Journal of the European Ceramic Society 36 (2016) 2341–2349

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Diffusion-based and creep continuum damage modelling of crack formation during high temperature oxidation of ZrN ceramics

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ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form
20 November 2015
Accepted 22 November 2015
Available online 22 December 2015

Keywords:
Oxynitride
Nitride
Oxidation
Micro-cracking
Continuum damage modelling

ABSTRACT

ZrN's good thermal and mechanical properties make it suitable for many commercial applications including in nuclear fuels. An understanding of its oxidation behaviour is essential to prevent catastrophic failures and ensure it is employed safely in nuclear power plants. Based on available experimental results on oxidation of ZrN in the temperature range 1173–1373 K, a continuum damage mechanics-based combined creep and time-dependent material oxidation model is proposed. The model allows for the development of a surface oxide layer combined with damage due to creep under an applied load. A representative grain structure has been modelled according to ZrN microstructural characteristics in order to allow intergranular cracking and individual oxidation damage rates for grains and grain boundaries. The proposed damage model is implemented as a user subroutine and runs in a coupled temperature-displacement analysis using the commercial finite element software Abaqus. Available data on ZrN are used to validate the capability of the model to predict oxidation damage in ceramics at high temperatures.

1. Introduction

Zirconium nitride is being considered for use in advanced nuclear power plants as inert matrix fuel (IMF) or as accident tolerant fuel particle coating due to its high thermal conductivity, low neutron capture cross section and chemical compatibility with existing fuel cycle technology [1]. Due to this increased interest in ZrN, recent work has focused on assessing thermophysical properties of ZrN and mixed phases of actinide nitrides dispersed in ZrN [2–11]. However, there have been few studies on the oxidation behaviour of ZrN which is an important factor to be considered especially under accident conditions such as occurs in a loss of coolant accident (LOCA).

The majority of oxidation studies of ZrN have been performed on thin films due to the extensive use of ZrN as a hard coating on cutting tools. Krusin-Elbaum and Wittmer [12] studied the oxidation kinetics of ZrN thin films (60 nm–1 μm) reporting the activation energy of oxidation to be $241 \pm 10\,\mathrm{kJ\,mol^{-1}}$ for 748–923 K with the oxide layer comprising monoclinic (m) and cubic (c) ZrO_2. Panjan et al. [13] showed the oxidation of ZrN coatings with thicknesses of 300 μm to have an activation energy of $229\,\mathrm{kJ\,mol^{-1}}$ from 773–1123 K and to obey a parabolic rate law, in agreement with Krusin-Elbaum and Wittmer.

ZrC has similar chemical properties and crystal structure to ZrN and its oxidation kinetics and mechanism in the bulk are better understood and thus will be discussed here. Shimada and Ishil [14] report the onset of oxidation occurring 653–750 K and observe a change in mechanism of ZrC oxidation with increasing temperature. At temperatures > 743 K, submicron c-ZrO_2 crystals nucleate from the amorphous $ZrO_2 + C$ layer and this forms a dense layer which becomes rate determining in regards to oxygen diffusion through the oxide scale. However, at temperatures > 823 K and increased oxidation times the small crystallites grow and strain arising from the volume expansion causes intergranular fracture, thus paths for oxygen diffusion in and CO_2 diffusion out are formed. Berkowitz-Mattuck [15] report the onset of oxidation of ZrC occurs at temperatures < 1470 K and the author observed a porous m-ZrO_2 scale which fractured due to intergranular oxidation. However, above 1470 K a dense ZrO_2 layer formed, attributed to sintering effects and resulted in the decreased diffusion rate of oxygen to the bulk in agreement with Shimada and Ishil [14]. Simultaneously the formation of dense scales of ZrO_2 has been proposed to provide effective oxidation resistance in ZrB_2–SiC [16] and ZrC–SiC [17] composites.

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.11.023

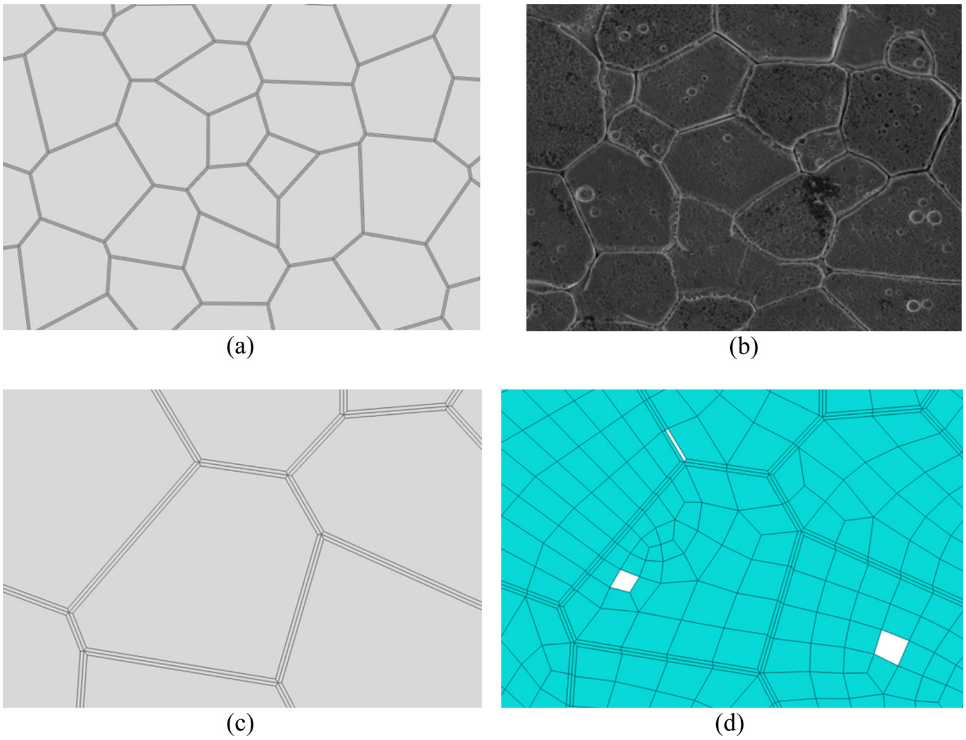

Fig. 1. (a) Microstructure generated using Voronoi tessellations, (b) actual ZrN microstructure on chemically etched sample, (c) close-up of a grain showing grain boundary regions and (d) microstructure after meshing showing voids coloured in white.

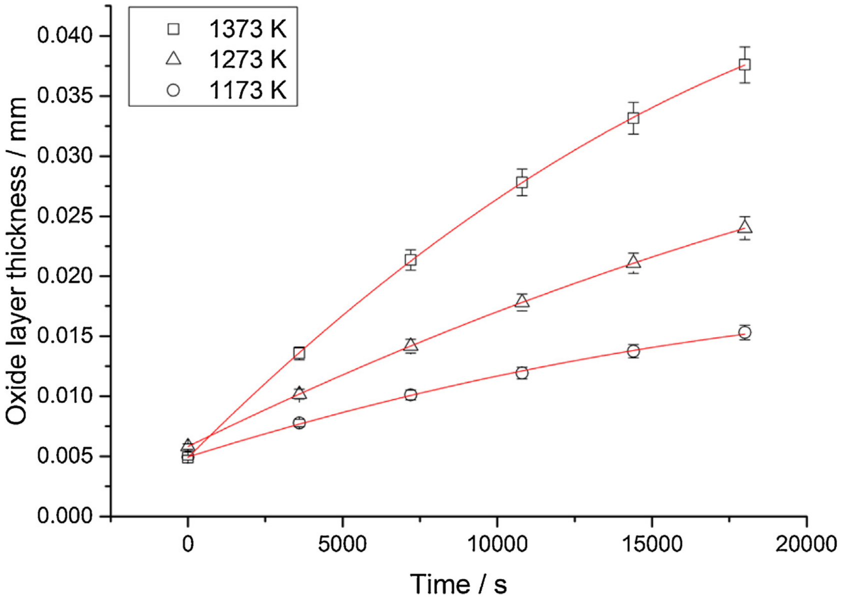

Fig. 2. Oxide layer thickness as a function of time.

Recent work on the oxidation of bulk ZrN ceramics [18] reveal the formation of this dense, protective ZrO_2 layer at temperatures of 1173 K which slows the rate of oxidation. However, above this temperature (1273–1373 K) the protective layer fails with ZrN grains near the oxide interface showing intergranular cracking and extensive grain boundary oxidation. This attack on the grain boundaries may occur by two mechanisms:

- Increased rate of oxygen diffusion through the oxide scale leads to oxidation of grain boundaries and subsequent intergranular fracture from stresses induced.
- Intergranular fracture of the surface ZrN grains due to strains from the advancing oxide layer, opening channels for oxygen ingress and therefore oxidation of the grain boundaries.

In this work a continuum damage model is proposed that aims to predict oxidation damage and compare to experimental results previously reported [18] to produce a failure mechanism of the grain boundaries during oxidation of ZrN. Due to lack of Young's modulus data for ZrN, values for ZrC have been used in the model [19,20]. The methodology can also account for creep damage [21] and is presented in a later section. This work focuses on oxidation