Effects of Final Annealing on the Corrosion Behavior and Hardness of Zr-Nb-Fe-P Alloy

Min-Young Choi, Chung-Yong Lee, Yoon-ho Kim, Yong-Kyoon Mok, Seung-Jae Lee, Jung-Min Suh
KEPCO Nuclear Fuel, 1047 Daedeokdaero, Yuseong-gu, Daejeon 305-353, Republic of Korea
E-mail: mychoi@knfc.co.kr

1. Introduction

Zr-based alloys have been used as a fuel cladding material for several decades since these alloys have revealed a good corrosion resistance and mechanical properties in reactor operating conditions [1]. For the development of advanced cladding materials, many researches have been studied to improve the corrosion resistance of Zr-based alloys [2-4]. They have reported that the corrosion resistance of Zr alloy were affected by the alloying elements and and adequate annealing condition. Many researchers have examined the effect of alloying elements and annealing conditions [5]. The corrosion properties of the Nb contained Zr-based alloys were influenced by microstructure properties such as second phase characteristics. Therefore, two kinds of P contained Zr-based alloys were designed and their compositions are Zr-1.1Nb-0.3Fe-0.01P and 0.02P in wt.%, respectively. The microstructural characteristic of Zr-Nb alloy was applied to the optimized final annealing condition. The purpose of this investigation is to get the optimized final annealing conditions of Zr-Nb-Fe-P alloys.

2. Experimental procedure

Zr-1.1 Nb- 0.3 Fe- 0.01P (alloy 1) and Zr-1.1 Nb- 0.3 Fe- 0.02P (alloy 2) were manufactured by a sequence of three vacuum arc-meltings to promote homogeneity of the alloying elements. A button of the melted Zr alloys were quenched from the β-region (maintained at 1020°C for 0.5hr and quenched to water at room temperature). The hot rolling was performed after a preheating at 640°C for 0.3hr, and cold rolled with intermediately annealed at 580°C for 3hr. The final annealing for the manufactured cold rolled sheets was applied at three different temperatures, i.e. 470°C, 540°C, and 600°C for 8hr to assess the effect of the final annealing temperature on the corrosion behavior and the hardness.

The microstructural characteristics were analyzed by using a TEM (Transmission Electron Microscope) equipped with EDS (Energy Dispersive Spectra). 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 50 um.

Hardness measurement of annealed specimen has been performed by Vickers hardness tester. Hardness analysis specimens of 10 mm x 10 mm x10 mm in size were cut from the annealed sheets and mounted. To measure hardness, mechanical polishing was performed.

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 15mm x 15mm x1 mm in size were cut from the annealed sheets and mechanically polished with SiC paper. ZIRLO and Zry-4 strips were used to compare the corrosion properties between commercially available Zr-alloys and Zr-Nb-Fe-P alloys. 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 gain of the corroded samples after suspending the corrosion test at a periodic term.

3. Results and discussion

The corrosion behaviors of the Zr-Nb-Fe-P alloys were investigated in 360°C water for 75 days. ZIRLO & Zry-4 samples were used as reference. The period of the corrosion test was 5, 15, 30, 45, and 75 days. Fig. 1 shows the weight gain of the alloy 1and 2. The weight gains of the water environment, all manufactured sheets were higher than those of the ZIRLO and Zry-4 strips.

The corrosion resistance of the Zr-Nb-Fe-P alloys shows the best result when it was annealed at 540°C compared to 470°C and 600°C. The temperature, 540°C, is within the range of partially recrystallized annealing, therefore the structure has deformation and recrystalline structures.

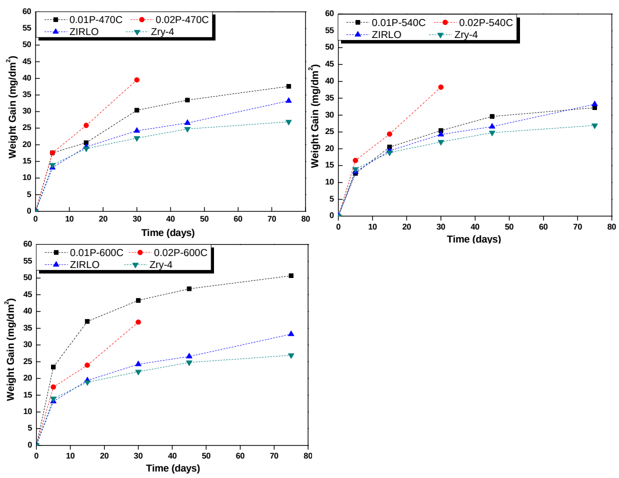

Fig. 1. Corrosion behavior of final annealed Zr-Nb-Fe-P alloys

The weight gain of the alloy 2 was higher than that of alloy 1 and after 30 days, the surface of the alloy 2 was turned into white oxide. Therefore the corrosion resistance of Zr-Nb-Fe-P alloy with 0.01wt.% phosphorous was higher than that of 0.02 wt.% one.

Fig. 2 shows the bright field and dark field TEM images of the alloy 1 that was annealing at 540°C. The deformation and recrystallization structures were observed in the microstructure. The alpha grains were observed in the matrix of the final annealed Zr-1.1Nb-0.03Fe-0.01P alloy and the second phase particles were formed in between the alpha grains. The size of precipitates is between 20 and 100 nm, and the precipitates showed round shapes. From TEM-EDS results, the second phase in the matrix was revealed as β-Zr phase.

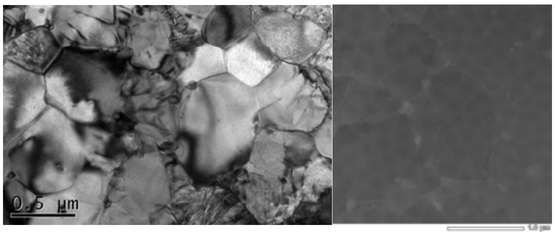

Fig. 2. The TEM image of Zr-1.1Nb-0.3Fe-0.01P alloy annealing at 540°C for 8 hr.

Fig. 3 shows the results of Vickers hardness tests of the Zr-Nb-Fe-P alloys at room temperature. Final annealing results in reduction of intercrystalline stresses level and degree distortion of crystal lattice therefore the α-Zr was softened. The hardness of the alloy 1 alloy was higher than those of alloy 2.

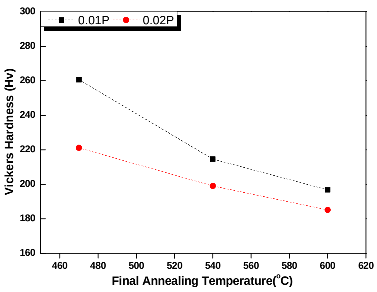

Fig. 3. The hardness of final annealed Zr-Nb-Fe-P alloys

4. Conclusion

The study on the effect of final annealing of Zr-Nb-Fe-P alloy on the Vickers hardness tests and corrosion tests in 360°C water environment was carried out with three kinds of final annealing and the microstructure was observed by TEM. The 540°C annealed Zr-1.1Nb-0.3Fe-0.01P alloy has deformation and recrystallization mixed structures with precipitates, which ultimately leads to the best corrosion resistance. The result showed that the 540°C annealing could be chosen as the candidate among the final annealing conditions.

Acknowledgment

This research has been carried out as a part of the nuclear R&D program of the Korea Institute of Energy Technology Evaluation and Planning funded by the Ministry of Trade, Industry and Energy in Korea.

REFERENCES

[1]Ramos C, Saragovi C, Granovsky M.S., Some new experimental results on the Zr-Nb-Fe system, J. Nucl. Mater., 366, 198-205 (2007)
[2] A.V. Nimulina, J. Nucl. Mater.,238,(1996) 205.
[3]R.J. Comstock, G. Schoenberger, G.P. Sabol, Zirconium in the Nuclear Industry, ASTM STP 1295, (1996) 710.[3] J.P. Mardon, D. Charquet, J. Senevat, ASTM STP 1354 (2000) 505.
[4]J.P. Mardon, D. Charquet, J. Senevat, ASTM STP 1354 (2000) 505.
[5] C.M.Eucken, P.T. Finden, S. Trapp-Pritsching, and H.G. Weidinger, Zirconium in the Nuclear Industry, ASTM STP 1023, (1989)113.