Oxide Layers on (0001) Plane of Zircaloy-4 After Corrosion at 360 °C in Lithiated Aqueous Solution

Shao-Qiu Gou · Bang-Xin Zhou · Mei-Yi Yao · Jian-Chao Peng · Chuan-Ming Chen · Qiang Li · Jin-Long Zhang

Received: 19 October 2014/Revised: 27 January 2015/Published online: 21 March 2015
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2015

Abstract The microstructures of the oxide layers formed on near (0001) plane of Zircaloy-4 were investigated by autoclave tests at 360 °C in lithiated aqueous solution. Oxygen-rich regions with hcp structure were observed at the undulating O/M interface, and the inner surface morphology of the oxide layers formed on (0001) was only concave–convex. Monoclinic, tetragonal and cubic phases and a kind of zirconium sub-oxide with bcc structure were detected in the oxide layer near the metal matrix. This zirconium sub-oxide layer had a coherent relationship with α -Zr matrix, and the growth direction of the zirconium sub-oxide layer was nearly parallel to the [0001] direction of α -Zr regardless of the orientation of metal matrix. The orientations scattering of columnar grains formed on near (0001) plane differ from that formed on near (10 $\bar{1}$ 0) plane.

KEY WORDS: Zircaloy-4 (0001) plane; Oxide/metal interfaces; Microstructure; Oxygen-rich regions; Zirconium sub-oxide

1 Introduction

Zirconium alloys are widely used as nuclear fuel cladding in light water nuclear reactors, while waterside corrosion resistance of the fuel cladding is a key factor to restrict service life of high burn-up fuel assemblies. Because of the hexagonal close-packed (hcp) crystal structure, zirconium alloys have a prominent anisotropic corrosion characteristic. Kim et al. [1] investigated the corrosion behaviour of the unalloyed Zr at 360 °C in water and found that the

oxidation rate of the (11 $\bar{2}$ 0) prismatic plane was faster than that of the (0002) basal plane. Aiming at the problem of corrosion anisotropy, a lot of researches have been done and many achievements were made [2–7]. Investigation of the fine-grained Zircaloy-4 specimens with rolling texture corroded at 360 °C in lithiated aqueous solution showed the growth of oxide layer on the rolling surface (S_N) with maximum (0001) texture factors had a worse corrosion resistance than the surface with minimum (0001) texture factors [4]. Zhou et al. [7] used Zircaloy-4 coarse-grained specimens to investigate the anisotropic growth of oxide layers at 360 °C in lithiated aqueous solution and reported that the oxide layers formed on those specimens, in which the surface orientations tilted from 15° to 30° away from (0001) plane were the thickest, showing a prominent anisotropic corrosion.

The oxide/metal (O/M) interface has been a particular focus of experimental observations because oxidation reaction of zirconium alloys always occurs at this interface. Some kinds of oxygen-rich regions with a complex

Available online at <http://link.springer.com/journal/40195>

S.-Q. Gou · B.-X. Zhou (✉) · M.-Y. Yao · C.-M. Chen · J.-L. Zhang
Institute of Materials, Shanghai University, Shanghai 200072, China
e-mail: zhoubx@shu.edu.cn

J.-C. Peng · Q. Li
Laboratory for Microstructures,
Shanghai University, Shanghai 200444, China

structure and a stoichiometry different from that of both the oxide layer and the metal matrix were observed at the O/M interface [8–12]. A consistent sequence of sub-oxide phases about 150–250 nm thick was also detected ahead of the ZrO_2 oxide front [13]. Moreover, tetragonal (t) and cubic (c) phases of zirconia, which are not stable at room temperature, were observed in the oxide layer near the metal matrix [14]. These metastable phases would transform into stable monoclinic (m) phase in the subsequent evolution of the oxide layers and have an effect on the growth of oxide layers. It is generally thought that the nucleation of oxide formed on α -Zr substrate has the most favourable orientations; thus, the orientation relationship between the zirconia and α -Zr substrate is another concern with corrosion behaviour of zirconium alloys. Gong *et al.* [15] reported that the relationship of $(111)_m // (10\bar{1}0)_{\alpha\text{-Zr}}$ between m- ZrO_2 and α -Zr matrix was observed at the O/M interface of Zircaloy-4. Peng *et al.* [16] also reported that m- ZrO_2 had an orientation relationship with the α -Zr matrix, and the values of the spacing for different crystal planes compared to that of the standard m- ZrO_2 were about 5–15% smaller because of a high compressive stress produced during the formation of the oxide layer. The microstructure of the oxide layers formed adjacent to O/M interface, which could be affected by the orientation of α -Zr matrix, plays an important role in the subsequent evolution of oxide layers, and the microstructure evolution will consequently have an effect on the growth of oxide and the corrosion resistance.

A texture of (0001) plane nearly parallel to the rolling surface for the majority of grains is easy to form after cold rolling and annealing. In the process of corrosion, the growth of oxide layers on the rolling surface is the major contribution of the weight gain for flat or tubular samples, and there is obvious transition on the curve of weight gain versus exposure time for Zircaloy-4 specimens corroded in lithiated aqueous solution at 360 °C [4]. Thus, the investigation of oxide layers formed on (0001) plane is a key to make better understanding of the corrosion mechanism. As a part of the systematic investigation, the current study only aimed to address the microstructure and crystal structure of oxide layers at the O/M interface formed on a coarse grain surface with (0001) orientation during corrosion tests in autoclave at 360 °C and under 18.6 MPa in 0.01 mol/L LiOH aqueous solution. The study of $(10\bar{1}0)$ orientation has been reported in previous paper [17].

2 Experimental

In order to minimize the effect of grain boundaries on the growth of the oxide layer and investigate the microstructure

of oxide layers formed on metal grains with a particular orientation, coarse-grained specimen was a good choice to achieve these. In this study, coarse grains can be grown by annealing the specimens at 800 °C in the high-temperature alpha-phase region after water quenching from β -phase region. The details of the specimen preparation technique are described elsewhere [7, 17]. Specimens with coarse grains of 0.2–0.8 mm in diameter were obtained finally.

The specimens were pickled in a mixed acid solution of 10 vol% HF, 45 vol% HNO_3 and 45 vol% H_2O and then rinsed in boiling deionized water. In order to obtain oxide layers grown at the pre-transition stage, corrosion tests were carried out in static autoclaves at 360 °C and 18.6 MPa in 0.01 mol/L LiOH aqueous solution for 70 days. Cross-sectional thin sample of the oxide layers for TEM examination was prepared by an FEI Helios 600i Dual Beam workstation, using focus ion beam and scanning electron microscopy (FIB-SEM) in situ lift-out technique. The microstructure and crystal structure of the oxide layers formed adjacent to O/M interface were characterized by JEM-2010F HRTEM with an acceleration voltage of 200 kV, which is equipped with an INCA energy dispersive spectrometer (EDS) system. The inner surface of the oxide layers was characterized by JSM-6700F SEM after etching away the metal substrate in a mixed acid solution as mentioned above. The preparation of inner surface samples has been described in Ref. [18].

Fig. 1 TEM image of the whole thin foil sample showing the oxide layer and O/M interface

3 Results and Discussion

3.1 Oxygen-Rich Region at the Oxide/Metal Interface

Figure 1 shows a typical cross-sectional TEM image from thin foil sample prepared by FIB sectioning on the surface of a single grain. The outermost Pt layer was a protective coating which was deposited to protect oxides of interest before FIB sectioning. The mean thickness of the oxide layer was determined to be about 2.6 μm , and several micro-cracks were observed. The O/M interface was undulating, which is often observed in corrosion specimens [19–21].

Figure 2a shows the bright-field image of the metal matrix, and the selected area electron diffraction (SAED) pattern is shown in Fig. 2b. These were obtained after slightly tilting the double-tilt specimen holder ($X = -6.9^\circ$, $Y = 3.0^\circ$), and the tilt axes X and Y were shown in the lower left part of Fig. 2a. The $[12\bar{1}0]$ zone axis was parallel to the beam axis of TEM, and the $[0001]$ direction was nearly perpendicular to the line of the average O/M interface in Fig. 2a. According to the tilting rules of TEM operations, the original orientation of this single grain before corrosion testing was tilted from (0001) plane by no more than 10° . Because it was hard to obtain the Zircaloy-4 grain with strict (0001) orientation, this grain with near (0001) orientation was a reasonable choice for investigating the characteristic of the oxide layer formed on (0001) plane.

It is clearly seen that a region about 300 nm thick that is adjacent to the O/M interface in Fig. 2a had a different contrast with the oxide layer and nearby underlying metal. The chemical composition at the positions marked by the numbers was analysed by EDS, and the results are listed in Table 1. According to the results of Zr/O ratio given in Table 1, there was a significant gradient of oxygen content at the O/M interface. The oxygen content in this region (EDS 4 and 5) were between that of the oxide layers (EDS 6, 7 and 8) and the underlying metal (EDS 1, 2 and 3), so it is called “oxygen-rich region” in this paper. Figure 2c

Table 1 EDS results of the positions in Fig. 2a marked by the numbers

Position	Zr content (at%)	O content (at%)	Zr/O ratio
1	96.04	3.96	24.3
2	96.30	3.70	26.0
3	97.15	2.85	34.1
4	85.15	14.85	5.7
5	83.16	16.84	4.9
6	59.79	40.21	1.5
7	61.56	38.44	1.6
8	56.75	43.25	1.3

shows the bright-field image of the oxygen-rich regions. According to the observation, oxygen-rich regions were distributed at the O/M interface discontinuously. Figure 2d shows the SAED pattern of the oxygen-rich region, and the oxygen-rich region had the same hcp structure with α -Zr matrix by analysing the SAED pattern. In addition, the SAED pattern was obtained after slightly tilting the double-tilt specimen holder ($X = -11.8^\circ$, $Y = 0.7^\circ$) again. Thus, the crystal orientation of oxygen-rich region had a slight deflection in comparison with α -Zr matrix nearby. This phenomenon was not only related with the high stress accumulated at the O/M interface during the oxidation process, but also related with the solid solution of oxygen.

3.2 Morphology of Oxide/Metal Interface

The undulating wavy O/M interface can be found in Fig. 1, and the growth of the oxide layers is in a manner of alternating forward [17]. Figure 3 shows the inner surface of the oxide layers formed on the grain surface with an orientation near (0001) after 70 days exposure. The inner surface was concave–convex in Fig. 3a, and there were some relatively small concave–convex on the ridge strips observed at higher magnification, as shown in Fig. 3b. Based on the discussion of Fig. 2, the oxygen-rich regions

Fig. 2 **a** Bright-field image of metal matrix; **b** SAED pattern of the metal matrix; **c** bright-field image of the oxygen-rich region; **d** SAED pattern of the oxygen-rich region

Fig. 3 Inner surface morphologies of the oxide layers formed on the grain surface with near (0001) plane: **a** the inner surface was concave-convex; **b** there were some relatively small concave-convex on the ridge strips observed at higher magnification

might exist at the depressions of the inner surface discontinuously. Zhou *et al.* [22] reported that the inner surface of the oxide layers formed on the rolling surface (S_N) of the fine-grained specimens was also concave-convex, and the majority of the metal grain orientations on S_N surface were concentrated around (0001) pole. Because the orientation of metal matrix etched away in Fig. 3 was yet near (0001), it was believable that the unique characteristic of the inner surfaces was mainly attributed to the effect of (0001) orientation. Otherwise, the inner surface of the oxide layers formed on the grain surface with an orientation near $(10\bar{1}0)$ after 70-day exposure was many ridge strips which were parallel to each other along one direction [17], and the oxidation characteristics of (0001) basal plane of the Zircaloy-4 specimens were obviously different from that of $(10\bar{1}0)$ prismatic plane. It seems that the different characteristics have a relationship with the crystallographic orientations of the metal grain.

As it is known, (0001) basal plane has isotropic characteristic because of high symmetry. This unique characteristic decides that the inner surface of the oxide layers formed on the basal plane shows isotropic characteristic which has no obvious directivity, and it is consistent with the observation in Fig. 3. Because the atomic arrangements along [0001], $[10\bar{1}1]$ and $[10\bar{1}0]$ crystallographic directions are different with each other, $(10\bar{1}0)$ prismatic plane has anisotropic characteristic. There is a most preferential crystallographic direction, along which the minimum energy of oxidation reaction on $(10\bar{1}0)$ prismatic plane is required. Thus, the inner surface of the oxide layers will show the anisotropic characteristic. It is also consistent with the previous observation in Ref. [17]. Based on the above discussion, it is clearly seen that the orientation of the metal grains plays an important role in the growth of oxide layers.

3.3 Microstructure of Oxide Layers Adjacent to the Oxide/Metal Interface

The crystal structure of the oxide layers at the O/M interface has attracted a particular focus of experimental observations. Monoclinic, tetragonal and cubic phases of zirconia were also detected at some local areas [13], and the microstructure of the oxide layers adjacent to the O/M interface was more complex. In order to further study the growth mechanism of the oxide layers which is affected by the crystal orientation of the metal matrix, it is important to investigate the microstructure of the oxide adjacent to O/M interface formed on near (0001) plane.

Due to the discontinuous distribution of the oxygen-rich region, two kinds of interfaces at the O/M interface may be considered. One type of interface marked by “①” in Fig. 2a was denoted as type 1 interface, in which the oxide layers directly contact the metal matrix; another type interface marked by “②” was denoted as type 2 interface, in which oxygen-rich region existed between the oxide layers and the metal matrix.

Figure 4 shows the HRTEM image of type 1 O/M interface. Analysing the fast Fourier transformation (FFT) pattern and measuring the line spacing, the metal matrix marked by “A” was hcp structure of α -Zr, and the d values of (0002), $(10\bar{1}0)$ and $(10\bar{1}1)$ planes were 0.262, 0.283 and 0.265 nm, respectively. According to the difference of the lattice pattern in HRTEM image, the image of oxide layer part was divided into areas “B”, “C”, “D” and “E”. FFT patterns indexed for each area were incorporated.

Area “B” about 30 nm thick was formed at the O/M interface, which was convex into the metal matrix. By analysis of the FFT pattern of area “B”, this zirconium oxide was not fitted with the known zirconium oxide, including monoclinic zirconia ($m\text{-ZrO}_2$), tetragonal zirconia

Fig. 4 HRTEM image of the type 1 O/M interface and FFT patterns for the areas marked by the letters (A α -Zr matrix, B bcc-ZrO_x, C m-ZrO₂, D c-ZrO₂, E undefined structure)

(t-ZrO₂) and cubic zirconia (c-ZrO₂), and had a same body-centred cubic crystal (bcc) structure. The d values of (10 $\bar{1}$), (1 $\bar{1}$ 0) and (0 $\bar{1}$ 1) planes were 0.264, 0.263 and 0.262 nm, respectively. (10 $\bar{1}$)_{bcc} plane was parallel to (0002) _{α -Zr} plane, and they had the similar spacing value. Thus, this zirconium sub-oxide (bcc-ZrO_x) was the same as reported in Ref. [17], and the same coherent relationship of (1 $\bar{1}$ 0)_{bcc}//(0002) _{α -Zr}, [111]_{bcc}//[11 $\bar{2}$ 0] _{α -Zr} with the α -Zr matrix. By analysing the FFT patterns and measuring the lattice spacing, area “C” was m-ZrO₂ (PDF: 37-1484), and the d values of (101), (010) and (111) planes were 0.324,

0.492, and 0.266 nm, respectively. (111)_m plane was parallel to (0 $\bar{1}$ 1)_{bcc} plane, and they had a similar spacing value of crystal plane. So the m-ZrO₂ had a coherent relationship of (111)_m//(0 $\bar{1}$ 1)_{bcc}, [10 $\bar{1}$]_m//[111]_{bcc} with bcc-ZrO_x. By analysing the FFT patterns, area “D” was c-ZrO₂ (PDF: 27-997). Zhou *et al.* [14] observed c-ZrO₂ in the oxide layer. The c-ZrO₂ was not the stable phase in oxide layer of zirconium alloys, but it would exist as a metastable oxide phase because of the high compressive stress in the oxide layers. Pilling-Bedworth (P. B.) ratio of ZrO₂/Zr is 1.56, and a large stress level in the underlying metal near the

Fig. 5 HRTEM image of the type 2 O/M interface and FFT patterns for the areas marked by the letters (A oxygen-rich region, B t-ZrO₂, C m-ZrO₂, D m-ZrO₂)

O/M interface would appear to be of the order of 1–1.3 GPa [23, 24]. The metastable oxide phase can be stabilized under high compressive stress at O/M interface [25].

Figure 5 shows the HRTEM image of type 2 O/M interface. The oxygen-rich region marked by “A” had hcp structure according the FFT pattern. According to the difference of the lattice pattern in HRTEM image, the image of the oxide layer was divided into areas “B”, “C” and “D”.

By analysing the indexed FFT patterns and measuring the line spacing, area “B” in Fig. 5 was t-ZrO₂ (PDF: 50-1089), which was about 15 nm in diameter at the O/M interface. The d values of (1 $\bar{1}$ 0), (011) and (101) planes were 0.255, 0.290 and 0.29 nm. The oxide layers that formed on zirconium alloys during autoclave tests are composed of monoclinic and tetragonal phases, particularly near the O/M interface [26, 27]. There are a number of factors to stabilize the tetragonal phase down to room temperature, which include compressive stress, grain size, oxygen vacancies and alloying elements [26–31]. Both of the areas “C” and “D” were m-ZrO₂, as analysed from the FFT patterns in Fig. 5. The d values of (100), (01 $\bar{1}$) and (11 $\bar{1}$) planes of m-ZrO₂ for area “C” were 0.255, 0.290 and 0.291 nm, respectively. (11 $\bar{1}$)_m plane of area “C” was parallel to (011)_t plane of area “B”, and they had the similar spacing value of crystal plane. Thus, the m-ZrO₂ of area “C” had a coherent relationship of (11 $\bar{1}$)_m//(011)_t, [011]_m//[11 $\bar{1}$]_t with t-ZrO₂. As the oxidation process was going on in the subsequent autoclave tests, the microstructure evolution of the oxide layers occurred. Tetragonal phase would transform into monoclinic phase, and

the volume of ZrO₂ would be about 3–5% bigger because of the $t \rightarrow m$ transformation. As a result, higher internal stress levels induced by this transformation would be produced, more columnar grains would be destroyed and transform to the equiaxed grains, and simultaneously more micro-cracks would be produced in oxide layers [28]. Conversely, these would promote further the microstructural evolution of oxide layers.

The inverse fast Fourier transformation (IFFT) images of (1 $\bar{1}$ 0), (101) and (011) planes for t-ZrO₂ of area “C” are shown in Fig. 6, respectively. The IFFT images indicated that the lattice fringes of this area had severe distortion, and a large number of dislocations existed, which are indicated by arrows. Because of the larger number of defects, there was high strain energy contained in this area. On the one hand, it was beneficial for the diffusion of the oxygen vacancies and promoted the oxidation process. On the other hand, the migration of dislocations and the release of stress provided a favourable condition for the transformation of $t \rightarrow m$ phase. The severe distortion and a large number of the dislocations would provide power in the subsequent microstructural evolution of the oxide layer.

3.4 Zirconium Sub-Oxide with Body-Centred Cubic Crystal Structure

Through the analysis of the microstructure and crystal structure of the oxide layer, the bcc-ZrO_x was not only observed at the O/M interface on the metal grain surface with an orientation near (0001), but also detected on that with an orientation near (10 $\bar{1}$ 0) [17]. They had the similar crystal

Fig. 6 Reconstruction of the phase-contrast image of the area marked by “B” in Fig. 5

Fig. 7 HRTEM images of bcc-ZrO_x that formed on metal grain with an orientation near (10 $\bar{1}$ 0)

structure and kept the same coherent relationship of $(1\bar{1}0)_{\text{bcc}}// (0002)_{\alpha\text{-Zr}}$, $[111]_{\text{bcc}}// [11\bar{2}0]_{\alpha\text{-Zr}}$ with the $\alpha\text{-Zr}$ matrix. Because of the coherent relationship, the formation of this bcc-ZrO_x as transient phase decreased the total energy of oxidation of zirconium alloys through $\alpha\text{-Zr} \rightarrow \text{bcc-ZrO}_x \rightarrow \text{m-ZrO}_2$ phase transformation [17]. This bcc-ZrO_x formed on both grains with different orientations and still kept the strict coherent relationship regardless of the matrix orientation. It is obvious that bcc-ZrO_x has a relationship with the anisotropic corrosion of zirconium alloys. Therefore, it was significant to figure out the relationship in order to further understand the mechanism of anisotropic corrosion.

Figure 7 shows the HRTEM images of bcc-ZrO_x that formed on metal grain with an orientation near (10 $\bar{1}$ 0). The corresponding FFT images of marked areas are incorporated in Fig. 7. The shape of bcc-ZrO_x formed directly on the $\alpha\text{-Zr}$ matrix was like a strip, and the length direction of this strip was nearly parallel to the [0001] crystallographic direction of $\alpha\text{-Zr}$ matrix. Figure 8 shows the HRTEM images of bcc-ZrO_x that formed on metal grain with an orientation near (0001). It was obvious that the area of bcc-ZrO_x as a finger was perpendicular to the O/M interface and inserted into the metal matrix. Combined with the FFT images of marked areas incorporated in Fig. 8, the growth

Fig. 8 HRTEM images of bcc-ZrO_x that formed on metal grain with an orientation near (0001)

direction of bcc-ZrO_x area was nearly parallel to the [0001] direction of α -Zr. Moreover, the convex direction of bcc-ZrO_x was also parallel to the same crystallographic direction of α -Zr in Fig. 4. Based on the above analysis, it was clearly seen that the bcc-ZrO_x could be detected in different locations at O/M interface, and the growth direction of them, which showed different shape, was nearly parallel to the [0001] crystallographic direction of α -Zr regardless of the orientation of metal matrix.

Based on the discussion of Fig. 3, it can be known that the inner surface morphology of oxide layers was mainly attributed to the orientation of metal grain. However, the reason why the inner surface morphology will be affected by the orientation of metal grains should be revealed. It seems that the unique morphology of inner surface is affected by the growth of bcc-ZrO_x, which has a coherent relationship with metal matrix. The shape of bcc-ZrO_x was similar to the directional ridge strip of inner surface on metal grain with an orientation near (10 $\bar{1}$ 0), and the growth direction of them was nearly parallel to the [0001] crystallographic direction of α -Zr. Thus, the [0001] might be the most preferential crystallographic direction, along which the less energy of oxidation reaction was required. When bcc-ZrO_x grew on the O/M interface with (0001) orientation of α -Zr matrix, the growth direction of bcc-ZrO_x was vertical to the O/M interface. Therefore, it can be

understood that the inner surface morphology of oxide layers formed on (0001) was only concave–convex surface without the directional ridge strips.

3.5 The Difference of Oxide Layers Formed on (0001) and (10 $\bar{1}$ 0) Planes of α -Zr Matrix

Figure 9 shows the SAED patterns and dark-field TEM images of the oxide layers formed on near (0001) plane and near (10 $\bar{1}$ 0) plane. The SAED patterns of each oxide layer were analysed in order to investigate the crystal structure of both oxide layers, and the results indicated that both oxide layers with extremely fine grains have a small amount of tetragonal phase besides the majority of monoclinic phase. Several investigators have suggested that the crystal structure and orientation distributions of nanometre grains in oxide layers formed on different metal grains were obviously different [32]. By comparing the SAED patterns in Fig. 9, it can be seen that a semi-continuous diffraction rings were formed in the SAED pattern of oxide on near (0001) plane, but a pattern similar to a single crystal diffraction were observed in the SAED pattern of oxide on near (10 $\bar{1}$ 0) plane. Therefore, it indicated that the scattering of grain orientations in the oxide layer formed on near (0001) plane was wider than that in the oxide layer on near (10 $\bar{1}$ 0) plane. This difference of orientation scattering can

Fig. 9 SAED patterns of the oxide layers formed on near (0001) plane **a**, near (10 $\bar{1}$ 0) plane **b**, the corresponding dark-field TEM images obtained from the oxide layers on near (0001) plane **c**, near (10 $\bar{1}$ 0) plane **d**

also be seen clearly by comparing the corresponding dark-field TEM images, which were taken with the same $(\bar{1}11)_m$ diffraction spots from two SAED patterns (see Fig. 9c, d), respectively. The columnar grain structure can be easily identified from dark-field images by bright/dark diffraction contrast. Some sub-grains, showing by small bright spots and <20 nm in size, can be also seen within a single columnar grain. The columnar grains were separated from each other in Fig. 9a, and it means that the orientation of columnar grains in oxide layer formed on near (0001) plane was much different. But more columnar grains were connected each other in Fig. 9b, and it means that the orientation of columnar grains in oxide layer formed on near (10 $\bar{1}$ 0) plane was coincident.

Some researchers had reported that the corrosion resistance of zirconium alloys, which is also the growth rate of oxide layers in other words, was related with the microstructural evolution of oxide layers during the corrosion process [14, 22]. However, the microstructural evolution was affected by several factors, which included the water chemistry, the composition of alloy and the initial microstructure of oxide layers formed at the O/M interface.

In this study, due to metal grains having the same composition of alloy and corroded at the same water chemistry, the microstructural evolution of oxide layers on two different metal grains was mainly determined by the initial microstructure of oxide layers. Yilmazbayhan *et al.* [8] reported that zirconium alloys with lower corrosion rates exhibited more well-oriented columnar grains in oxide layers, whereas zirconium alloys with higher corrosion rates exhibited smaller equiaxed grains and mis-oriented columnar grains. During the corrosion process, the microstructural evolution of oxide layers can be easily promoted in the oxides with high stress, high density of defects and large scattering of columnar grain orientations. In Fig. 9, the orientation scattering of columnar grains formed on near (0001) plane had much of a difference, and the microstructure of oxide layers was more complicated than the oxides on near (10 $\bar{1}$ 0) plane, so the growth rate of oxide

layers formed on the near (0001) plane would show a worse corrosion resistance in subsequent corrosion tests at 360 °C and 18.6 MPa in 0.01 mol/L LiOH aqueous solution. These results have been confirmed by the results in Ref. [7], and it is believed that the microstructural difference of oxide layers affected by the orientation of α -Zr matrix at O/M interface plays an important role in the microstructural evolution of oxide layers and has an indirect effect on the corrosion resistance of zirconium alloys.

4 Conclusions

The investigation of the microstructure and crystal structure of oxide layers formed on near (0001) plane was carried out using Zircaloy-4 coarse-grained specimens by autoclave tests at 360 °C and 18.6 MPa in 0.01 mol/L LiOH aqueous solution for 70 days. The main conclusions are as follows:

- (1) Oxygen-rich regions in discontinuous distribution were observed at the O/M interface, which had the same hcp structure with α -Zr matrix. The inner surface morphology of the oxide layers was concave-convex, and this unique morphology of oxide layers was mainly attributed to the near (0001) orientation of metal matrix.
- (2) The microstructure and the crystal structure of the oxide layers at the O/M interface were very complex. Monoclinic, tetragonal and cubic phases were detected in the oxide layer near the metal matrix, and the m-ZrO₂ had a coherent relationship of $(11\bar{1})_m // (011)_t$, $[011]_m // [11\bar{1}]_t$ with t-ZrO₂. A zirconium sub-oxide layer with bcc structure was observed between underlying metal and m-ZrO₂, which had a finger shape inserted into the metal matrix and had an coherent relationship of $(1\bar{1}0)_{bcc} // (0002)_{\alpha-Zr}$, $[111]_{bcc} // [11\bar{2}0]_{\alpha-Zr}$ with α -Zr matrix and $(0\bar{1}1)_{bcc} // (111)_m$, $[111]_{bcc} // [10\bar{1}]_m$ with m-ZrO₂.

- (3) The growth direction of zirconium sub-oxide layer was nearly parallel to the [0001] direction of α -Zr regardless of the metal matrix with near (0001) plane or (10 $\bar{1}0$) plane. The growth direction of zirconium sub-oxide layer might affect the unique morphology of inner surface of oxide layers.
- (4) The orientation distribution of columnar grains in oxide layer formed on near (0001) plane was more scattered than that formed on near (10 $\bar{1}0$) plane. The microstructural evolution of oxide layers can be promoted in the oxides with high stress, high density of defects and large scattering of columnar grain orientations. The growth of oxide layers formed on the near (0001) plane would show a worse corrosion resistance in subsequent corrosion tests in LiOH aqueous solution at 360 °C.

Acknowledgments The authors would like to express their thanks to Dr. Pengfei Hu, Mrs Xue Liang and Mr. Yuliang Chu of Instrumental Analysis and Research Centre of Shanghai University for help in the microstructure analysis. This study was financially supported by the National Natural Science Foundation of China (Nos. 51171102 and 51271104).

References

- [1] H.J. Kim, T.H. Kim, Y.H. Jeong, J. Nucl. Mater. **306**, 44 (2002)
- [2] G. Bakradze, P.H. Jeurgens, J. Mittemeijer, Surf. Interface Anal. **42**, 588 (2010)
- [3] D. Charquet, R. Tricot, J.F. Wadier, paper present in: Zirconium in the Nuclear Industry, 8th International Symposium, West Conshohocken, ASTM STP 1023, (1989), pp. 374–388
- [4] G.C. Sun, B.X. Zhou, M.Y. Yao, S.J. Xie, Q. Li, Acta Metall. Sin. **48**, 1103 (2012). (in Chinese)
- [5] J. Favregeon, T. Montesin, G. Bertrand, Oxid. Met. **64**, 253 (2005)
- [6] C.S. Zhang, B.J. Flinn, I.V. Mitchell, P.R. Norton, Surf. Sci. **245**, 373 (1991)
- [7] B.X. Zhou, J.C. Peng, M.Y. Yao, Q. Li, S. Xia, C.X. Du, G. Xu, paper present in: Zirconium in the Nuclear Industry: 16th International Symposium, ASTM STP 1529, ASTM International, (2011), pp. 620–646
- [8] A. Yilmazbayhan, E. Breval, A.T. Motta, R.J. Comstock, J. Nucl. Mater. **349**, 265 (2006)
- [9] P. Bossis, G. Lelievre, P. Barberis, X. Iltis, F. Lefebvre, L. Thomas, M. Maguire, paper present in: Zirconium in the Nuclear Industry: Twelfth International Symposium, ASTM International, (2000), pp. 918–945
- [10] B. Wadman, Z. Lai, H.O. Nystrom, L.A. Nystrom, P. Rudling, H. Pettersson, paper present in: Zirconium in the Nuclear Industry: Tenth International Symposium, ASTM International, Baltimore, (1993), pp. 579–598
- [11] S. Abolhassania, G. Barta, A. Jakobb, J. Nucl. Mater. **399**, 1 (2009)
- [12] H. Anada, K. Takeda, paper present in: Zirconium in the Nuclear Industry: Eleventh International Symposium, American Society for Testing and Materials, Garmisch-Partenkirchen, Germany, (1995), pp. 35–54
- [13] Y. Dong, A.T. Motta, E.A. Marquis, J. Nucl. Mater. **442**, 270 (2013)
- [14] B.X. Zhou, Q. Li, M.Y. Yao, W.Q. Liu, Y.L. Chu, Corros. Prot. **30**, 589 (2009)
- [15] W.J. Gong, H.L. Zhang, Y. Qiao, H. Tian, X.D. Ni, Z.K. Li, X.T. Wang, Corros. Sci. **74**, 323 (2013)
- [16] J.C. Peng, MS Thesis, Shanghai University, 2009
- [17] S.Q. Gou, B.X. Zhou, C.M. Chen, M.Y. Yao, J.C. Peng, X. Liang, J.L. Zhang, Q. Li, Corros. Sci. **92**, 237 (2015)
- [18] M.Y. Yao, B.X. Zhou, Q. Li, W.Q. Liu, X. Geng, Y.P. Lu, J. Nucl. Mater. **374**, 197 (2008)
- [19] M. Paris, R. Foerch, G. Cailletaud, J. Phys. IV France **9**, 311 (1999)
- [20] D.S. Balint, J.W. Hutchinson, Acta Mater. **51**, 3965 (2003)
- [21] V. Likhanskii, M. Kolesnik, Corros. Sci. **87**, 416 (2014)
- [22] B.X. Zhou, Q. Li, W.Q. Liu, M.Y. Yao, Y.L. Chu, Rare Met. Mater. Eng. **35**, 1009 (2006). (in Chinese)
- [23] D.J. Park, J.Y. Park, Y.H. Jeong, J. Nucl. Mater. **412**, 233 (2011)
- [24] H.J. Beie, A. Mitwalsky, F. Garzarolli, H. Ruhmann, H.J. Sell, paper present in: Zirconium in the Nuclear Industry: 10th International Symposium, ASTM STP 1245, ASTM International, (1994), pp. 615–643
- [25] H. Arashi, M. Ishigame, Phys. Stat. Solidi A **71**, 313 (1982)
- [26] H.X. Zhang, D. Fruchart, E.K. Hill, L. Ortega, Z.K. Li, J.J. Zhang, J. Sun, L. Zhou, J. Nucl. Mater. **396**, 65 (2010)
- [27] E. Polatidis, P. Frankel, J. Wei, M. Klaus, R.J. Comstock, A. Ambard, S. Lyon, R.A. Cottis, M. Preuss, J. Nucl. Mater. **432**, 102 (2013)
- [28] W. Qin, C. Nam, H.L. Li, J.A. Szpunar, Acta Mater. **437**, 280 (2007)
- [29] R.C. Garvie, J. Phys. Chem. **69**, 218 (1965)
- [30] S. Fabris, A.T. Paxton, M.W. Finnis, Acta Mater. **50**, 5171 (2002)
- [31] P. Ghigna, G. Spinolo, U. Anselmi-Tamburini, F. Maglia, M. Dapiaggi, G. Spina, L. Cianchi, J. Am. Chem. Soc. **121**, 301 (1999)
- [32] C.X. Du, J.C. Peng, H. Li, B.X. Zhou, Acta Metall. Sin. **47**, 887 (2011). (in Chinese)