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Corrosion behavior and microstructure of Zirconium-Yttrium alloy

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1. Introduction

Zirconium-based alloys, such as Zircaloy-4, ZIRLO, M5, E110 and HANA etc., have been widely used as cladding and structural materials in nuclear reactor due to their low thermal neutron capture cross-section, adequate mechanical properties and good corrosion resistance [1]. However, as the demands for the high burn-up operation and the high temperature performance, new kinds of alloys which have a higher corrosion resistance have been continuously researched.

This study is the basic research for the new alloy design based on Zirconium-Yttrium (Zr-Y). Because yttrium has potential value as a structural material in nuclear reactor design due to its relatively low neutron cross-section, high melting point and other desirable properties according to the several researches [2, 3, 4], Yttrium metal, Yttrium oxide(Y_2O_3) and Yttria-stabilized zirconia(YSZ) are experimented as the alloying element. Also, this study is focused on that Y_2O_3 and YSZ are dispersed in the Zr alloy. It is expected that the dispersed elements existed as the rule of the seed of pre-oxide, which may be able to enhance corrosion resistance in Zr alloy

The current study examines the microstructural analysis to identification of the elements with TEM and the corrosion test in 360^{o}C water. The results are compared with pure Zr, ZIRLO and Zircaloy-4.

2. Experimental Procedure

Zr-Y and pure Zr ingots as shown in Table 1, are prepared by a method of vacuum arc-melting. To improve the homogeneity of alloying elements, three times of arc-melting were carried out. The ingot buttons were quenched from the β-region (maintained at 1020^{o}C for 30min and quenched to water at room temperature).

Table. 1. Chemical composition (wt %) of Zr-Y and Zr alloys.

	YSZ (3mol% YSZ)	YSZ (8mol% YSZ)	Y_2O_3 (> 50nm)	Y (metal)	Zr (sponge)
L00	0.5	1			balance
L01		1	0.5		balance
L02		1		0.5	balance
Zr					100

The microstructural characteristics were analyzed by using TEM(Transmission Electron Microscope) equipped with EDS(Energy Dispersive Spectra). Specimens for the TEM analysis were prepared by a twin-jet polishing with a solution of ethanol (90 vol%) and perchloric acid (10 vol%) after a mechanical polishing to about 70μm with SiC paper.

The corrosion test of three alloys was performed with static autoclave of 360^{o}C water under a saturated pressure of 186 bar. Corrosion specimens were cut from the quenched alloy to the specimens of 15mm x 15mm x 1mm in size and mechanically polished with the SiC paper. And the polished specimens for the corrosion test were pickled in a solution of H_2O (45 vol%), HNO_3 (45 vol%) and HF (10 vol%). Pure Zr, ZIRLO and Zircaloy-4 strips were prepared with similar preparation of the corrosion specimens and tested with to compare the corrosion behavior between commercial Zr alloys and the test alloys. The corrosion resistance was evaluated by measuring the weight gain of corroded samples suspending the corrosion test at a periodic term.

3. Results and Discussion

3.1 TEM Observation

For the detail microstructural observation, TEM analysis was carried out. In Fig 1 (a), the polygon shape particle was observed in L01. In the EDS result in Fig. 1 (b), the peaks of the polygon particle (Red circle in Fig. 1 (a)) was determined Y_2O_3.

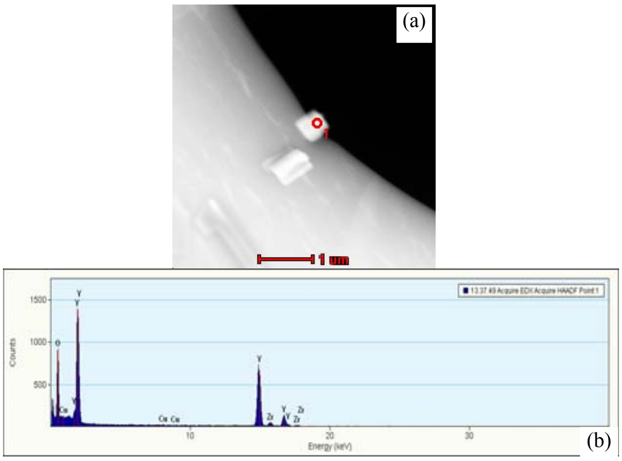

Fig. 1. Microstructure of Y_2O_3 particle (polygon-type) (a) and EDS results with Yttrium and Oxygen peaks (b) from L01 alloy.

Also, another TEM observation in L01, the acicular-type particle (Fig. 2 (a)) was observed which has similar peaks with the polygon-type Y_2O_3 in Fig 2 (b).

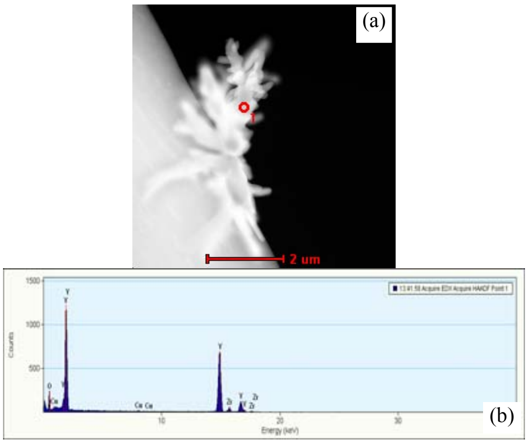

Fig. 2. Microstructure of Y_2O_3 particle (acicular-type) (a) and EDS results with Yttrium and Oxygen peaks (b) from L01 alloy.

In Fig. 3(a) and (b), there were observed YSZ particles from L01 and L02, respectively, with TEM analysis. Both alloys were observed spherical-type particles. The size ranges of particles were around 200 ~ 300 nm and the particles were dispersed homogeneously in the both ingots.

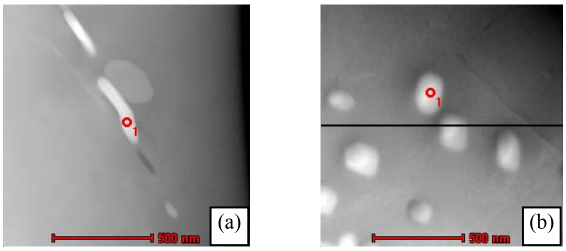

Fig. 3. TEM observed Spherical-type particles of L01 (a) and L02 (b) alloy

According to the EDS results in Fig. 4 and Fig. 5, those spherical-type particles in Fig. 3 were determined YSZ particles owing to the peaks of Yttrium, Zirconium and Oxygen.

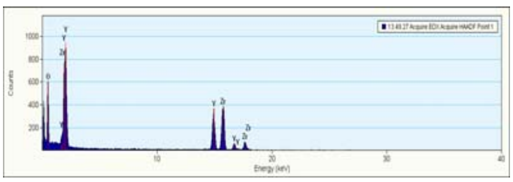

Fig. 4. EDS results of YSZ(spherical-type particle) peaks in L01 alloy

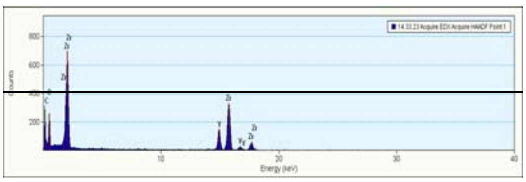

Fig. 5. EDS results of YSZ(spherical-type particle) peak in L02 alloy

3.2 Corrosion Test

The corrosion behavior of three kinds of alloys and reference specimens (ZIRLO and Zircaloy-4) were investigated in 360°C pure water for 35 days. Fig. 6 shows the weight gain of the alloys. The weight gains of all three kinds of alloys were higher than those of ZIRLO and Zircaloy-4 reference specimens.
After 5 days, the white oxides were occurred on the surface of L00, L01 and L02 alloys. Furthermore, L00 specimen was spalled to the white flake. After 10 days corrosion test, L02 specimen started to break off the white flakes similar as L00. After 35 days, L01 was started to spall.

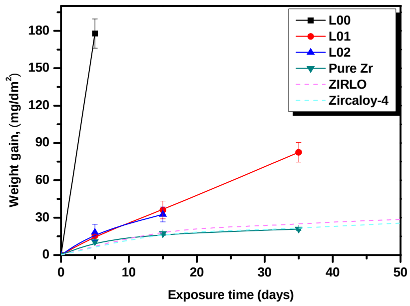

Fig. 6. Corrosion test results in 360°C water

4. Conclusion

In the present study, the three kinds of alloy are successfully manufactured. Also, the YSZ and Y_2O_3 existed and were dispersed in particle shape in Zr alloys. YSZ is remained the spherical-type particle, and Y_2O_3 exist as the polygon or acicular-type particle. In the corrosion test, the addition of yttrium, yttrium oxide and YSZ tends to increase weight gain and changed to white oxide in 360°C water under a saturated pressure of 186 bar.

Acknowledgements

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REFERENCES

[1] D. Q. Peng, X. D. Bai, X. W. Chen, Q. G. Zhou, X. Y. Liu, and R. H. Yu, Comparison of electrochemical behavior of zirconium and zircaloy-4 implanted with Y and Ce ions, Applied Surface Science 221. pp. 259–271, 2004.

[2] I.S. Batra, R.N. Singh, P. Sengupta, B.C. Maji, K. Madangopal, K.V. Manikrishna, R. Tewari and G.K. Dey, Mitigation of Hydride embrittlement of Zirconium by Yttrium, Journal of Nuclear Materials 389, pp 500 ~ 503, 2009.

[3] B. J. S. Wilkins and J. Chater, The microstructures and kinetics of internally oxidized dilute zirconium-yttrium alloys, Journal of Nuclear Materials 31, pp 288 ~ 299, 1969.

[4] R. W. Fisher and C. B. Fullhart, Feasibility Studies on Molten Metal Reactor Components, USAEC Report, ISC-1020, June, 1958.