A study into the impact of interface roughness development on mechanical degradation of oxides formed on zirconium alloys

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ABSTRACT

As a cladding material used to encapsulate nuclear fuel pellets, zirconium alloys are the primary barrier separating the fuel and a pressurised steam or lithiated water environment. Degradation mechanisms such as oxidation can be the limiting factor in the life-time of the fuel assembly. Key to controlling oxidation, and therefore allowing increased burn-up of fuel, is the development of a mechanistic understanding of the corrosion process. In an autoclave, the oxidation kinetics for zirconium alloys are typically cyclical, with periods of accelerated kinetics being observed in steps of $\sim$2 μm oxide growth. These periods of accelerated oxidation are immediately preceded by the development of a layer of lateral cracks near the metal-oxide interface, which may be associated with the development of interface roughness. The present work uses scanning electron microscopy to carry out a statistical analysis of changes in the metal-oxide interface roughness between three different alloys at different stages of autoclave oxidation. The first two alloys are Zircaloy-4 and ZIRLO™ for which analysis is carried out at stages before, during and after first transition. The third alloy is an experimental low tin alloy, which under the same oxidation conditions and during the same time period does not appear to go through transition. Assessment of the metal-oxide interface roughness is primarily carried out based on the root mean square of the interface slope known as the R_{dq} parameter. Results show clear trends with relation to transition points in the corrosion kinetics. Discussion is given to how this relates to the existing mechanistic understanding of the corrosion process, and the components required for possible future modelling approaches.

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1. Introduction

Zirconium alloys are used as cladding to encapsulate fuel pellets in pressurised and boiling water nuclear reactors. Research into oxidation of these alloys has been significant since the introduction of the material. However, the microstructure and electro-chemical processes during oxidation are complex and many questions still remain unanswered. One such issue is the formation of lateral cracks near the metal-oxide interface. Small cracks have been seen to form continuously during oxidation, with large scale networks of lateral cracks forming cyclically every $\sim$2 μm of oxide growth. These networks of cracks can be correlated with acceleration in the corrosion kinetics [1–7]. These lateral cracks might enable the link up of nano pores along grain boundaries perpendicular to the metal/oxide interface as reported in [8,9]. Experiments using Synchrotron X-Ray Diffraction (S-XRD) by both Polatidis et al. and Petigny et al., have separately shown that oxides formed on Zirca-

loy-4 are composed of monoclinic and stabilised tetragonal phases, with an $\sim$7% reduction in the tetragonal phase fraction from 1 to 3 μm oxide growth [4,10]. One theory is that the lateral cracks may destabilise the tetragonal phase close to the metal-oxide interface. The phase transformation has an $\sim$6% expansion associated with it, which could lead to fracture perpendicular to the metal-oxide interface, thereby generating fast ingress routes for oxygen containing species [11,12].

Work by Bossis et al. [2], Ly et al. [5], and Ni et al. [13], have all indicated an increase in interfacial roughness with oxidation of zirconium alloys. However, connecting this with transition in the corrosion kinetics can be more problematic. When considering the interface undulations to be similar to a sinusoidal wave, Bossis et al. have said that the interface develops a fairly consistent wavelength of $\sim$1 μm, and that the amplitude increases progressively up to transition in the corrosion kinetics. The rapid oxidation reduces the amplitude, which would in theory allow the process to cycle [2,14]. Ni et al. used FIB slice and view to characterise the development of interface roughness and lateral crack formation in 3D [13].

The root mean square of the interface roughness appears to increase up to transition and then drop sharply in line with the work by Bossis et al. [2]. Ly et al. could not identify a typical wavelength using Fast Fourier Transform, and although interface roughness increases with oxidation no clear link to transition could be identified [5].

There are two probable causes of interface roughness formation. The first is that this is a deformation mechanism designed to relieve some of the stresses induced by the expansion as the metal transforms into oxide [15–17]. Indeed finite element analysis predicts the plastic deformation of the metal substrate in the presence of interface roughness [18]. TEM carried out by Tejland et al. has seen evidence of dislocation clusters and sub-grain formations. The paper details why this is most likely to be a result of localised deformation due to interface roughness development [19]. The second possibility is that interface roughness forms due to variation in oxygen diffusion rates through the oxide layer [17,20]. Oxides formed on zirconium alloys are composed of monoclinic and tetragonal phases, both of which demonstrate high levels of compressive stress [4]. This has the potential to impact oxygen diffusion through the lattice and along grain boundaries. High resolution SIMS analysis of ^{18}O doping oxidation tests indicated that the lateral cracks might locally impede oxygen diffusion, thereby contributing to interface roughness development [21].

Lateral cracks have been seen to form preferentially above peaks in the interface roughness, or delays in the advancing oxidation front [2,13,14,22]. Finite element analysis has indicated that the expansion of newly formed oxide above interface peaks should result in a strong tensile stress perpendicular to the metal-oxide interface [18]. These tensile stresses could potentially cause the localised fracture of the oxide layer, or separation of the metal-oxide interface. Isolated cracks have been observed to form continuously during the oxidation process [2,5,13]. Although they have been seen to initiate above emerging SPPs (second phase particles) above a certain size, many lateral cracks form in the absence of SPPs meaning another mechanism must be primarily responsible [5]. There is some disagreement relating crack formation with transition in the corrosion kinetics. Bossis et al. and Ly et al. have both said that networks of lateral cracks form at transition (~2 μm oxide growth), i.e. before the acceleration in the corrosion kinetics [2,5]. The work by Ni et al. states that the crack volume fraction increases linearly with oxide thickness, and therefore the layers of lateral cracks, that are present at ~2 μm intervals, form during the accelerated oxidation phase rather than immediately before.

Other materials which form strongly compressed oxide layers during high temperature oxidation have been seen to form interface roughness, and subsequently separation of the interface or fracture of the oxide [16,17,23,24]. A common approach has been the application of fracture mechanics to develop energy models of the oxidation process. The basic theory being that a compressed oxide layer contains stored elastic energy which can be relaxed by increasing the interfacial area [16,23]. However, this increases the interfacial energy and leads to strain hardening of the substrate. Therefore, at some stage it becomes energetically favourable to induce spallation of the oxide layer [15,20]. Research of this type is significant and worth considering when analysing oxidation of zirconium alloys.

The aim of the work presented here is to analyse the development of roughness at the metal-oxide interface for a range of zirconium alloys and connect this with the transition points and associated acceleration in the corrosion kinetics. This will be used to enhance the current mechanistic understanding of zirconium alloy corrosion.

2. Experimental

The materials that have been assessed are Zircaloy-4 (sheet), ZIRLO™ (tube), and A-0%Sn (tube). The samples were prepared by pickling using a dilute hydrofluoric acid solution, followed by autoclave testing in 360 °C primary water at ~18 MPa by EDF-R&D at Moret-sur-Loing, France. Further experimental details can be found in [4] and [25]. The weight gain measurements for Zircaloy-4 have been converted into average oxide thicknesses and can be found in Fig. 1a. The Zircaloy-4 sheet exhibits transition and acceleration in the oxidation kinetics somewhere between 160 and 200 days. Assessing the alloy chemistries shown in Table 1 it can be seen that the A-0%Sn tube material is very similar to that of the ZIRLO™ tube but with <0.0% Sn. This makes the direct comparison of the oxidation behaviour of these materials very valuable. The weight gain measurements for ZIRLO™ and A-0%Sn can be seen in Fig. 1b. The ZIRLO™ appears to go through transition between 140 and 160 days, whereas the A-0%Sn does not go through transition during the period analysed.

Samples from these materials were mounted in cross-section, ground, and polished with a colloidal silica OPS (oxide polishing solution). Analysis of the metal-oxide interface was carried out using an FEI Quanta 200 Scanning Electron Microscope (SEM) in backscattered electron mode. The samples that have been mounted and analysed have been circled in Fig. 1a and b. For the Zircaloy-4 material 7 samples were analysed, with ~100 images taken at random across a distance of ~30 mm per sample. For the Zircaloy-4 material the surface of the oxide layer remained largely intact after sample preparation, allowing analysis of the oxide thickness and comparison of interface roughness with oxide thickness for each image. 5 samples of the ZIRLO™ and A-0%Sn material were analysed, with ~30 images taken at random across a distance of ~10 mm per sample. For the ZIRLO™ and A-0%Sn materials, small amounts of damage to the surface of the oxide layer during sample preparation made analysis of the oxide thickness via SEM
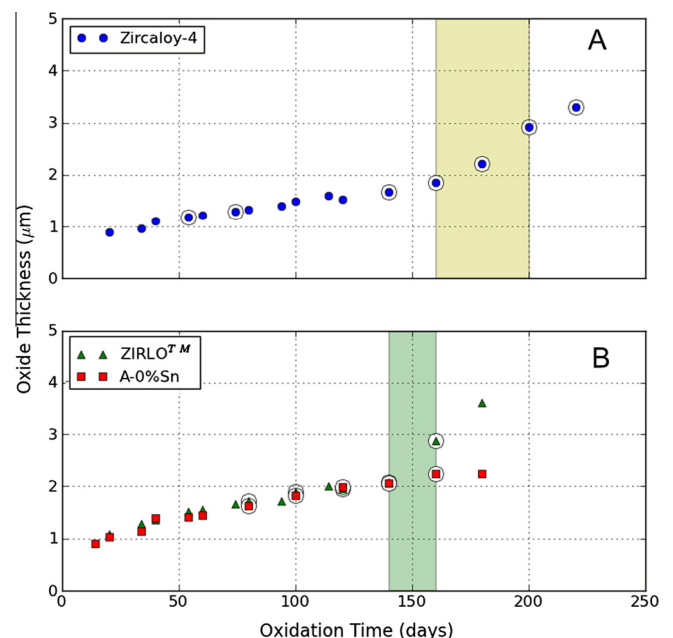

Fig. 1. The oxidation kinetics for Zircaloy-4 sheet material (A), and ZIRLO™ & A-0%Sn tube materials (B), in 360 °C primary water, with the light yellow and green bars representing the interval in time when transition appears to have occurred for the Zircaloy-4 and ZIRLO™ materials respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)