

Corrosion Behavior and Microstructure of Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr Alloy with a Annealing

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1. Introduction

For the development of advanced cladding materials, many researches have been implemented to improve the corrosion resistance of Zr-based alloys [1-3]. They have reported that the corrosion kinetics of Zr alloy were affected by the alloying element and the precipitates that are formed by various alloying elements. Since the combination of an alloying element such as Nb, Sn, Fe, Cr etc., is a very important factor to obtain good properties of an alloy such as fuel claddings, many researchers have tried to establish the ideal alloying elements and their amounts [3, 4]. At KAERI, many of the Zr alloys which were systematically controlled by an alloying element were then tested for various properties such as their corrosion, tensile, creep, and high temperature oxidation. Therefore, a high Nb-containing Zr-based alloy was designed and its composition is Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr in wt.%. So, the purpose of this investigation is to obtain the optimized β -annealing conditions for the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy.

2. Experimental procedure

Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy was manufactured by a sequence of four vacuum arc re-meltings to promote a homogeneity of the alloying elements. To study the β -annealing temperature effect, a button of the melted Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy was quenched from the β -regions of 960, 1050, and 1200 °C. And to study the cooling rate effect, another button of this alloy was also applied to a different cooling rate for a water quenching and air cooling from the β -region of 1050 °C. The cooling rate of the water quenching was about 1000 °C/sec and that of the air cooling was about 4 °C/sec. Therefore, Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloys with different β -annealing conditions were manufactured. The microstructural characteristics were analyzed by using a transmission electron microscope equipped with energy dispersive spectra. Specimens for the TEM observation were prepared by a twin-jet polishing with a solution of C₂H₅OH (90 vol.%) and HClO₃ (10 vol. %) after a mechanical thinning to about 70 μ m.

The corrosion test was performed in a static autoclave of 400 °C steam under a 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 with 1200 grit SiC paper. Also, the ground specimens for the corrosion test were pickled in a solution of H₂O (40 vol.%), HNO₃ (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. The cross-sectional oxide preparation method was used to observe the oxide characteristics and then the oxide microstructure was observed by using a transmitted optical microscope.

3. Results and discussion

Fig. 1 shows the corrosion behavior of the β -annealed Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy corroded in a static autoclave with a 400 °C steam condition for up to 90 days.

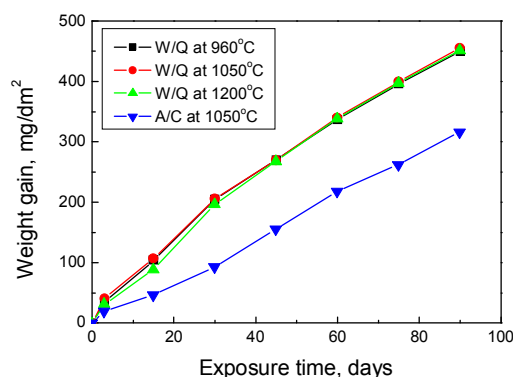


Fig. 1 Corrosion behaviors of β -annealed Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy

The weight gain of the water quenched Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy reached about 450 mg/dm² at the corrosion test time of 90 days. Since an effect of the β -annealing temperature was not observed in the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy, the corrosion resistance of the water quenched alloy was not affected by the β -annealing temperatures. And the corrosion resistance of the air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy from the β -region of 1050 °C was increased when compared to that of the water quenched alloy from the β -region of 1050 °C. Therefore, the corrosion resistance was increased when the β -Zr phase in the matrix of the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy was formed by a slow cooling.

Fig. 2 shows the TEM micrographs of the water quenched and air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr

alloy at different annealing temperatures from 960 to 1200°C. The martensite structure which was mixed with dislocations and twins was formed on the fast cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy regardless of the β -annealing temperature range of 960 to 1200°C and the Widmanstätten structure which was mixed with an elongated α -grain and β -phase was formed on the slow cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy.

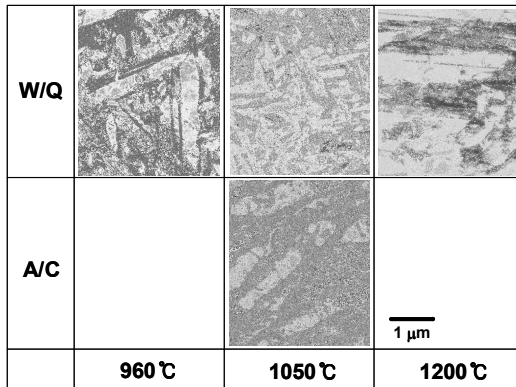


Fig. 2 TEM micrographs of the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy with different annealing temperatures and cooling rates from the β -region

Fig. 3 shows the cross-sectional optical micrographs of the oxides of the water quenched and air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy which were corroded for 60 days. The oxide thickness of the water quenched and air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy matched well with the weight gain of the corrosion data of 60 days. The roughness of the metal/oxide interfaces was shown differently with the cooling rates of the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy. In general, the uniform roughness of metal/oxide interfaces was formed in the good corrosion resistance alloy, however, the oxide formed in the air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy has more irregular metal/oxide interfaces, although the air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy has a better corrosion resistance than the water quenched alloy. It was caused by the matrix homogeneity of the alloying element. From the inhomogeneity of the alloying element between the α -phase and the β -phase, the corrosion rate was differently in a local area. Therefore, irregular metal/oxide interfaces were formed in the air cooled Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy. But it was shown that the corrosion resistance of the Zr-1.5Nb-0.4Sn-0.2F-0.1Cr alloy was increased by an air cooling from the β -region, because the oxide thickness of the air cooled Zr-1.5Nb-0.4Sn-0.2F-0.1Cr alloy was thinner than that of the water quenched Zr-1.5Nb-0.4Sn-0.2F-0.1Cr alloy.

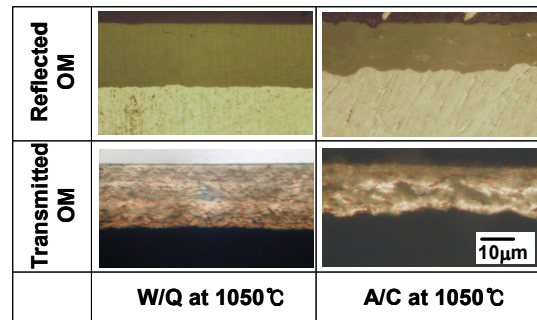


Fig. 3 Reflected and transmitted optical micrographs of the oxide formed on the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy with different cooling rates

4. Conclusion

The corrosion resistance of the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy was not affected by the different β -annealing temperatures of 960, 1050, and 1200°C, however, the corrosion resistance of this alloy was increased by a slow cooling when compared to a fast cooling. Although the corrosion behavior was improved by applying a slow cooling, a good homogeneity could not be obtained by a slow cooling condition. Therefore, it is concluded that a fast cooling rate after a β -solution annealing should be applied to the Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr alloy to obtain a good homogeneity of the alloying element.

ACKNOWLEDGMENTS

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