Transactions of the Korean Nuclear Society Fall Meeting
Changwon, Korea, October 20-21, 2022

Beta phase transformation in Zr-2.5%Nb pressure tube material

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1. Introduction

The pressure pipe of CANDU (CANada Deterium Uranium) reactor is manufactured by hot extrusion and cold drawing after water quenched Zr-2.5%Nb ingot in α-Zr+ β-Zr region. Stress relief treatment was performed at 400°C for 24 hours to eliminate the effect of cold drawing. Because of this manufacturing history, the microstructure of the pressure tube is composed of two phases: α-Zr+β-Zr[1-4].

Since β-Zr is a metastable phase, it is known that β-Zr precipitates ω-phase and transforms into β-Nb phase when exposed to heavy water operation environment or heat treatment at reactor operating temperature[5]. Also, during this process, Nb dissolved in α-Zr, which is the main phase, is discharged from α-Zr and precipitated as β-Nb phase. Ultimately, Zr-2.5%Nb alloy becomes the material of the α-Zr+β-Nb phase.

As such, in the pressure tube material, β-Zr is decomposed during operation and Nb is redistributed. From what is known so far, it is known that pressure tube materials are precipitated as β-Nb when heat treated at 400° C. for 24 hours. However, the decomposition behavior of β-Zr is not known in detail. Therefore, in this study, the decomposition process of β-Zr was systematically studied by heat treatment at 400°C for 50 hours and performing differential scanning calorimeter (DSC) analysis.

2. Experiment

The Zr-2.5%Nb alloy used in the experiment is a quadruple melt pressure tube D084 material. Its composition is as shown in Table 1. This specimen was heat treated at 400°C for 2, 5, 10, 20, 32, and 50 hours. This specimen was subjected to DSC analysis up to 950°C to investigate the β-Zr and ω-phase decomposition processes. DSC analysis was used to determine the activation energy for the degradation process of the β-Zr phase.

The as received specimens are scanned in different rate of 10, 20, 40k/min by DSC in order to determine the activation energy for the exothermic reaction. The activation energy for the ordering reaction is calculated as follows [6,7];

$$\ln((\alpha_2 T_1^2/\alpha_1 T_2^2) = Q/R(1/T_1-1/T_2) \quad (1)$$

where T_1 and T_2 are peak temperatures at scan rate α_1 and α_2 and R is gas constant.

Table 1. Chemical composition of D084 Zr-2.5%Nb (wt %).

elements	Zr	Nb	Fe	Ta	Cr	Ti	W	O	H
composition	Balance	2.6%	980 ppm	100 ppm	<100 ppm	<50 ppm	<50 ppm	1100 ppm	<3 ppm

3. Results and Discussion

Figure 1 shows the results of DSC analysis at 400°C up to 50 hours. The pressure tube in the as received state shows an endothermic reaction at 511°C, but not at 800°C. However, in the specimens heat treated at 400°C for 2, 5, and 10 hours, the endothermic reaction at around 511°C is smaller than that of the as-received specimen, but it shows an endothermic reaction of 10 J/g at around 750-850°C. Specimens heat-treated at 400°C for 20 hours do not show endothermic reaction near 800°C.

As described above, β-Zr undergoes ω-phase and transforms into β-Nb phase. When heat treatment is performed at 400°C for 2-10 hours, it seems that ω-phase is precipitated. However, when heat treatment is carried out at 400°C for 20 hours or more, it is understood that the ω-phase phase does not precipitate. But β-Zr is transformed to β-Nb immediately since enough time is applied at 400°C for 20 hours or more, so an endothermic reaction does not occur near 800°C.

The DSC results are shown in table. 2. Figure 2 shows the activation energy obtained during the decomposition of β-Zr in the as received Zr-2.5%Nb alloy. Q=326 kJ/mol. This value is considered to be the activation energy required for the phase transformation of the β-Zr phase of the BCC structure to the ω-phase of the HCP structure.

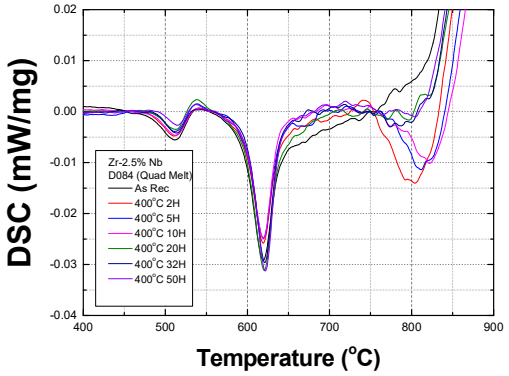

Fig. 1. DSC results of variously treated Zr-2.5%Nb pressure tube material (quadruple melt D084) aged at 400°C.

Table 2. Peak temperature variation with heating rate in water quenched mild steel.

Material condition	Heating Rate (α, ℃/min)	Peak Temperature (Tp, ℃)	1/T [K^{-1}]	α/Tp2
As received Zr-2.5%Nb (D084)	10	504.7	0.001286	1.65275E-05
	20	515.7	0.001268	3.21396E-05
	40	525.8	0.001252	6.26644E-05

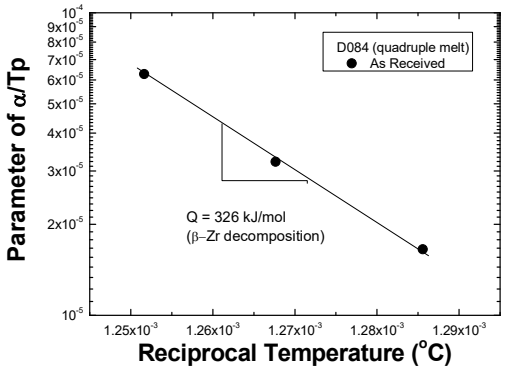

Fig. 2. Determination of activation energy for beta-Zr phase in Zr-2.5%Nb pressure tube material (quadruple melt, D084).

4. Conclusion

1. In the 400℃ heat treatment experiment for Zr-2.5%Nb pressure tube material, the time for β-Zr to decompose into ω-phase is completed in 10-20 hours.
2. The temperature at which β-Zr is decomposed into ω-phase is about 511℃, and the temperature at which ω-phase is transformed into β-Zr is about 750-850℃.
3. The activation energy of the transformation of β-Zr into ω-phase near at 511℃ is about 326 kJ/mol.

Acknowledgments

This work was supported by the NRF of Korea (NRF) grant funded by the Korea government (ministry of Science and ICT). (Project No. RS-2022-00155533)

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