Microstructure and corrosion behavior of a Zr-Sn-Nb-Fe-Cu-O alloy fabricated by α+β quenching processing

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Abstract. In this work, the microstructure of a Zr-Sn-Nb-Fe-Cu-O alloy fabricated by α+β quenching processing (ABQ sample) was investigated by the combined utilization of scanning electron microscopy, electron backscatter diffraction and transmission electron microscopy. The results showed that the polygonal grains evenly distributed in ABQ sample and triangular grains distributed at triple junctions of polygonal grains with densely second phase particles (SPPs). The textures of 0002  directions tilted approximately 25° from normal direction and the rolling direction spreading along the 1120  - 1010  were found in the sample, which was also detected in the regularly cold rolled and annealed sample. The occurrence of corrosion kinetics transition of ABQ sample was sight earlier than that of RAX sample. Due to a higher solid solubility of β-Zr, SPPs re-dissolved into β-Zr during α+β annealing and precipitated out afterward in those areas. Finally, discrepant corrosion rate of metal matrix and SPPs led to the formation of protrusions of matrix, which could concentrate stress and generate cracks in the oxide.

Keywords: zirconium alloys, microstructure, corrosion, α+β quenching, second phase particles

1. Introduction

Because of low thermal neutron absorption cross-section, excellent waterside corrosion resistance, and appropriate mechanical properties, zirconium alloys have been successfully utilized as structural materials in nuclear industry [1-7]. The corrosion resistance of zirconium alloys has been considered as one of the most important properties to control the performance and the safety of nuclear reactors [8-10]. During corrosion, a thin oxide film forms on the metal surface by reacting with coolant [10]. This oxide can protect metal from the ingestion of oxidant. Thus, the corrosion rate decreases with the ongoing of corrosion [9]. Once the oxide reaches to a certain thickness, it splits into two layers and the corrosion kinetic transition occurs [11]. Then the corrosion resistance of alloys degrades.
The characteristics of oxide film are significantly influenced by the microstructures of alloys which are based on the processing procedure [12-15]. Ly et al. [15] suggested that a “soft” metal substrate could release the in-plane stress of oxide via creep, thus recrystallized Zircaloy-4 possessed better corrosion resistance. Park et al. [16, 17] found that HANA-4, HANA-6 and Zr–1.1Sn–0.2Nb–0.35Fe–0.15Cr–0.1Cu (in wt.%) alloys with lower final annealing temperature had better corrosion resistance and lower oxide growth. Kim et al. [14] studied the microstructure of Zr–0.4Sn–1.5Nb–0.2Fe–0.1Cr fabricated by α/β annealing after β-quenching and discovered that the increased corrosion resistance was caused by a decreased the supersaturated Nb content in the matrix by formation of β-Zr. Chen et al. [18, 19] also presented the quality of oxide is highly depend on the microstructure which is on the basis of processing procedures. Therefore, to optimize performance of zirconium alloys, it is necessary to explore new processing procedure.

In our previous work, we were successful in improving the corrosion resistance of two Zr-Sn-Nb alloys by the second β-quenching processing [18-20]. In this work, α+β quenching processing was added into the regularly cold rolled and annealed processing procedure, and then the microstructure and corrosion behavior of as-received sample were investigated. Autoclave corrosion tests were conducted up to 200 days and weight gain changes were observed as the measure of corrosion resistance of alloy. To study the corrosion mechanism, oxide cross-sectional microstructure of sample was also characterized. This work aimed to under the microstructure and corrosion behavior of a Zr-Sn-Nb-Fe-Cu-O alloy fabricated by α+β quenching processing.

2. Materials and methods

2.1. Samples preparation

Zr-Sn-Nb-Fe-Cu-O alloy was prepared by vacuum arc re-melting for three times to obtain chemical homogeneity. The alloy contains 0.55% Sn, 0.32% Fe, 0.35% Nb, 0.05% Cu, and 0.079% O and with Zr as the balance (in wt. %), where the contents of Sn, Fe, Nb and Cu were analyzed by inductively coupled plasma atomic emission spectrometry and the content of O was determined by Nitrogen/Oxygen Exterminator (TC600, LECO Corporation). The disk-shape ingot was 110 mm in diameter and 50 mm in height. After forged at 1000 °C, the height of ingots was reduced to 10 mm and then the ingots were β-quenched at 1050 °C. Afterward the sample was processed by the regularly rolled and annealed procedure [19]. Before the sample was rolled into 0.6 mm, the intermediate annealing was replaced by α+β quenching. This sample is denoted as ABQ in current work and was compared with the normal regularly cold rolled and annealed processing procedure.

2.2. Microstructure analysis

Microstructures were characterized using a FEI Sirion 200 field emission gun scanning electron microscope (SEM) and a JEOL-2100F transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector with an accelerated voltage of 200 kV. Samples for SEM observations were polished according to standard metallographic techniques and then etched in the solution containing H2O : HNO3 : HF of 9 : 9 : 2 (in vol.%). Specimens for TEM observations were prepared using a twin-jet polishing with a solution (C2H5OH : HClO4 = 9 : 1 in vol.%) at a voltage of 20 V and a temperature of −30 °C. In order to obtain the oxide cross-section fracture surface, the corroded samples were etched in the solution for 15 min to dissolve the metal substrates. Then, the oxide films extruding the metal substrates were gently fractured using a tweezer. The cross-sectional oxides and their fracture surface were coated with a gold film to improve the electrical conductivity before SEM observation.

Electron back scattering diffraction (EBSD) measurements were carried out with an AZtec HKL Max system, installed on a NOVA NanoSEM 230 scanning electron microscope. Samples prepared for EBSD measurements were polished by colloidal silica after etching. EBSD patterns were analyzed by the channel 5 software. The grain boundary angle condition used to define a grain was fixed to 10°.
The channel 5 software can also identify the degree of recrystallization via comparing the collected crystallographic data with the existing data in database.

2.3. Corrosion tests
Samples used for autoclave corrosion testing were 15 mm × 20 mm in size and chemically polished using a pickling solution (H₂O : HNO₃ : H₂SO₄ : HF = 3 : 3 : 3 : 1 in vol.%) at 30–50 °C and finally cleaned by deionized water. The corrosion resistance of the sample was evaluated by measuring their weight gain per unit surface area in relation to the exposure time (i.e. 3, 7, 14, 42, 70, 100, 130, 160, and 200 days). The corroded samples were named after their procedure number and exposure time (e.g. sample 1#-100 stands for the sample 1# after 100 days exposure, and so on). According to the ASTM-G2/88 (Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F or in Steam at 750 °F) [21], corrosion tests were conducted with a static isothermal autoclave in deionized water and 0.01 mol/L LiOH aqueous solution at 360 °C under a saturation pressure of 18.6 MPa, respectively.

3. Results and discussion

3.1. General microstructural characteristics
Figure 1 shows the general microstructural characteristics of the sample. Two shapes of grains could be found. Polygonal grains are evenly distributed and have high proportion in the sample. Triangular grains distribute at triple junctions of polygonal grains with densely SPPs as indicated by white solid arrows (figure 1(a)). Figure 1(b) is the magnified image of the dash line rectangle in figure 1(a). It is rather clean in the interior of the polygonal grains (α-grains), none of SPPs can be discovered.

![Figure 1. SEM micrographs of (a) the experimental sample, (b) is the magnified micrograph for the square regions marked in (a). The SPPs located areas are indicated as white solid arrows. The prior β grains are indicated by white hollow arrows.](image)

Figure 2 presents the TEM image for SPP in the sample studied. The particle possess face-center cubic (FCC) structure via the selected area diffraction pattern (SADP) analysis (the inset in figure 2). The chemical compositions of SPPs obtained by EDS are in a range of 3.0–8.7% Nb, 21.6–25.7% Fe, 3.5–5.9% Cu (in wt.%) and the balance is Zr. Therefore, the particles are identified as C15 type (Zr, Nb, Cu)₂Fe precipitates, which are coincide with our previous work [19, 22]. The type of SPPs has not been changed in the event of more alloying elements concentrated in the triangular grains.

β-Zr is produced at triple junctions of polygonal grains when sample is annealed at α+β region[23]. Due to larger solid solubility of β-Zr, SPPs which precipitate in the former processing steps dissolve into β-Zr grains again [24, 25]. Thus the contents of solid solution alloying elements are unbalance in different grains when α-Zr and β-Zr grains coexist. After quenching, solid solution alloying elements are kept in the prior β-Zr grains (transformed α-Zr grain). However, solid solubility of prior β-Zr is
much lower than that of β-Zr, SPPs precipitate once again at afterward processing steps. On the other hand, it is speculated that the content of alloying elements in α-Zr grains is no more than solid solution limit of α-Zr since no SPP redissolves into them while the sample is annealed at α+β region. Therefore, none of SPPs precipitate out after final annealing. This is the main reason accounting for areal distribution of SPPs.

Figure 2. TEM images of the experimental sample. The inset is the SADP of SPP.

3.2. EBSD result and texture

Figure 3 reveals EBSD inverse pole figure (IPF) map of sample. This result is good agreed with the SEM observation of microstructure. The polygonal grains with grain size of about 20–40 μm are surrounded by imperfectly identified regions. These regions are triangular grains with intensively SPPs in figure 1. Due to the small size of SPPs, EBSD analysis could not work well in distinguishing them. Nevertheless, the imperfectly analysis confirms the features of microstructure observed by SEM, and also demonstrates that the SPPs are areal distribution.

Figure 3. EBSD inverse pole figure maps for the experimental sample.
Figure 4 presents the EBSD inverse pole figure of sample. It can be easily found that strongly \( <0002> \) directions are tilted approximately 25° from the normal direction of sample (ND) and the rolling direction (RD) tends to spread along the \( <11\bar{2}0>-<10\bar{1}0> \) symmetry boundary of the stereographic triangle. Such kind of texture is always found in cold rolling or at a low temperature annealing (below 600 °C) after cold rolling zirconium alloys [19, 26-28]. In present work, cold rolling and a low temperature final annealing were carried out after \( \alpha+\beta \) quenching. It implies that compared to the regularly cold rolled and annealed processing procedure, \( \alpha+\beta \) quenching processing added into processing procedure before the last cold rolling and final annealing has not significant effect on the texture of sample. Therefore, the influence of textural variation on corrosion behavior of sample can be neglected. Furthermore, the quantitative relationship between texture and corrosion resistance has not been impeccably built up to now [28-30].

![Figure 4. EBSD inverse pole figures for the experimental sample.](image)

### 3.3. Corrosion behaviour

Figure 5.

![Figure 5. Autoclave corrosion weight gain profile of the experimental alloy (ABQ) and the regularly cold rolled and annealed sample (RAX) after 200 days at 360 °C/18.6 MPa in (a) deionized water and (b) 0.01 mol/L LiOH aqueous solution.](image)

The results of corrosion tests are obtained as shown in figure 5, which are examined in deionized water and 0.01 mol/L LiOH aqueous solution at 360 °C under a saturation pressure of 18.6 MPa, respectively. The weight gains of the regularly cold rolled and annealed sample (denoted as RAX) at same experimental conditions are used to compare with the corrosion result of ABQ, which is published in our previous work [18]. As seen from figure 5, both samples have comparative weight gains before corrosion kinetics transition. This phenomenon means both samples have almost same corrosion rate at the initial stage of corrosion experiments. Once transition occurs, an obvious gap could be found between the weight gains of ABQ and RAX in both conditions. The corrosion resistance depends significantly on the transition point. Higher corrosion resistance is related to a
longer pre-transition period [18, 31]. Hence, it indicates that the transition of ABQ takes place earlier than that of RAX. The corrosion resistance of ABQ is worse than that of RAX under the conditions of this work. Since the corrosion kinetics transition phenomenon is closely related to the oxide formed on the matrix [20], the cross-sectional microstructure of oxide of ABQ is thus investigated.

Figure 6. (a) SEM micrograph representative of the experimental alloy of oxide (cross-section) in deionized water, (b) is the magnified micrograph for the square regions marked in (a).

Figure 6 represents the cross-sectional microstructure of oxide of ABQ sample at 100 days in deionized water. The sample is still in pre-transition and a continuous oxide layer can be found. Beneath the oxide, the microstructure of metal matrix can be clearly observed in figure 6(a), which is as same as the description in figure 1. The undulated interface of oxide and metal matrix is produced by stress in oxide and matrix or diffusion of oxygen ions [18, 31-34], which is also observed in figure 6. Figure 6(b) is the magnified image of the dash line rectangle in figure 6(a). As shown by white solid arrow, the oxide is much thinner in this area. Below this area, densely located SPPs area is presented. It manifests that the corrosion of matrix is much slower in such area. Hence, discrepant corrosion rate of metal matrix and SPPs leads to the formation of protrusions of matrix. Meanwhile, such protrusions on matrix can lead to the redistribution of planar stress of oxide and trigger cracks in the oxide [20, 29, 31-33]. Therefore, the slower corrosion of matrix in densely located SPPs area may be the main reason accounting for the earlier corrosion kinetics transition of ABQ.

3.4. The possible corrosion mechanism
The precondition to obtain excellent corrosion resistance of zirconium alloys is uniform corrosion which means the corrosion rate is equivalent in the everywhere of metal surface [22, 36-38]. During inward diffusion of oxygen ions, the matrix gets oxidized. The corrosion rate has significant difference between metal matrix and precipitates [39], which depends on the nature of type of SPPs. Although SPPs can improve the corrosion resistance of zirconium alloys, they also play an important role in triggering cracks in the oxide due to their slower corrosion rate than that of matrix. More energy is needed for Fe and Nb to form oxide than Zr [40, 41]. C15 type precipitate is found in this work (figure 2), which was reported that has a slower corrosion rate than matrix [20, 39-41]. In the triangular grains area, SPPs are highly aggregated. These SPPs postpone the corrosion of alloy in such areas. Due to discrepant corrosion rate of metal matrix and SPPs, the thickness of oxide is uneven during corrosion. Therefore, protrusions form as shown in figure 6. Once protrusions form, stresses are apt to concentrate in these segments of oxide and then cracks are generated. It was reported that the cracks on the protrusions are the key factor influencing the occurrence of transition [20, 42]. Compared to the RAX sample the SPPs are evenly distributed [18], ABQ sample is liable to degrade earlier during corrosion tests. Hence, the corrosion resistance of ABQ sample is slightly worse than that of RAX sample. This work advances the understanding of applying appropriate processing procedure to keep
evenly distribution of SPPs is an important prerequisite to ensure uniform corrosion of zirconium alloy.

4. Conclusions
In this paper, the microstructure of a Zr-Sn-Nb-Fe-Cu-O alloy prepared by vacuum arc re-melting and fabricated by α+β quenching processing is investigated by the combined utilization of SEM, EBSD and TEM. The corrosion behavior and morphology of cross-sectional oxide are also studied. Some key conclusions can be drawn as follows:

β-Zr is produced at triple junctions of polygonal grains when sample is annealed at α+β region. Most alloying elements concentrate at β-Zr grains due to their larger solid solubility. SPPs precipitate out from these areas in the afterward processing. Therefore, areal distribution of SPPs forms. Strongly <0002> directions are tilted approximately 25° from the normal direction of sample and the rolling direction tends to spread along the <1120>-<1010> symmetry boundary of the stereographic triangle. This kind of texture is always found in cold rolled or at a low temperature annealing (below 600 °C) after cold rolled zirconium alloys. It indicates that adding α+β quenching into processing procedure has no significant effect on the texture of sample.

The ABQ has an earlier corrosion kinetics transition compared to RAX. The reason is that the corrosion rate of SPPs is slower than that of matrix. Therefore, the corrosion rate is much slower in the densely SPPs located area. Result from non-uniform corrosion, protrusions which concentrating stress and generate cracks in the oxide forms on the matrix. Consequently, the corrosion resistance of ABQ is worse than that of RAX.

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