On the oxidation behavior of (Zr,Nb)₂Fe under simulated nuclear reactor conditions

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Abstract: The corrosion behavior of Zr alloys was affected by second phases, especially by those containing Fe and Nb. Ti₂Ni-type (Zr,Nb)₂Fe compound was melted and exposed to H₂O₂ water solution at 320 °C and 16.4 MPa for 60 hours. The oxide layer was analyzed by X-ray diffraction and high-resolution transmission electron microscope (HRTEM). The formation of nano-crystalline tetragonal ZrO₂ (Fe-rich area) and amorphous ZrO₂ (Fe-deficient area) was observed. HRTEM analysis identified α-Fe could stabilize tetragonal ZrO₂ due to the epitaxial growth. ZrxFeyNb alloys with different iron were melted and corroded similarly. The result was consistent with the proposed mechanism.

Key words: A. Zirconium; B. X-ray diffraction; B. TEM; C. Oxidation

1. Introduction

Zr alloys are extensively used in nuclear reactor as cladding materials, which should tolerate the exposure to the coolant (high temperature water, liquid metals, gas, or liquid salts), stress, vibration, intense field of high energy neutrons, or gradients in temperature. The degradation of Zr alloys in reactor core can lead to decrease of

performance and even sudden failure of materials. Thus, efforts should be taken to increase the properties of Zr-based alloys at high burn-up environment. This can be achieved through the introduction of alloying elements with low absorption cross-section of thermal neutrons to induce solution and/or precipitate strengthening while maintaining good corrosion resistance. Therefore, only a limited number of alloying elements are suitable for addition into cladding Zr alloys, with their acceptable contents being fairly low. So far, the recognized alloying elements for such materials include Nb, Sn, Fe, Cr, O etc. Due to the limited solubility of alloying elements in α -Zr, most of them tend to precipitate as second phase particles (SPPs), which strongly influences the properties of Zr alloys [1-10].

Numerous researches have reported that the size distribution and type of precipitates have a significant impact on the oxidation and corrosion of Zr alloys, especially on the microstructure of oxide layer. The optimized corrosion performance of Zr alloys was achieved when the fine second phase particles were uniformly precipitated in α -Zr matrix [11-12]. Rudling et al. showed that the SPPs distribution and chemical composition heavily affected the corrosion behavior, since the barrier layer (dense zirconia) which influence the diffusion of oxygen ions was closely related to the SPPs [13]. On the other hand, the defects of precipitates make them prone to amorphization and elemental migration, which would change the stability of precipitates and the chemical composition of matrix, thereby lowering the working performance of Zr alloys [4-7, 14]. Therefore, the evolution of SPPs during the service condition, exposure to oxidation and corrosion, should be further characterized.

During oxidation, an oxide layer would form on the metal-oxide / water interface, which can effectively prevent the further corrosion of Zr alloys [15-16]. The oxide layer normally consists of monoclinic ZrO_2 ($m\text{-ZrO}_2$) and tetragonal ZrO_2 ($t\text{-ZrO}_2$). Refs [4, 17-18] reported that the corrosion resistance of zirconium alloys was improved when the amount of tetragonal zirconia near the metal-oxide interface increased, which would form a dense oxide layer. It has been confirmed that the tetragonal phase could be stabilized by the surrounding strain generated during the phase transformation. Refs [1, 19-21] showed that the stability of zirconia can also be

affected by the redistribution of iron during oxidation process. Iron and niobium as main alloying elements also affect the corrosion resistance of advanced Zr-based alloys such as E635 or Zirlo. However, by far it is still an open question about the roles that precipitates play during the corrosion process. The relationship between the precipitates and the stabilization of zirconia is also not well established. Thus special interest should be paid to the behavior of precipitates in the working environment. It is necessary to build up the relationship between the structural evolution of oxide layer and elemental migration of precipitates in Zr-based alloys during the oxidation process.

The cubic Ti_2Ni -type $(\text{Zr},\text{Nb})_2\text{Fe}$ has a homogeneity range of 2.4-13 at.% Nb and 31-33 at.% Fe in the Zr-rich corner, which is an usual precipitate in Zr-alloys. It was reported that the formation of Ti_2Ni -type $(\text{Zr},\text{Nb})_2\text{Fe}$ would improve the oxidation resistance, compared with C14-type $\text{Zr}(\text{FeNb})_2$ phase. The origination of the significant improvement was attributed to the stabilization of $t\text{-ZrO}_2$ [4]. However, the stabilization mechanism is still unknown. At the same time, the formation of stress induced microcracks on the precipitate/matrix interface would make it complicated to analyze the oxidation mechanism [21].

In this study, to clarify the role that Ti_2Ni -type $(\text{Zr},\text{Nb})_2\text{Fe}$ played as precipitate in the oxidation process, single phase $(\text{Zr},\text{Nb})_2\text{Fe}$ bulk was fabricated and oxidized under a super critical condition. The oxidation of single bulk intermetallic compound would exclude the influence of stress and acquire a relatively reliable oxidation model.

2. Experimental methods

Intermetallic compound ingots (composition: 60 at.% Zr-7 at.% Nb-33 at.% Fe based on [22-23]) were produced in an arc furnace with a non-consumable tungsten electrode in a high purity argon atmosphere. Sponge zirconium (nuclear grade) and high purity of Niobium (99.99 wt.%) and iron (99.8 wt.%) were used to prepare the compound. Repetitive melting was carried out to achieve a satisfactory chemical and phase homogenization. The as-cast ingots were cut into small sheets with the thickness of 1.5 mm. Herein the sheets used for the corrosion test were in a complete

bulk state without crack. Before corrosion test, the sheets were mechanically grinded with grit of 400#, 800#, 1500#, 2000#, 4000 # and cleaned in deionized water.

The corrosion test was performed in a static autoclave with 1 % H₂O₂ pure water solution under the simulated PWR environment (320 °C and 16.4MPa) [24] for 60 hours. H₂O₂ was introduced into autoclave to improve the corrosivity / oxidation ability of the environment, which helps to get sufficient oxides layer thickness and diminishes the destroy of the sample. After oxidation, the samples were dried with absorbent paper after ultrasonic cleaning in deionized water.

The crystallographic information was obtained through X-ray diffractometer (XRD) (Rigaku Ultima IV) at a speed of 2° / min in the 20° - 90° range using a Cu anticathode at room temperature. Focusing and parallel beam models were employed for the bulk and oxide layer scanning, respectively. The microstructure of oxide layer was studied using transmission electron microscope (TEM) (FEI Tecnai G² F20) equipped with energy dispersive X-ray spectrometer (EDS). Cross-section samples were cut from the oxidized samples, which were glued surface to surface. After grinded to 70 - 80 μm in thickness, the sample was dimpled using a Gatan Model 656 Dimple Grinder with the dimple centered near the oxide-oxide interface. The thickness of the sample at the center of the dimpled region was controlled in the range of 10-20 μm. The final thinning was performed using a Gatan Model 691 PIPS instrument.

3. Results and discussion

The XRD patterns of the as-cast (Zr,Nb)₂Fe and the referred standard PDF pattern [23] are shown in Fig. 1(a). It can be seen that single Ti₂Ni-type (Zr,Nb)₂Fe phase was fabricated. The wonderful agreement in the position and intensity of two patterns indicated that there was no evident residual stress in the sample. After oxidation, XRD pattern of oxide layer was also shown in the bottom of Fig. 1(a). The peaks corresponding both to *m*-ZrO₂ (monoclinic ZrO₂ [25]) and *t*-ZrO₂ (tetragonal ZrO₂ [26]) were observed. The broad and weak peaks indicated a poor crystallinity of zirconia during the oxidation process. It is known that a more appreciable percentage

of $t\text{-ZrO}_2$ was observed in the initial stage of oxidation process than post-transition oxide layers [14-15, 27]. Metastable $t\text{-ZrO}_2$ would transform into monoclinic phase kinetically with the oxidation proceeds [15, 27] Consequently, major $m\text{-ZrO}_2$ and minor $t\text{-ZrO}_2$ were observed.

The High-angle annular dark-field (HAADF) image and EDS line-scan result of the oxide layer are shown in Fig. 1(b). The elemental distribution of oxygen, iron, zirconium and niobium in the layer was demonstrated based on O K α , Fe K α , Zr L and Nb L. Even though the oxidation rate of SPPs is generally slower than that of $\alpha\text{-Zr}$ [2-7, 28-30], EDS result shows an oxide layer with the thickness of approximately 4 μm after autoclaved for 60 hours. As it can be seen from Fig. 1(b), the distribution of zirconium and niobium has a similar tendency and a small range of Nb / Zr aggregation can be observed nearby the oxide surface. Meanwhile, in the outer surface, the distribution of Fe is apparently different. Significant peaks can be identified, which indicates that the Fe element was discontinuously segregated in the middle area (400 nm away from the outer surface) of oxide layer. The redistribution and aggregation of Fe during oxide process was identified. Refs [19, 21, 31] reported that iron migrated from the oxidized SPPs in the oxide to the oxide/metal interface, then formed iron oxides. Therein, it was hypothesized that the iron elements probably segregated as $\alpha\text{-Fe}$ initially, which was supported by EDS mapping without any structural characterization [31].

TEM cross-section images of the oxide layer nearby the outer surface are shown in Fig. 2. It is observed that nano-crystalline particles distributed on the oxide matrix. The selected area diffraction (SAD) pattern inserted in Fig. 2(a) is halo rings with small spots corresponding to the nano-crystalline phases, which indicates that the dominant matrix phase is amorphous ZrO_2 . The local high-resolution transmission electron microscope (HRTEM) image demonstrated that the nano-crystalline particle can be indexed as $m\text{-ZrO}_2$ (Fig. 2b,c). The formation of dislocations (indicated by arrows) due to the stress of phase transformation was also identified from the inverse fast Fourier transformation (IFFT) image of the $m\text{-ZrO}_2$ phase. In this region (nearby outer surface), the oxide was largely in an amorphous state with small amounts of

nano-crystalline *m*-ZrO₂.

Fig. 3 shows a region approximately 600 nm away from the oxide-water interface. It is interesting to note that there is obvious diffraction contrast from the bright field image (shown in Fig. 3a). EDS analysis of ‘1’ and ‘2’ indicated that the particles on the matrix with black and gray contrast mainly correspond to iron-rich phase and zirconium oxide, respectively. As shown in Fig. 1(b), the Fe element was enriched somewhere with relatively low Zr content (indicated by dotted line). The SAD pattern inserted in Fig. 3(a) from the area close to the surface shows a similar result as observed in Fig. 2. However, the SAD pattern corresponding to the area 600 nm away from the outer surface, which was marked as ‘B’ in Fig. 3(a), shows a typical characteristic of nano-crystalline phase that can be indexed as tetragonal ZrO₂ (Fig. 3b). To figure out more structure information of the nano-particles, a typical iron-rich phase and the surrounding area was analyzed by HRTEM and presented in Fig. 3(c). One can see from the lattice fringe image in Fig. 3(c-2) that two crystalline particles grown with an orientation relationship (OR). The phase interface was marked with red dot line. These two crystal particles can be identified as *t*-ZrO₂ and α -Fe [32], respectively, as shown in the insert of Fig. 3(c). The corresponding OR was identified as $[010]_{t\text{-ZrO}_2} // [001]_{\alpha\text{-Fe}}$, $(200)_{t\text{-ZrO}_2} // (110)_{\alpha\text{-Fe}}$. It can be figured out that the mismatch on the conjunct planes was recognized as $4d_{t(200)} = 5d_{\alpha(110)}$. In previous study, the relation of iron redistribution and phase selection of zirconia has been reported [20]. They mainly attributed the stabilization of *t*-ZrO₂ to the accumulation of iron in zirconia and the lattice defects.

On the oxidation, oxygen will diffuse inward and react with Zr preferentially due to the higher affinity of them and higher diffusion coefficient of O ($2.8 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ at 350 °C) [33]. The formation of zirconia is also far more favored kinetically than that of iron oxide since the effective oxygen partial pressure to trigger the oxidation of Zr and Fe is 10^{-75} atm and 10^{-34} atm, respectively [21, 31]. In addition, iron tends to stay at the area with low O₂ concentration and always migrate out of area with high local O. In the Ti₂Ni-type (Zr,Nb)₂Fe, Fe exists at the lattice site of 32e while Zr and Nb

occupy the position of 48f and 16c [34]. During the initial state of oxidation, iron diffused inward from the surface area and gradually aggregated at a certain distance. With the growth of oxide layer, Fe began to saturation since negligible small amounts can be incorporated into the zirconia [31]. The diffusion coefficient of iron in zirconia is as low as $10^{-26} \text{ m}^2 \text{ s}^{-1}$ at the experiment temperature [20], thus the diffusion of Fe fell behind the formation of $t\text{-ZrO}_2$. It is interesting to find the formation of $\alpha\text{-Fe}$ surrounded by $t\text{-ZrO}_2$ with semi-coherent interface (Fig. 3c). Thus it is quite reasonable to conclude that $\alpha\text{-Fe}$ could stabilize tetragonal ZrO_2 . The epitaxial formation of $\alpha\text{-Fe}$ and $t\text{-ZrO}_2$ provided a strong anchoring between $(200)_{t\text{-ZrO}_2}$ and $(110)_{\alpha\text{-Fe}}$, which suppressed the martensitic transformation from $t\text{-ZrO}_2$ to $m\text{-ZrO}_2$. It has been reported that the epitaxial formation with orientation relationship could be an import factor for the stabilization of the growing phases [35-37].

To further identify our point, $\text{Zr}_x\text{Fe}_y\text{Nb}$ ternary system with different Fe / Nb ratio was also melted and corroded at same corrosion environment. X-ray diffraction patterns were scanned over the Bragg angle range from 26° to 38° , which contains the most prominent diffraction peaks of $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$. Fig. 4 shows that the content of $t\text{-ZrO}_2$ phase increases with the iron content.

4. Conclusions

The oxidation process of Ti_2Ni -type $(\text{Zr},\text{Nb})_2\text{Fe}$ under simulated reactor conditions is discussed. The effect of iron on the oxide characteristics was investigated for the non-irradiated Zr-Fe-Nb ternary system. As for the oxide layer formed on Ti_2Ni -type $(\text{Zr},\text{Nb})_2\text{Fe}$ intermetallic, dominant $m\text{-ZrO}_2$ and typical nano-crystalline $t\text{-ZrO}_2$ were found. The defects and dislocations formed in $m\text{-ZrO}_2$ may contribute to its amorphization. The redistribution of Fe was confirmed, which resulted in the formation of an epitaxial growth of $\alpha\text{-Fe}$ and $t\text{-ZrO}_2$. The orientation relationship between $t\text{-ZrO}_2$ and $\alpha\text{-Fe}$ was: $[001]_{t\text{-ZrO}_2} // [010]_{\alpha\text{-Fe}}$, $(200)_{t\text{-ZrO}_2} // (110)_{\alpha\text{-Fe}}$. The $t\text{-ZrO}_2$ was retained around / by the $\alpha\text{-Fe}$. The fact that $t\text{-ZrO}_2$ could be stabilized by Fe addition was further verified by the ternary compounds with different Fe content.

Acknowledgement

The authors acknowledge the financial support from the State Nuclear Baoti Zirconium Industry Company (SNZ), the National Science Foundation of China [grant number: 51001091, 51571182, 111174256, 52110774]. This work was also supported partially by Henan province education department [grant number: 13A430643].

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Figure caption:

Fig. 1 (a) XRD patterns of the as-casted $\text{Zr}_{60}\text{Nb}_7\text{Fe}_{33}$ sample before and after oxidation, Rietveld plot of Ti_2Ni -type phase reported by Ref [23] was shown as reference; (b) HAADF pattern of the oxide film formed in the $\text{Zr}_{60}\text{Nb}_7\text{Fe}_{33}$ sample; the chemical composition of Zr, Fe, Nb, O measured using EDX detector across the line marked '1'. The oxide surface and metal substrate was indicated.

Fig. 2 Oxide film formed on the oxide-water interface of the sample: (a) bright field image, SAD pattern of the dotted circle was also inserted; (b, c) HRTEM patterns from region marked with black square and IFFT was also inserted. The defect was indicated by a black arrow.

Fig. 3 Oxide film formed in the middle of the sample: (a) bright field image and SAD pattern corresponding to the circle 'A' was also inserted; (b) SAD pattern corresponding to the circle 'B'; (c) HRTEM pattern of a small particle marked 'C' and around region. The insert in (c) shows the FFT pattern from the two particles. The HRTEM of tetragonal ZrO_2 and interface region was also shown as (c-1) and (c-2), respectively. EDS result from area "1" and "2" was inserted.

Fig. 4 X-ray diffraction patterns of dominant peaks of ZrO_2 from the samples with different Fe/Nb ratios obtained after corroded in simulated PWR environment.

Fig. 1

Fig. 2

Fig. 3

Fig. 4