Journal of the Korean Nuclear Society
Volume 32, Number 4, pp.372~378, August 2000

Effect of Alloying Elements on the Thermal Creep of Zirconium Alloys

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(Received February 28, 2000)

Abstract

The effect of alloying elements on the creep resistance of Zr alloys was investigated using thermal creep tests that were performed as a part of advanced fuel cladding development. The creep tests were conducted at 400℃ and 150 MPa for 240 hr. A statistical model was derived from the relationship between the steady-state creep rate and the content of individual alloying elements. The creep strengthening effect decreased in the following sequence : Nb, Sn, Mn, Cr, Mo, Fe and Cu. The high creep resistance of Sn and the opposite effect of Fe on zirconium alloys seem to be associated with their lowering and enhancing, respectively, the self-diffusivity of the zirconium matrix.

Key Words : thermal creep, zirconium alloy, alloying effect, advanced fuel cladding, power-law creep, multiple linear regression

1. Introduction

The environmental conditions of nuclear fuel cladding in light water reactors are becoming more severe, because of high burnup and increased coolant temperature, driven primarily by the desire to operate reactors more economically. To fulfill these demands and improve the fuel pin integrity, the new zirconium alloys have been developed worldwide as substitutes for Zircaloy-4 or Zircaloy-2. The prerequisites for these new zirconium alloys are improvements in dimensional stability and corrosion resistance compared to existent Zircaloys. The in-reactor dimensional changes of cladding materials are mainly due to thermal creep, irradiation creep and irradiation growth. The main contributors influencing these properties are the alloying elements. However few studies have been performed on the effect of alloying elements on thermal creep resistance of zirconium alloys, while the effect on corrosion resistance has been extensively studied [1].

Also, in Korea, several hundred new alloys have been designed and tested mechanically and chemically so that a considerable database has been developed. The results of thermal creep

Table 1. Database of Alloys for Analysis and Maximum Solubility of Alloying Elements in Alpha Zirconium

Alloying Elements	Sn	Nb	Fe	Cr	Mo	Cu	Mn	*Others
Alloying frequency	104	101	92	38	19	35	18	12
Alloying range, wt%	≤1.5	≤1.0	≤1.0	≤0.3	≤0.3	≤1.0	≤0.2	≤0.2
Solubility, wt%	1.6	0.6	0.02	0.16	0.18	0.2	0.1	-
Ref. for solubility	[2]	[3]	[4]	[4]	[5]	[5]	[5]	-

*Others = V+Sb+Ta+O

experiments were taken from the database and the alloying element effect was investigated by using a statistical approach, the multiple linear regression. The effectiveness of individual alloying elements on creep strength and the origin of the difference are also discussed.

2. Experiments and Analysis Method

Generally steady-state creep is emphasized over primary or tertiary creep due to the relatively large fraction of creep life associated with this regime. In addition, the importance of steady-state creep is apparent from the Monkman-Grant relationship, in which time to rupture is inversely proportional to steady-state creep rate. This indicates that the fracture process can be predicted from its secondary creep rate response. Thus the steady-state creep rate is one of the most important parameters in determining the creep strength as well as fracture resistance of a material.

All creep tests were performed using sheet specimens with a 25 mm gauge length and 0.9 mm thickness at constant load. Load was applied parallel to the rolling direction. The tests were carried out at 400℃ and 150 MPa for 240 hours. The steady-state creep rate was determined using the first order least square method.

The manufacturing process, especially the final state of cold working and heat treatment, may influence the creep resistance of an alloy even if it has same chemical composition. To avoid these effects, only data for specimens that had a similar fabrication process was evaluated. The final state of manufacturing process of the alloys investigated in this work was cold-worked in the range of 50~60% and stress relieved at the annealing temperature of 470 ~ 500℃.

The total number of alloys used in this analysis was 115, and Table 1 shows the range of alloying elements with their terminal solubility [2~5] in alpha zirconium.

The multiple linear regression [6] method was applied to the analysis of the effect of alloying elements. This method assumes that a single dependent variable is affected by several independent variables, and that no dependency is exist between independent variables. By applying this method to creep analysis, the steady-state creep rate was expressed as follows,

$$\dot{\varepsilon}_s = a \cdot XSn + b \cdot XNb + c \cdot XFe + \ldots \quad (1)$$

where a, b, c represent the proportional constants and XSn, XNb, XFe are weight fraction of each alloying elements. In this article, the commercial software Microcal Origin 5.0 [7] was used to calculate the proportional constants. When the proportional constants are determined in multiple regression form, the creep rate can be predicted with a given alloying system. Furthermore, the alloying effect can be evaluated by comparing the

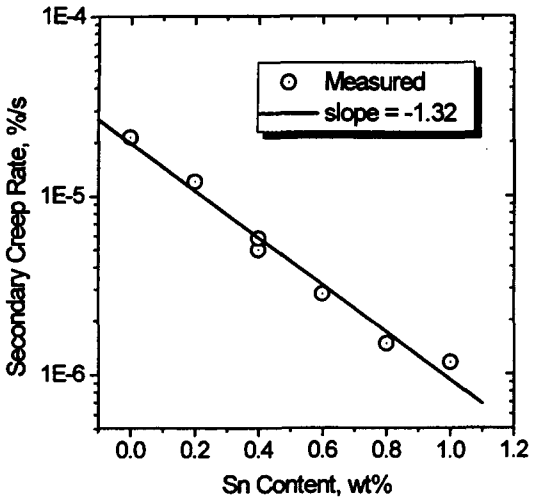

Fig. 1. Effect of Sn Content on the Steady-state Creep Rate of Zr-0.8Nb-xSn Alloys

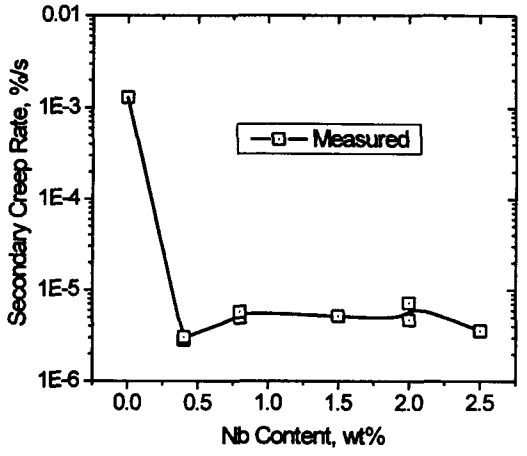

Fig. 2. Effect of Nb Content on the Steady-state Creep Rate of Zr-0.4Sn-xNb Alloys

constants.

The reliability of the model prediction can be evaluated by the R^2 (correlation coefficient) value that lies between 0 and 1, which represents random and perfect prediction of the model, respectively.

3. Results and Discussion

3.1. Model Development

In addition to the alloying elements and fabrication process, there are many other factors that may affect the creep characteristics of an alloy in a given microstructural state, such as grain size, dislocations, precipitations, subgrain intercept, etc. In this work, however, the microstructural state was neglected since it was assumed that the state is controlled primarily by the alloying elements only. One of the factors that affect the creep properties of Zr alloys is their crystallographic texture developed during fabrication process. However this effect was not considered in this analysis since all the samples were fabricated similarly and tested in same direction, rolling direction, as described in previous section.

As shown in Table 1, the main alloying elements were Sn, Nb and Fe. Considering the solubility limits of Sn and Fe, it is expected that all of Sn could be soluble in alpha zirconium, whereas almost all of Fe was precipitated as second phase particles due to its extremely low solubility. In case of high Nb alloys, such as 1wt% Nb alloy, a considerable amount of the element would be precipitated, and the rest would remain in solid solution. The impact of alloying element on creep resistance differs if it is solid solution versus precipitated.

Prior to proceeding with the statistical analysis, Figures 1 and 2 show the creep rate dependency on alloying content for Sn and Nb, respectively. The addition of Sn decreased the logarithmic creep rate in a continuous manner, and matched with the linear fitting quite well. The addition of Nb near the solubility limit, presumably 0.5 wt%, drastically dropped the creep rate. However, no discernable effect on creep resistance was evident when Nb was increased above the solubility limit. The discontinuity of creep rate with Nb addition

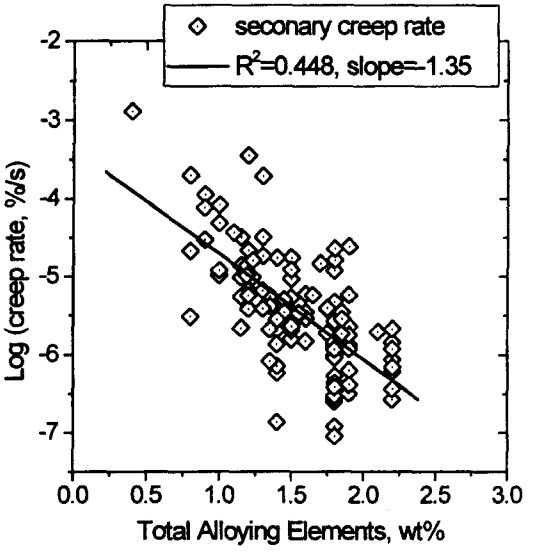

Fig. 3. Creep Rate Variation of Zirconium Alloys as a Function of the Total Alloying Content

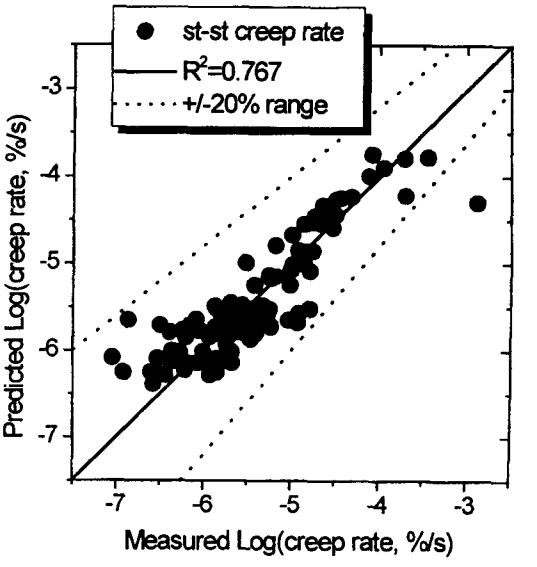

Fig. 4. Comparison of the Measured Steady-state Creep Rates with Those Predicted by the Statistical Model

seems to be associated with solubility limit of Nb. Based on these experimental results, the statistical model was established with the following assumptions.

- A linear relationship exists between the logarithmic creep rate and alloying content.
- The addition of Nb content above 0.5wt% does not affect the creep rate.

Figure 3 plots the secondary creep rate of zirconium alloys as a function of alloying content, without distinguishing the individual alloying elements. There must be a significant effect of specific alloying elements on creep strength since the difference in creep rate is three orders of magnitude even though the total amount of alloying elements is constant.

With regard to individual alloying elements, the equation from the statistical model for Nb < 0.5 wt% is :

$$\log \dot{\varepsilon}_s = -3.67 - 1.56XSn - 1.74XNb - 0.08XFe + 0.64XCu - 0.17XMo - 0.73XMn - 0.61XCr - 1.83X(V + Sb + Ta + O)$$

The applicability of this model equation is limited to the range of alloying addition as listed in Table 1. Comparison of the proportional constants in the equation above indicates that the creep strengthening effect on alloying additions decreases in the following sequence : Nb, Sn, Mn, Cr, Mo, Fe, and Cu. The additions of Sn and Nb are especially effective in increasing the creep resistance at concentrations up to their solubility limits. On the other hand, the addition of Fe or Cu is not effective or even has a deleterious effect on the creep resistance of zirconium alloys.

Figure 4 shows the comparison of the measured and predicted creep rates. The parameter R^2 increased from 0.448 to 0.767, indicating a significant improvement of the model prediction by considering the effect of individual alloying elements on the creep of zirconium alloys.

3.2. Alloying Element Effect

The creep strengthening of various alloying

elements was evaluated in a previous section. It seems that Sn content plays a major role in creep strength of the alloys analyzed, and the slopes in Figures 1 and 3 are similar at -1.32 and -1.35, respectively. In this section, we will discuss the reason why Sn is effective in improving creep strength while Fe is not. Pahutova, et al [8] suggested that the addition of Sn lowers the stacking fault energy, and hence increases the creep resistance of zirconium alloys by the increased interaction between solid solution alloying elements and extended dislocations. This mechanism has been widely accepted qualitatively; however, no clear evidence has been provided, such as the measurement of stacking fault energy.

Several authors [9,10] have suggested that the creep mechanism of Zircaloy-2 and 4 was diffusion-controlled climb of dislocations under test conditions similar to those in the database that was evaluated. Thus it is appropriate to continue discussion of the power-law creep theory that characterizes the steady-state creep rate in terms of the applied stress σ to a power n. This law is generally expressed in the following phenomenological equation [11]:

$$\dot{\varepsilon}_s = A\frac{DG\Omega}{kT}\left(\frac{\sigma}{G}\right)^n \qquad (3)$$

Here D is the lattice self-diffusion coefficient, G is shear modulus, Ω is activation volume, and A is a constant that depends primarily on the stacking fault energy of metal. This equation can be simplified because of the identical conditions of test temperature and applied stress for all of the alloys analyzed. In addition to this, since Ω is proportional to the spacing between obstacles l ($\Omega = \mathbf{b}l^2s$), and approximating l^2 depends inversely upon alloy concentration c, Eq. (3) becomes,

$$\dot{\varepsilon}_s = A\frac{D\Omega}{G^{n-1}} \approx \frac{A\cdot D}{\sqrt{c}\cdot G^{n-1}} \qquad (4)$$

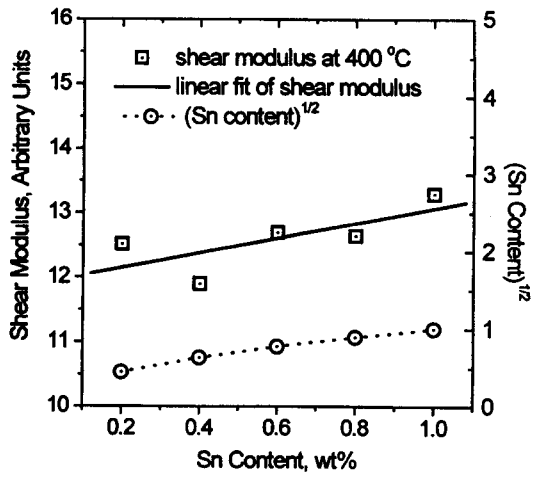

Fig. 5. Change of Shear Modulus at 400℃ and Square Root of Sn Content of Zr-0.2Nb-0.4Fe-0.2Cu-xSn Alloys as a Function of Sn Content

According to this relation, varying the chemical composition may change the stacking fault energy, self-diffusivity, alloying content and shear modulus. To estimate the rate controlling factor on creep rate, a quantitative analysis was performed for the alloys with a variation in Sn content. Unfortunately the effect on stacking fault energy as a function of Sn content was not evaluated because of the lack of experimental data.

In general, the change in G with chemical composition is caused by the atomic size difference between solid solution and matrix elements. The change in c is related to the number density of obstacles to dislocation movement. Figure 5 shows the change in shear modulus at 400℃ and square root c for Zr-0.2Nb-0.4Fe-0.2Cu-xSn alloys as a function of Sn content. When the Sn content increased from 0.2 to 1.0 wt %, the increments in both the shear modulus and square root of Sn content were below 10 %. Knorr [9] used a stress exponent n of 4.5 to describe the creep of Zircaloy-2 at 400℃ and above 70 MPa. Even we

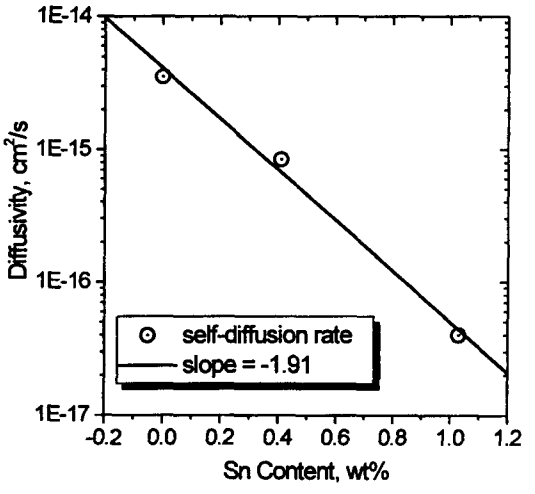

Fig. 6. The Self-diffusion Coefficient of Zr-xSn Alloys at 400℃ Cersus Sn Addition. Data was Extrapolated from Reference [12]

use this figure on G^{n-1} factor, the effect of rigidity on creep rate versus Sn content is not very large. Therefore the changes of rigidity and concentration are not enough to explain >100X difference in creep rate with Sn content shown in Figure 1.

It is known that the addition of Sn significantly decreases the self-diffusivity of alpha zirconium. As shown in Figure 6, the self-diffusion coefficient of Zr-xSn alloys can be extrapolated down to 400℃ from ref.[12]. The slope for the diffusion rate versus Sn content, -1.91, exhibits a similar trend to that of the creep rate in Figure 1. This indicates that the variation in the self-diffusion coefficient with Sn content is a more dominant factor in determining creep rate than rigidity and concentration effects. From this point of view, the small effect of Fe on creep strengthening may be interpreted in terms of its effect on lattice diffusion coefficient, as Fe enhances the self-diffusion coefficient of alpha zirconium [13,14].

4. Summary and Conclusions

Over one hundred new zirconium alloys were manufactured as sheet specimens, and creep tests were conducted at 400℃ and 150 MPa for 10 days. Using this database, the effect of alloying elements on the creep resistance of zirconium alloys was evaluated by multiple linear regression. A statistical model was derived for steady-state creep rate versus the content of individual alloying elements. The model indicates that the creep strengthening effect of alloying additions decreases as follows : Nb, Sn, Mn, Cr, Mo, Fe and Cu. It was noted that up to their solubility limits Sn and Nb are especially effective in enhancing creep strength, whereas Fe and Cu are not effective, when these elements are alloyed in zirconium matrix.

The power-law creep theory was modified and employed to explain the creep resistance as a function of Sn content. As a result, the variation in lattice self-diffusion coefficient with Sn content is more dominant than the contributions of rigidity and concentration effects. The reason for highly beneficial effect of Sn and the minimal effect of Fe on zirconium alloys may be explained by their reduction and enhancement, respectively, of the self-diffusion coefficient of zirconium matrix.

Acknowledgement

This work has been carried out under the Nuclear R & D Program by Ministry of Science and Technology (MOST), Korea.

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