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CREEP BEHAVIORS OF ZR-NB-CU ALLOYS OXIDIZED AT HIGH TEMPERATURE

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Abstract: *The loss of creep ductility and fracture of nuclear cladding tubes caused by brittle oxides may pose a threat to the reliability and cost-effectiveness of the nuclear reactor. Creep characteristics of oxidized Zr-Nb-Cu alloy nuclear claddings were studied. Creep rate of Zr-Nb-Cu nuclear claddings oxidized at 700°C for a day in air were found to be apparently faster than those annealed at 700°C for 3 hours with negligible oxidation in vacuum. The creep rates of Zr-Nb-Cu nuclear cladding tubes accelerated by oxidation. The increase of creep rate after oxidation is caused by the presence of increased volume fraction of brittle oxide and the ready initiation of cracks in oxide layer and propagation into Zr-Nb-Cu alloy matrix. The stress exponents of Zr-Nb-Cu alloy after annealing for 3 hours were observed to be in the range of 5.0~6.6 whereas stress exponents after oxidizing for 24 hours were in the range of 3.7~5.3. The decrease of the stress exponent in the oxidized alloy after annealing for 24 hours can be attributed to the presence of thick oxide film and the microstructural modification. The activation energy for creep in oxidized Zr-Nb-Cu alloy nuclear claddings annealed for 3 hours was in the range of between 259~336 KJ/mole whereas that of Zr-Nb-Cu alloy nuclear claddings oxidized for 24 hours was 296~368 KJ/mole.*

Keywords: *Zr-1.1Nb-0.05Cu, oxide layer, oxidation, creep rate, crack propagation*

INTRODUCTION

Nuclear cladding materials are required to exhibit excellent creep strength and corrosion properties, good mechanical reliability, and low neutron absorption properties. Zr base alloys have been developed and used as nuclear cladding tubes [Godlewski, 1994; Hong & Lee, 2005; Lee & Hong, 2011; Lee & Hong, 2012;]. In-reactor performance of Zr nuclear cladding alloys including creep and corrosion resistances, mechanical reliability, and irradiation growth are strongly dependent on its chemical composition and mechanical processing and thermal treatments during pilgering [Yan & Burseva & Billone, 2009; Steinbruck & Bottcher, 2011; Lee & Hong, 2012; Lee, Kim & Jeon, 2016; Muthucumaran, Pathmarajah, Mowjood, 2015].

The enhancement of nuclear safety and economy of nuclear power plants have been achieved by the development of advanced Zr base alloys including Zirlo™

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(produced by Westinghouse Electric Co.) and M5™ (produced by AREVA NP) alloys. Niobium and tin are essential alloying elements in the advanced nuclear cladding tubes such as Zirlo™ (Zr-Nb-Sn-Fe) and M5™ (Zr-Nb-O) nuclear tubes. Creep resistance and high temperature strength have been found to be improved by the addition of Sn while the corrosion resistance in Zr base nuclear cladding tubes is deteriorated by Sn [Lee & Hong, 2012; Kim & Hong, 2016;]. On the other hand, the corrosion resistance and irradiation-induced growth resistance are known to be enhanced by the addition of Nb. Recently, Zr-Nb-Cu alloys have been reported to have excellent oxidation resistance.

The loss of ductility and the fracture of nuclear cladding tubes caused by brittle oxides may pose a threat to the reliability and cost-effectiveness of the nuclear reactor. The probable release of radioactive materials to the primary and secondary coolant loops and even to the air could be a serious health hazard to human. The crack formation and spallation associated with the presence of oxide layer are believed to have an influence on the overall mechanical reliability of oxidized nuclear cladding tubes. To enhance the oxidation resistance of advanced Zr alloy cladding tubes, tin content was suggested to be lower than 1 wt. % in Zirlo™, lower than 1.36 wt. % in Zircaloy-4. Furthermore, no tin was added in M5™ to enhance the corrosion resistance at the expense of mechanical properties. The creep resistance of Zr–Nb alloy nuclear claddings without tin addition was reported to be lower than that of Zr-Nb-Sn-Fe alloy nuclear claddings with 1 wt. % Sn. In order to optimize the creep resistance and oxidation resistance, Zr-Nb alloys with an optimum Sn content, lower than 1 wt. % have been developed. In this study, the influence of oxidation on the creep performance and reliability of Zr-Nb-Cu alloy cladding tubes were examined.

EXPERIMENTAL

Zr-1.1Nb-0.05Cu alloy nuclear cladding tubes were used in this study for creep test. Zr-1.1Nb-0.05Cu alloy nuclear cladding tubes underwent cold-pilgering with double intermediate heat treatments and post-cold-pilgering stress-relief at 460 °C for 7 hours [Lee & Hong, 2011;]. The ring-type creep specimens were transversely sectioned and machined from the Zr-Nb-Cu nuclear cladding tubes, for high-temperature heat treatments for oxidation and creep testing. The outer diameter and the length of the ring-type creep specimens were ~9.6mm and 4mm respectively, and both ends of the ring-type creep specimens were polished carefully for oxidation heat treatment and creep testing. All ring-type creep specimens were chemically cleaned in a solution of 45% HNO3, 5%HF and 50% H2O. The oxidations of ring-type creep specimens were heated at 700°C in air for 3 hours and 24hours. Oxidized samples were creep-tested at 450°C~500°C, 80MPa~120MPa, to investigate the influence of oxidation on the on creep performance Zr-Nb-Cu alloy nuclear cladding tubes. Some specimens were annealed at 700°C for 3 hour in argon atmosphere to anneal the matrix without oxide formation on the surface. The schematics of the ring-type tensile and creep tests are displayed in Fig. 1.

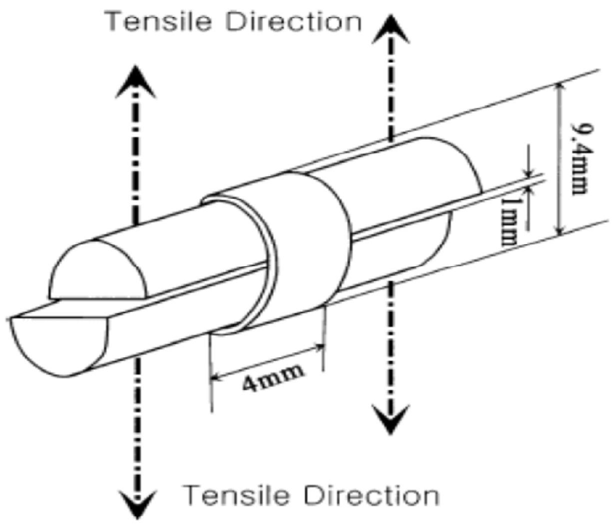

Figure 1: Schematics of ring specimen and grips for creep testing

RESULTS AND DISCUSSION

In Fig. 2(a) and (b), the SEM micrographs of the cross sectioned surface of the sample annealed for 3hours (a) and oxidized in air for 24 hours (b). It is apparent that the oxide layers thickened with increase of heat temperature and time for oxidation. Oxide film thickness of Zr-Nb-Cu cladding tubes oxidized at 700°C for 3hours and 24 hours is 0.011mm and 0.151mm, respectively. The ring-type creep specimens oxidized at 700°C for 3hrs and 24hrs (Fig. 2(a) and 2(b)) shows the presence of cracks in both outer and inner sides of the nuclear cladding tube. However, the oxide film thickness is negligible after annealing for 3hours compared to those oxidized for 24 hours. The formation of cracks is probably caused by the greater volume expansion due to the oxidation and phase transformation associated with the monoclinic ZrO2. The presence of initial cracks is likely to accelerate the oxidation rate by providing easy access of oxygen and promoting diffusion rate of oxygen (Fig. 2(b)), which in turn increases the volume expansion rate and crack formation. The population and size of cracks were observed to be increased with increase of volume expansion and subsequent oxidation rate. Metastable tetragonal ZrO_2 with a protective film was reported to be formed in the initial stage of oxidation. As oxidation in progress with increases of time and temperature, the protective tetragonal ZrO_2 film is partly replaced by monoclinic ZrO_2, with a non-protective nature. The oxidation kinetics in Zr and Zr base alloys are known to

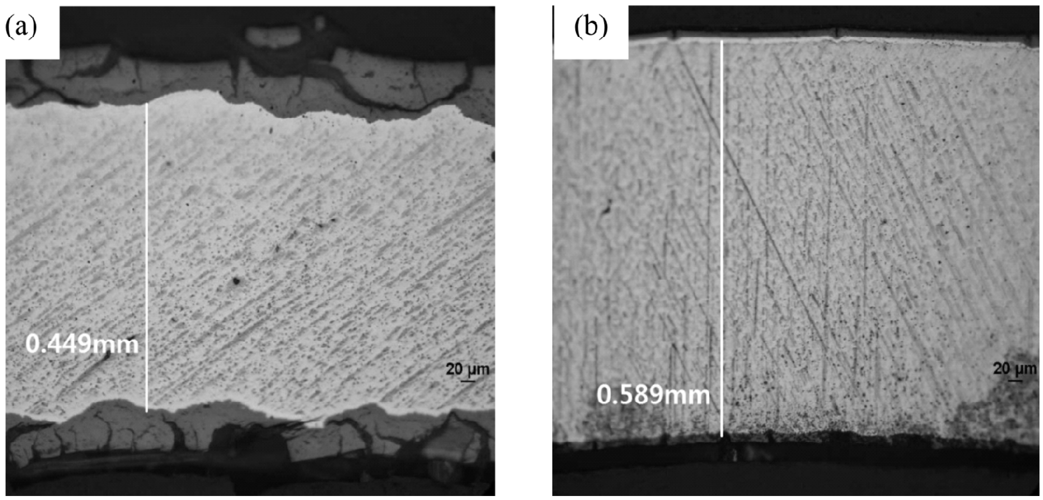

Figure 2: SEM micrographs of the cross sectioned surface of Zr-1.1Nb-0.05Cu annealed for 3 hours (a) and for 24 hours (b)

accelerate in the presence of monoclinic ZrO_2 [Godlewski, 1994; Yan & Burtseva & Billone, 2009; Steinbruck & Bottcher, 2011;].

Figure 3 shows the creep behaviors of Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for 24 hours and 3hours. Creep rate of Zr-Nb-Cu alloy nuclear cladding tubes also increased with creep temperature and stress. Creep rate of Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for 24 hours were faster than those of Zr-Nb-Cu alloy nuclear cladding tubes annealed at 700°C for 3 hours with negligible oxide film. Zr-Nb-Cu alloy nuclear cladding tubes annealed at 700°C for 3 hours exhibited less pronounced primary creep and smaller total creep fracture strain compared to the Zr-Nb-Cu alloy nuclear cladding tubes cladding tubes oxidized at 700°C for 24 hours. It should be emphasized that the steady-state creep rates are much slower in the Zr-Nb-Cu alloy nuclear cladding tubes annealed at 700°C for 3 hours than in Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for 24 hours at all loading conditions and testing temperatures.

In Fig. 4(a) and 4(b), the steady-state creep rates of oxidized at 700°C for 3 hours (a) and 24 hours (b) Zr-Nb-Cu alloy nuclear cladding tubes are plotted against the stress. In Fig. 4(a), stress exponents of Zr-Nb-Cu alloy nuclear cladding tubes after oxidizing for 3 hours were observed to be in the range of 5.0~6.6 whereas stress exponents after oxidizing for 24 hours were in the range of 3.7~5.3. The steady-state creep rates of the oxidized Zr-Nb-Cu alloy nuclear cladding tubes alloy claddings for 24 hours (b) are lower than those of the annealed claddings for 3 hours (a). The stress exponent increased with increase of temperatures from 3.67 to 5.41 as the temperature increased from 450°C to 500°C in oxidized alloys for 24

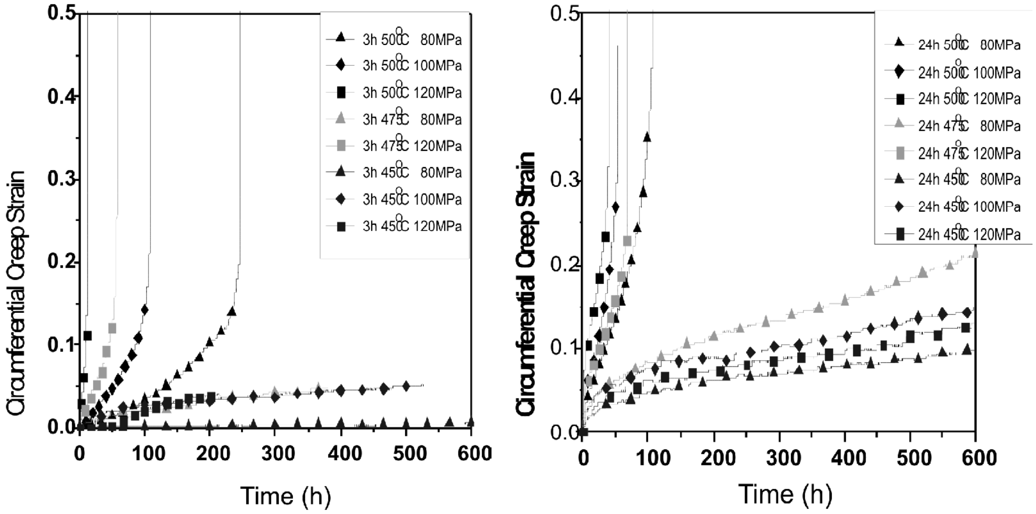

Figure 3: Creep curves of Zr-1.1Nb-0.05Cu alloy cladding tubes oxidized at 700°C for 3 hours (a) and 24 hours (b)

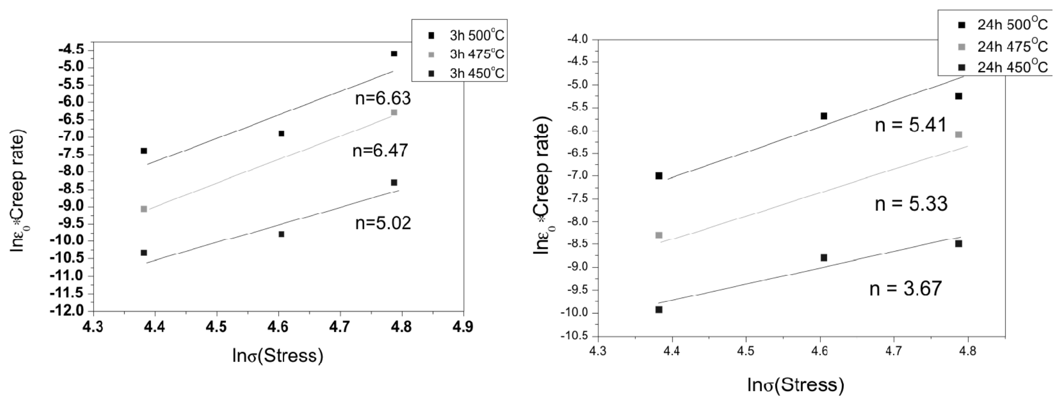

Figure 4: Double-log plots of steady state creep rate vs. stress on annealed at 700°C for 3 hours (a) and oxidized at 700°C for 24 hours (b) Zr-1.1Nb-0.05Cu alloys at various temperatures

hours. The reason for the lower stress exponent for the oxidized alloy is not clear, but can be attributed to the presence of thick oxide film and the microstructural modification during annealing [Steinbruck & Bottcher, 2011; Lee & Hong, 2012; Kim & Hong, 2016;].

In Fig. 5(a) and 5(b), the steady state creep of Zr-Nb-Cu alloy nuclear cladding tubes oxidized for 3 hours (a) and 24 hours (b) are plotted against the reciprocal of temperature. The activation energy for creep in oxidized Zr-Nb-Cu alloy nuclear cladding tubes for 3 hours in Fig. 5(a) was observed to be in the range of between

259~336 KJ/mole whereas that of Zr-1.1Nb-0.5Cu alloy tube oxidized for 24 hours was found to be 296~368 KJ/mole (Fig. 5(b)). Activation energy of Zr alloy was found to be increased with stress. The activation energy of creep in Zr-1.1Nb-0.05Cu alloy was found to increase with increase of oxidation time (oxide thickness). The activation energy for creep of Zr-Nb-Cu alloy nuclear cladding tubes for 3 hours in this study was observed to be similar to the activation energy of creep for stress-relieved Zr-1Nb-1Sn-0.1Fe (240~260 kJ/mol and that (300 kJ/mol) of Zr at high temperatures(660°C) [Lee & Kim & Hong, 2009; Ko & Hong & Kim, 2010; Jeong & Kim & Hong, 2016; Kim & Hong, 2016;].

In Fig. 6, the polished cross-sectional surface of crept Zr-1.1Nb-0.05Cu oxidized for 24 hours is shown. Long fatal cracks were observed to be formed at the oxide layer. One interesting observation is that cracks initiated in the oxide layer continue to propagate into the matrix because of the stress concentration adjacent to the crack tip. The crack propagation into the matrix can also be influenced by the local dislocation structure in Zr alloys [Hong, 1986;]. The presence of brittle cracks in the oxide and the propagation of cracks into Zr-Nb-Cu alloy matrix at the tensile strain of Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for 24 hrs, resulting in the acceleration of creep rate and reduction of creep life in Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for 24 hrs.

CONCLUSIONS

The creep behaviors and propagation of cracks for Zr-Nb-Cu alloy nuclear cladding tubes were studied and following conclusions were obtained.

1. Creep rate of Zr-Nb-Cu alloy nuclear cladding tubes oxidized at 700°C for a day were faster than those of Zr-Nb-Cu alloy nuclear cladding tubes annealed at 700°C for 3 hours with negligible oxidation. The propagation

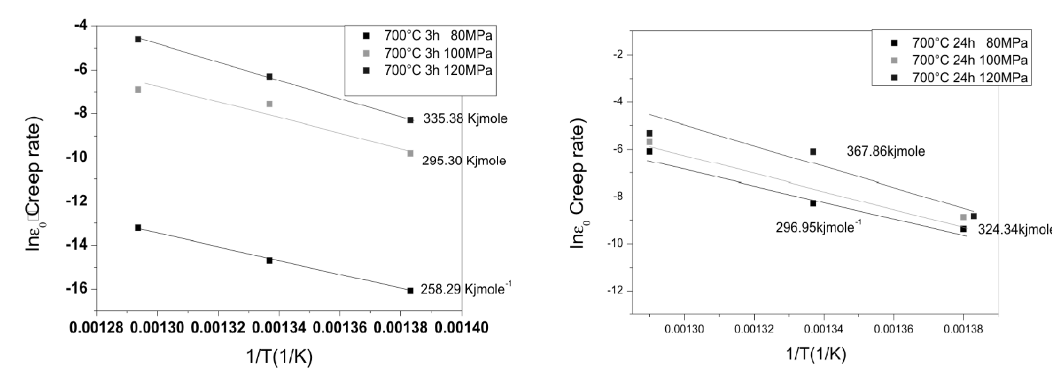

Figure 5: Variation of creep rate plotted against the reciprocal of temperature. Creep activation energy for oxidized Zr-1.1Nb-0.05Cu alloy at 700°C for 3 hours (a) and 24 hours (b) were obtained for various applied stresses

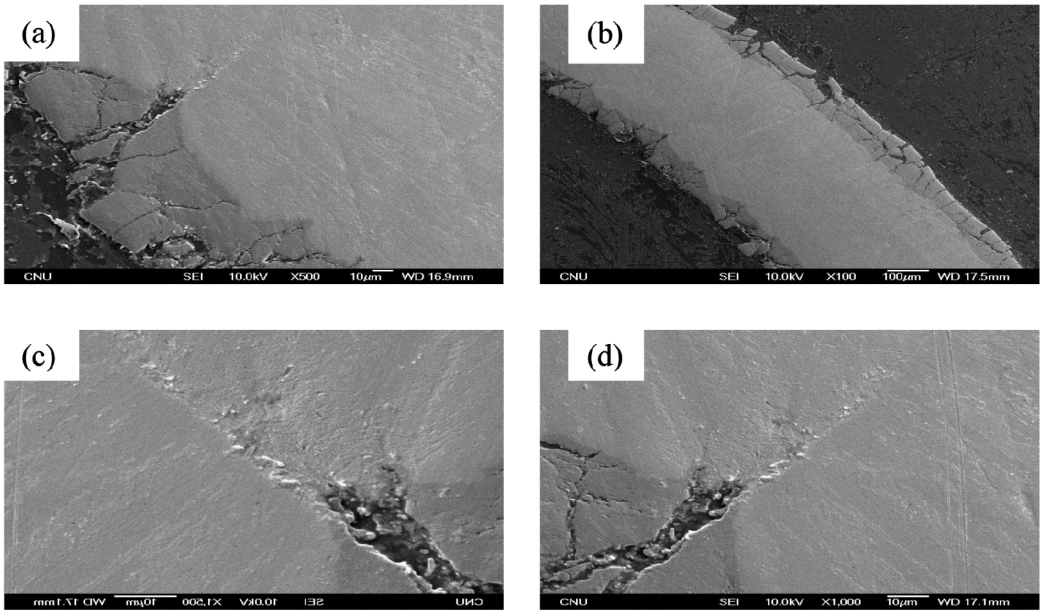

Figure 6: Microstructure of the Zr-1.1Nb-0.05Cu alloy with oxidation for 24 hours; (a) x100, (b) x500, (C) x1000, (d) x1500

of cracks from oxide to Zr-1.1Nb-0.05Cu matrix contributed the acceleration of creep rates.

2. The stress exponents of Zr-1.1Nb-0.05Cu after oxidizing for 3 hours were observed to be in the range of 5.0~6.6 whereas stress exponents after oxidizing for 24 hours were in the range of 3.7~5.3. The reason for the lower stress exponent for the oxidized alloy for 24 hours can be attributed to the presence of thick oxide film and the microstructural modification during annealing at high temperature.
3. The activation energy for creep in oxidized Zr-1.1Nb-0.05Cu alloy claddings for 3 hours was observed to be in the range of between 259~336 KJ/mole whereas that of Zr-1.1Nb-0.5Cu alloy tube oxidized for 24 hours was found to be 296~368 KJ/mole. The activation energy of creep in Zr-1.1Nb-0.05Cu alloy was found to increase with increase of oxidation time (oxide thickness). The activation energy for creep was observed to be similar to those for Zr-1Nb-1Sn-0.1Fe (240~260 kJ/mol) and of Zr (300 kJ/mol).
4. The acceleration of creep rate and reduction of creep life after oxidation at 700^{o}C for 24 hours is caused by the volume expansion of brittle oxide layers and the raedy propagation of cracks from oxide into Zr-Nb-Cu alloy matrix.

Acknowledgments

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