Transactions of the Korean Nuclear Society Spring Meeting
Gwangju, Korea, May 30-31, 2013

Serrated Grain Boundary Formation in Ni-Based Alloy 690

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1. Introduction

A lot of damage in Ni-based alloys from applied and/or residual stress at high temperature is closely associated with a crack initiation and subsequent growth on the grain boundary. An intergranular creep fracture by a grain boundary sliding represents the typical example of such damage[1,2]. Stress corrosion cracking in the primary water environments occurs as the form of intergranular cracking in the same way, that is, the cracks nucleate at the grain boundaries on the surface, and propagate inwards along the grain boundaries[3]. If the straight grain boundary is modified into a serrated type, the resistance to intergranular cracking can be considerably improved. In the present study, the conditions for the grain boundary serration were investigated for a solid solution strengthened Ni-based Alloy 690 (Ni-30wt%Cr-8wt%Fe), which has been used as a new structural material in nuclear power plants. The mechanism of grain boundary serration in this alloy was examined through an analysis on the obtained results.

2. Methods and Results

2.1 Experimental procedures

Alloy 690 tubes were obtained in a 74.2 % cold-pilgered (690CP) condition, and thermally-treated at 720 ℃ for 10 hours (690TT). The chemical compositions of the Alloy 690CP and 690TT were identical, and measured as (wt%) 75.8 Ni, 15.45 Cr, 6.98 Fe, 0.055 C, 0.48 Si, 0.60 Mn, 0.18 Ti, 0.06 Co, 0.17 Al, 0.03 Cu, 0.005 P, and 0.001 S. First, the solid solution temperature (or Cr carbide dissolution temperature) of Alloy 690CP was determined by an isothermal treatment for 1 hour. After that, the specimens were control-cooled from the above solid solution temperature with the cooling rates between 100 and 0.5 ℃/min to precipitate intergranular Cr carbides, and at the same time, to change the grain boundary shapes. Specimens from Alloy 690TT were used in the as-received state in all experiments.

The specimens for the optical microscope and SEM were prepared by chemical etching in a solution of 2 % bromine + 98 % methanol. Transmission electron microscopy (TEM) specimens were prepared by cutting longitudinal strips from the tubes, grinding them to flat slabs approximately 60 ㎛ thick, and finally electro polishing the 3 mm discs. A 7 % perchloric acid + 93 % methanol solution cooled to -40 ℃ was used, and a current of approximately 50 mA was applied for the jet polishing. TEM observation was carried out with a JEOL 2000 FXII (operating voltage 200 kV).

2.2 Grain growth kinetics

The microstructure of Alloy 690CP, as a starting material, had grains elongated along the rolling direction, and Cr carbides were precipitated on the grain boundaries during the tube fabrication. Since the pre-existing carbides can have an additional effect on the grain boundary motion, they were completely dissolved during the heat treatment for grain growth. The dissolution temperature of Cr carbides was determined as 1106 ℃. The heat treatment for grain growth was done above the carbon solubility temperature to completely dissolve the pre-existing Cr carbides. Since a grain boundary migration is a thermally activated process, its kinetics followed an Arrhenius type temperature dependency in the alloy. The activation enthalpy of grain boundary migration in Alloy 690 was calculated as 1.27×10^5 J/mol.K.

2.3 Isothermal and controlled cooling treatments

The intergranular Cr carbides in Alloy 690 were consistently identified as Cr-rich $M_{23}C_6$, irrespective of the types of heat treatment. It is well known that Cr-rich $M_{23}C_6$ has a cube-cube orientation relationship such as $\{100\}_\gamma // \{100\}_{M23C6}$, $<100>_\gamma // <100>_{M23C6}$ with one grain. The intergranular Cr-rich carbide morphologies and grain boundary shapes in the isothermal and controlled cooling treatments are shown in Fig. 1.

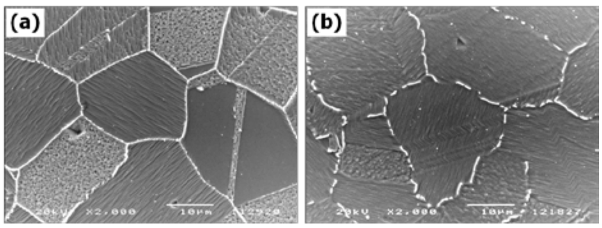

Fig. 1 IG Cr carbides and grain boundary shapes in Alloy 690 due to (a) isothermal treatment at 720 ℃ for 10 hours, and (b) controlled cooling with a cooling rate of 10 ℃/ min.

The carbides precipitated during the isothermal treatment had tiny and globular forms, and were densely distributed on the straight grain boundaries (Fig. 1(a)). However, coarse and plate-like shaped carbides were infrequently arranged along the grain boundaries in a slow cooled specimen, and the grain boundaries had wavy (or, serrated) shapes (Fig. 1(b)). The average size of intergranular Cr carbides in the serrated specimens was incomparably larger than that in the isothermally treated specimens. From the above results, it can be assumed that the grain boundary serration occurs owing to the interaction with coarse intergranular carbide precipitation during the cooling process.

2.4 Effects of grain size and cooling rate on the degree of serration

It was found that the heat treatment condition for the grain boundary serration of Alloy 690 was very restrictive. Serration with a significant precipitation of intergranular Cr carbides was possible only when the annealing temperature decreased from 990℃ and reached 950℃. The degree of serration was found to be dependent on the average grain size and the cooling rate. When the average grain size of a specimen increased, grain boundary serration occurred at a higher temperature and the degree of serration also increased, compared with those of a small grain size. As the cooling rate decreased, the number density of precipitated carbide is also decreased; however, the individual ones lengthened and thickened. The effect of cooling rate on the degree of serration in the specimens with the same grain size of about 30 ㎛ is shown in Fig. 2. As shown in the figures, as the cooling rate decreases from 10 of 10 ℃/ min. to 2 ℃/ min., the degree of serration increases.

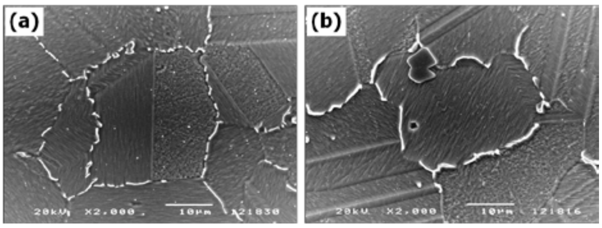

Fig. 2 Pricipitation morphologie of intergranuar carbide and grain boundary shapes in Alloy 690 with a cooling rate of (a) 10 ℃/ min. and (b) 2 ℃/ min

2.5 The mechanism of grain boundary serration

From the above results, it can be confirmed that the grain boundary serration is closely correlated with the precipitation behavior of intergranular Cr carbides. The driving force for carbide precipitation is originated from the supersaturated carbon content in a solid solution state. As the average grain size decreases, the total grain boundary area in a given volume increases, and the carbon content necessary for carbide precipitation on grain boundaries would then be insufficient in this case, making a low degree of serration.

The size, shape, and number density of intergranular carbide and the rate at which they form are primarily influenced by the kinetics of the phase transformations, that is, nucleation and growth of the second phases[4]. When the heat treatment temperature is relatively low, many nuclei form, however, their growths are very sluggish. If the temperature becomes higher, the reciprocal phenomena begin to occur. Therefore, when the specimen is cooled slowly, sparsely nucleated carbides can grow very fast at the high temperature range once they nucleate, as shown in Fig. 2.

The significantly grown intergranular carbides can act as obstacles to grain boundary migration. When a moving grain boundary encounter fixed particles, the grain boundary is then pinned by the interaction with the adjacent particles, which is a well known effect as the Zener drag[5]. The local segments of a grain boundary between the pinning particles can move further freely until the driving force for boundary migration vanishes. As the result, the grain boundary changes its shape from a straight form into the serrated one. As the particles have a more planar shape and/or are more sparsely distributed on a grain boundary, the amplitude and wavelength of the serration become larger.

3. Conclusions

The dissolution temperature of Cr carbides in the test alloy was determined as 1106℃, and the activation enthalpy of the grain boundary migration was calculated as 1.27 x 10^5 J/mol.K. The grain boundary had a straight shape in the case of an isothermal treatment; however, grain boundary serration occurred by controlled cooling processes. The degree of serration was dependent on the average grain size and cooling rate of a test specimen. As the average grain size increased and/or the cooling rate became low, the degree of serration increased. The mechanism of grain boundary serration could be explained by the pinning effect of intergranular carbides on the moving grain boundary

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