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

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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.

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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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.