppression of grain growth, because X element has low solubility in alpha-zirconium[4,5]. Therefore, X element contained zirconium alloys without Sn were designed to improve corrosion resistance and maintain mechanical strength. Therefore, the purpose of this work is to study the good corrosion behavior of Zr-Nb-X experimental alloys. The effect of final heat treatment condition on the corrosion resistance is also discussed in this study.

2. Experimental procedure

The experimental specimens were Zr-Nb-X alloys were manufactured as sheets and the process is shown in figure 1.

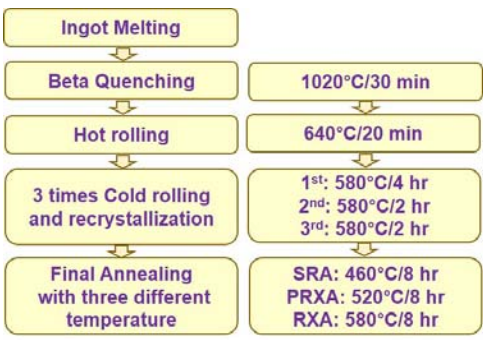

Fig 1. The manufacturing process of Zr-Nb-X experimental alloys

For homogenizing of the alloying elements, several meltings and beta-heat treatment were performed. The prepared specimens were hot and cold rolled to have about 1 mm thickness. The intermediate heat-treatments were performed subsequent to every cold rolling to restore ductility after a cold deformation. The final annealing was performed at three different temperatures; i.e. SRA(460°C), PRXA(520°C), and RXA(580°C) for 8 hours to assess the effect of the final annealing temperature on the corrosion behavior.

The corrosion tests were performed with a static auto clave of 360°C water under a saturated pressure of 18.6 MPa. To compare the corrosion properties of manufactured alloys, commercially available zirconium alloys were used (such as Zry-4, A, HANA-6 tubes and strips). The specimens for corrosion test were cut from the final annealed sheets and mechanically polished with SiC paper. The polished specimens were pickled in a solution of H_2O (45 vol.%), HNO_3 (45 vol.%), and HF(10 vol.%). The corrosion resistance was evaluated by measuring the weight of the samples after suspending the corrosion test at a periodic term.

The microstructural characteristics were analyzed by using a TEM (Transmission Electron Microscope). The 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 70 μm.

3. Results and discussion

The corrosion behavior of the manufactured sheets and commercial Zr alloys was investigated in 360°C water for 165 days in the periods of 16, 46, 80, 110, 160 and 165 days. Figure 2 shows the weight gain of manufactured alloys with different temperature and amount of alloys.

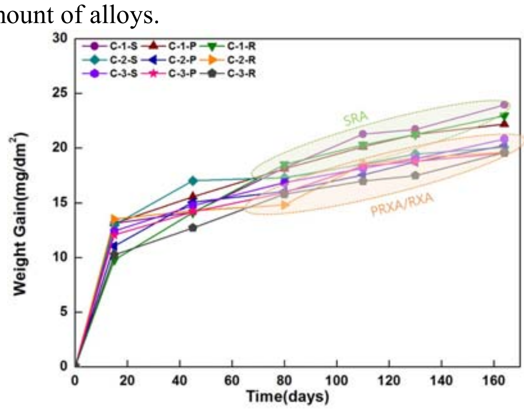

Fig. 2. Corrosion behaviors of manufactured alloys as function of final annealing temperatures; S (460°C), P (520°C), and R (580°C)

As the final annealing temperature increases, the weight gain was slightly decreased. Regarding the effect of the alloying elements, the alloy of more reduced content of Nb showed a good corrosion resistance, but its influence was slightly small. Therefore, there was little difference in accordance with the amount of alloying element.

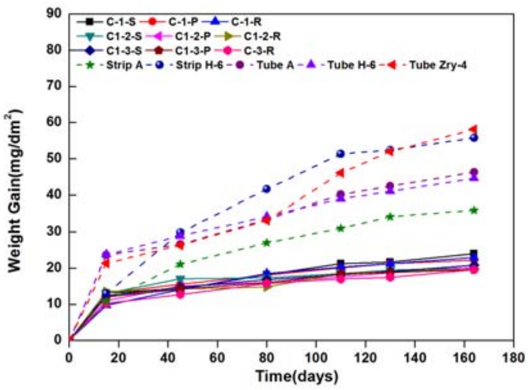

Fig. 3. Corrosion behaviors of manufactured alloys and commercial zirconium alloys with different annealing temperatures; S (460°C), P (520°C), and R (580°C)

Figure 3 shows weight gain of manufactured Zr-Nb-X alloys and commercial zirconium alloys. The solid lines show the weight gains of Zr-Nb-X alloys and the dotted lines show those of the commercial zirconium alloys. In the case of 360°C water corrosion environment, the weight gains of all Zr-Nb-X alloys were lower than those of the commercial zirconium alloys. Generally, the addition of Nb and the reduction of Sn improve corrosion resistance. Therefore, the beneficial effect on corrosion behavior of the removal of Sn might be achieved in Zr-Nb-X alloys.

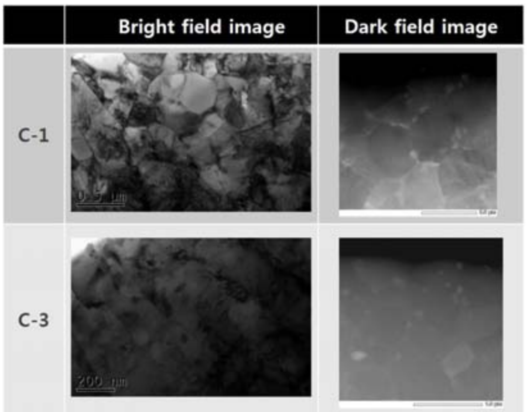

Fig. 4. The TEM image of Zr-Nb-X alloys which were annealed at 520°C for 8 hr.

Figure 4 shows the bright field and dark field TEM images of the C-1 and C-3 alloys which were annealed at 520°C for 8 hours. The deformation and recrystallization structures were observed in the microstructure. The alpha grains were observed in the matrix of the final annealed sheets and the second phase particles were formed in the alpha grains. There were no difference on the size, shape and distribution of precipitates in these specimens. It seems that there are almost no difference in the microstructure according to the amounts of alloying element, so the corrosion properties were similar.

4. Conclusions

The corrosion behavior and microstructure characteristics of Zr-Nb-X alloys (Sn free) were investigated. The microstructure shows that there were no differences with alloying elements of the alloys. Therefore, it seems that the effects of final heat-treatment and alloying elements were not remarkable in corrosion behavior of Zr-Nb-X. Zr-Nb-X experimental alloys showed much lower weight gain than commercial zirconium alloys. . It can be concluded that the Zr-Nb-X alloys have improved corrosion resistance. Also, it can be inferred that removal of Sn or addition of new alloying element have significant effect on corrosion behavior.

Acknowledgment

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