



Short Communication

The role of alloying elements in the initiation of nanoscale porosity in oxide films formed on zirconium alloys



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ABSTRACT

Zr–Nb–Y alloys were used to investigate the initiation mechanism of nanoscale pores in the oxide films formed on zirconium alloys. Based on the experimental results, we propose that these nanoscale pores are generated by the enrichment of Y at columnar oxide grain boundaries and subsequent unequal diffusion of Y and Zr cations in oxide crystals, which is validated in other two zirconium alloys of M5[®] and N18. As the generation of porosity is attributed to the characteristics of alloying elements, this work provides a new insight into the effect of alloying elements on the corrosion behaviour of zirconium alloys.

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1. Introduction

Zirconium alloys are widely used as fuel cladding materials in nuclear power plants, while waterside corrosion limits their application for high burn-up and extended fuel cycle operations. Oxidation of zirconium alloys always exhibits a kinetics transition, where the oxidation rate abruptly increases following a parabolic or cubic law [1,2]. The transition shows a periodic characteristic, giving a periodically layered structure of oxides [3,4]. Many factors such as tetragonal ZrO₂ content [5], undulations of the oxide/metal interface [6], and residual stresses in the oxide films [7] are thought to be responsible for the transition of the oxidation. So far the reported mechanisms are still in debate. As the oxidation of zirconium alloys is controlled by oxygen diffusion through the oxides to the oxide/metal interface, there should be short circuits for oxygen diffusion just before the abrupt transition [1]. Recently, interconnection of nanoscale pores at grain boundaries of the columnar oxides is newly proposed to determine the transition of Zr oxidation [8–10], which is arousing considerable interest. The interconnected pores can provide a channel for fast oxygen diffusion through the oxides.

The initiation mechanism of the nanoscale pores in zirconium oxide films is still not clear. These pores have been supposed to initiate firstly in Zr substrates near the oxide/metal interface through the Kirkendall effect and then incorporate into the Zr oxide films [8]. The proposed initiation process is inspired by void formation

in Ni–Cr–Al alloys [11]. However, such an assertion is argued because the characteristics of porosity are different for the two kinds of alloys. In the Ni–Cr–Al alloys, the pores are identified to initiate in the metal substrates [12]. As the oxidation progresses, these pores reside at the oxide/metal interface and never go into the oxides [11]. In the zirconium alloys, to the best of the authors' knowledge, no pores have been observed in the Zr substrates but only identified in the oxide films [8]. Moreover, the above-mentioned initiation process cannot interpret well why the nanoscale pores are located just at grain boundaries of the Zr oxides.

In order to clarify the initiation mechanism of the oxide pores, we design a ternary Zr–Nb–Y alloy. The nanoscale pores are identified in the oxides formed on the Y-containing Zr alloys by scanning electron microscope (SEM). The initiation of porosity in the oxides by the Kirkendall effect is suggested in this study. The proposed mechanism is further proved by the observations of the oxides formed on the M5[®] and N18 zirconium alloys.

2. Experimental

Zr_{1.0}Nb_xY ($x = 0, 0.1, 0.4$ wt.%), as-received N18 (Northwest Institute for Non-ferrous Metal Research, China), and M5[®] alloys (AREVA, France) were investigated. Table 1 shows the chemical compositions of the five alloys. Zr–Nb–Y ingots were prepared by the vacuum arc re-melting method using sponge zirconium (Guangdong Orient Zirconic Industry, China), high purity niobium (Zhuzhou Cemented Carbide, China), and yttrium (General Research Institute for Nonferrous Metals, China) as the starting materials. The chemical compositions of the starting materials are given

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Table 1
Chemical compositions of the alloys investigated in this study (wt.%).

Alloy	Nb	Sn	Y	Fe	Cr	O	Zr
Zr1.0Nb	0.97	–	–	0.058	0.0071	0.067	Bal.
Zr1.0Nb0.1Y	0.96	–	0.070	0.029	0.0042	0.064	Bal.
Zr1.0Nb0.4Y	0.92	–	0.34	0.042	0.0081	0.067	Bal.
M5 [®]	0.92	–	–	0.046	0.0067	0.14	Bal.
N18	0.39	0.93	–	0.31	0.08	0.048	Bal.

Table 2
Chemical compositions of zirconium, niobium, and yttrium as the starting materials to prepare the Zr–Nb–Y alloys (wt.%).

Element	Zirconium	Niobium	Yttrium
Si	<0.01	0.002	–
Cl	<0.06	–	–
O	0.038	0.12	0.5
N	0.001	0.036	–
Al	0.001	–	0.01
Cr	0.004	–	–
Fe	0.012	0.008	–
Mn	0.0018	–	–
Ni	0.0001	–	–
Pb	0.0004	–	–
Ti	0.0038	<0.005	0.21
Hf	0.0065	–	–
C	0.01	0.012	–
Mg	0.0003	–	0.0007
W	–	0.005	–
Mo	–	0.005	–
Ta	–	0.12	–
Cu	–	0.001	–
TREM ^a	–	–	≥99
Y/TREM	–	–	≥99.5
Ca	–	–	0.0025
Zr	Bal.	–	0.007
Nb	–	Bal.	–

^a TREM = total rare earth metals.

in Table 2. The ingots were β -solution heat-treated at 1300 °C for 30 min in an argon atmosphere, hot-rolled after pre-heated to 800 °C and soaked for 30 min, and then cold-rolled twice to sheets with a final thickness of ~ 1 mm. During the rolling intervals, the sheets were intermediate-annealed at 580 °C for 3 h. The final cold-rolled sheets were also annealed at 580 °C for 3 h to obtain a fully recrystallized microstructure. Second phase particles (SPPs) in the prepared Zr1.0Nb x Y specimens were characterized by SEM (JEOL JSM7001F, Japan). Prior to SEM observations, the specimens were electropolished at 0 °C in a solution of 5 vol.% HClO₄ and 95 vol.% C₂H₅OH. Due to low solubility in α -Zr matrix and no reaction with Zr or Nb [13,14], the alloying element Y was found to be present as Y SPPs with a size of ~ 100 nm, as shown in Fig. 1.

Corrosion tests were performed in 400 °C/10.3 MPa pure steam for 70 days according to ASTM G2-88. After the corrosion tests, cross-sections of the formed oxide films were characterized by SEM (Zeiss AURIGA, Germany), with a limiting resolution of 1 nm at 15 kV accelerating voltage. In order to obtain the cross-sections, the corroded specimens were etched in a solution of 10 vol.% HF, 45 vol.% HNO₃, and 45 vol.% H₂O for 20 min to dissolve the metal substrates. Then, the oxide films extruding the metal substrates were gently fractured using a tweezer. Before SEM observations, the fractured cross-sections were coated with a gold film to improve the electrical conductivity. Layered structures and grain morphology of the oxide films were thus revealed by the fractured cross-sections. Crystal structures of the oxides were characterized by Raman spectroscopy (Jobin Yvon HR800, France) using a 532 nm

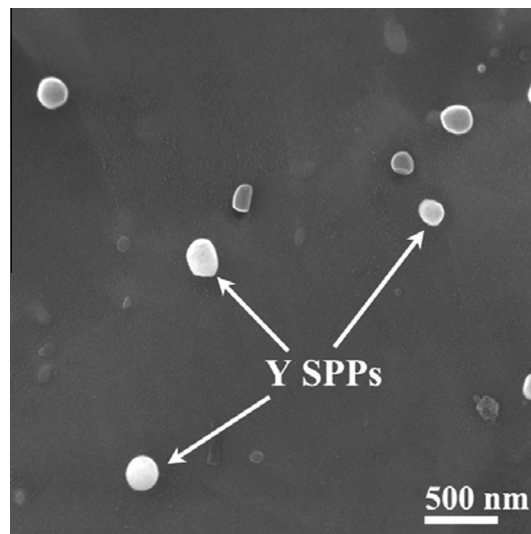


Fig. 1. SEM observation of Y SPPs in the Zr1.0Nb0.1Y alloy.

excitation line of a solid laser. Systematic line scans with a step of 0.6 μ m were performed on the polished cross-sections of the oxide films. After base line subtraction and intensity normalization, representative Raman spectra extracted from the line scans were used to investigate variations of tetragonal ZrO₂ (t-ZrO₂) content with respect to distance from the oxide/metal interface.

3. Results and discussion

3.1. Characteristics of oxide films

Fig. 2 shows the cross-sections of the oxide films formed on the zirconium alloys. The results of the corrosion tests in pure steam at 400 °C for 70 days are summarized in Table 3. The thickness of the oxides formed on the M5[®] alloy was nearly equal to that on the N18 alloy, both of which were thinner than the Zr1.0Nb x Y alloys. With increasing Y content, the thickness of the oxides on the Zr1.0Nb x Y alloys was increased, indicating a reduced corrosion resistance. The oxide films on the M5[®] alloy displayed one integral layer, while two layers were found on the N18 alloy. In the case of the Zr1.0Nb x Y alloys, the number of periodic layers was increased with increasing Y content, suggesting a lowered corrosion resistance. The formation of the periodic layers is caused by the periodic transitions of corrosion kinetics [2]. Interconnection of nanoscale pores in oxides is thought to be responsible for the periodic transitions [10], since the oxygen diffusion rate can be abruptly increased. The corrosion result indicates that Y addition introduces additional transitions into the corrosion kinetics of the Zr1.0Nb alloys.

Fig. 3 shows the cross-sectional morphology of the oxide films near a boundary between two transition layers. The oxide films mainly consisted of columnar grains aligned parallel to the growth direction of the oxides. Fig. 3a presents that no oxide pores were observed for the Zr1.0Nb alloy. Compared with the tightly aligned columnar oxide grains formed on the Zr1.0Nb alloy, nanoscale spherical pores in strings were observed at grain boundaries of the columnar oxides formed on the Zr1.0Nb0.1Y (Fig. 3b) and Zr1.0Nb0.4Y alloys (Fig. 3d). The size (<10 nm), shape, and location of these pores are all in good agreement with the TEM observations using Fresnel contrast [8]. The oxide pores can be well characterized on the cross-sections by SEM, although they are nanoscale in size. The size of the oxide pores increased from <10 nm

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