Evaluation of An-isotropy of Pilgered Zirconium Alloys by Neutron Scattering and Its Effect on Hydride Formation and Corrosion Behavior

M. Kim[1], Y. Choi[2], J. W. Choi[3], S. C. Kwon[1]

1) Principal Researcher, Surface Technology Research Center, KIMM, Changwon, Kyungnam, Korea
2) Professor, Dept. of Electronic Materials Eng., Sunmoon University, Asan, Korea (yochoi@sunmoon.ac.kr)
3) Head, COTEC, Changwon, Kyungnam, Korea

ABSTRACT

Neutron scattering technique was applied to study on the effect of crystallographic orientation of pilgered zirconium alloys on the hydride formation and corrosion behavior. Neutron scattering showed that pilgering of the zirconium alloys results in making unique crystallographic orientation such that most of (002) poles are oriented along radial direction that results in significantly influencing corrosion behavior. The longitudinal and transverse directions of corrosion potentials and rates of the pilgered zirconium with hydride in 40wt.% HCl-500ppm $FeCl_3$ aqueous solution were -1.70 mV_{SHE}, 3.86×10^{-5} A/cm^2, and -1.78 mV_{SHE}, 4.62×10^{-5} A/cm^2, respectively. The corrosion behavior is related to crystallographic an-isotropy of the specimen.

INTRODUCTION

Zirconium alloy tubing has been used for many years in chemical and nuclear engineering applications involving severe combinations of temperature and reactive environments. The alloy tubing is generally produced by pilgering process, which is one of plastic deformation techniques for making seamless tube. The pilgering process results in making unique microstructure of the materials such as texture and crystallographic orientation. Since the crystallographic orientation is dependent upon the degree of plastic deformation like the number of deformation process and also changed thermally at a high temperature service condition. Metallurgical point of view, a study of the crystallographic effect on the performance of the alloy is one of important because it influences various mechanical and chemical properties.[1] In this study, neutron scattering was applied to analyze texture of zirconium alloy to determine crystallographic orientation and evaluate effect of hydride formation on corrosion behavior of the materials with pilgering direction. Emphasis is on the effect of crystallographic an-isotropy on the corrosion behaviors.

EXPERIMENTAL METHOD

Pilgered zirconium alloy tubes supplied by the Korea Nuclear Fuel Company were used in this study. The chemical composition of the zirconium alloys is in Table 1. The pilgered zirconium alloy was cut 5x5x5 mm in length, ground with from 320 grit to 600 grit emery papers, rinsed in deionized water, and introduced into electron microscope and neutron scattering facility. Microstructure of the tube was observed by scanning electron microscopy (Jeol JSM 2400). Zirconium hydride was formed by high temperature cathodically hydrogen charging (HTCHC) method [2]. Crystallographic orientation of the specimen for longitudinal and transverse directions was determined with a four-circle diffractometer using a neutron beam of wavelength 0.99 Å, at the HANARO reactor of the Korea Atomic Energy Research Institute. Three pole figures were measured for each phase. First, the texture was determined by usual complete pole figures. In this procedure, pole figures were scanned on both the radial angle α and azimuth angle β with a constant interval of 5^o. Corrosion behavior was determined by electrochemical method in 40%-hydrochloric acid solution (Gammy 200).

Table 1. Chemical composition of Zirconium alloy specimen

Element	Sn	Fe	Cr	Fe+Cr	O	C	Si	H	Zr
wt.%	1.2-1.45	0.18-0.24	0.09-0.13	0.28-0.37	0.10-0.37	0.01-0.135	0.08-0.012	20ppm	bal.

RESULTS AND DISCUSSION

Fig. 1 is microstructure of the specimen with pilgering direction. As shown in figure 1, the zirconium alloys have similar grain size with almost equi-axed shape. The average grain size is about 8.7 μm. Since the specimen thickness is about 10 mm, neutron scattering technique was applied to evaluate crystallographic an-isotropy of the specimen. Since the most common method for representing crystallographic orientation is through the construction of stereographic pole figures, basal pole (002) or (0001) was determined in this study. As shown in figure 2, crystallographic an-isotropy was well observed such that the most of (002) poles are oriented along radial direction, whereas, lots of (100) poles are mainly oriented to longitudinal direction and partially oriented to redial direction, respectively. This kind of crystallographic an-isotropy occurred by the preferential orientation effect during deformation. Since zirconium has the hexagonal cross packed structure with axial ratio of c/a axis less than 1.633, the slip of the zirconium during deformation occurs to the direction of the lowest resolved shear stress. This is well agreement with previous reports [3].

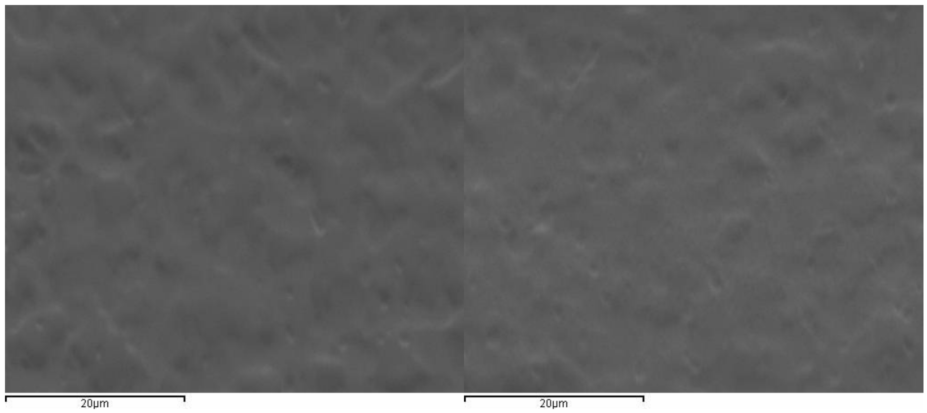

Fig. 1. Cross sectional view of zirconium alloy : (a) transverse (b) longitudinal

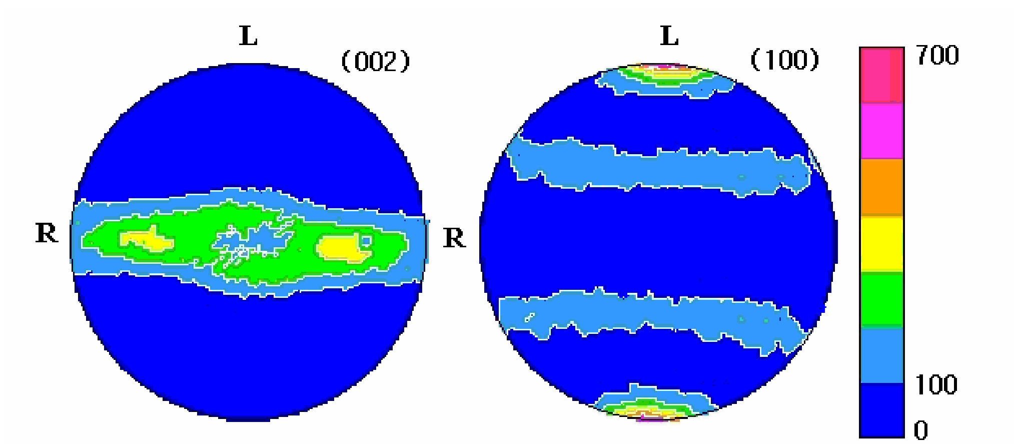

Fig. 2. Crystallographic orientation of pilgered tube

Table 2 is the corrosion potential and rate of the pilgered zirconium alloys after hydriding with deformation direction and content of chloride. As shown in Table 2, corrosion behavior depended on tube direction. The longitudinal and transverse directions of corrosion potentials and rates of the pilgered zirconium with hydride in 40wt.% HCl-500ppm $FeCl_3$ aqueous solution were -1.70 mV_{SHE}, $3.86\times10^{-5}A/cm^2$, and -1.78 mV_{SHE}, $4.62\times10^{-5}A/cm^2$, respectively. It is interested in why corrosion behavior is so different after pilgering. Metallurgical point of view, there are so many parameters to influence corrosion behavior such as grain boundary, crystallographic orientation and precipitates. Among these, grain boundary is one of important areas to be corrosion attacked. As shown in figure 1, the grains of the specimen with pilgering direction are similar size of about 8.7 μm. This means that effect of grain boundary area on corrosion resistance is similar for the given specimen.

In order to study the hydride effect on the corrosion behaviors, the zirconium was high temperature cathodically hydrogen charging (HTCHC) followed by annealing at 150 ^oC for 24 hours. As shown in Table 2, corrosion potential and rate depended on pilgering direction and significantly decreased with hydride formation. It is known that the hydride in zirconium was formed on basal plane (0001) and grown across grain boundary [4]. This means that hydride formation on the specimen with equi-axed grains is not a main parameter to give different corrosion behaviors in Table 2. Since the pilgering makes crystallographic orientation change of the grains, the crystallographic an-isotrpy of the grains results in influencing corrosion behavior. In case of corrosive ions like chloride ion in aqueous solution, chloride ions can not corrosively attack zirconium hydride but the passive film on metallic zirconium to be corroded [5]. Accordingly, corrosion rates of the specimen with hydride is related to the relative area effect of anode and cathode region [6]. Hence, the corrosion behavior observed in this study is more predominantly related to crystallographic orientation than grain boundary and hydride.

Table 2. Corrosion behaviors of the pilgered zirconium alloys with pilgering direction in HCl-500ppm $FeCl_3$ at 25 ^oC

Zirconium alloy	Observed direction	Ecorr[mV]	Icorr[×10-5A/cm^2]
as-received	longitudinal	72.0	6.07
	transverse	31.0	18.1
with hydride	longitudinal	-1.70	3.86
	transverse	-1.78	4.62

CONCLUSIONS

The pilgered zirconium tube with average grain size of 8.7 μm has crystallographic orientation, in which the most of (002) poles are oriented along radial direction, whereas, lots of (100) poles are mainly oriented to longitudinal direction and partially oriented to redial direction, respectively. The longitudinal and transverse directions of corrosion potentials and rates of the pilgered zirconium with hydride in 40wt.% HCl-500ppm $FeCl_3$ aqueous solution were -1.70 mV_{SHE}, 3.86×10^{-5}A/ cm^2, and -1.78 mV_{SHE}, 4.62×10^{-5}A/ cm^2, respectively. The corrosion behavior is related to crystallographic an-isotropy of the specimen.

ACKNOWLEDGEMENT

This study was supported by NRL program of Korea Science and Engineering Foundation (KOSEF) and Ministry of Science and Technology (MOST), Korean government.

REFERENCES

1. W. Evans, J. A. L. Robertson, The Physical Metallurgy of Zirconium, CRNL-1208, (1974).
2. Y. Choi and S. I. Hong, “Hydride Formation by High Temperature Cathodic Hydrogen Charging Method and its Effect on the Corrosion Behavior of Zircaloy-4 Tubes in Acid Solution”, Journal of Nuclear Mataterials, vol. 256, p. 124 (1998).
3. Yu. Perovich, M. Grekhov, M. Isaenkova, V. Fesenko, B. Kalin, V. Yakushin, “Bulk Texture and Structure Changes in Tubes of Zr Alloy due to the Long-Range Effect of Ion-Plasma Surface Treatment”, Materials Science Forum, vol. 495, p. 687, (2005).
4. C. E. Ellis, "Hydride Precipitates in Zirconium Alloys", Journal of Nuclear Materials, vol. 28, p. 129 (1968).
5. T. L. Yau and Maguire, “Electrochemical Protection of Zr aginst SCC by Oxidizing HCl Solution”, Corrosion, vol. 14(7), p. 397 (1985).
6. 4. D. A. Jones, Corrosion Processes, Englewood, (1982).