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Microstructure and Corrosion Characteristics of HANA Alloys with β-annealing

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1. Introduction

The corrosion resistance of fuel claddings has been considered to be one of the important properties to control the performance and the safety of nuclear reactor. Zr-based alloy such as Zircaloy-4 has been used as fuel cladding materials for the last few decades. Since, the corrosion of fuel claddings is the most critical issues in high burn-up operating condition in PWRs, the development of the advanced Zr-based fuel cladding with an improved corrosion resistance was demanded.

The HANA alloy designed in KAERI was one of the newly developed materials having an improved corrosion resistance. It was reported that the corrosion properties of the Nb contained Zr-based alloys were very sensitive to the some factors such as Nb-content and second phase characteristics which was controlled by the heat-treatment [1-3]. The microstructural characteristics of Zr-based alloy were determined by the heat-treatment conditions. Therefore, to obtain the good corrosion resistance, the Zr-based alloy as a fuel cladding was applied to the optimized β-annealing conditions. The purpose of this investigation is to get the optimized β-annealing conditions of HANA alloy.

2. Experimental procedure

The three types of HANA-3, HANA-4, and HANA-6 alloys as shown in table 1 were manufactured by the sequence of the vacuum arc re-melting of 4 times to promote the homogeneity of the alloying element. To study the β-annealing temperature effect, the one series of the melted HANA alloys were quenched from the β region of 960, 1050, and 1200℃. And to study the cooling rate effect, the other series of the melted HANA alloys were also applied to different cooling rate of water quenching and air cooling from the β region of 1050℃. Therefore, the three types of HANA alloys having different β-annealing conditions were manufactured.

The microstructure with annealing temperature was observed using optical microscope with polarized light. The precipitate characteristics were analyzed using transmission electron microscope equipped with energy dispersive spectra. Specimens for TEM observation were prepared by twin-jet polishing with a solution of C_2H_5OH (90 vol.%) and $HClO_3$ (10 vol. %) after mechanical thinning to about 70μm.

The corrosion test was performed in a static autoclave of 400℃ steam under saturated pressure of 10.3 MPa. Corrosion testing specimens of 15mm x 25mm x 1mm in size were cut from the annealed samples and mechanically ground up to 1200 grit SiC paper. Also, the ground specimens for the corrosion test were pickled in a solution of H_2O (40 vol.%), HNO_3 (30 vol.%), HCl (25 vol.%) and HF (5 vol.%). The corrosion resistance was evaluated by measuring the weight of the corroded samples after suspending the corrosion test at a periodic term.

Table 1. Chemical composition of HANA alloys

Alloy	Chemical composition wt.%					
	Nb	Sn	Fe	Cr	Cu	Zr
HANA-3	1.5	0.4	0.1	-	0.1	Bal.
HANA-4	1.5	0.4	0.2	0.1	-	Bal.
HANA-6	1.1	-	-	-	0.05	Bal.

3. Results and discussion

The microstructure observation was performed to evaluate the grain shape and precipitate characteristics with the β-annealing temperature of 960, 1050, 1200℃ and the cooling rate from β region of 1050℃, since it is well known that corrosion properties of Zr alloys is highly depended on the microstructural characteristics [3].

Fig. 1 shows the TEM micrographs of water quenched HANA alloys with the β-annealing temperature of 960, 1050, and 1200℃. Because the dislocations and twins were observed in the matrix of the quenched HANA-3, HANA-4 and HANA-6 alloys, the martensite structure (prior β phase) was formed at water quenched HANA alloys from the β region. The alloying elements of HANA alloys were homogeneously supersaturated in the martensitic matrix, since the precipitates were not observed in the martensite structure formed by water quenching. However, the β-annealing temperature of 960℃ is approach to the α+β/β transformation temperature [4] and that temperature of 1200℃ is too high in the focus on the manufacturing economy. Therefore, the β-annealing temperature of HANA alloys was considered as 1050℃.

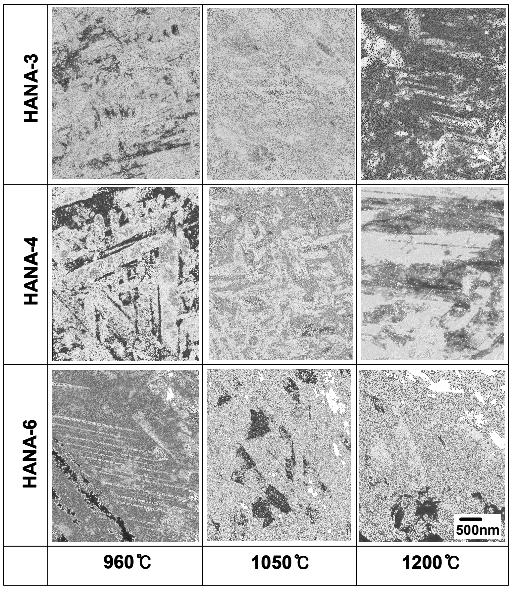

Fig. 1 TEM micrographs of water quenched HANA alloys with different β-annealing temperature

Fig. 2 shows the TEM micrographs of air cooled HANA alloys from the β region of 1050℃. The alpha grain was observed in the matrix of the air cooled HANA alloys and the second phase was formed in between the alpha grains. From the result of precipitate analysis by using TEM-EDS, the second phase in the matrix was revealed as β-Zr phase.

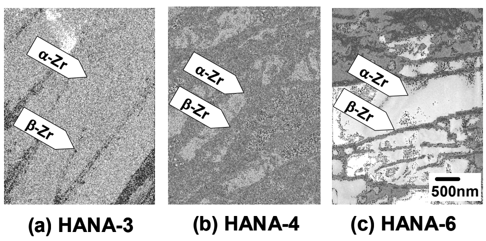

Fig. 2 TEM micrographs of air cooled HANA alloys from β region

Fig. 3 shows the corrosion behavior of β-annealed HANA alloys corroded in an autoclave of 400℃ steam condition up to 60 days. The corrosion resistance of water quenched HANA alloys was not affected by the β-annealing temperatures. However, the HANA-6 alloy showed good corrosion resistance than HANA-3 and HANA-4 alloy. It could be thought that the corrosion rate was affected by the Nb content as an alloying element, because the Nb content in HANA-6 alloy was lower than other HANA alloys. The corrosion resistance of the air cooled HANA alloys from β region of 1050℃ was increase compared to that of the water quenched HANA alloys from β region of 1050℃. Therefore, the corrosion resistance was increased when the β-Zr phase in matrix of HANA alloys was formed by slow cooling. However, inhomogeneity of alloying element was formed by the formation of β-Zr.

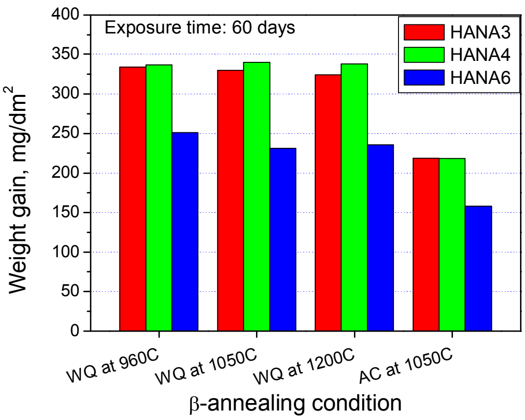

Fig. 3 Corrosion behaviors of β-annealed HANA alloys

4. Conclusion

The newly developed HANA alloys which were designed in KAERI were investigated in order to get the optimized β-annealing conditions. From the results of the microstructural observation and corrosion test, the martensite structure was formed by water quenching and the β-Zr phase was formed by air cooling. The corrosion resistance of HANA alloys was not affected by the β-annealing temperature of 960, 1050, and 1200℃. However, the corrosion resistance of HANA alloys was increased by the slow cooling as compared to the fast cooling.

ACKNOWLEDGMENTS

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REFERENCES

[1] G.P. Sabol, G.R. Kilp, M.G. Balfour, E. Roberts, ASTM STP 1023 (1989) 227.
[2] H, Anada, B.J. Herb, K. Nomoto, S, Hagi, R.A. Graham, T. Kuroda, ASTM STP 1295 (1996) 74.
[3] J.P. Mardon, D. Charquet, J. Senevat, ASTM STP 1354 (2000) 505.
[4] H.G. Kim, J.Y. Park, Y.H. Jeong, J. Nucl. Mater., 347 (2005) 140.