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TEM study on the initial oxidation of Zircaloy-4 thin foil specimens heated in a low vacuum air condition at 280–300 °C

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ABSTRACT

As one of the important structural materials in nuclear industry, the corrosion resistance of zirconium alloy limits their in-pile application. Therefore, it is necessary to investigate the corrosion mechanism of zirconium alloys. The zirconium-oxygen reaction at the O/M interface is one of the factors that affect the oxidation process. There are few reports in this regard. Ideally, the reaction process at the O/M interface has certain relevance with the initiation oxidation of zirconium, which provided a new way to investigate the reaction process by observing the initiation oxidation behaviours. To investigate the oxidation behaviours of zirconium alloy at the initial stage, in this paper, zircaloy-4 TEM thin foil specimens in 3 mm diameter were studied by TEM observation after heating in air condition with a vacuum of 3 Pa at 280 °C, 290 °C and 300 °C for 30 min exposures. The results show that, ZrO_2 begin to nucleate at a size of 3–5 nm at a high Zr/O ratio of 10.4 and oxide layer formed while Zr/O was 4.6. As a result of stress caused by the P.B ratio of Zr, slip bands formed and a bcc structure sub-oxide b-ZrOx ($a = 0.51$ nm) grew up along with the slip bands was observed. At both sides of b-ZrOx, two hcp structure sub-oxides having the same **a**-axis lattice parameter and different **c**-axis lattice parameter were detected.

1. Introduction

Zirconium alloys, as one of the important structural materials in nuclear industry, have been widely used as the fuel cladding material and the structural materials of fuel assemblies in pressurized water reactors for its low thermal neutron absorption cross section and adequately mechanical properties and corrosion resistance [1–3]. Researchers have done many works on the investigation of the corrosion resistance and the corrosion mechanism of zirconium alloys, aiming to guide the research and development of advanced zirconium alloys.

Zirconium alloys would react with high temperature and high pressure water to form an oxide layer. The oxidation process of zirconium alloys is considered to be controlled by the rate of oxygen ions diffusing through a dense protective oxide layer to the oxide/matrix (O/M) interface [4]. Therefore, the investigation on the microstructure of the oxide layer and its evolution during the corrosion process is of meaningful. Indeed, some phenomenon and microstructure of the oxide layer have been investigated by various techniques [5–15]. However, no unified theory for the corrosion mechanism of zirconium alloys was reported so far.

In recent years, people come to realize that the corrosion process of zirconium is not only controlled by the diffusion of oxygen atoms from the outside surface to the O/M interface but also the zirconium-oxygen reaction process at the O/M interface [16,17]. Different zirconium-oxygen reaction process results in different nucleation process, strain and phase composition of oxide at the O/M interface, which affects the microstructure evolution of the whole oxide layer. Therefore, to clearly understand the corrosion mechanism of zirconium alloys, it is necessary to investigate the zirconium-oxygen reaction process at the O/M interface. However, it is difficult to observe the reaction process and ZrO_2 nucleation process at the O/M interface because that it occurs at a thin region. Ideally, the reaction process at the O/M interface has relevance with

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the initiation oxidation on the surface of zirconium, which provided a new way to investigate the reaction process by observing the initiation oxidation behaviours.

The results obtained by recent studies [16–20] have demonstrated that, oxidation behaviours in the initial stage, including the variation of the crystal structure along with the increase of oxygen contents before the formation of zirconia (ZrO_2), are very complex. The oxidation behaviour at the initial stage and the growth process of the oxide layer later do have some relationships, even though there are some differences between each other. Therefore, the investigation on the oxidation behaviours at the initial stage has an important influence on the understanding of the corrosion mechanism of zirconium alloys.

However, due to the limitation of the experimental methods and equipment, the investigation on the nucleation process of ZrO_2 and the evolution of the crystal structure at the initial stage is a hard work. Previous results [21–23] show that oxygen atoms would diffuse into α-Zr lattice with an oxygen content up to 28 at.%, forming a solid solution at the initial stage. Sanz *et al* [24] observed that, 2–5 nm thick oxide layer was firstly formed on the surface of zirconium under air condition at the room temperature. Wadman [25] and Hudson [26] *et al* reported that the oxide layer formed at the initial stage was composed of amorphous and fine-grained ZrO_2 at a size of 5–10 nm, which was thought to be consisted of unstable sub-oxide ZrO_{1-x}. However, the nucleation process of ZrO_2 at the initial stage and the influence of corrosion conditions on the nucleation process have not been entirely understood.

To investigate the oxidation behaviours of zirconium alloy at the initial stage, we once studied the nucleation of ZrO_2 by using the TEM thin foil specimens for coarse-grained Zircaloy-4 corroded at 250 °C and 280 °C in 0.01 mol/L LiOH aqueous for a short time exposure [27]. A crystal structure evolution varied along with the increase of oxygen contents before the formation of ZrO_2, a commensurable long period super-lattice 9a-2H, an ordered hcp structure Zr_3O and an ordered fcc structure ZrO were detected. In order to further study the influence of corrosion conditions on the oxidation behaviours of zirconium alloys at the initial stage, in this experiment, TEM thin foil specimens for coarse-grained Zircaloy-4 were heated in a tubular furnace with a vacuum of 3 Pa at 280 °C, 290 °C and 300 °C for 30 min exposures and the oxidation behaviours were studied by TEM observation.

2. Experimental procedure

2.1. The preparation of TEM thin foil specimens using coarse-grained samples

In order to investigate the influence of corrosion conditions on the oxidation behaviours of zirconium alloys at the initial stage, coarse-grained specimens should be prepared to minimize the effect of grain boundaries on the nucleation and growth process of ZrO_2. In this experiment, coarse grains formed by annealing the specimens at 800 °C in the high temperature α phase region after water quenching from β phase region. According to the experimental methods of the past [16,28], Zircaloy-4 samples with a composition of 1.5% Sn, 0.2% Fe, and 0.1% Cr (in mass fraction), and 8×25 mm^2 in size, were cut from a 1 mm thick plate, and pickled in a mixed acid solution of 10% HF + 45% HNO_3 + 45% H_2O (in volume), and finally cleaned in deionized water. They were vacuum sealed under 5×10^{-3} Pa in quartz capsules, solution treated at 1020 °C in β phase region for 30 min, and then quenched into water while simultaneously breaking the quartz capsules. The specimens were annealed again in a vacuum at 800 °C for 10 h to grow coarse grains after removing the thin blue oxide on the specimen surface caused by water quenching. The detail experimental procedures have been reported in the previous paper [16,27]. Finally, coarse-grained samples were annealed at 700 °C in a vacuum for 100 h to reduce the supersaturated solid solution of alloying elements in the α-Zr matrix. The average grain size of zircaloy-4 is about 0.5 mm. Coarse-grained Zircaloy-4 samples were firstly chemical polished to 70 μm thick using mixed acid solution of 10%HF + 45% HNO_3 + 45%H_2O (in volume), then punched to small discs in 3 mm diameter. Thin foil specimens for TEM observation were prepared by double-jet electro-polishing method in an electrolyte solution of 95%C_2H_5OH + 5%$HClO_4$ (in volume) at −30 °C with DC 30 V.

2.2. Oxidation tests

The oxidation rate is not easy to be controlled to form a thin oxide layer meeting the need of the observation of the microstructure and crystal structure evolution at the initial oxidation stage when the thin foil specimens are heated in the air. Therefore, a tubular furnace with a vacuum of 3 Pa (air) obtained by a vacuum pump is used for oxidation tests. In addition, the heating temperature and holding time also need to be considered to prevent the specimens from over-oxidizing. After many attempts, the oxidation tests are determined to be heated at 280 °C, 290 °C and 300 °C for 30 min in the air condition with a vacuum of 3Pa.

2.3. Observation and analysis for oxidized specimens

Energy dispersion spectrometer (EDS) and selected area electron diffraction (SAED) equipped on a JEOL-2010F are used to determine the qualitative oxygen contents and crystal structure in the regions around the hole after oxidation tests. The size of the aperture used for the SAED is 175 nm.

The EDS results are inaccurate for light elements such as carbon, nitrogen and oxygen. Therefore, the EDS result of oxygen in this experiment is qualitative. We need a comparable value to measure the oxidation level of the TEM foil specimen. What should be clear is that, in this experiment, the oxygen content is the average level of the region containing matrix and oxide layer but not the oxygen content of an oxide layer. The EDS-affected zone passed by the electron beam is a cylinder (see Fig. 1). Supposing that x_0 is the oxygen concentration per unit volume in the oxide layer and the zirconium concentration per unit volume is $1\text{-}x_0$, and then, the number of oxygen and zirconium atoms in the EDS-affected zone are $N_1 = 2\pi r^2 x_0 h$ and $N_2 = 2\pi r^2 h(1\text{-}x_0) + \pi r^2 (H\text{-}2h)$, respectively. The Zr/O atomic ratio could be determined as:

$$\text{Zr/O ratio} = N_2/\,N_1 = H/2hx_0 - 1 \qquad (1)$$

where x_0 is a constant value, therefore, the Zr/O ratio could partially reflects the oxidation level of this region. The Zr/O ratios can be used to compare the oxidation level in the region of approximately equal thickness.

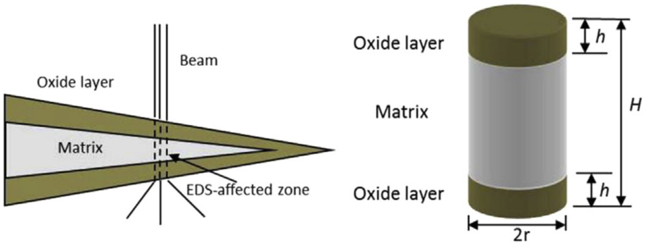

Fig. 1. The schematic diagram of the oxidized TEM foil specimen and the EDS-affected zone.