Atom Probe Tomography Study of Fe Segregation at Phase Interface in Zr–2.5Nb Alloy

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Abstract

β -Nb is a typical second phase in Zr–Nb-based alloys used as fuel claddings in water-cooled nuclear reactors. The segregation of alloying element Fe may affect the corrosion resistance of Zr–Nb-based alloys. In this work, the Fe segregation at the interface between β -Nb phase and α -Zr matrix in Zr–2.5Nb alloy was studied using atom probe tomography and focused ion beam. The results suggested that the Fe concentration was much lower than Nb concentration in α -Zr matrix, while Fe selectively segregated at the β -Nb/ α -Zr phase interface, leading to a Fe concentration peak at some interfaces. The peak Fe concentration varied from 0.4 to 1.2 at.% and appeared at the position where Zr concentration was approximately equal to Nb concentration. The selective segregation of Fe should be affected by the heat treatment and structure defects induced by cold rolling.

Keywords Zr–Nb alloy · β -Nb phase · Phase interface · Segregation · Atom probe tomography

1 Introduction

Zr alloys have been widely used as structural materials (e.g., fuel cladding) of reactor pressure vessel (RPV) in light water reactors due to their low thermal neutron penalty, desired mechanical property and high corrosion resistance. The waterside corrosion of Zr alloys in RPV is known to directly affect the structure integrity of the relevant components. However, the underlying corrosion mechanism of Zr alloys still remains unclear as the corrosion process in high-temperature water is dominated by multiple factors. The secondary phases and the trace alloying elements in the alloy matrix play a key role in the corrosion process.

The Zr–Nb alloy is a promising candidate material for fuel cladding in pressurized water reactors due to the low thermal neutron penalty and strengthening effect of Nb. The corrosion resistance of Zr–Nb alloy is closely related to the solubility of Nb and the oxidation of β -Nb phase in α -Zr matrix [1]. The equilibrium solid solubility of Nb in α -Zr matrix of Zr–Nb binary alloy is 0.2–0.3 wt% [2–4]. It was reported that the Zr–Nb binary alloy with the Nb content at this equilibrium solid solubility exhibited the best corrosion resistance, while the supersaturation of Nb in α -Zr matrix accelerated the corrosion process [3–6]. Generally, the Nb supersaturation leads to precipitation of β -Nb phase, in which the Nb concentration is higher than 80 at.% [7, 8]. As a typical second phase in Zr–Nb alloy, β -Nb precipitates retarded the corrosion process in deionized water, endowing the commercial Zr–2.5Nb alloy with excellent corrosion resistance even under irradiation condition [4–6]. On the other hand, previous studies revealed that the oxidation of β -Nb particles enhanced the corrosion of Zr–Nb alloy in lithiated water or dissolved oxygen environment [9]. The role of β -Nb precipitates is susceptible to the water chemistry.

The interactions between the alloying elements could affect the maximum solid solubility of Nb and β -Nb precipitation in α -Zr matrix [4, 10]. A small amount of Fe was reported to increase the Nb solid solubility to 0.29–0.49 wt% and inhibit the β -Nb precipitation [3]. Therefore, Fe may

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affect the corrosion process through altering the maximum solubility of Nb and the kinetics of β -Nb precipitation. Recently, researchers have investigated the chemistry inhomogeneity of Sn, Ni and Fe at the grain boundary and its effect on the oxidation process [11–13]. Fe and Ni segregation at the grain boundary was thought to be associated with the enhancement of hydrogen pickup by Zr–2.5Nb alloy [11]. Metallic Sn particles with a size up to 20 nm were found to accelerate the corrosion process in surrounding Zr–2 matrix due to the fact that Sn depletion in the surrounding ZrO_2 grains could lead to transformation of chemically stabilized tetragonal phase to monoclinic ZrO_2 [12]. The segregation and clustering of Fe and Sn at the grain boundary in the Zr–2 alloy were also reported to have implications with the waterside corrosion kinetics of the alloy [14, 15]. However, little attention was paid to the distribution of Nb and Fe and the relationship between the element distribution and β -Nb phase in Zr–Nb alloy. In addition, the alloying element content in Zr alloys is quite low, leading to a difficulty of precise examination of the alloying element. For example, the Fe solubility in Zr–Sn–Nb–Fe alloy determined by electron probe was (0.1 ± 0.3) at.%, which was quite different from that calculated based on the Zr–Sn–O phase diagram (0.12 at.%) [16, 17]. The difference would be larger if there is segregation or clustering of Fe in the matrix. Therefore, accurate analysis of Fe distribution in Zr–Nb alloy is necessary.

The atom probe tomography (APT) is known for the high atomic scale resolution and the good chemistry sensitivity in three dimensions (3D) [18]. In this work, the 3D distribution

of Zr, Nb and Fe in bulk Zr–2.5Nb alloy was investigated using APT, in order to clarify the relationship between Fe segregation and β -Nb phase.

2 Experimental

The material used in this study was Zr–2.5Nb alloy plate with a thickness of 1.4 mm, which was supplied by the Northwest Institute for Non-ferrous Metal Research. The plate was homogenized at 1030 °C for 40 min; then, it was cold rolled to about 0.7 mm, followed by an annealing treatment at 580 °C for 5 h. The chemical composition of the Zr–2.5Nb alloy was determined to be 2.5% Nb, 0.012% Fe, 0.008% Cr and Zr balance (wt%), using inductively coupled plasma atomic emission spectrometry. The microstructure was examined by a JEM-2010F transmission electron microscope (TEM).

The needle-tip specimen for APT analysis was fabricated using a FEI 600i focused ion beam (FIB) instrument according to the lift-out method [19]. Figure 1 shows the detailed fabrication process of the APT specimen. It is worth mentioning that Pt was previously deposited as a protective layer. At the last milling stage, a small energy of 2 keV was used to remove the remaining Pt and to minimize the irradiation damage of Ga ions. A tip size of no more than 50 nm was finally obtained for all APT specimens.

The accurate chemical composition analysis was performed by using a CAMECA LEAP-4000X HR APT system which operated in a local electronic atom probe and

Fig. 1 Fabrication process of APT specimen by using FIB: **a** select an area of $10\ \mu\text{m} \times 2\ \mu\text{m}$ on the surface; **b** isolate the volume, weld it to a micromanipulator and lift it out; **c** move the volume to a silicon post; **d** weld the volume to the silicon post; **e, f** cut off the volume with the micromanipulator; **g** milling stage; **h** cleaning-up to finish the fabrication of APT tip

laser pulsing mode. To avoid the rupture of the APT specimen, a pulse repetition rate of 200 kHz and a laser energy of 70–100 pJ were used [18]. During the APT test, the temperature of the specimens was maintained at ~ 50 K while the standing voltage varied automatically to maintain a detection rate of 0.005 ion/pulse. The collected APT data were reconstructed and analyzed using the IVAS 3.6.8 software. The default value of the image compression factor was set as 3.3, and the evaporation field of Zr was 28 V/nm [20] for the APT data reconstruction.

3 Results and Discussion

The TEM micrograph of the Zr–2.5Nb alloy sheet is shown in Fig. 2, which is consisted of partially recrystallized α -Zr matrix and a dispersion of fine precipitates. The numerous spherical precipitates were detected as β -Nb phase, while the rod-like ones with a small amount were identified to be residual β -Zr phase. The β -Nb and β -Zr phases are common precipitates in Zr–2.5Nb alloy [8].

Figure 3 shows the reconstructed atom maps of Zr, Nb and Fe in the Zr–2.5Nb alloy sheet. No second phase precipitates or clusters were detected in this APT dataset. All the elements were homogeneously distributed. The Nb content in the α -Zr matrix was determined as approximately 0.67 at.%.

Figure 4 shows the reconstructed atom maps of Zr, Nb and Fe in the Zr–2.5Nb alloy sheet from different regions of interest, which clearly shows the Fe segregation (Fig. 4b) and Nb-enriched clusters (Fig. 4c). These clusters were defined as β -Nb precipitates under TEM observation (Fig. 2). For a better visualization, the β -Nb precipitates are surrounded by the 80 at.% Nb

Fig. 2 TEM micrograph of Zr–2.5Nb alloy showing spherical β -Nb precipitates and rod-like β -Zr phase in the α -Zr matrix

Fig. 3 APT reconstructed atom maps of Zr, Nb and Fe in the Zr–2.5Nb alloy, showing homogeneous distribution of Zr, Nb and Fe atoms. The size of the volume analyzed is 114 nm $\times$ 113 nm $\times$ 289 nm

iso-concentration surface (Fig. 4d). Figure 4b and d shows that the Fe atoms appeared to segregate at the interface between the β -Nb precipitates and the α -Zr matrix (i.e., β -Nb/ α -Zr phase interface). The proxigram profiles corresponding to two β -Nb precipitates (P1 and P3) marked in Fig. 4d are shown in Fig. 4e, f. The results indicated that the Nb content in most β -Nb precipitates was close to 100 at.%, which is consistent with the result of above 80 at.% reported in Ref. [5]. In addition, Fe atoms were detected to segregate at the β -Nb/ α -Zr phase interface, resulting in a concentration peak of Fe at the phase interface. The peak concentration of Fe varied from 0.4 to 1.2 at.% for different precipitates. Further, the concentration peak of Fe appeared at the position where the Zr content was approximately equal to Nb content. The Fe contents at the positions far away from the β -Nb precipitates were much lower, which is consistent with the results shown in Fig. 3.

Figure 5 shows the reconstructed atom maps of Nb and Fe and proxigram from the third APT dataset. Nb-enriched clusters (i.e., β -Nb phase) were observed in Fig. 5a. Slight Fe segregation was also found at the β -Nb/ α -Zr interfaces in Fig. 5b, c. Nevertheless, the magnitude of Fe segregation was weak with the peak Fe concentration of less than 0.1 at.%, as shown in Fig. 5d. This result indicated that not all the β -Nb/ α -Zr phase interfaces were obviously enriched with Fe and the Fe segregation at the β -Nb/ α -Zr phase interfaces was selective.

Figure 6 shows the interface structure between the large β -Nb phase and α -Zr matrix in the Zr–2.5Nb alloy. Obvious lattice distortion and mismatch at the interface was found in the high-resolution transmission electron microscopy (HRTEM) image, which is a kind of structure defect induced by cold rolling.

Fig. 4 **a–c** APT reconstructed atom maps of Zr, Fe and Nb in the Zr–2.5Nb alloy, showing Fe segregation and β -Nb precipitates in the matrix. The size of the volume analyzed is $90 \times 88 \times 284 \text{ nm}^3$, **d** Fe atom map and 80 at.% Nb iso-concentration surface. All the precipitates are marked by arrows, **e, f** proxigram profiles for Zr, Nb and Fe of two selected β -Nb precipitates (P1 and P3, respectively) shown in **d**

The APT results shown in Figs. 3, 4 and 5 suggested that not all the β -Nb/ α -Zr phase interfaces were obviously enriched with Fe. The selective segregation of Fe was likely to be dependent on the heat treatment. Following the homogenization annealing at 1030 °C for 40 min, uniform β -Zr phase was formed in the Zr–2.5Nb alloy. At the slow cooling stage of the homogenization annealing, some β -Zr phases decomposed to form the β -Nb precipitates (i.e., proeutectoid β -Nb phase). Subsequent cold rolling and annealing treatment induced dense structure defects around these β -Nb particles (Fig. 6). Therefore, these β -Nb particles were easier to grow up due to the accelerated diffusion rate of solute atoms by the structure defect. In addition to the proeutectoid β -Nb phase, eutectoid β -Nb phase was formed by the decomposition of β -Zr phase into α -Zr matrix and β -Nb phase following the annealing treatment at 580 °C. With consideration to the results shown in Figs. 4 and 5, obvious Fe segregation occurred at the interfaces between the larger β -Nb particles (P1 and P3) and the α -Zr matrix rather than those between the smaller particles (P7) and matrix. This result indicated that Fe tended to segregate at the interface between the

proeutectoid β -Nb phase and the α -Zr matrix. According to the study reported by Sundell et al. [16], the degree of Fe segregation was higher in the deformed Zr–2.5Nb alloy. In addition, Toyama et al. [21] reported that Fe segregation occurred at the structure defects around the precipitates in Zr–Nb alloy. These two studies demonstrated that the crystal structure defect in the Zr–2.5Nb alloy matrix played a key role in the Fe segregation. Therefore, in addition to the heat treatment, the effect of cold rolling on Fe segregation in the Zr–2.5Nb alloy cannot be neglected.

4 Conclusions

- (1) Nb content in α -Zr matrix was about 0.67 at.% while Fe content was much lower in α -Zr matrix.
- (2) Fe was found to segregate at the β -Nb/ α -Zr phase interface, leading to a concentration peak of Fe. The peak Fe concentration varied from 0.4 to 1.2 at.%, which appeared at the position where Zr content was approximately equal to Nb content.

Fig. 5 **a, b** APT reconstructed atom maps of Nb and Fe in the Zr–2.5Nb alloy, **c** 50 at.% Nb iso-concentration surface showing β -Nb precipitates, **d** proxigram profiles for Zr, Nb and Fe of the β -Nb precipitates marked by P7 in **c**

Fig. 6 HRTEM image of interface structure between the large β -Nb phase and α -Zr matrix in the Zr–2.5Nb alloy

- (3) Not all the β -Nb/ α -Zr phase interfaces were obviously enriched with Fe. The selective segregation of Fe was likely to be affected by the heat treatment and the structure defects induced by cold rolling.

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