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The microstructure and microtexture of zirconium oxide films studied by transmission electron backscatter diffraction and automated crystal orientation mapping with transmission electron microscopy

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Abstract

A detailed characterization of nanostructured thin zirconium oxide films formed during aqueous corrosion of a nuclear-grade zirconium alloy (Zircaloy-4) has been carried out by means of two novel, ultra-high-spatial-resolution grain mapping techniques, namely automated crystal orientation mapping in the transmission electron microscope (TEM) and transmission electron backscatter diffraction (t-EBSD). While the former provided excellent spatial resolution with the ability to identify tetragonal ZrO_2 grains as small as ~5 nm, the superior angular resolution and unambiguous indexing with t-EBSD enabled verification of the TEM observations. Both techniques revealed that in a stress-free condition (TEM foil prepared by focused ion beam milling), the oxide consists mainly of well-oriented columnar monoclinic grains with a high fraction of transformation twin boundaries, which indicates that the transformation from tetragonal to monoclinic ZrO_2 is a continuous process, and that a significant fraction of the columnar grains transformed from stress-stabilized tetragonal grains with (0 0 1) planes parallel to the metal–oxide interface. The TEM analysis also revealed a small fraction of size-stabilized, equiaxed tetragonal grains throughout the oxide. Those grains were found to show significant misalignment from the expected (0 0 1) growth direction, which explains the limited growth of those grains. The observations are discussed in the context of providing new insights into corrosion mechanisms of zirconium alloys, which is of particular importance for improving service life of fuel assemblies used in water-cooled reactors.

Keywords: Zirconium oxide; Texture; EBSD; TEM; Corrosion

1. Introduction

The motivation for understanding the microstructure and texture of zirconium oxide films comes from the requirement to improve the aqueous corrosion performance and minimize hydrogen pickup of zirconium alloys, which are used to clad nuclear fuel in light and heavy water reactors. The microstructure of the oxide has been found to directly affect the corrosion performance of zirconium alloys; for example, alloys with low corrosion rates have been observed to exhibit large columnar grains [1]. Their superior corrosion performance is attributed to a reduction in grain boundary area in oxides with large grains, as the grain boundary diffusion coefficient is 10^8 times higher than the bulk diffusion coefficient of the oxide [2]. The grain-to-grain misorientation has also been linked to aqueous

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corrosion performance [3], with more highly textured oxides exhibiting reduced levels of hydrogen pickup and improved corrosion performance. This is attributed to the high fraction of low-angle grain boundaries in highly textured oxide and their associated low mobility for diffusing species. Hydrogen pickup is a major concern for the nuclear industry because it results in hydride formation and embrittlement and can lead to cladding failure via a mechanism known as delayed hydride cracking (DHC) [4]. Despite the correlation between oxide grain orientation and hydrogen pickup, there has been relatively little work attempting to link the microtexture, and thus the grain boundary character distribution in the oxide, to the corrosion performance of zirconium alloys. Previously, zirconium oxide corrosion films have provided a significant challenge for grain orientation mapping due to their fine grain size (some grains are less than 30 nm), high levels of residual stress, complex microstructural morphology and dual phase nature, a mixture of metastable tetragonal and stable monoclinic zirconia [1].

The technique of electron backscatter diffraction (EBSD) has made considerable advances in recent years; with improvements in both hardware and software it has now become possible to detect, and accurately index, Kikuchi patterns from ultra-fine-grained materials such as zirconium oxide. The best possible resolution is achieved on electron-transparent samples in transmission geometry, using a technique termed transmission EBSD (t-EBSD) [5,6]. Automated crystal orientation mapping in the transmission electron microscope (TEM) can also be used to map the phase and orientation of such fine-grained microstructures [7]. The electron beam is scanned across the sample and transmission electron diffraction spot patterns are recorded and matched to calculated templates in order to deduce phase and orientation information. This TEM technique offers improved lateral spatial resolution over t-EBSD; however, angular and phase detection accuracy are reduced due to the low sensitivity and ambiguity of electron diffraction spot patterns. Overlapping grains can also cause problems when using transmission techniques on such a fine-grained microstructure as zirconium oxide. The overlapping of grains in the TEM will result in the formation of composite diffraction patterns, which can lead to problems during the template matching process. However, in t-EBSD, the Kikuchi patterns have been shown to originate primarily from the exiting surface of the sample [6], therefore the occurrence of composite patterns from overlapping grains is reduced. In the present study the strengths of both transmission-based orientation-mapping techniques were combined to investigate the microstructure, microtexture and grain boundary distribution of oxide films formed on a zirconium alloy as a consequence of extended corrosion in superheated pressurized water.

Previous attempts to measure the orientation of the grains that make up the oxide formed on Zircaloy-4 have been carried out using X-ray diffraction (XRD) [8–11] texture measurements. These investigations have demonstrated that a strong fibre texture forms in the monoclinic oxide on Zircaloy-4 during aqueous corrosion, with the $(10\bar{3})$ [11], $(10\bar{4})$ [8] or $(10\bar{5})$ [10] planes parallel to the sample surface. The discrepancy between these studies is due to the fact that the monoclinic grains can adopt a range of orientations. Theoretical calculations have shown that monoclinic grains with orientations ranging between $(10\bar{3})$ and $(10\bar{6})$ reduce the in-plane surface area and so minimize the transformation stress associated with the metal-to-oxide transformation during oxide growth [12]. The orientation of the tetragonal phase has also been measured using XRD [11]; a (001) texture was found to form on Zircaloy-4, which is again the orientation with the smallest in-plane surface area for this phase. It is important to note that texture measurement via XRD is a bulk technique sampling a comparatively large volume and the non-destructive nature of these measurements allows the stress state in the oxide to be maintained. However, it does not allow for direct characterization of grain-to-grain misorientations. TEM observations have shown qualitatively a similar texture in the monoclinic phase formed on Zircaloy-4, and also revealed a more well-defined texture away from the metal–oxide interface [1]. These observations were made using a large diffraction aperture, which samples the average texture over a relatively large area of hundreds of nm, and as such are not correlated with the oxide microstructure. High resolution TEM (HRTEM) has been utilised to directly measure the orientations of individual oxide grains [13–16]. The observations reveal that the oxide consists of a large proportion of well-oriented columnar monoclinic grains, and a small number of more randomly oriented equiaxed monoclinic and tetragonal grains. It is important to note that XRD analysis of the oxide generally reports significantly higher volume fractions of tetragonal phase than TEM analysis on foils where the stresses have been relieved [13,16]. The oxide has also been observed to contain a high fraction of twin boundaries [15], which are thought to form as a result of the tetragonal-to-monoclinic transformation during oxide growth. However, due to the time-consuming nature of manual TEM orientation analysis, these TEM investigations tend to concentrate on a small number of grains and thus lack statistical significance, which is of concern considering the heterogeneity of the oxide microstructure [16].

Zircaloy-4 exhibits cyclic corrosion kinetics during aqueous corrosion in an autoclave environment, as shown in Fig. 1. At a critical oxide thickness, the oxide loses its protectiveness and accelerated corrosion kinetics are observed; this region in the corrosion curve is often termed the transition. After the transition, the oxide regains its protectiveness and the process repeats itself in a cyclic manner until a period of approximately linear growth develops, known as breakaway corrosion. During oxide growth, the transformation from zirconium to zirconium oxide causes high levels of compressive stress in the oxide, which has been shown to decrease with distance from the interface [9,17]. Stress relaxation in the oxide is postulated to be