

# Effect of O and Fe Concentration on Phase Boundary of Zr-Nb alloy

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## 1. Introduction

The development of advanced cladding materials with an improved corrosion resistance has been widely carried out in many countries operating nuclear power plants for the last few decades [1-3]. Nb is an important alloying element in the advanced Zr-based alloys. Although a number of researches [1-5] were carried out to optimize the Nb content and annealing conditions in the Nb-containing Zr alloys, the optimum Nb content for a good corrosion resistance was differently reported since the optimum Nb content for corrosion resistance of the Nb-containing Zr alloys was depended on the impurities which were assumed to change the Nb solubility and the monotectoid temperature in alloy system. Therefore, it is essential to investigate the phase stability of the commercial grade Zr-Nb binary alloy system for developing advanced fuel cladding materials with a superior corrosion resistance. The phase diagram of the Zr-Nb binary system was extensively studied using iodide Zr of a high purity [6].

However, the commercial grade sponge-type Zr, which is actually being used in the manufacturing of the fuel cladding, contains O and Fe as impurities in the range of  $10^2$ - $10^3$  ppm. Therefore, it is not reasonable to apply the previous results on the Zr-Nb phase stability directly to the heat treatment conditions for the development of advanced Zr-alloys. In this study, the phase stability of the Zr-Nb binary alloy system was investigated using Zr containing 1400ppm O which was amount in most fuel claddings and 700ppm Fe.

## 2. Experimental procedure

The chemical compositions of the Zr alloys used in this study are Zr-xNb system ( $x=0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 2.0$  and  $10.0$  wt.%). Nb of a high purity (99.9%) and Zr containing the 1400ppm O which was additionally added in commercial grade sponge-type Zr and the 700ppm Fe were used for manufacturing the experimental alloys. Button ingots, approximately 300 g, were prepared by arc melting under an argon atmosphere and remelted at least five times to promote the homogeneity of the as-cast structure. The arc-melted ingots were solution-treated at  $1050^\circ\text{C}$  for 30 min in a vacuum furnace, hot-rolled after pre-heating at  $700^\circ\text{C}$  for 30 min, and cold-rolled three times to a final thickness of 1mm. Between the rolling

steps, the cold-rolled sheets were intermediately annealed at  $600^\circ\text{C}$  in a vacuum furnace for 2 hrs to obtain the fully recrystallized structure. The final cold-rolled sheets were quenched into water with the cooling rate of about  $1200^\circ\text{C}/\text{sec}$  after heat treatment at the  $\beta$  phase field ( $1050^\circ\text{C}$ ), and then isothermally annealed at various temperatures for a long time to reach the equilibrium phase from 3 hrs to 3 months. The microstructures of the alloys were examined using OM and TEM equipped with an EDS. The TEM specimens were prepared by a twin-jet polisher with a solution of 10 vol.%  $\text{HClO}_3$  and 90 vol.%  $\text{C}_2\text{H}_5\text{OH}$  after mechanical thinning to  $70\ \mu\text{m}$ .

## 3. Results and discussion

The phase equilibria of the alloys is characterized by the structural change which was observed by the optical microscope. Fig. 1 shows the phase boundary of the Zr-rich region in the Zr-Nb system as a function of temperature and Nb content. On the basis of the microstructural observation using OM in this study, it was possible that the phase boundary in commercial grade Zr-Nb containing 1400ppm O and 700ppm Fe could be determined.

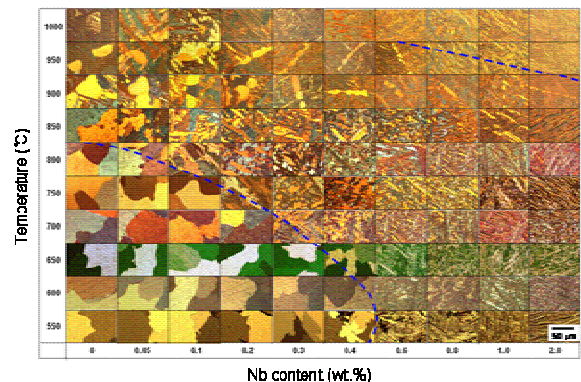


Fig. 1 Optical micrographs of Zr-xNb alloys containing 1400ppm O and 700ppm Fe annealed from 550 to 1000

The martensitic microstructure which had been initially formed by fast cooling at the  $\beta$  phase region was changed with variation of the annealing conditions and the Nb contents. After isothermal annealing at various temperatures for a long time, the new microstructures such as  $\alpha$  and  $\alpha'$ (prior  $\beta$ ) phase were formed at some conditions. So, it was possible that the phase state of

alloys with various annealing temperatures and Nb contents could be defined by microstructural characterization. In the sponge Zr containing 1400ppm O and 700ppm Fe, the fully recrystallized  $\alpha$  phase was observed by annealing at 800 . And the mixed  $\alpha$  and  $\alpha'$  (prior  $\beta$ ) phase, and the  $\alpha'$  phase were observed at the annealing temperature at 850 to 950 , respectively. These microstructural changes such as  $\alpha$  and  $\alpha'$  (prior  $\beta$ ) phase were similarly observed at other Zr-xNb alloys containing 1400ppm O and 700ppm Fe, and the  $\alpha/(\alpha+\beta)$  and  $(\alpha+\beta)/\beta$  transus temperatures were decreased with increasing Nb content.

Fig. 2 shows the TEM micrographs and EDS spectra for the precipitates of the Zr-xNb ( $x=0.1, 0.2$  and  $0.3$ ) alloys.

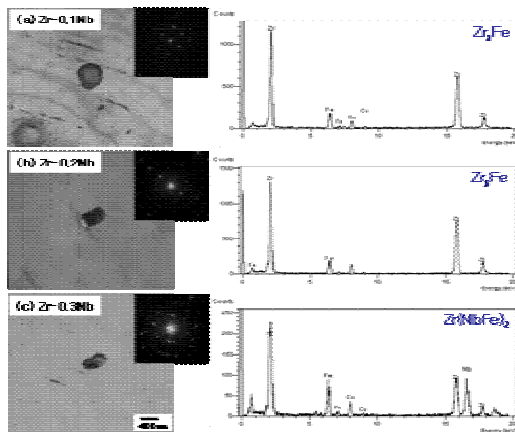


Fig. 2 TEM micrographs of Zr-xNb alloys containing 1400ppm O and 700ppm Fe annealed at 580 for 3 months.

It was observed that the precipitates in the Zr-0.1Nb and Zr-0.2Nb alloys was consisted of Zr and Fe from the EDS results, while the precipitates in the Zr-0.3Nb alloys was consisted of Nb as well as Zr and Fe. The precipitates type in the Zr-xNb alloys was reported in the previous study. The Fe containing precipitate was originated from Fe contained in the sponge Zr because the Fe content (700ppm) in the all tested samples was much higher than the Fe solubility in  $\alpha$ -Zr (about 100ppm). Although the  $\beta$  phase was not observed in the analyzed alloys (to 0.3 wt.% Nb), it was frequently observed in the Zr-0.6Nb alloy. It was suggested that 0.3Nb was higher than the Nb solubility in  $\alpha$ -Zr because the Nb was precipitated in the second phase. It should be thought that the Nb solubility in  $\alpha$ -Zr was affected by the impurity such as Fe which had been known as one of the  $\beta$  stabilizing elements. Consequently, the Nb solubility in  $\alpha$ -Zr was determined to be approximately 0.2 wt.% because the Nb containing precipitates were found in the 0.3 wt.% Nb alloy. The Nb

solubility in  $\alpha$ -Zr obtained by the TEM observation was not consistent with the result from the OM observation (0.5 wt.%Nb).

#### 4. Conclusions

The  $\alpha/(\alpha+\beta)/\beta$  transformation temperature, the solubility limit of Nb, and the monotectoid temperature of the Zr-Nb binary system were investigated using commercial grade Zr containing 1400ppm O and 700ppm Fe and different Nb with a high purity. The microstructure characterization was carried out using OM and TEM. From the microstructure examination using OM, it was revealed that the  $(\alpha+\beta)$  region was expended in commercial grade Zr containing 1400ppm O and 700ppm Fe. From the microstructure characterization using TEM, it was revealed that the Nb solubility in  $\alpha$ -Zr was determined to be approximately 0.2 wt.%, which was lower than that of the previous result (0.6wt.% Nb).

#### ACKNOWLEDGMENTS

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