



Grain morphology and crystal structure of pre-transition oxides formed on Zircaloy-4

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ABSTRACT

Grain morphology and crystal structure of pre-transition oxides formed on a Zircaloy-4 alloy were investigated. The results show that monoclinic columnar grains align tightly in inner oxides, whereas porous monoclinic equiaxed grains exist in outer oxides. Small-sized tetragonal equiaxed grains are embedded in monoclinic columnar grains, with tetragonal phase content declining from the inner to the outer oxides. The crystallographic orientation relationship of $(111)_m // (10\bar{1}0)_{\alpha-Zr}$ was identified, which explains well the formation of monoclinic texture on the zirconium substrate. This work advances the understanding of corrosion properties before transition of oxidation of zirconium alloys.

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1. Introduction

Zirconium alloys have been used as fuel cladding materials in nuclear power plants since 1950s due to their low thermal neutron absorption, reasonable mechanical properties, and good corrosion resistance. In the last twenty years, higher burn-up and extended operating time are becoming a great challenge to the corrosion resistance of nuclear claddings in water-cooled reactors. Several new zirconium alloys including ZIRLO[®], M5[®], HANA-4, and HANA-6 have accordingly been developed. The understanding of waterside oxidation mechanism is necessary for the improvement of corrosion resistance of new zirconium alloys. So far numerous researches have been carried out to clarify the correlation between zirconium oxide structure and corrosion properties of zirconium alloys. A transition behavior of the oxidation kinetics is widely reported. Interestingly, the oxide layers and their grain morphology are consistent with a transition periodicity [1–6]. The transition is generally thought to be related to the change in oxide microstructure. These include phase transformation of ZrO₂ from tetragonal to monoclinic, grain morphology transformation from columnar to equiaxed, accumulation of compressive stresses induced by volume expansion, and development of large-scale cracks and porosity [2,7]. Recently, undulations of the oxide/metal interface that promote nucleation of microcracks in the vicinity of the interface are also suggested relevant to the transition [8,9]. It is still

argued in literature which is the decisive factor responsible for the transition of oxidation kinetics.

The grain morphology and crystal structure of oxides formed on zirconium alloys are essential to the interpretation of transition of oxidation kinetics. The grain morphology and crystal structure are mainly characterized by microbeam X-ray diffraction (XRD) [2,3], Raman spectroscopy [10] and transmission electron microscopy (TEM) [4,6,11]. The characterization methods would cause a problem when determining the correlation between grain morphology and crystal structure. The oxide grain size is calculated from peak broadening of XRD [2,6]. Nevertheless, the calculation of grain size by the Scherrer equation could be inaccurate, since the peak broadening is not only connected to small grain size but also to stresses in oxides [2]. Raman spectroscopy is capable of examining the crystal structure along the depth to the oxide/metal interface; however, the grain morphology of oxides cannot be detected. High resolution transmission electron microscopy (HRTEM) is thus needed to simultaneously identify the grain morphology and crystal structure. Kim et al. [12] investigated the pre-transition oxides formed on a Zr–0.4Nb alloy by high voltage electron microscopy (HVEM) and found a complex morphology of equiaxed and columnar grains. But in their study, a thick TEM sample (>100 nm) is prepared and two or more oxide grains can be involved along the direction parallel to electron beam. The thick sample greatly restricts the characterization of grain morphology and crystal structure of oxides. To the best of the authors' knowledge, explicit correlation between grain morphology and crystal structure of oxide films formed on zirconium alloys is rarely reported. Recently, focus ion beam (FIB) is widely used for the preparation of TEM foils

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with a thickness <100 nm [9,13]. In this study, we have performed detailed characterization on pre-transition oxides formed on Zircaloy-4 by using HRTEM with the aid of FIB-prepared samples. Based on the high-quality HRTEM images achieved, the correlation between grain morphology and crystal structure in the pre-transition oxides can be established. We demonstrate that a tetragonal equiaxed grain with a small size is embedded in monoclinic columnar grains with a large size. This finding proves that ZrO_2 tetragonal phase can be stabilized by small grain size in addition to compressive stresses.

The formation mechanism of textured oxide films is another concern with corrosion behavior of zirconium alloys. It is well known that intensive textures exist in both zirconium alloys and monoclinic oxide films grown on zirconium substrate [6,14–16]. The monoclinic texture in the oxide films is mainly characterized by XRD. Yilmazbayhan et al. [6] show that the $(200)_m$ and $(002)_m$ planes of oxides on Zircaloy-4 are oriented nearly parallel and perpendicular to the oxide growth direction, respectively. Lin et al. [16] detected different monoclinic oxide textures formed on Zircaloy-4 and Zr–2.5Nb. Both researches [6,16] state that the monoclinic oxide texture does not vary with distance from the oxide/metal interface. Moreover, the crystallographic orientation relationship between oxide texture and zirconium substrate is not presented. As a main phase of the oxide films, the monoclinic texture determines the integrity of oxide layers and therefore dominates the oxidation kinetics. The formation mechanism and microstructural evolution of the monoclinic oxide texture are required in order to elucidate both the pre- and post-transition behavior of zirconium alloys. In this study, the formation mechanism of monoclinic oxide texture on Zircaloy-4 is proposed based on the orientation relationship of $(111)_m // (10\bar{1}0)_{\alpha-Zr}$ identified at the oxide/metal interface.

The present work is to give new insights into the formation mechanism of pre-transition oxides on Zircaloy-4, allowing for a better understanding of corrosion behavior of zirconium alloys in an oxidizing environment at high temperature. To this end, the grain morphology and crystal structure of the oxide films are characterized as a function of distance from the oxide/metal interface. The crystallographic orientation relationship between the formed oxides and zirconium substrate is also clarified.

2. Experimental

Zircaloy-4 sheets (Northwest Institute for Non-ferrous Metal Research, China) were employed, with chemical compositions as given in Table 1. The microstructure of the as-received alloy was examined by a polarized light optical microscope (OM, Zeiss Axio Imager, Germany). Prior to OM observations, the alloy was electro-polished at 0 °C in a solution of 5 vol.% $HClO_4$ and 95 vol.% C_2H_5OH . As shown in Fig. 1, the alloy displayed fully recrystallized equiaxed grains with a grain size of $\sim 3.8 \mu m$.

Samples of $30 \times 25 \times 4$ mm in size were cut from the as-received sheets, mechanically ground with 2000 grit SiC paper, and then pickled in a solution of 40 vol.% H_2O , 30 vol.% HNO_3 , 25 vol.% HCl , and 5 vol.% HF . In order to obtain pre-transition oxides, a short-term corrosion test was conducted for 72 h in a static autoclave, in 400 °C/10.3 MPa pure steam to simulate a nuclear reactor environment according to ASTM G2-88. After corrosion tests, the thickness of the oxide films formed was estimated by

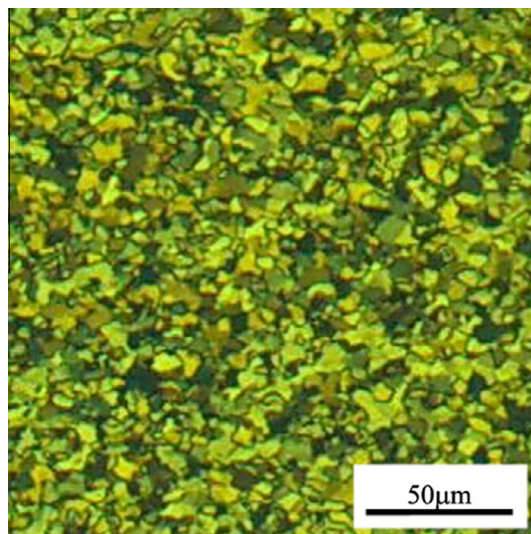


Fig. 1. Optical microscopy of the as-received Zircaloy-4 alloy.

measuring the weight gain of sample. The thickness was determined to be $\sim 1.26 \mu m$ according to the relationship of $1 \mu m = 15 \text{ mg/dm}^2$ [2].

The phase structure of the oxide films was analyzed by using grazing incidence X-ray diffraction (GIXRD, Rigaku D/max2550HB+/PC, Japan). The XRD was performed on the surface of the oxide films. Based on the thickness of $\sim 1.26 \mu m$ of oxide films determined by the weight gain method, grazing incidence angles 1° , 2° , and 3° were chosen for XRD characterization and the corresponding X-ray probing thickness was estimated to be 0.5, 1.2, and $2.0 \mu m$, respectively [15]. The results are shown in Table 2. A peak to peak analysis of the XRD patterns was carried out in the diffraction angle range of $20\text{--}40^\circ$ for phase identification [15,17]. The textures in both the zirconium substrate and oxides were characterized by a $\theta\text{--}2\theta$ scan in XRD (Cu $K\alpha$ radiation, Rigaku SmartLab, Japan). The 2θ angles of 32.02° , 31.47° and 28.22° were used to determine the pole figures of $(10\bar{1}0)_{\alpha-Zr}$, $(111)_m$ and $(\bar{1}11)_m$, respectively. In order to improve the precision of determination, a fine step of 2° was used for the azimuthal angle α ($0\text{--}70^\circ$) and a step of 1° for the polar angle β ($0\text{--}360^\circ$). Pole figures were recalculated using a programme named THCLXPD (Tsinghua University, China).

Cross-sectional samples of the oxide films were prepared by FIB with 2–30 kV Ga^+ incident beam voltage and 50 pA–16 nA beam current. The FIB-prepared sample was observed by scanning electron microscopy (SEM, Zeiss AURIGA CrossBeam workstation, Germany) using an acceleration voltage of 5 kV. The FIB technique avoids stresses induced by mechanical polishing and provides better quality of SEM images for oxides. The cross-sectional samples were further thinned to <100 nm by FIB milling to prepare foils for TEM observations. Low-energy (2 kV, 50 pA) gallium ions were used in the final milling step to remove FIB-induced damages. Grain morphology and crystal structure of the oxides as a function of distance from the oxide/metal interface were characterized by TEM (FEI Tecnai F20, The Netherlands). An accelerating voltage of

Table 2
Calculated t-ZrO₂ contents for different grazing incidence angles.

Grazing incidence angle (°)	Probed thickness (μm)	t-ZrO ₂ content (%)
1	0.5	4.3
2	1.2	7.4
3	2.0	12.5

Table 1
Chemical compositions of the Zircaloy-4 alloy investigated (wt.%).

Sn	Fe	Cr	O	Zr
1.46	0.22	0.11	0.12	Bal.

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