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Effect of alloying elements (Cu, Fe, and Nb) on the creep properties of Zr alloys

Hyun-Gil Kim *, Yang-Hoon Kim, Byoung-Kwon Choi, Yong-Hwan Jeong

Advanced Core Materials Lab, Korea Atomic Energy Research Institute, 150, Doekjin-dong, Yuseong-gu,
Daejeon 305-353, Republic of Korea

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Abstract

The thermal creep behaviors of Zr-based alloys containing Cu, Fe and Nb were investigated under constant load stress at temperatures of 280 and 330 °C, and a stress range of 100–140 MPa. To evaluate an alloying effect on a creep, Zr-based alloys were selected as the binary and ternary systems of Zr–0.3Cu, Zr–0.3Fe, Zr–0.5Nb–0.3Cu and Zr–0.5Nb–0.3Fe. The final annealing of these alloys was performed at 510 °C for 8 h to obtain a recrystallization structure for all the tested alloys. A microstructure characterization test was carried out for the samples before and after the creep test by using TEM, and the results were used to understand the creep mechanism. Creep tests were performed for up to 70 h, which showed a steady-state secondary creep rate in all the alloys. The value of the stress exponent was about 5.5 in all the alloys. The dislocation density was increased by increasing the applied stress, regardless of the alloy system. From the results of this study, it was revealed that the Nb as an alloying element showed the strongest effect on the creep resistance among the added alloying elements, and Fe was more effective than Cu from the viewpoint of creep resistance.

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1. Introduction

Zirconium alloys have been widely used for the fuel cladding and other core components in nuclear reactors and among them Zircaloy-4 has been mainly used as a fuel cladding material for pressurized water reactors (PWR) for a long time. However, since the PWR operating conditions such as higher burn-up, increased operating temperature and high pH operation have been implemented to improve the reactor efficiency, advanced Zr-based alloys are necessary. Because the development of the advanced cladding materials was focused on corrosion resistance, the alloy composition of the most newly developed alloys was changed to decrease the tin content and to increase the niobium content [1,2]. The results of this trend are a decrease of the creep strength of the zirconium alloys. Most of the alloying elements were added to the zirconium alloys to increase the corrosion resistance and the creep strength. It is well known that the creep strength of zirconium alloys is affected by alloying elements such as tin [3,4], niobium [5], oxygen [4], carbon [6] and sulfur [2,7,8] in solid

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[*] Corresponding author. Tel.: +82 42 868 2522; fax: +82 42 862 0432.
E-mail address: hgkim@kaeri.re.kr (H.-G. Kim).

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solution. For a study of the alloying element effects on zirconium thermal creep, the additions of tin and niobium are especially effective for enhancing the creep strength at concentrations up to their solubility limits [9]. Although, alloying elements such as copper were incorporated in the HANA-5 alloy (Zr–0.4Nb–0.8Sn–0.30Fe–0.15Cr–0.1Cu in wt%) [10] and iron was incorporated in most of the types of zirconium fuel cladding, a study of the copper and/or iron effects on the creep properties has not performed for the zirconium binary alloys.

The present work was undertaken to provide the creep behavior of Zr–Cu and Zr–Fe binary alloys and also Zr–Nb–Cu and Zr–Nb–Fe ternary alloys at the reactor operation temperature range of 280–330 °C. And a microstructural observation by using TEM was applied to the before and after creep test samples to evaluate the creep mechanism.

2. Experimental procedure

The chemical compositions of the Zr-based alloys used in this study are the binary Zr–0.3Cu and Zr–0.3Fe and also the ternary Zr–0.5Nb–0.3Fe and Zr–0.5Nb–0.3Fe systems. Cu, Fe and Nb of 99.9% and Zr containing 700 ppm O and Fe, which was incorporated in commercial grade sponge-type Zr were used for manufacturing the creep test sheet material. Button ingots, of 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 1020 °C for 30 min in a vacuum furnace, hot-rolled after a preheating at 590 °C for 10 min, and cold-rolled three times to obtain a final thickness of 1 mm. Between the rolling steps, the cold-rolled sheets were intermediately annealed at 580 °C in a vacuum furnace for 2 h and the final cold-rolled sheets were also annealed at 510 °C in a vacuum furnace for 8 h to obtain a fully recrystallized structure.

Creep specimens were machined from the sheet along the RD direction with a gauge length and width of 25 mm and 5 mm, respectively. Creep tests were carried out under a constant load stress at temperatures of 280 and 330 °C and a stress range from 100–140 MPa. The axial creep strains were monitored by using an LVDT (Liner Variable Differential Transformer) extensometer. Creep samples were tested at given temperature for 70 h.

TEM observation was performed on the before and after creep test samples. TEM specimens were prepared by a twin-jet polisher with a solution of 10 vol.% $HClO_3$ and 90 vol.% C_2H_5OH after a mechanical thinning to 70 μm and then examined for the dislocation microstructure.

3. Results and discussion

3.1. Effect of an alloying element on the creep behavior

Generally, the creep behavior is affected by certain parameters such as the chemical composition, microstructural characteristics of the grain size, dislocation density and the precipitates. Due to the very low solubility of copper [11] and iron [12] in zirconium at a low temperature, it was impossible to study the solute range effect of both elements in this study. Therefore, the creep behavior in this work would be affected by the solid solution as well as the precipitates which would be determined by the type of alloying elements and the amount of alloying elements.

Figs. 1 and 2 show the creep curves of the binary and ternary Zr-based alloys with different applied stresses. In all the cases, normal curves containing a primary region and a steady state region were obtained during a 70 h test. Fig. 1 shows the creep strain of the Zr–0.3Cu (a) and Zr–0.3Fe (b) alloys as a function of the creep strain and the test time. Creep strain of the binary alloys was increased by increasing the applied stress at the test temperature of 280 °C and the creep strain of the Zr–0.3Cu alloy was higher than that of the Zr–0.3Fe alloy. Although the amount of copper and iron was the same in wt%, the creep strains of both alloys were quite different, with a dependency on the type of alloying elements. At each applied stress of 100, 120 and 140 MPa, the creep strains of the Zr–0.3Cu alloy were about three times higher than those of the Zr–0.3Fe alloy. If the creep mechanism of the binary alloy containing copper or iron is controlled by solute diffusion, it is assumed that the creep rate is mainly affected by the diffusion rate of both the alloying elements in the zirconium. According to Sweeney's study [13] on the diffusivity of various alloying elements with zirconium, it was reported that the diffusivity of copper was higher than that of iron. Therefore, it is reasonable to suppose that the difference in the creep strength between the Zr–0.3Cu and Zr–0.3Fe alloys would be caused by their diffusivity in the zirconium.

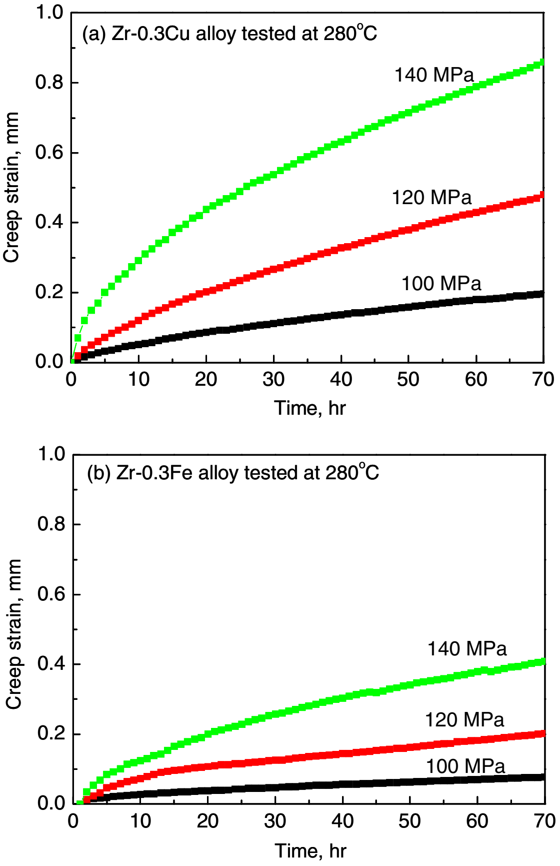

Fig. 1. Thermal creep properties of the binary zirconium alloys with a different applied stress, tested at 280 °C.

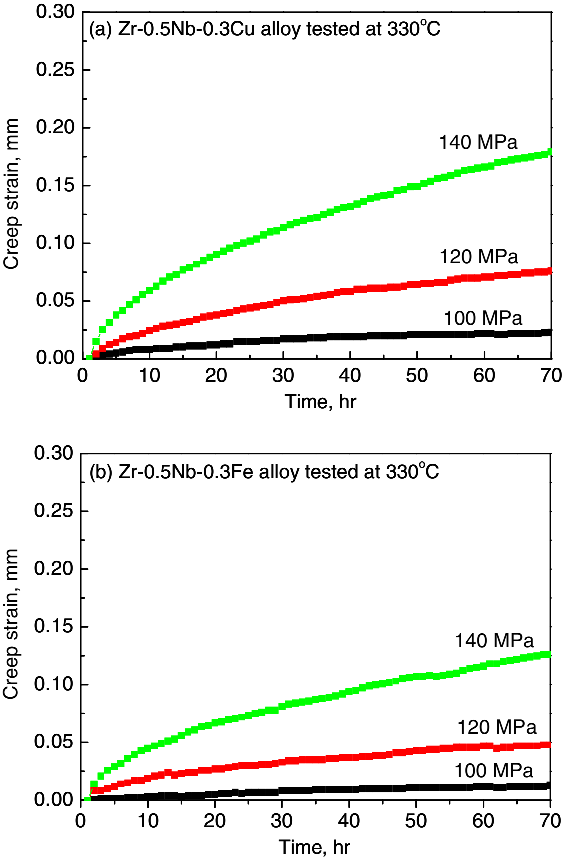

Fig. 2. Thermal creep properties of the ternary zirconium alloys with a different applied stress, tested at 330 °C.

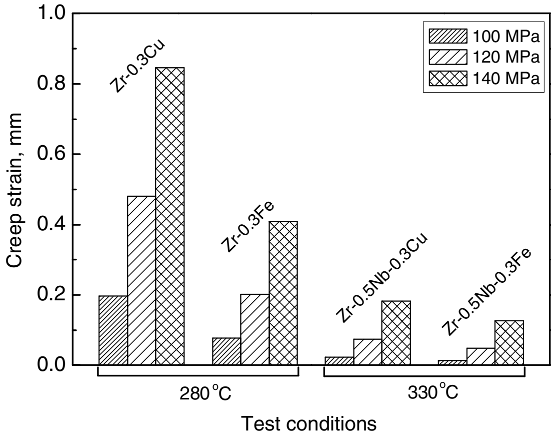

Fig. 3. Thermal creep strain after the creep test of the zirconium alloys with an applied stress range from 100 to 140 MPa and different test temperatures of 280 and 330 °C after 70 h.

Fig. 2 shows the creep strain curves of the Zr–0.5Nb–0.3Cu (a) and Zr–0.5Nb–0.3Fe (b) alloys. The creep strain behavior of the ternary Zr-based alloys was similar to that of the binary Zr-based alloys and the creep rate of the copper containing ternary alloy was higher than that of the iron containing ternary alloy. However, the total creep strain of the ternary alloys at the same tested time was much lower than that of the binary alloys, even though the test temperature of the ternary alloys was higher than that of the binary alloys. This result was due to the Nb addition to the zirconium alloys. From the results of the alloying element effects on the creep strength [9], niobium is especially effective for enhancing the creep strength at concentrations up to their solubility limits.

Fig. 3 shows the creep strain of the tested binary and ternary alloys at the same test time of 70 h. Creep strain changed with the applied stress and the alloying elements. From the viewpoint of the applied stress, the creep strain of all the tested alloys was increased by increasing the applied stress, and the applied stress effect was significant in the binary alloys. A constant increase of creep strain by the applied stress from 100 to 140 MPa was observed in the tested alloy system. The creep strain behaviors with various alloying elements of copper, iron and niobium are clearly observed in Fig. 3. The creep strain of the copper containing binary alloy was two times higher than that of the iron containing binary alloy, but the creep strain of the ternary alloy which contained niobium plus copper was somewhat higher than that of the ternary alloy which contained niobium plus iron. This result shows that the creep strength of the zirconium alloys was changed, with a dependency on the type of alloying elements.

It could be thought that the creep strength due to the addition of alloying elements was controlled by two factors; the diffusivity of each alloying element and the solubility limit of the alloying element in the alpha zirconium. Although, the diffusivity of the alloying element in the alpha zirconium was not studied in this work, it is known that niobium has the lowest diffusion rate among the added alloying elements and that iron has a lower diffusion rate than copper in zirconium from previous studies [13,14]. Also, from a study for the solubility limit of an alloying element such as copper [11], iron [12] and niobium [15], it is known that the niobium solubility limit is much higher than the copper or iron solubility limits in alpha zirconium. Therefore, it could be assumed that both factors of a diffusivity and a soluble amount of the alloying elements would control the creep strength of the zirconium-based alloys.

3.2. Stress exponent and microstructural characteristics

The stress dependency of the creep rate is obtained from the log-liner plots as a function of the creep rates and stresses. The stress dependency of a thermal creep is described by the following equation:

$$\dot{\varepsilon}_s = B\sigma^n, \qquad (1)$$

where $\dot{\varepsilon}$ is the steady-state or minimum creep rate, B is a material constant, σ is the applied stress, n is a stress exponent. Fig. 4 shows the log-liner plot with the creep strain rate and the applied stress of the binary and ternary zirconium-based alloys. The relation between the strain rate and the applied stress follows a log-linear rate law. The stress exponent and the total creep strain of the binary and ternary alloys are summarized in Table 1. The stress exponent value of the binary and ternary alloys was about 5.5 in the stress range of 100 to 140 MPa. This range of the stress exponent n corresponds to region III which was clearly indicated by dislocation glide and climb as the rate-controlling mechanism [16]. And the zirconium-based alloys in this work corresponded to the Class A alloys (solid solution alloys) which were governed by the rate of the dislocation glide controlled by the rate of the diffusion of the solute atoms and this creep mechanism is usually referred to as a viscous glide [17]. On the bases of these theories, it could be assumed that the solute atoms such as copper, iron and niobium could be locked on to the dislocation glide and climb. So, the niobium as an alloying element showed the strongest effect for the creep strength among the added alloying elements, and iron was more effective than copper from the view point of the dislocation locking effects of the solute atoms.

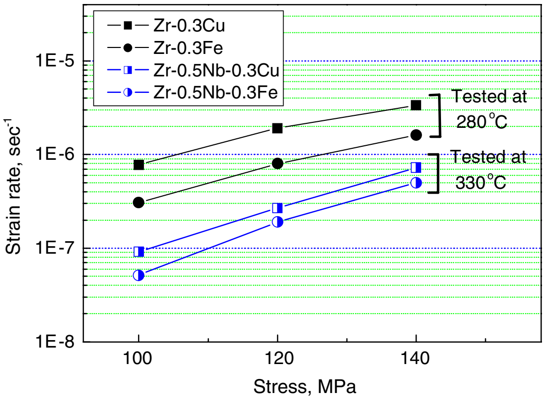

Fig. 4. Log-linear plot of the creep strain vs. applied stress of the zirconium-based alloys with a different applied stress range from 100 to 140 MPa and a different test temperature at 280 and 330 °C.

Table 1
Stress exponent and the total creep strain of the binary and ternary zirconium alloys

Alloys	Factors			
	Stress exponent, n	Total strain, %		
		100 MPa	120 MPa	140 MPa
Zr–0.3Cu	5.0	0.784	1.924	3.384
Zr–0.3Fe	5.4	0.308	0.808	1.636
Zr–0.5Nb–0.3Cu	5.7	0.092	0.3	0.732
Zr–0.5Nb–0.3Fe	5.8	0.052	0.192	0.504

Fig. 5 shows the bright field TEM micrographs of the sample before and after the creep test of the binary and ternary zirconium alloys. The recrystallized grains were formed on all the zirconium alloys since the final annealing was performed at 510 °C for 8 h. From the TEM/EDS analysis for the precipitates, the precipitate was composed of the added alloying elements in each alloy system as shown in Table 2. The iron detection in the precipitates of the Zr–Cu and Zr–Nb–Cu alloys was caused by an iron impurity in the sponge-type Zr. The mean size of the precipitate was somewhat changed by the alloy system. The precipitate size of the ternary alloy was smaller than that of the binary alloy whereas the number density of the precipitate of the ternary alloy was increased than that of the binary alloy. It is related to the Nb because the diffusivity of Nb is lower than the other alloys. Also, dislocations were not observed in the binary and ternary alloys before the creep test. However, after the creep test, some dislocations were formed in the grain interiors and the dislocation density was increased with an increase of the creep strain in all the tested specimens. It is well known that a deformation of the

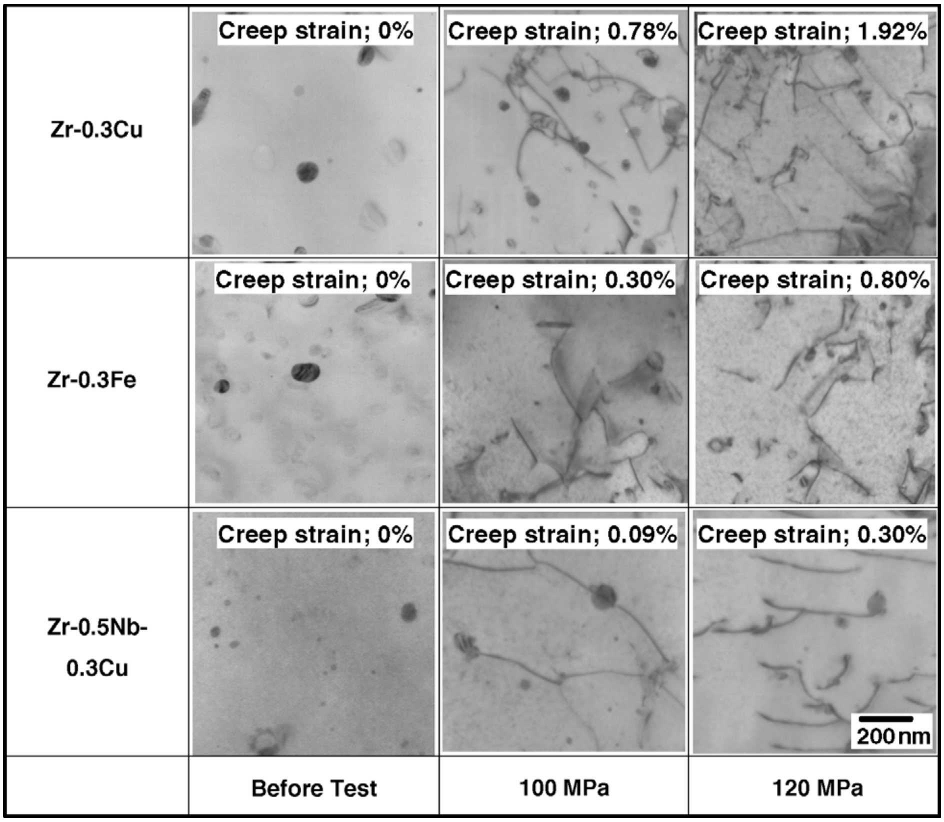

Fig. 5. TEM micrographs of the before and after creep test samples of the binary zirconium alloys tested at 280 °C and the ternary zirconium alloy tested at 330 °C.

Table 2
Precipitate mean size and precipitate composition of the binary and ternary zirconium alloys

Alloys	Factors				
	Precipitate mean diameter, nm	Precipitate composition, at.%			
		Cu	Fe	Nb	Zr
Zr–0.3Cu	76.4	30 ± 5	1.5 ± 0.5	–	Bal.
Zr–0.3Fe	86.8	–	20 ± 5	–	Bal.
Zr–0.5Nb–0.3Cu	59.4	30 ± 5	1.5 ± 0.5	25 ± 5	Bal.
Zr–0.5Nb–0.3Fe	51.8	–	17 ± 5	25 ± 5	Bal.

zirconium and zirconium alloys is caused by a dislocation slip in the $\langle a \rangle$ or $\langle a+c \rangle$ direction under high temperature and low stress conditions. And the dislocation Burgers vector and the density of the crept Zircaloy-4 by using a transmission electron microscopy were confirmed by Ecob and Donaldson [18]. Since the transmitted beam direction was nearly the [0001] zone axis during the transmission electron microscopy application in this study, all the visible dislocations could be confirmed as $\langle a \rangle$ type or $\langle a+c \rangle$ type dislocations. The observed dislocations were uniformly distributed in the grain interiors regardless of the alloying compositions of copper, iron and niobium and also a dislocation sub-cell structure was not observed in the electron micrographs.

From the microstructural characteristics in the Class A alloys, a steady-state creep is governed by the rate of a diffusion of the solute atoms and this creep mechanism is usually referred to as a viscous glide [16]. So, from the results of the stress exponent values and the dislocation characteristics in this study, it is thought that the creep behavior of the binary and ternary zirconium alloys containing copper, iron and niobium are controlled by a dislocation glide creep. Because a dislocation glide creep is related to a diffusion of the atoms, the diffusivity of an alloying element in zirconium is one of the main factors to determine the creep strength at temperatures of 280 °C and 330 °C. Niobium as an alloying element showed the highest effect on the creep resistance and iron was more effective than copper in the zirconium-based alloy which is consistent with an alloying element diffusivity and solubility.

4. Conclusions

The creep characteristics of binary and ternary zirconium-based alloys containing copper, iron and niobium were evaluated at the stress range of 100–140 MPa and at a temperature of 280 and 330 °C. From the creep strength results of the zirconium alloys, niobium showed the strongest effect on the creep resistance among the alloying elements and iron was more effective than copper as an alloying element from the viewpoint of a creep resistance of the zirconium alloy. The creep mechanism of the binary and ternary zirconium alloys containing copper, iron and niobium was controlled by a dislocation glide creep from the results of the stress exponent values and the dislocation characteristics.

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