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Microstructural characteristics of β precipitates in Zr–1Nb alloy

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ABSTRACT

The β phase precipitates in a Zr–1Nb alloy annealed at 600 °C and 700 °C (below and above the monotectoid temperature, respectively) for 3 h were investigated by transmission electron microscopy. It was found that the uniformly distributed β phase obtained at 600 °C was spherical, with diameter of 30–60 nm, volume fraction of ~2.5% and Nb content of ~68 wt.%. However, the β phase obtained at 700 °C was stick-shaped, with ~100 nm in diameter and ~300 nm in length, volume fraction of ~9.8% and Nb content ~10 wt.%. The distinctions in volume fractions and compositions were consistent with the lever rule of the Zr–Nb phase diagram. The distinction in shapes resulted from the change in the interfacial structure, which depended on the lattice misfit. The orientation relationship between α matrix and stick-shape β precipitates satisfied Burgers' orientation relationship, i.e., $(10\bar{1}0)_\alpha//(1\bar{1}2)_\beta$ for the broad face, $(0001)_\alpha//(110)_\beta$ for the side facet and $(11\bar{2}0)_\alpha//(\bar{1}11)_\beta$ for the edge. The outline of the stick-shaped β precipitates was composed of straight and curved interfaces, and the broad faces and side facets together formed the straight interface, and the edges formed the curved one. As the Nb content of β phase increased, the lattice misfits on broad face and side facet increased and their interfacial structures changed from coherent (obtained at 700 °C) into incoherent (obtained at 600 °C), and the misfits of edge decreased, and their interfacial structures were always incoherent for the two heat treatments. Therefore, the curved interfaces had a higher growth rate than the straight interfaces at 700 °C and stick-like β phase precipitate was formed. While the three planes have a comparable growth rate at 600 °C and spherical β phase precipitate was formed.

1. Introduction

Zr–1Nb alloy has been used as fuel cladding and structure materials in Russian VVER and in France nuclear reactors for many years [1,2]. In this alloy, precipitates have an intense influence on the physical, mechanical and corrosion properties. Therefore, lots of efforts have been made over several decades to reveal the influence of hot working, heat treatment and service conditions on the characterizations of the precipitates, such as crystal structure, composition, shape, size, volume fraction and distribution.

There are many possible solid phase transformations in Zr–1Nb alloy, such as 1) β → α (α′) during cooling from the β phase field, 2) β → ω during quenching from the β phase field or aging at low temperature, 3) β → α + β_1 (Nb-impoverished), 4) β → α + β_2 (Nb-enriched) monotectoid reaction and 5) α' → α + (β_1 or β_2) [6,15]. It has been reported that the precipitates in Zr–1Nb alloy are mainly Nb-impoverished or Nb-enriched β phase precipitates [3–8], and a small amount of intermetallic compounds [8–11]. Generally, annealing below the monotectoid temperature for a long time Nb-enriched β_2 phase precipitate could be formed, while annealing above the monotectoid temperature or for a short time Nb-impoverished β_1 phase precipitates could be formed [12–14]. As almost all the studies on the relationship between precipitates and corrosion properties show that an increase in the amount of Nb-impoverished β_1 phase precipitate increases the corrosion rate, the microstructure containing stable Nb-enriched β_2 phase precipitate is preferred for materials stability under corrosive conditions [4,14]. Now the investigation on the β → α + β_2 phase transformations and the crystal structure of β_2 precipitate in Zr–1Nb alloy have been extensively undertaken, however little effort has been made to study the composite-phase transformation

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($\beta_2 \rightarrow \beta_1 + \alpha \rightarrow \beta_1$) and associated crystallographic characteristics.

In the present study, the β phase particles in a Zr–1Nb alloy annealed below and above the monotectoid temperature were investigated by transmission electron microscopy.

2. Experimental procedures

The as-received material was Zr–1Nb (wt.%) alloy manufactured by the State Nuclear Baoti Zirconium Industry Company (SNZ). The alloy was forged in the β phase field and quenched to room temperature, and then hot and cold rolled into a rod 9.6 mm in diameter below the monotectoid temperature, finally the rod was annealed at 600 °C and 700 °C (below and above monotectoid temperature, respectively) for 3 hours to obtain a fully recrystallized structure. Transmission electron microscopy (TEM) and composition analysis were performed using a FEI Tecnai G^2 20 transmission electron microscope equipped with energy dispersive X-ray (EDX) analyzer. TEM foils were mechanically thinned to 50 μm in thickness and further reduction was carried out using a Tenupol-5 twin-jet electrolytic polisher in a solution of 10% perchloric acid and 90% ethanol (volume fraction).

3. Results

Fig. 1 shows the changes in the micro-hardness with annealing time at 600 °C and 700 °C respectively. Generally the samples annealed at 600 °C had higher micro-hardness than that at 700 °C. In the first hour the micro-hardness of both samples increase. After 2 h' annealing at 600 °C or 3 h annealing at 700 °C, the micro-hardness for the annealed samples became constant. Thus the samples annealed at 600 °C for 3 h (600 °C/3 h-AC) and at 700 °C for 3 h (700 °C/3 h-AC) were chosen for detailed TEM study.

Fig. 2 shows the typical bright-field TEM microstructure of the 600 °C/3 h-AC sample. The spherical precipitates were uniformly distributed within the equiaxed α grains. The diameter was 30–60 nm and the volume fraction was ~2.5%, as shown in Fig. 2a and b. The selected area electron diffraction (SAED) pattern revealed that the precipitates were β phase with body-centered cubic crystal structure, as shown in Fig. 2c. EDX analysis under TEM indicated that the precipitates contain ~68 wt.% Nb.

Fig. 3 shows the typical bright-field TEM microstructure of the 700 °C/3 h-AC sample. The morphologies of the precipitates were obviously different from that in the 600 °C/3 h-AC sample. The precipitates had a stick-shaped morphology ~100 nm in diameter and ~300 nm in length. The volume fraction was ~9.8%, as shown in Fig. 3a and b. Selected area electron diffraction (SAED) revealed that the precipitates were also β phase with body-centered cubic crystal structure, as shown in Fig. 3c. The TEM-EDX analysis indicated that the precipitates contained ~10 wt.% Nb. In this case, through the combination of bright- and dark-field imaging with the consideration of magnetic rotation, it was noticed that the straight boundary of the needles corresponded to the $(10\bar{1})$ plane of the β-Zr precipitate, and this β particle plane is also parallel to the (0001) plane of the α-Zr matrix. When a dark-field image was taken using the $(10\bar{1})_\beta$ diffraction spot from a β-Zr precipitate, almost all precipitates containing the same axial direction were highlighted in the DF image, which suggested that these precipitates maintained an orientation relationship with the α-Zr matrix.

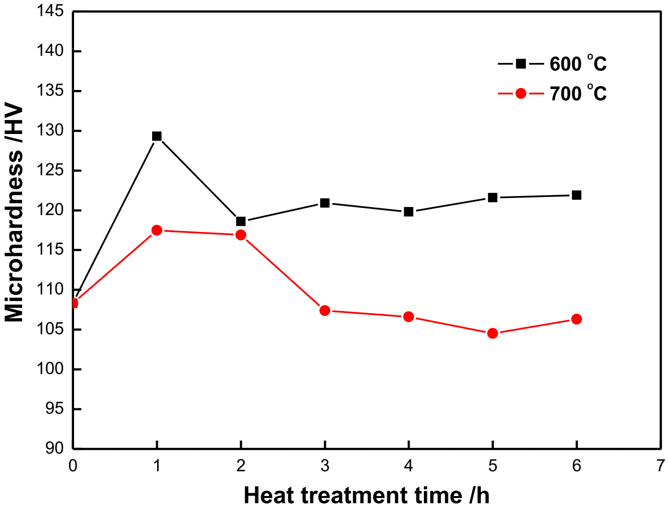

Fig. 1. Micro-hardness with annealing times at 600 °C and 700 °C, respectively.

4. Discussions

Comparing the characteristics of precipitates in the 600 °C/3 h-AC and 700 °C/3 h-AC samples, one noted that when the annealing temperature changes from 600 °C (below monotectoid temperature) to 700 °C (above monotectoid temperature), the volume fraction increased from ~2.5% to ~9.8%, while the Nb content decreased from ~68 wt.% to ~10 wt.%. At the same time, the size increased and the morphology changed from spherical to stick-shaped. The changing trends in volume fraction and composition are consistent with the lever rule of the Zr–Nb binary phase diagram. The Zr–Nb phase diagram shows that at 600 °C α and β_2 (Nb-enriched) phases exist. The Nb content of β_2 (Nb-enriched) phase is ~93 wt.% and the volume fraction is ~0.2%. At 700 °C α and β_1 (Nb-impoverished) phases exist. The Nb content of β_1 (Nb-impoverished) phase is ~11 wt.% and the volume fraction is ~3.7%. The distinctions between the experimental and theoretical data may result from several factors. On the one hand, the impurities, such as Fe, O, N, H, etc, will change the phase boundaries in Zr–Nb binary phase diagram. On the other hand, the annealing time was not long enough to reach full equilibrium. Because the compositions of α, β_1 (Nb-impoverished) and β_2 (Nb-enriched) phases are substantially different, the growth rate of β precipitates will be mainly controlled by the diffusion coefficients of Nb and Zr atoms.

Fig. 4 shows the HRTEM image of the boundary between α-Zr matrix and β precipitate in Zr–1Nb alloy with annealing of 700 °C for 3 h/AC. The outline of the stick-like β-precipitates is composed of straight and curved interfaces from the longitudinal section point of view. As showed in Fig. 4, the orientation relationship between α and stick shaped β phase precipitate for a straight interface is $(0001)_\alpha//(1\bar{1}\,0)_\beta$, and the [111] zone axis of the β phase precipitate is parallel to the $[11\bar{2}\,0]$ zone axis of α-Zr matrix, so the orientation relationship between α-matrix and β phase precipitate satisfies Burgers orientation relationship, i.e., $(10\bar{1}\,0)_\alpha//(1\bar{1}\,2)_\beta$ for the broad face, $(0001)_\alpha//(110)_\beta$ for the side facet and $(11\bar{2}\,0)_\alpha//(\bar{1}11)_\beta$ for the edge, just like the orientation relationship of phase transformation from β-matrix to α lath [15]. Therefore the broad faces and side facets together form the straight interface perpendicular to the S-axis, and the edges form the curved one perpendicular to the L-axis, as shown in Fig. 5.

The distinction in the morphologies of β phase precipitates indicates that at 600 °C the growth rate of β_2 (Nb-enriched) is isotropic while at 700 °C the growth rate of β_1 (Nb-impoverished) is anisotropic. A lot of studies have revealed that the migrating rate of the phase interface is intensely influenced by the interfacial structure. The more disordered the arrangement of atoms in the interface is, the faster migrating rate of the phase interface is. The extent of disorder can be reflected by the lattice misfit. As the increase of Nb content of β phase, the lattice parameter of β phase