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Effects of annealing on the corrosion and creep resistance of Zr-Nb- Mo or P alloys.

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1. Introduction

Zr alloys have been used in nuclear industry for several decades because they have a good corrosion resistance and mechanical properties in reactor operating conditions[1]. For the development of advanced cladding materials, many researches have been studied for advanced Zr-Nb alloys instead of Zircaloy-4 to satisfy more severe operating condition such as higher burn-up and increased operation temperature. They have reported that the fabrication processes including especially the different annealing treatments have a significant effect on corrosion and creep ressistance of Zr-Nb alloys. So many researchers have studied to establish the ideal alloying elements and their amounts [2-4].

In this study, two kinds of alloys were designed to improve corrosion and creep resistances. One is Zr-Nb –P alloy; P system (P-1~4), the other is Zr-Nb-Mo alloys; Mo system (Mo-1~3). The purpose of this investigation is to get the more effective alloying system and annealing temperature which has good corrosion and creep resistance.

2. Experimental Procedure

Zr-Nb-Fe-P/Mo alloys were designed amount of the solute atoms of Fe, P, Mo, and Ta added to a pure sponge zirconium. The chemical composition of the Zr-Nb alloy used in this study is presented table 1.

Table 1. Chemical composition of Zr-Nb alloys
(unit: wt%)

	Zr	Nb	Fe	Mo	P	Cu	Ta
P-1~4	Bal	1.1~ 1.2	0.2	-	0.005~ 0.01	-	0.03 ~0.1
Mo-1~3	Ba.	0.5~ 1.2	0.2	0.4 ~0.8	-	0.1	-

For homogenizing of the alloying elements, triple vacuum arc-meltings were performed. The melted buttons of the melted Zr alloys were β-quenched at 1020°C for 0.5 hours. The quenched ingots were hot and cold-rolled with intermediately annealing. For the comparison, final annealing for the cold rolled sheets was applied at three different temperatures, i.e. S; 460°C, P; 520°C, and R; 580°C, for 8hours to study the effect of the final annealing temperature on the corrosion and creep resistance.

The corrosion tests were performed with a static auto clave of 360°C water under a saturated pressure of 18.6 MPa. Corrosion testing specimens of 20 mm x 20 mm x1 mm in size were cut from the annealed sheets and mechanically grounded with 1200 grit SiC paper. The polished specimens for corrosion test 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. For comparison of the creep properties with commercially available Alloy-A tube was used.

Creep test were carried out under a 120 MPa at 350°C for 240 hours. Creep specimens were machined from the sheet along the longitudinal direction with a guage length and width of 25 mm and 5 mm, respectively. The axial creep strains were recorded on every 3600 second. For comparison of the creep properties, commercially available Zr-alloys Alloy-A sheets were used which manufactured same manufacturing process.

3. Results and Discussion

The corrosion behavior of the manufactured sheets were investigated up to 260 days. Figure 1 shows the weight gain of manufactured alloys with different final heat temperature and amount of alloys. As the final annealing temperature increases, the weight gain was slightly decreased in both systems. The differences between different thermal treatments could be due to the degree of recrystallization and intermetallic precipitates, because a recrystallized alloy oxidizes more slowly than a cold work stress relieved alloy[5].

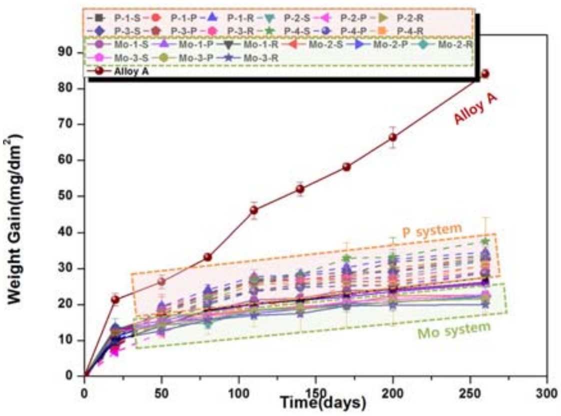

Fig. 1. Corrosion behavior of manufactured alloys as function of alloying elements and final annealing temperature. (S; 460°C, P: 520°C, R: 580°C)

Regarding the effect of the alloying elements amount, there was little difference in the amount of alloying element.

The weight gains of the water environment, all manufactured sheets were much lower than those of Alloy-A. Therefore, both P and Mo are effective element which improve the corrosion resistance of Zr-Nb alloys. Comparing the corrosion behavior between P and Mo system, the weight gains of the Mo system were lower than that of P system. The result shows that Mo is more effective element which improve the corrosion resistance.

Figure 2 shows the TEM images of the P and Mo system which were annealed at 520°C for 8 hours. The deformation and recrystallization structures were observed in the microstructure. As shown in this figure, Mo system containing more precipitation in grain and grain boundaries which causes more improving corrosion resistance than P system.

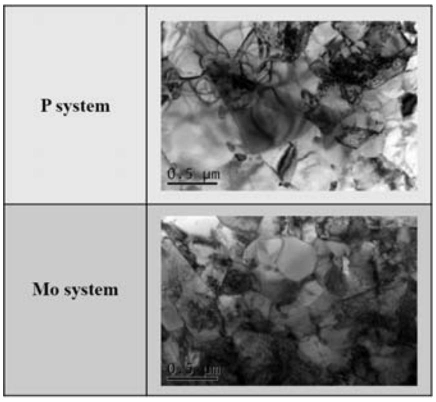

Fig. 2. The TEM image of P or Mo system which annealed at 520°C for 8 hours.

The creep behavior was affected by alloying elements, microstructural characteristics of the grain size and precipitates. Figure 3 shows the creep properties of the manufacture Zr-Nb alloys with respect to the different alloying elements. The blue line shows the creep strain of reference value of the alloy-A which manufactured same manufacturing process.

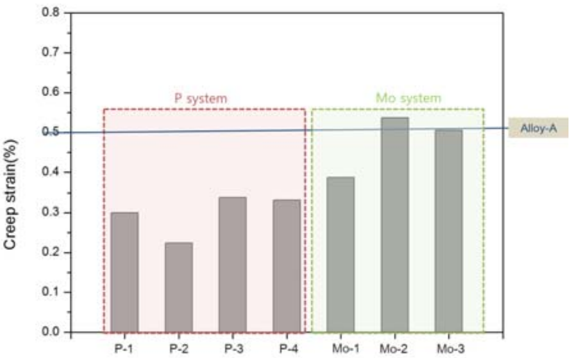

Fig. 3. Creep strain of manufactured alloys which annealed at 460°C for 8 hours.

The creep strains of Zr-Nb alloys with P or S were lower than those of Alloy-A except Mo-2. The result shows that both P and Mo are effective on creep resistance. P and Mo has a very low solubility in zirconium at a low temperature, however the effect of precipitates on creep was different. Chang and Hong et al, the enhance the creep property mechanism of S or P containing Zr alloys can be explained by the dislocation interaction mechanism.[6] Therefore, the creep strains of the P system were lower than that of Mo-systems. P or S atoms interacted to oxygen atoms could be affected the dislocation density as shown in figure 2. From this result, P is the more effective element to enhance the creep resistance. As the amount of alloying elements were increased, the creep strain was decreased.

4. Conclusion

The effects of the alloying elements and annealing conditions for the Zr-Nb alloys with P or Mo were investigated. The corrosion resistance of P system alloys were worse than that of Mo system alloys. Because Mo system alloys contain more precipitates that causes more improving corrosion resistance than P system alloys. In the same alloying system, as the heat treatment temperature increased, the corrosion resistance were improved. The creep resistances of P system alloys was better than that of Mo system alloys. This is because the creep resistance of the P containing Zr alloys controlled by dislocation mechanism which result enhancing the creep resistance.

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REFERENCES

[1] F. H. Ruddy, A. R. Dulloo, J. G. Seidel, F. W, Hantz, and L. R. Grobmyer, Nuclear Reactor Power Monitoring Using Silicon Carbide Semiconductor Radiation Detectors, Nuclear Technology, Vol.140, p. 198, 2002.

[2] F. H. Ruddy, A. R Dulloo, J. G Seidel, J.W.Palmour, and R. Singh, The Charged Particle Response of Silicon Carbide Semiconductor Radiation Detector, Nuclear Instruments and Methods In Physics Research, Vol.505, p.159, 2003.

[3] G. Lutz, Semiconductor Radiation Detector, Springer, New York, 1999.

[4] S. Kass and W. W. Kirk, "Corrosion and hydrogen absorption properties of nickel-free Zircaloy-2 and Zircaloy-4," ASM transactions quarterly, vol. 55, p. 77-100, 1962.

[5]"Waterside corrosion of zirconium alloys in nuclear power plants," Vienna: IAEATECDOC-996 1998.

[6] Hong SI. Influence of dynamic strain aging on theapparent activation energy for creep. Mater Sci Eng 1984;64:L19–21.