



Finite element analysis of the tetragonal to monoclinic phase transformation during oxidation of zirconium alloys



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ABSTRACT

Corrosion is a key limiting factor in the degradation of zirconium alloys in light water reactors. Developing a mechanistic understanding of the corrosion process offers a route towards improving safety and efficiency as demand increases for higher burn-up of fuel. Oxides formed on zirconium alloys are composed of both monoclinic and meta-stable tetragonal phases, and are subject to a number of potential mechanical degradation mechanisms. The work presented investigates the link between the tetragonal to monoclinic oxide phase transformation and degradation of the protective character of the oxide layer. To achieve this, Abaqus finite element analysis of the oxide phase transformation has been carried out. Study of the change in transformation strain energy shows how relaxation of oxidation induced stress and fast fracture at the metal–oxide interface could destabilise the tetragonal phase. Central to this is the identification of the transformation variant most likely to form, and understanding why twinning of the transformed grain is likely to occur. Development of transformation strain tensors and analysis of the strain components allows some separation of dilatation and shear effects. Maximum principal stress is used as an indication of fracture in the surrounding oxide layer. Study of the stress distributions shows the way oxide fracture is likely to occur and the differing effects of dilatation and shape change. Comparison with literature provides qualitative validation of the finite element simulations.

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1. Introduction

Oxides that form on nuclear grade zirconium alloys during autoclave testing in water or steam are not only composed of monoclinic but also tetragonal phase, particularly near the metal/oxide interface [1–6]. This is despite only the monoclinic phase being stable in pure zirconia below ~1200 °C [7]. However there are a number of factors relating to naturally forming oxides that contribute towards stabilising the tetragonal phase down to room temperature. This includes compressive stress, grain size, oxygen vacancies and alloying elements. Synchrotron X-ray Diffraction (S-XRD) has repeatedly shown that the oxide is strongly compressed [1–6], something which is known to stabilise the tetragonal phase in zirconium oxides [7–12]. Garvie demonstrated that ~30 nm represents a critical size below which pure tetragonal zirconia can be stabilised by grain size alone [13]. Transmission electron microscopy (TEM) has been used to show that oxides formed on Zircaloy-4 and ZIRLO™ consist of equiaxed grains 10–30 nm in

diameter, and columnar grains 14–40 nm wide and 135–230 nm long [14]. It is therefore plausible that grain size is a contributing factor in the stabilisation of the tetragonal phase present in the oxide. Zirconium alloys oxidise almost entirely due to the inward migration of oxygen ions [15]; this requires the generation of oxygen vacancies at the metal–oxide interface which migrate outwards. The impact of oxygen vacancies on the lattice structure is a leading theory for the stabilisation of manufactured tetragonal zirconia [10,16–18]. Finally, zirconium alloys contain a range of alloying elements some of which, such as iron and chromium, have previously been shown to stabilise the tetragonal phase when used as a dopant [19–23]. However it must be noted that these alloying elements will be present in the oxide in very small quantities when compared with typical dopants used in manufactured zirconia.

The corrosion kinetics of zirconium alloys out of reactor, in aqueous solution at ~360 °C, can be summarised as follows: initial rapid corrosion associated with a non-protective layer of equiaxed grains between 300 and 500 nm thick, this is followed by the formation of long columnar grains and the reduction of corrosion kinetics [14]. Synchrotron X-ray diffraction, TEM, and t-EBSD have indicated that the equiaxed grains are often tetragonal and that the columnar grains are typically monoclinic [24–26]. It could be implied then that the equiaxed region near the surface of the oxide

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may have a higher tetragonal phase fraction. These two stages give a kinetics curve somewhere between parabolic and cubic. In commercial, nuclear grade zirconium alloys a breakdown of the protective character of the oxide is usually seen after $\sim 2 \mu\text{m}$ of oxide growth, followed by acceleration in the corrosion kinetics. This process of breakdown and acceleration is referred to as transition. Oxide growth is then cyclical, repeatedly forming almost identical layers separated by transition points in the corrosion kinetics every $\sim 2 \mu\text{m}$ [15,27].

Experiments using S-XRD by both Polatidis and Petigny have separately shown an $\sim 7\%$ reduction in the tetragonal phase fraction from 1 to 3 μm oxide growth on Zircaloy-4 [4,5]. This indicates that there may be destabilisation of the tetragonal phase. From a mechanical point of view there are two key features that occur during the oxidation process. Firstly is the relaxation of compressive stresses in the oxide [4,5]. Which could relate to oxidation induced creep and hydrogen induced strain in the metal substrate [28–30]. Secondly there is the formation of micro-scale lateral cracks at or near the metal oxide interface (see Fig. 1). Although some small cracks appear to be present throughout the oxidation process, larger numbers of micro-scale cracks have been associated with the transition points in the corrosion kinetics [5,6,24,27]. Finite element analysis has indicated that these cracks may be formed by localised out-of-plane stresses associated with undulations at the metal–oxide interface. In this analysis the maximum principal stress is at the metal–oxide interface, raising the question over whether these cracks form due to fracture of the oxide or de-bonding at the interface [31]. In manufactured partially stabilised zirconia, the zone of tensile stress ahead of an advancing crack causes the tetragonal phase to transform to monoclinic. Although the transformation can arrest micro-scale cracks, it can also generate smaller cracks typically along grain boundaries [8,32]. The formation of small cracks perpendicular to the metal oxide interface would allow fast ingress routes for oxygen containing species providing part of the explanation for transition in the corrosion kinetics [33].

The present work incorporates experimental data and theoretical calculations into a finite element analysis of the tetragonal to monoclinic phase transformation. The dilatation and shear effects are separated, and analysis includes the energy of transformation and stress distributions in the surrounding oxide. In this way mechanical destabilisation of the tetragonal phase and degradation of the oxide layer can be considered.

2. Model construction

2.1. Microstructural representation and boundary conditions

All simulations have been carried out using the Abaqus finite element system. The models are 3D linear elastic consisting of a single grain surrounded by a homogenous oxide (Fig. 2). The single grain has been simulated as a truncated octahedron in order to use

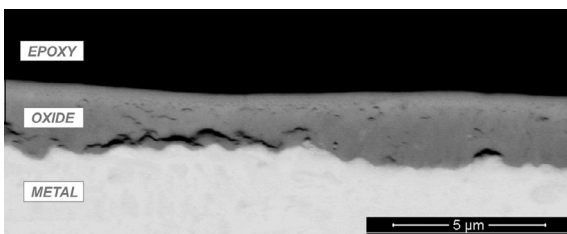


Fig. 1. Back-scattered SEM cross section image of Zircaloy-4 oxidised in primary water for 180 days at 360 °C. This shows the lateral cracks that form in the oxide at the first transition point in the corrosion kinetics.

a symmetrical shape that approximates an equiaxed grain. With relation to the metal–oxide system (Fig. 1) directions 1 and 2 are parallel to the metal–oxide interface (in-plane) whilst direction 3 is perpendicular (out-of-plane). A symmetry boundary condition has been placed on the bulk model at one of the faces normal to each direction, fixing displacement and rotation. For each direction, the opposite face has an equation constraint ensuring the entire face strains evenly. This combination of boundary conditions and constraints allows the model to be representative of a small cube in the centre of an infinite oxide.

These simulations are then used to represent two basic stress states relating to destabilisation of the tetragonal phase. The first represents relaxation of the biaxial compressive stress induced by the oxidation process, potentially due to creep or hydrogen induced strain. This involves application of a compressive stress in the in-plane 1 and 2 directions. Experimental results offer a wide range of values for in-plane compressive stresses in oxides formed on zirconium alloys, with significantly higher values at the metal–oxide interface compared to the outer surface [6]. For thin oxides, S-XRD gives average stress values in the order of -1 GPa for the monoclinic phase and -2 GPa for the tetragonal phase [5]. These values frequently show a gradual relaxation in the average in-plane stress over time as the oxide thickens [1–6]. The effect is simulated in these models by running the phase transformation under a range of bi-axial compressive stresses from -2.2 GPa down to -0.1 GPa .

The second stress state is a tri-axial tensile stress designed to represent the zone ahead of an advancing crack tip. Micro-scale lateral cracks have been observed in the oxide layer, and appear to form very close to or at the metal–oxide interface (Fig. 1). Finite element analysis by Parise et al. indicated that these cracks form as a result of localised tensile stresses above peaks in the metal–oxide interface roughness [31]. These cracks are considered separate to any nano-scale cracks that might result from the tetragonal to monoclinic phase transformation. An assumption is made here that whether the micro-scale lateral cracks form via fracture of the oxide or by de-bonding at the interface a triaxial tensile stress state will still be present. In manufactured partially stabilised zirconia cracks would be expected to destabilise the tetragonal phase. This is simulated by applying tensile stress in direction 1, 2 and 3. As this the maximum stress at the crack tip is not known, the applied tensile stresses cover a range from 0.1 GPa up to a maximum stress value of 2.2 GPa as it is approximately equal to three times the fracture strength of bulk fracture strength for manufactured stabilized zirconia [34]. For the biaxial compressive and triaxial tensile stress states it is the trends in behaviour rather than the absolute values that are considered of greatest importance for this work.

The 3D elements used in the present model are fully integrated 4 node tetrahedrons with 10 integration points (C3D10). The overall dimensions of the models are $150 \times 150 \times 150 \text{ nm}^3$, which represents the surrounding oxide. In the centre there is a truncated octahedron with a width of 50 nm in direction 1, 2, and 3, which characterises the grain that will be transformed. It has been reported previously that tetragonal grains with a diameter of about 30 nm can be size stabilised. Hence a slightly larger grain might be typical for a stress stabilised tetragonal grain. The elastic constants that have been incorporated to represent orthotropic material behaviour in 3D are shown in Table 1 [35,36]. It should be noted that the tetragonal elastic constants are taken for 12 mol% Ce-TZP (Cerium stabilised tetragonal zirconia polycrystal) [36].

2.2. Model limitations

A finite element model at such scale raises the question of whether the constitutive equations used in Abaqus will be able to truly represent the behaviour of a materials microstructure at

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