THE KINETICS OF PRECIPITATE COARSENING IN ZIRCALOY-2

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ABSTRACT

THE KINETICS OF PRECIPITATE COARSENING IN ZIRCALOY-2. Zircaloy-2 has been used as fuel element cladding material in both light and heavy water power reactors. The aims of the experiment are to study the kinetics of precipitate coarsening during isothermal α-annealing and to characterize the nucleation and growth of precipitate affected by the variations of cold work and heat treatment. The results of the experiment show that all specimens annealed at 650°C have the average precipitate diameter less than 0.1 μm whereas those at 750°C have the average size larger than 0.1 μm except for one annealed for less than 5 hours. The average size of precipitates is 0.07 μm for specimens deformed before β-quenching and 0.168 μm for specimens deformed after β-quenching. The deformed specimens after β-quenching have more homogeneous size distribution than that of undeformed specimens and specimens deformed before β-quenching. The kinetics of precipitate coarsening depends on the changes in annealing temperature and time, and cooling rate from the β-phase region. The nucleation and growth of precipitates have been influenced by the variations of cold work and heat treatment.

Key words: Zircaloy-2, Kinetics of precipitate coarsening, Fuel element cladding

ABSTRAK

KINETIKA PENGASARAN PRESIPITAT DALAM ZIRCALOY-2. Zircaloy-2 digunakan sebagai material kelongsong elemen bakar reaktor daya berpendingin air ringan atau air berat. Penelitian ini bertujuan untuk mempelajari kinetika pengasaran presipitat selama anil-α isothermal serta karakterisasi pengintian dan pertumbuhan presipitat sebagai fungsi pengerjaan dingin dan perlakuan panas. Hasil penelitian menunjukkan bahwa semua spesimen yang dianil pada 650°C mempunyai diameter presipitat rerata lebih kecil dari 0,1 μm, sedangkan pada 750°C diameter presipitat rerata lebih besar dari 0,1 μm kecuali spesimen yang dianil kurang dari 5 jam. Ukuran rerata presipitat spesimen yang dideformasi sebelum β-*quenching* adalah 0,07 μm, sedangkan untuk spesimen yang dideformasi setelah β-*quenching* adalah 0,168 μm. Spesimen yang dideformasi setelah β-*quenching* mempunyai distribusi ukuran presipitat lebih homogen dibandingkan spesimen yang belum dideformasi dan telah dideformasi sebelum β-*quenching*. Kinetika pengasaran presipitat bergantung pada perubahan temperatur dan waktu anil, serta laju pendinginan dari daerah fasa-β. Pengintian dan pertumbuhan presipitat dipengaruhi oleh variasi pengerjaan dingin dan perlakuan panas.

Kata kunci: Zircaloy-2, Kinetika pengasaran presipitat, Kelongsong elemen bakar

INTRODUCTION

It is well known that zircaloy-2 is mainly used as cladding and structure materials in the core of both light and heavy water nuclear reactors. It has an exellent corrosion resistance in high-water temperature, and also high mechanical strength at elevated temperature, high melting point, high thermal conductivity and low absorption of thermal-neutron cross section. Cladding is required to protect the fuel from direct contact with coolant and to prevent the fission product release from fuel to coolant. The structure material is required to support the reactor core and to prevent fuel element distortion from various forces or stress imposed as a result of fission process within the fuel.

In zirconium alloy corresponding to zircaloy-2, main phases occuring succesively on heating are hcp α, (hcp α + bcc β) and bcc β; hcp generally exists between room temperature and 865°C, while the coexisting of (hcp α + bcc β) presents in the range of 865°C and 985°C and bcc β is in the region above 985°C [1].

Some investigations on microstructure features with respect to the mechanical and physical properties, and also the effects of heat treatments and microchemistry on the corrosion of zircaloys have been conducted [2,3,4]. The variations of cold work and heat treatment, and the changes of their conditions, however, play a significant role on the kinetics of precipitate coarsening that is associated with their contributions as a basic information on the design

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material of zircaloy. High coarsening rate of precipitates formed in zircaloy should be prohibited because it can increase the corrosion rate and electrical resistivity and also decrease the hardness of the material.

The objectives of this work are to evaluate the kinetics of precipitate coarsening during isothermal α-annealing and to characterize the nucleation and growth of precipitates with respect to their size distribution affected by variations of cold work and heat treatment.

MATERIALS AND METHODS

The material used in this experiment was as-forged zircaloy-2 with the composition of Zr-1.6 wt.% Sn-0.2 wt.% Fe-0.1wt.% Cr-0.05 wt.% Ni, supplied by Kobe Steel Co., Japan. Specimens were distinguished by three steps.

In the first step, specimens were β-annealed then water quenched (wq) at about 400°C/s. It was used as an initial state. The β-quenched specimens were subsequently annealed in the α-phase for various durations followed by water quenching as tabulated in Table 1. In the second and third steps, specimens were deformed (rolled) before and after β-quenching, and then both were annealed at 650°C and 750°C for 5 hours, as shown schematically in Figure 1 and Figure 2, respectively.

Table 1. Heat treatment history (first step)

Specimen	Category	Heat Treatment
B15	β-quenched	1050°C/15 min, wq
B15-750/0.5 H	α-quenched	B-15/750°C/0.5 h, wq
B15-750/2 H	idem	B-15/750°C/2 h, wq
B15-750/5 H	idem	B-15/750°C/5 h, wq
B15-750/48 H	idem	B-15/750°C/48 h, wq
B15-750/120 H	idem	B-15/750°C/120 h, wq
B15-650/0.5 H	idem	B-15/650°C/0,5 h, wq
B15-650/2 H	idem	B-15/650°C/2 h, wq
B15-650/5 H	idem	B-15/650°C/5 h, wq
B15-650/48 H	idem	B-15/650°C/48 h, wq
B15-650/120 H	idem	B-15/650°C/120 h, wq

Thin foils for TEM were prepared by a twin-jet electropolishing technique in the polishing solution of 10 vol.% perchloric acid (60%) and 90 vol.% methanol (99.8%). The solution temperature was maintained between - 45°C and - 35°C with the voltage varied from 9 to 20 volt during thinning. TEM examinations was conducted with a JEM-2000 EXII.

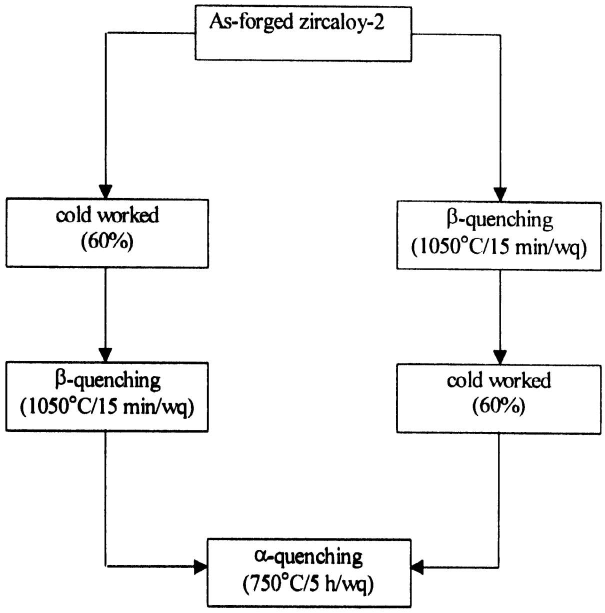

Figure 1. Scheme of second step heat treatment

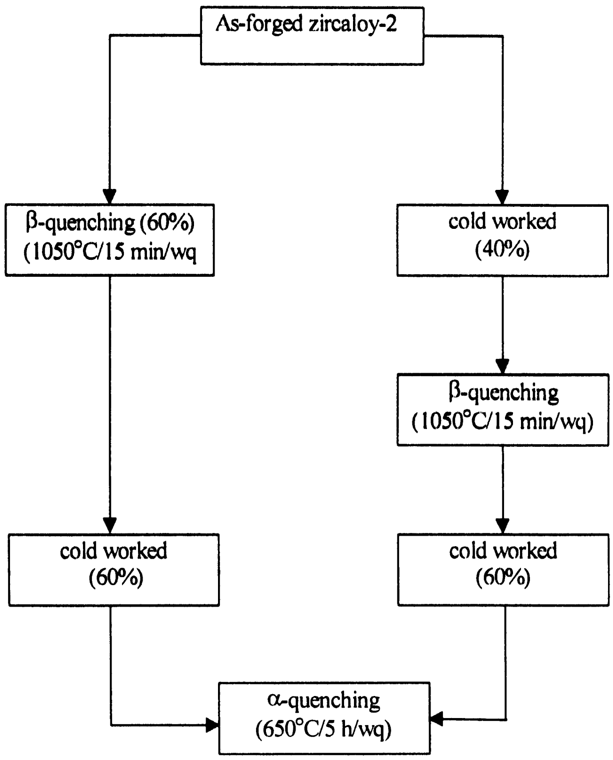

Figure 2. Scheme of third step heat treatment

RESULTS AND DISCUSSION

Coarsening of precipitates

The size of precipitates tends to become coarser with increasing annealing time and temperature. As the precipitates become coarser, however, their number becomes lower. By increasing the annealing temperature, the growth of the precipitates becomes more profound than by increasing the annealing time. This finding agrees with that of Maussner et.al [5] who conducted study on zircaloy-4.

When a precipitate nucleates, its growth is as fast as the diffusion of solute from the surrounding matrix. During this period, the volume of the precipitates increases and the solute content of the matrix decreases. After the solute concentration of the matrix has decreased to a near-equilibrium level, the microstructures become static. On this basis, solute content in equilibrium with smaller precipitates will be greater than that with larger precipitates. It causes flux of solute atoms from smaller to larger precipitates. This flux results in the shrinkage of the small precipitates and the growth of the larger ones [6].

The kinetics of precipitate coarsening during isothermal α-annealing is illustrated in Figure 3. It shows that all specimens annealed at 650°C have the average precipitate diameter less than 0.1 μm whereas those at 750°C have the average size larger than 0.1 μm except for one annealed for < 5 hours. Precipitates formed in the specimens were mostly distributed at the grain boundaries.

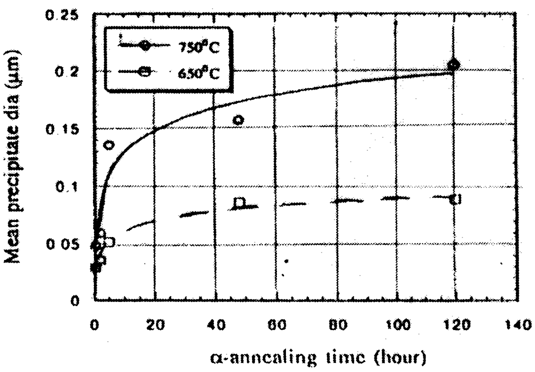

Figure 3. Coarsening of isothermal a-annealing precipitate

The coarsening of precipitates has been considerably extended by a diffusion rate that follows the simplified model of the Oswald ripening. The equations (1) as follows

$$d^3 - do^3 = k' . D . t . \exp(-Q/R.T) \quad (1)$$

If do is assumed to be small compared with d, then

$$d^3 = k' . D . t . \exp(-Q/R.T) \quad (2)$$

where

d = mean diameter of precipitates, m
k'= constant, m
D= diffusion constant, m^2/s.
t = time, s
T = absolute temperature, K
Q = activation energy = J/mole
R = gas constant = 8.3143 J/mole.K

The variation of the cube of precipitate diameter with time and temperature is given in Figure 4, Q and k'.D are 192 kJ/mole and 1.19×10^{-7} m^3/s, respectively.

Another investigation [5] shows that zircaloy-2 rolled sheet isothermally annealed at 750°C and 800°C after

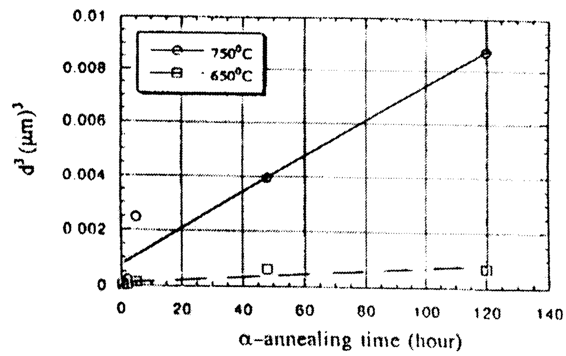

Figure 4. Dependency of volume precipitate on time and temperature.

β-quenching with cooling rate of 800°C/s gave Q = 250 kJ/mole and k'.D = 0.9×10^{-3} m^3/s. According to the discrepancy in the value of the activation energy between these two investigations, there could be an effect of cooling rate from the β-phase region on the coarsening rate of the precipitates, that has been controlled by the diffusion of the alloying elements through the matrix into the precipitates.

Effects of cold work and heat treatment variations

Taking into account the observation results in the first step, the average size of precipitates less than 0.1 μm was formed in specimens annealed either at 650°C for 5 hours or at 750°C for less than 5 hours. The specimens might have been indicated as relatively good materials with respect to low corrosion rate tendency.

Based on the above conditions, the effects of deformation (cold work) before and after β-quenching were conducted on the nucleation and growth of precipitates. The difference of precipitate coarsening formed in the specimens in the second step and that in the undeformed specimens annealed at 750°C can be clearly observed from the electron micrographs as shown in Figure 5. The average size of precipitate is 0.07 μm for specimens deformed before β-quenching and 0.168 μm for specimens deformed after β-quenching. It can be said that the coarsening rate

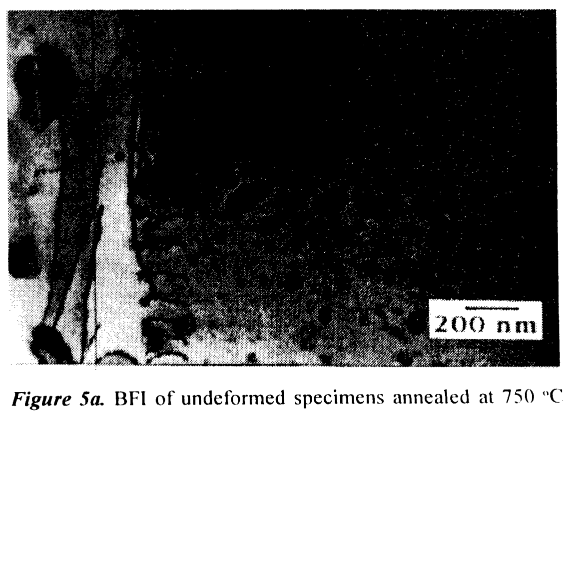

Figure 5a. BFI of undeformed specimens annealed at 750 °C

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Figure 5b. BFI of deformed specimens annealed at 750 °C

of precipitate in the specimen deformed after β-quenching tends to be higher than that of the undeformed specimens and specimens deformed before β-quenching. According to the size distribution of the precipitates, however, the deformed specimens have more homogeneous size distribution.

On the other hand, specimens prepared in the third step have relatively low in average size of precipitate. It is 0.03 μm for specimens deformed after β-quenching and 0.05 μm for specimens deformed for both before and after β-quenching. The comparison of their precipitate sizes is depicted in Figure 6.

Normally the specimens deformed after β-quenching form a zone with quite high dislocation density which creates high concentration of vacancy. These play more role in the precipitation (nucleation and growth) which is controlled by migration of atoms in the alloy.

Figure 6a. BFI of undeformed specimens annealed at 650 °C

Figure 6b. BFI of deformed specimens annealed at 650 °C

CONCLUSION

According to the evaluation and observation results of precipitate coarsening, it can be pointed out that the kinetics of precipitate coarsening depends on the changes in the annealing temperature and time, and the cooling rate from the β-phase region that has been controlled by the diffusion of alloying elements through the matrix into the precipitates. The variations of cold work and heat treatment have also strongly influenced the nucleation and growth of precipitates which have been controlled by migration of atoms.

Among all specimens examined in this work, the specimens annealed at 750°C for more than 5 hours and specimens deformed after β-quenching then annealed at 750°C cannot be classified as good materials owing to their high rate of precipitate coarsening.

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