



The effect of Sn concentration on oxide texture and microstructure formation in zirconium alloys



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ARTICLE INFO

Article history:

Received 8 April 2015

Accepted 1 August 2015

Available online 14 August 2015

Keywords:

Zirconium oxide

Texture

Microstructure

TEM

EBS

ABSTRACT

The development of oxide texture and microstructure formed on two zirconium alloys with differing Sn contents (Zr–1Nb–1Sn–0.1Fe, i.e. ZIRLO™ and Zr–1.0Nb–0.1Fe) has been investigated using transmission Kikuchi diffraction (TKD) in the scanning electron microscope (SEM) and automated crystal orientation mapping in the transmission electron microscope (TEM). Bulk texture measurements were also performed using electron backscatter diffraction (EBSD) in order to quantify and compare the oxide macrotexture development. The Sn-free alloy showed significantly improved corrosion performance by delay of the transition region and reduced levels of hydrogen pickup. The macroscopic texture and grain misorientation analysis of the oxide films showed that the improved corrosion performance and reduced hydrogen pick up can be correlated with increased oxide texture strength, the improved oxide grain alignment resulting in longer, more protective columnar grain growth. A lower tetragonal phase fraction is also observed in the Sn-free alloy. This results in less transformation to the stable monoclinic phase during oxide growth, which leads to reduced cracking and interconnected porosity and also to the formation of larger, well-aligned monoclinic grains. It is concluded that the Zr–1.0Nb–0.1Fe alloy is more resistant to hydrogen pickup due to the formation of a denser oxide with a larger columnar grain structure.

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1. Introduction

Ever since the development of the first zirconium alloy, Zircaloy-1, which was alloyed with 2.5% Sn, a reduction in Sn content has been correlated with improved corrosion performance [1–4]. However, this improvement is coupled with a reduction in creep resistance and yield stress [5] and therefore modern Nb-containing Zr alloys contain small amounts of Sn in order to maintain adequate mechanical properties. There have been numerous studies providing evidence that alloys with reduced levels of Sn exhibit a low tetragonal phase fraction in the oxide film [2–4,6]. A recent study [4] has suggested that Sn enables the stress stabilization of the tetragonal phase, and therefore induces increased transformation to the stable monoclinic phase during later stages of oxide growth. The large shear strain and volume expansion associated with this transformation has previously been postulated to cause cracking and porosity in the oxide and to lead to the onset of accelerated corrosion kinetics [7–10]. It has also been suggested that Sn segregation to oxide grain boundaries and the subsequent

expansion during oxidation could induce transformation and create porosity at the oxide grain boundaries [3].

The crystallographic orientation of oxide grains that form during corrosion of zirconium alloys has previously been shown to affect the corrosion properties of the oxide. Glavicic demonstrated by X-ray diffraction (XRD) analysis that as the oxide texture strength was increased on a Zr–2.5% Nb alloy, there was a reduction in both oxidation rate and hydrogen pickup [11]. Yilmazbayhan et al. used TEM to show qualitatively that alloys with improved corrosion performance showed a higher proportion of well-aligned columnar monoclinic grains [12]. This relationship between grain orientation and corrosion performance is thought to be due to the fact that well aligned oxide grains should exhibit a high fraction of coherent grain boundaries, and the diffusivity along these grain boundaries is related to their interfacial energy [13]. A number of studies have also indicated that oxide grain boundaries are likely paths for hydrogen through the protective oxide [14–17]. TEM studies have shown interconnected porosity at oxide grain boundaries [9,18], which could provide a transport mechanism for hydrogen through the oxide. This is supported by recent atom probe tomography observations of deuterium

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enrichment at oxide grain boundaries in samples exposed to heavy water [17].

A strong texture has been observed via XRD [19,20] and TEM [12,21] analysis to form in the monoclinic oxide during corrosion. The formation of this texture in conventionally processed single-phase zirconium alloys is thought to be driven by the transformation stress induced by the zirconium-zirconia transformation [20,22]. The oxide orientations which occupy the smallest in-plane surface area will grow preferentially as they minimise the compressive stress that arises during oxidation of the metal [22]. Therefore a fibre texture is formed with the $(1\ 0\ \bar{3})$ – $(1\ 0\ \bar{5})$ planes oriented parallel with the sample surface [19,20,23]. A (001) fibre texture has also been observed using XRD to form in the tetragonal phase of oxidised Zircaloy-4 [23]. The growth of these orientations will also minimise the transformation stress as they have the smallest in-plane surface area. It has previously been suggested that transformation of these favourable tetragonal orientations could lead to the formation of the observed monoclinic texture [10]. However, laboratory XRD measurements of the tetragonal phase rely on the measurement of only a single diffraction peak due to the complex nature of the ZrO_2 diffraction spectrum [20,24]. In addition, microtexture measurements rely on the preparation of electron transparent samples, which results in the transformation of the majority of the tetragonal grains [10,25]. Precise measurement of the orientation of the tetragonal grains is therefore difficult with these techniques.

The present study focuses on a comparison between the commercial alloy ZIRLO™ and an experimental alloy, Zr–1.0Nb–0.1Fe developed by Westinghouse, which has the same composition except that no Sn was added to the alloy (Table 1). A previous study has shown a similar distribution of monoclinic $(\bar{1}\ 1\ 1)$ poles in the oxide formed on these alloys as measured by laboratory XRD [4], however only a single contoured pole figure is presented from each alloy in the pre-transition region and therefore a more detailed analysis of the effect of Sn on oxide texture formation is required. The aim of the present study was to investigate the effect of Sn reduction on oxide texture formation and microstructure development and to link this to the corrosion performance of the alloys, both in terms of oxidation and hydrogen pickup. The complementary use of conventional EBSD, transmission Kikuchi diffraction (TKD) and the automated crystal orientation mapping TEM technique allows for analysis of a large number of oxide grains [10]. It thus provides a more statistical approach, including texture and misorientation distribution analysis, than conventional TEM techniques [12,21,26,27]. In addition, removal of the outer portion of the oxide via mechanical grinding and polishing, and the subsequent examination with EBSD, allowed for examination of the monoclinic and tetragonal texture evolution whilst maintaining the in-plane stress state in the oxide. The hydrogen pickup behaviour of the alloys was also measured as part of this work in order to determine if the differences in behaviour can be correlated with the degree of oxide texture and type of grain misorientation distribution. Such a correlation would provide evidence for oxide grain boundaries providing a preferential transport route for hydrogen through the protective oxide.

2. Experimental methods

2.1. Sample selection

Two alloys were selected for this study; the commercial alloy, ZIRLO™ (Zr–1Sn–0.1Fe), and the developmental alloy, Zr–1.0Nb–0.1Fe, both supplied by Westinghouse. Both alloys were in tube form in the recrystallised condition. The measured composition of the alloys is shown in Table 1. The alloys were exposed to

Table 1

Composition in wt.% of zirconium alloys used in this study, measured by EDF using an inductively coupled plasma atomic emission spectrometer (ICP-AES). Balance is zirconium.

Alloy	Cr	Fe	Nb	Ni	Sn
ZIRLO™	<0.01	0.09	0.87	<0.01	0.92
Zr–1.0Nb–0.1Fe	<0.01	0.08	0.91	<0.01	0.01

simulated primary water chemistry at 360 °C for a total of 540 days as part of a previous research program (MUZIC-1) [9]. The corrosion kinetics are shown in Fig. 1 and each data point is an average weight gain from at least 5 samples. More detail on the corrosion testing can be found in Ref. [28]. In order to have samples with a similar oxide thickness for comparison, one sample was selected from each alloy (circled on Fig. 1). The ZIRLO™ sample had been exposed for a total of 360 days and had an oxide thickness of ~6.4 µm, as measured by weight gain measurements (1 µm of oxide is equivalent to a weight gain of 15 mg dm² [29]). The Zr–1.0Nb–0.1Fe sample had been exposed for a total of 540 days in primary water chemistry and also received an additional exposure to deuterated water for 45 days (for NanoSIMS analysis, which is not covered here). The total oxide thickness after 585 days exposure was ~5.4 µm from weight gain measurements. The exposure to deuterium accounted for only an additional 0.2 µm of oxide growth and is not expected to have caused any changes to the microstructure of the pre-existing oxide.

The approximate time to the first transition in the corrosion kinetics¹ are labelled on Fig. 1. For ZIRLO™ this region can be estimated from the accelerated corrosion kinetics after transition. For Zr–1.0Nb–0.1Fe, however, this was not possible as there are insufficient data points beyond 300 days of corrosion. The transition region was therefore estimated from comparison of the oxidation kinetics to the oxide microstructure, as will be discussed in more detail later.

2.2. Sample preparation

The samples were prepared for bulk EBSD measurements by sectioning a ~6 × 4 mm piece (with the long direction parallel to the axial direction of the tube) and grinding flat using 4000 grit SiC paper. The use of such a fine grit allowed for the preparation of a flat surface without complete removal of the relatively thin oxide. The samples were subsequently polished in a colloidal silica suspension for an extended period of time to remove the grinding scratches. After polishing, a series of cross sections were produced across the tube length using a focussed ion beam (FIB) instrument in order to measure the thickness of the remaining oxide, as shown in Fig. 2. The oxide removal rate was found to vary significantly from the centre to the outside edge of the tube samples, with very little oxide removed from the centre of the tube and all of the oxide removed at each end. The resulting thickness gradient allowed for the measurement by EBSD of bulk oxide texture as a function of oxide thickness. Electron transparent cross-sectional samples for microtexture analysis were prepared by FIB milling using the in situ lift-out technique [30]. Sample preparation using FIB milling is essential for producing large samples of uniform thickness from oxide/metal composites. The samples were prepared with the axial direction of the tube in the plane of the sample. After thinning, low energy FIB cleaning was performed on the samples, which has been shown to remove the surface regions damaged by the ion beam during preparation [31]. After final thinning the typical foil

¹ Zr alloys are known to exhibit cyclic corrosion kinetics. The corrosion kinetics are initially of parabolic to cubic nature before a point at which the protectiveness of the oxide breaks down causing a transition in corrosion kinetics. At this stage the second cycle starts.

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