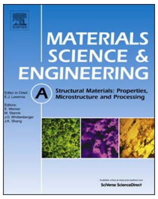
Materials Science & Engineering A 684 (2017) 191–195

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea



Transition of creep mechanism by solute hydrogen in Zircaloy-4

Tetsuya Matsunaga[a,b,*], Hiromichi Hongo[a], Masaaki Tabuchi[a], Yuhki Satoh[b], Hiroaki Abe[b]

[a] *National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Miyagi 980-8577, Japan*

ARTICLE INFO

Keywords:
Zircaloy-4
Creep
Solute hydrogen
Straight dislocation
Dislocation network
Cross-slip

ABSTRACT

The effect of solute hydrogen up to 200 ppm on the creep mechanism of Zircaloy-4 was discussed to ascertain the safety of nuclear power plants. Creep tests performed at 673 K and revealed that the addition of solute hydrogen decreased the creep rate in intermediate stress regions. According to the followed transmission electron microscopy, the phenomenon reflected the change of rate-controlling mechanisms without or with solute hydrogen: cross-slip in a non-hydrogenated sample with H=10 ppm; solute-atmosphere dragging process in hydrogenated samples with H=100 and 200 ppm. Because cross-slip works as the annihilation process for the glide dislocations in Zircaloy-4, it is considered that the suppression of cross-slip by solute hydrogen leads to a decrease in the creep rate.

1. Introduction

Zircaloy-4 is used as a fuel cladding material in nuclear power plants because of its good chemical and mechanical properties as well as small absorption cross-section for thermal neutrons at the operation temperatures of nuclear power plants. Therefore, high-temperature creep mechanisms have been carefully investigated for about half a century [1–9]. These mechanisms have been summarized in a deformation mechanism map [1,2]. In particular, the creep mechanism at coolant temperature is important to ascertain the safety of cladding tubes. Hayes et al. reported that such a creep occurs in diffusion-controlled dislocation creep regions and has a stress exponent (n) of 6.4 [7]. Recently, Moon et al. [9] and Morrow et al. [10,11] adapted the modified jogged-screw (MJS) model and obtained similar n values (4–5). In a previous study, we also obtained an n value of 6.5 at 673 K [12]. However, the value obtained from the interrupted creep tests at strains (ε) of < 0.05 and the actual stress exponent using the minimum creep rate was 14 at a high strain of ~0.15. The transition of the n value is related to the following deformation modes: (1) individual dislocation motion at low strains (stage I); (2) development of dislocation structures at high strains (stage II). To ascertain the safety of the plant, the creep strain should be limited during the operation of the plant because the acceleration of creep begins at $\varepsilon > 0.15$. Therefore, stage I deformation, i.e., the individual dislocation motion, is an important deformation mode in Zircaloy-4 used in nuclear power plants.

In addition, cladding materials suffer from degradation due to the usage environment, e.g., hydrogenation from the coolant water. It is well known that hydrogenation leads to embrittlement because of hydride precipitates [13–15]. On the other hand, solute hydrogen increases the dislocation velocity in thin films [16,17] and fosters an individual dislocation motion by decreasing the elastic interaction and enhancing the kink-pair generation. Moreover, Yamanaka et al. [18] claimed that solute hydrogen decreases Young's modulus, and Mallipudi et al. [19] proposed that the creep rate is increased by a decrease in Young's modulus according to a constitutive equation.

However, the present study shows the different experimental result mentioned above, i.e., the addition of solute hydrogen decreases the creep rate in the hydrogenated samples (H=100 and 200 ppm) and changes the rate-controlling process. It means that investigating the effect of solute hydrogen on high-temperature creep is necessary to discuss not only by the decrease in Young's modulus [18,19] but also by the deformation mechanism to ascertain the safety of nuclear power plant. Therefore, the present study discusses and focuses on the microstructure during the creep in solute hydrogen-containing and solute hydrogen-free Zircaloy-4.

2. Experimental procedures

A rolled-sheet of Zircaloy-4 was used in this study. Its chemical composition is given in Table 1. The alloy was annealed at 873 K for 3 h prior to the tests. The grain size was 30 µm as evaluated using the intercept length, and a recrystallized texture was observed. The non-hydrogenated sample had a small hydrogen content of 10 ppm.

Next, hydrogen absorption tests were performed in an argon and hydrogen atmosphere at 633 and 773 K on the samples with H =100 and 200 ppm, respectively. In addition, the effect of hydrogen on

---

[*] Corresponding author at: National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.
E-mail address: MATSUNAGA.Tetsuya@nims.go.jp (T. Matsunaga).

http://dx.doi.org/10.1016/j.msea.2016.12.057
Received 29 July 2016; Received in revised form 9 December 2016; Accepted 11 December 2016

Table 1
Chemical composition of the sample.

Sn	Fe	Cr	Al	Hf	O
1.4	0.2	0.1	0.001	0.005	0.1
N	C	H	Zr		
0.009	0.002	0.001	Bal.	[wt%]	

Young's modulus (E) of Zircaloy-4 was evaluated using the following equation [18]:

$$E_H = E - 0.0173\,H\,(\text{GPa}), \quad (1)$$

where E_H is Young's modulus at a given hydrogen content. In this study, the E value was calculated using the equation given in an earlier report [20]. The E value was calculated to be 74 GPa. The H values were less than the reported value of the solid solubility limit of hydrogen, i.e., 202 ppm at 673 K [21].

The creep tests were performed under tension using a dead-load creep frame at 673 K. The specimens were prepared using a wire electrical discharge machine with the loading direction perpendicular to the rolling direction. The gauge section dimensions were 10 mm×3.5 mm×0.9 mm. The displacement was measured using displacement transducers. The data for the non-hydrogenated sample with H=10 ppm has been reported in Ref. [12].

Transmission electron microscopy (TEM) observations were conducted to elucidate the intragranular deformation mechanism. The TEM samples were prepared by mechanically grinding the specimens, followed by electro-polishing with a solution of 50 ml of perchloric acid and 950 ml of methanol at 20 V and room temperature.

3. Results and discussion

Fig. 1 shows the creep test result, i.e., a double logarithmic plot of creep rate vs. modulus compensated applied stress (σ/E_H) at 673 K. Each sample showed a power-law breakdown (PLB) region with a large stress exponent at $\sigma/E_H > 10^{-3}$, which is shown by dashed lines in the figure. However, the data was separated by the hydrogen content in the intermediate stress region. The non-hydrogenated sample showed a stress exponent of 6.5. This value is consistent with the previously reported n values [7,9,12]. On the other hand, the samples with H=100 and 200 ppm showed a smaller n value (=2.5) in this region. However, at low stresses, these samples showed an n value of 6.5, which is the same as that of the non-hydrogenated sample. In addition, the creep rate decreased with the addition of solute hydrogen at $\sigma/E_H=5\times10^{-4}–1\times10^{-3}$, despite a decrease in Young's modulus by hydrogenation as described by Yamanaka et al. [18]. Therefore, a transition in the creep mechanism with the addition of solute hydrogen in the intermediate stress region is clearly evident.

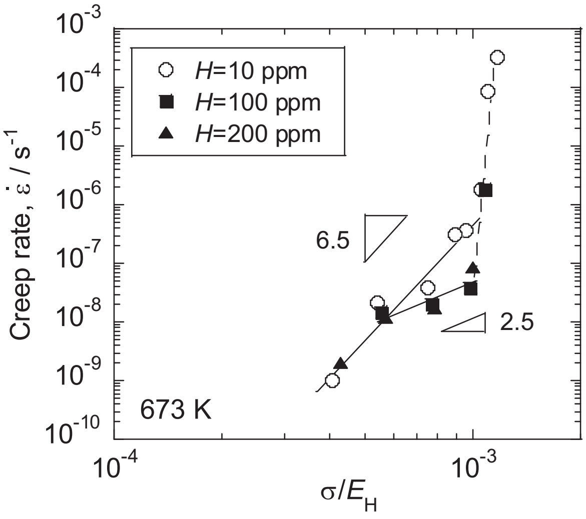


Fig. 1. Double logarithmic plot of creep rate vs. modulus compensated applied stress of each sample. Dashed line shows the PLB region. The data of the sample with H =10 ppm has been reported [12].

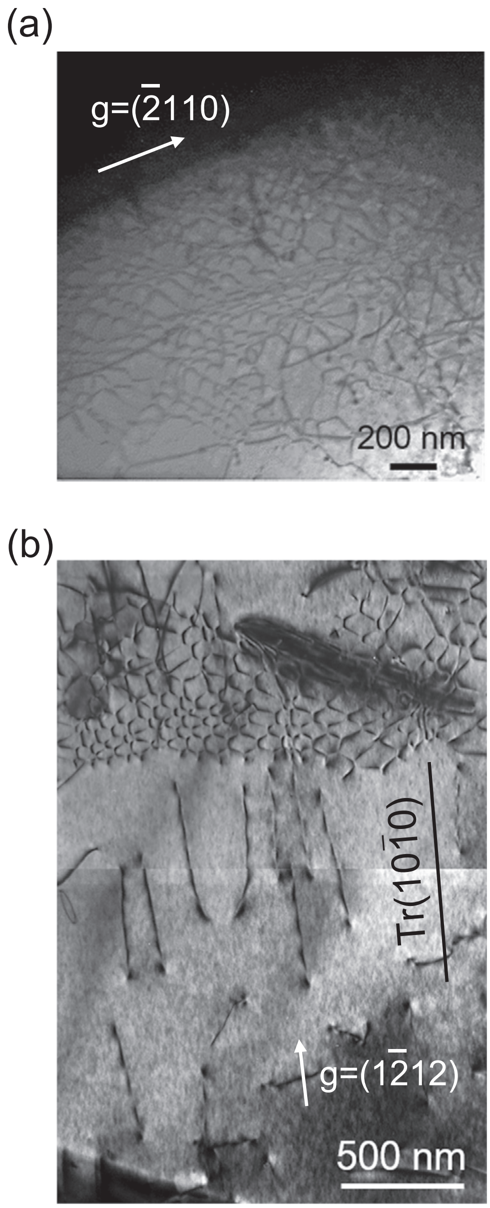


Fig. 2. TEM bright-field images of the sample with H=10 ppm taken after the creep tests at (a) 71 MPa and (b) 40 MPa. Dislocation network in the non-hydrogenated sample with H =10 ppm. Beam directions were (a) [0001] and (b) [$1\bar{2}1\bar{3}$].

To investigate the change in the creep behavior due to the addition of solute hydrogen, the TEM images were recorded after the creep tests. Fig. 2 shows the dislocation structure in the non-hydrogenated samples crept at 71 MPa ($\sigma/E_H=9.4\times10^{-4}$) and 40 MPa ($\sigma/E_H=5.4\times10^{-4}$). Straight dislocations lied on the ($10\bar{1}0$) prismatic plane at 40 MPa but a dislocation network was observed at both the applied stresses. Armas et al. [3] and Kombaiah et al. [22] also observed dislocation networks in non-hydrogenated Zircaloy-4 crept at over 773 K and claimed that the screw dislocations lying on the prismatic planes generated dislocation networks on the basal plane by cross-slip. On the basis of this discussion, it can be stated that the dislocation structure in the non-