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A study into stress relaxation in oxides formed on zirconium alloys

P. Platt [a,*], E. Polatidis [a], P. Frankel [a], M. Klaus [c], M. Gass [b], R. Howells [b], M. Preuss [a]

[a] University of Manchester, School of Materials, Materials Performance Centre, Manchester M13 9PL, UK
[b] AMEC, Walton House, Faraday Street, Birchwood Park, Risley, Warrington WA3 6GA, UK
[c] Helmholtz Zentrum Berlin für Materialien und Energie, Albert-Einstein Strasse 15, 12489 Berlin, Germany

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ABSTRACT

Pressurised and boiling water reactors contain zirconium alloys, which are used as nuclear fuel cladding. Oxidation of these alloys, and the associated hydrogen pick-up, is a limiting factor in the lifetime of the fuel. To extend the burn-up of nuclear fuel requires control of the oxidation, and therefore development of a mechanistic understanding of the cladding corrosion process. Synchrotron X-ray diffraction (S-XRD) has been used to analyse oxide layers formed during in-situ air oxidation of Zircaloy-4 and ZIRLO™. Analysis shows that as the oxide thickness increases over time there is a relaxation of the stresses present in both the monoclinic and meta-stable tetragonal phases, and a reduction in the tetragonal phase fraction. To better understand the mechanisms behind stress relaxation in the oxide layer, finite element analysis has been used to simulate mechanical aspects of the oxidation process. This simulation was first developed based on stress relaxation in oxides formed in autoclave, and analysed ex-situ using S-XRD. Relaxation mechanisms include creep and hydrogen-induced lattice strain in the metal substrate and creep in the oxide layer. Subsequently the finite element analysis has been extended to stress relaxation observed by in-situ S-XRD oxidation experiments. Finite element analysis indicates that the impact of creep in the oxide is negligible, and the impact of both creep and hydrogen-induced lattice strain in the metal substrate metal is small. The implication is that stress relaxation must result from another source such as the development of roughness at the metal–oxide interface, or fracture in the oxide layer.

1. Introduction

Zirconium alloys are used as fuel cladding in pressurised and boiling water nuclear reactors. As such these materials are exposed to a large number of environmental factors that will promote degradation mechanisms such as oxidation. At high burn-ups, i.e. extended service life, oxidation and the associated hydrogen pick-up can be a limiting factor in terms of fuel efficiency and safety. The oxidation kinetics for many zirconium alloys are cyclical, demonstrating a series of approximately cubic kinetic curves separated by transitions [1–5]. These transitions are typified by a breakdown in the protective character of the oxide and are potentially linked to a number of mechanical issues. Understanding how these issues influence oxidation is a key to developing a full mechanistic understanding of the corrosion process.

Synchrotron X-ray diffraction (S-XRD) experiments have shown that oxides formed on zirconium alloys are strongly compressed and composed of both monoclinic and stabilised tetragonal phases. Published results suggest residual stresses ranging from −3800 MPa to −80 MPa, and tetragonal phase fractions ranging from 50% to 5%, depending upon the position on the corrosion kinetics curve and alloy composition [4–8]. Although there is some variation close to transition in the corrosion kinetics, each of these papers show that over several microns of oxide growth there is a gradual reduction in both the average compressive stress and the tetragonal phase fraction. It is implied from this that some combination of mechanisms are relaxing the compressive stress and destabilising the tetragonal phase. Possible mechanical factors include oxidation-induced creep and strain, or crack formation in the oxide layer [9–11]. The tetragonal to monoclinic phase transformation is considered as a key component in the oxidation process as it could potentially cause the crack and pore formation observed using TEM [11,12]. This would provide fast ingress routes for oxygen containing species thereby accelerating the corrosion kinetics, and degradation of zirconium alloy components.

A number of attempts have been made to experimentally define oxidation-induced strain in the metal substrate as a result of creep and hydrogen pick-up. Donaldson et al. oxidised samples of cold work stress relieved Zircaloy-4 tube in air, with wall thicknesses between 0.58 and 0.08 mm, at temperatures in the range of

* Corresponding author at: Material Performance Centre, Room D10, Manchester Materials Science Centre, The University of Manchester, Grosvenor Street, Manchester M1 7HS, UK. Tel.: +44 7753431684.
E-mail address: Philip.Platt@manchester.ac.uk (P. Platt).

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350–450 °C for times ranging from 152 to 753 days. Axial strains were measured at regular intervals. Across the temperatures measured, total strains at the end of the tests ranged between 0.0016–0.0265 in the thinnest tube and 0.0003–0.0047 in the thickest. In particular, the elevated strain with decreasing substrate thickness is evidence of oxidation-induced creep as reducing substrate thickness would increase the oxidation-induced stress in the metal substrate [13]. Both Blat et al. and Barberis et al. have attempted to measure strains resulting from both oxidation-induced creep of the metal substrate and hydrogen-induced lattice strain [9,10]. Blat et al. oxidised recrystallised 0.45 mm thick Zircaloy-4 sheet at 360 °C, with simulated primary water chemistry. Oxide thicknesses ranged from 2.1 to 7.3 μm, i.e. 100–400 days exposure. Including both hydrogen pick-up and oxidation-induced creep, strains ranged from 0.00012 to 0.00066. Barberis et al. carried out a significant number of tests into oxidation-induced strain due to creep and hydrogen pick-up. Oxidising recrystallised M5 tube in 360 °C water for ~220 days resulted in an oxide ~3.7 μm thick and a diametral strain of ~0.00015 [10]. Although measuring such small levels of strain is problematic, these papers show clear evidence of creep deformation in the metal substrate as a direct result of oxidation.

In-reactor zirconium alloys are exposed to a range of stresses from sources such as channel bowing, oxidation, and pellet clad interaction (PCI). These factors can limit the lifetime and safety of the fuel, hence research into creep mechanisms in zirconium alloys is significant [14–16]. The most commonly researched creep mechanism is power law creep, which is based on dislocation climb and glide. Although near surface S-XRD of the metal substrate has given stress values of 50–100 MPa [5], this does not correlate with calculations for the bulk metal balancing stress based on the average in-plane stress in the oxide layer measured using S-XRD. Instead, Barberis et al. calculate bulk tensile stresses present in the metal substrate that are of the order of ~15 MPa [10]. Extrapolating the stress measured at the near surface to the bulk of the metal substrate is problematic due to potential for localised stress effects relating to roughness at the metal–oxide interface [17]. Taking the bulk stress to be ~15 MPa puts oxidation-induced creep in a low stress regime. Numerous mechanisms have been presented in the literature to explain creep in this regime including Coble, Nabarro-Herring, Harper-Dorn, Ashby-Verrall and Grain Boundary Sliding (GBS) [16]. Assignment of a specific creep mechanism is based on stress, temperature, and grain size [15,16,18–22]. In the three main pieces of work that study oxidation-induced creep, all strains in the substrate are measured empirically; and no discussion is given to assigning an actual creep mechanism to the observed behaviour [9,10,13].

For many years manufactured samples of tetragonal and cubic zirconia (ZrO_2) have been known to be superplastic and capable of significant levels of strain under the appropriate experimental conditions. Strain rates of up to $1 \times 10^{-3}\ s^{-1}$ have been recorded at 1150 °C for nanocrystalline, yttria stabilised tetragonal zirconia [23]. This has led to a significant amount of research into creep [23–28], and a number of tracer element diffusion tests designed to define the diffusion coefficients have been conducted [29–32]. However this temperature is much higher than would be observed in reactor under normal operating conditions, and the morphology of the oxides are very different. As yet there appears to be no experimental work that directly confirms the presence of creep in the oxide layer during oxidation at 360 °C.

The hydrolytic component of the zirconium corrosion process leads to the generation of hydrogen, a percentage of which is known to be absorbed into the metal substrate [1]. As an interstitial element it occupies the tetrahedral sites between lattice planes and causes growth of the metal substrate. Blat et al. used a gaseous hydrogen charging technique to measure the hydrogen-induced lattice strain. Results taken between 300 and 2000 wppm hydrogen predict strains in recrystallised Zircaloy-4 sheet of 1.15×10^{-6} per wppm [9]. Vizceno et al. aimed to quantify this effect by heating cathodically charged Zircaloy-4 tube to 300 °C in a push-rod differential dilatometer. Hydrogen concentrations in the range of 150–400 wppm gave an axial elongation of 5.21×10^{-6} per wppm [33].

The following work combines newly presented in-situ S-XRD data on the development of phase fraction and stress as an oxide grows, existing ex-situ S-XRD measurements on autoclave tested samples, and significant finite element analysis of the oxidation process. The aim of the work is to establish if a combination of mechanisms including creep and hydrogen-induced lattice strain could explain oxide stress relaxation observed experimentally.

2. Experimental

2.1. Materials

Materials included samples of recrystallised Zircaloy-4 and ZIRLO™ sheet, cut into coupons with respective dimensions of $30 \times 20 \times 0.6\ mm^3$ and $30 \times 20 \times 0.45\ mm^3$. Sample preparation involved pickling in HF solution (5%HF, 45%HNO_3 and 50%H_2O) [34]. All materials were provided by Westinghouse, and the chemical compositions for these materials can be found in Table 1.

2.2. In-situ synchrotron X-ray diffraction

All synchrotron X-ray diffraction experiments were carried out at the EDDI beam-line at BESSY II (Berlin, Germany) [35]. EDDI is a polychromatic energy dispersive beam-line allowing rapid acquisition of the diffraction peaks in the energy range of 8–120 keV. The classical $\sin^2\psi$ technique was used to characterise the biaxial in-plane compressive residual stress in the oxide layer by tilting the sample through a range of ψ angles and measuring diffraction patterns through each angle. The specific peaks of interest for measuring residual stress in thermally grown zirconium oxides are the $(\bar{1}\,1\,1)_m$ monoclinic and $(1\,0\,1)_t$ tetragonal peaks. In addition to these two reflections the $(1\,1\,1)_m$ monoclinic peak was incorporated into the Garvie–Nicholson formula for defining the tetragonal zirconia phase fraction [36]:

$$f_{tet} = \frac{I_{t(1\,0\,1)}}{I_{t(1\,0\,1)} + I_{m(1\,1\,1)} + I_{m(\bar{1}\,1\,1)}} \quad (1)$$

where I_{xxx} are the averaged integrated intensities of each reflection along the range of ψ angles. These techniques have been used for both the previously published ex-situ analysis of samples oxidised in an autoclave [5], and the in-situ air oxidation experiments presented here. More detailed description of the $\sin^2\psi$ and Garvie–Nicholson techniques used in similar experiments can be found in [5]. The key in-situ oxidation experiments used a heated sample stage, allowing diffraction patterns to be recorded every 4.5 min as the oxide layer is formed. Samples from each of the alloys were subjected to the thermal profiles discussed in the following section, and the evolution of each oxide phase was recorded. By calculating the stress in the monoclinic and tetragonal phases and weighting them based on the corresponding phase fraction it is possible to define an average bulk oxide in-plane compressive stress.

The previously presented S-XRD experiments involved removing a number of samples from the autoclave at different oxidation

Table 1
Chemical compositions for zirconium alloys (wt%).

Materials	Sn	Fe	Cr	Ni	Nb
Zircaloy-4	1.24	0.17	0.1		<0.01
ZIRLO™	0.92	0.09			0.91