



An elastic phase field model for thermal oxidation of metals: Application to zirconia



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ARTICLE INFO

Article history:

Received 26 November 2013

Received in revised form 17 March 2014

Accepted 21 March 2014

Available online 18 April 2014

Keywords:

Oxidation

Zirconium

Phase field model

Finite element method

Growth stress

ABSTRACT

A multi-phase field model was developed for non-selective oxidation of metals which captures both the oxidation kinetics and stress generation. Phase field formulation involved a non-conserved phase field variable as the marker for the metallic substrate, oxide scale, and a fluid phase containing oxygen, and a conserved phase field variable representing the concentration of oxygen. The evolution equations of the phase field variables were coupled to the mechanical equilibrium equations to investigate the evolution of stress generation in both the oxide scale and the underlying metal. The governing equations were solved in a finite element framework. This phase field model predicts the oxygen composition depth and stress profiles in the oxide layer and at the metal–oxide interface. The model was proven successful in predicting the observed evolution of oxide thickness and growth stresses for Zircaloy-4 oxidized at 900 °C. The results of phase field simulations showed that the generation of stresses upon oxidation tends to slow down the oxidation kinetics, and this substantially improved the model predictability of experimental data.

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1. Introduction

Metals and alloys exposed to high temperatures during service and operating in aggressive environments usually suffer from oxidation at their free surfaces. Oxidation is considered as one of the most important lifetime limiting factors for metallic components used in high temperature applications [1–8]. Oxidation resistance can be obtained if metals form a protective oxide layer called the thermally grown oxide (TGO). The TGO must be able to grow uniformly and continuously on the substrate while maintaining a good adherence and structural health. Alumina is the most common TGO found in engineering applications requiring long thermal exposures. Alumina layers grown on alumina-forming alloys have a particularly low diffusivity of oxygen, an excellent creep resistance, and are able to remain adherent and compact at temperatures exceeding 1300 °C. Alumina-forming alloys are exemplified by nickel aluminides used as bond coats in thermal barrier coating (TBC) systems, and by iron–chromium–aluminum (FeCrAl) alloys which find use in TBCs and in catalytic converters [9] and heat exchangers [10]. Chromia can also form a stable TGO in chromium-containing ferritic steels. However, chromia is much more

unstable than alumina and as such not often utilized in structural components undergoing oxidation above 600 °C, unless the electronic conductivity of the oxide is a major concern, as in interconnects in semiconductor devices.

A particular high temperature application disqualifying both alumina and chromia as TGO layers is the fuel-rod cladding for nuclear reactors. The cladding material must be transparent to neutrons with high thermal creep resistance, and this fact renders only low-alloy zirconium alloys, namely Zircaloy grades [11–14], usable. Thus, the oxidation resistance of Zircaloy relies on the growth of zirconia (ZrO₂), usually at temperatures between 320 °C and 600 °C, or, at much higher temperatures, in the case of undesirable power ramps. Zirconia, however, is substantially more prone to cracking and spalling than thin alumina and chromia layers [15]. Cracking has actually emerged in the last decade as a major factor reducing the durability of Zr cladding [16–21]. In fact, the oxidizing environment in most nuclear reactors is water, and upon its reduction by the zirconium oxidation, it produces hydrogen. Hydrogen diffuses faster through cracks and other fast diffusion paths leading to an increase in the hydrogen uptake (HU) by the zirconium substrate. HU leads to a variety of embrittlement phenomena such as formation of hydride blisters and rims as well as an acceleration of the oxidation kinetics. Because of the remarkable susceptibility of zirconia to develop cracks upon oxidation, HU is considered as the most critical source of environmental

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degradation of zirconium cladding. Regardless of whether the TGO layer is alumina, zirconia or chromia, stresses induced in the metal and in the TGO by an isothermal oxidation process plays a major role in TGO cracking and spallation mechanisms. Internal stresses can be of two natures:

1. Growth stresses [22–27] develop due to either dislocation climb-glide return at the interface [28–36] or interdiffusion [34,36,37]. While interdiffusion occurs only in alloys where selective oxidation is substantial, interfacial misfit dislocation activities contribute to stress generation for any oxidizing metal within both the metal and the oxide scale. Growth stresses in the oxide and metal can be in the order of tens of GPa [1] and have been involved in several forms of damage in the oxide scale and in the metal rushing breakaway oxidation [36,38–42]. In addition to these effects, growth stresses induce mass transport and mismatch strains at the metal–oxide interface, which cause the interface to corrugate, and thus the oxide scale to wrinkle and pattern stresses and cracks [35,43–51]. For example, the present authors recently showed that mismatch elastic stresses due to the lattice dilatation and interdiffusion at the solid–fluid interfaces can cause interface corrugation without any contribution from an external force [51].
2. Transformation stresses develop due to phase transformation within the oxide or within the metal upon oxidation. Phase transformation in the oxide scale was observed to occur in both of alumina and zirconia. In alumina, metastable polymorphs of cubic (γ -phase) and/or monoclinic (θ -phase) structures transform to the stable α -phase, thereby generating high stresses under the large difference of the atomic volumes between these allotropic phases [40,52–54]. Tetragonal to monoclinic transformation has also been observed to occur in thin zirconia layers grown over Zircaloy-2 and Zircaloy-4 [55–61]. Based on the recent observations by Park et al. [62] and the scaling mechanisms put forward by Martin et al. [63], transformation stresses may play a tacit and significant role in the generation and patterning of cracks observed in oxide scales developed over Zircaloy [15,64–66].

Modeling, via the sharp interface approach, of growth stresses due to misfit dislocation activities upon the thickening process of the TGO is a convoluted problem. In fact, such models must count the dislocations leaving the interface to accommodate metal recession and those returning to the interface to maintain epitaxiality. Although Suo et al. [34] attempted to formulate governing equations incorporating the dislocation-based mechanisms identified by Pieraggi et al. [29,33], their models were essentially phenomenological as they did not introduce any type of dislocation densities. There is in fact no physical model in the literature that incorporated the mechanisms put forward by Pieraggi et al. [33]. Moreover, the numerical implementation and investigation of Suo's [34] and El Kadiri's [36] models beyond a one-dimensional case are extremely difficult as the necessity to track the interface is computationally impractical. Accordingly, all current oxidation models are essentially continuum models that rely on the Pilling–Bedworth ratio (PB ratio or PBR) and calculate growth stresses thereupon. Moreover, continuum models for growth stresses did not take into account the effect of growth stress gradient on the diffusion according to Stephenson's Law [37]. Krishnamurthy and Srolovitz [67,68] presented a continuum model to study stress distribution in growing oxide films. Using the mass balance of the chemical reaction, these authors derived the reaction–diffusion governing equations, then followed Larch and Cahn's theory [25] to relate the chemical (or diffusion) potential to the stress; the chemical potential is the sum of the stress-free chemical potential and a function which linearly depends on the dilatational stress.

Similar approach was used by Zhou et al. [69,70] to study stress–oxidation interaction for Fe–Cr alloys exposed at high temperatures.

The phase field method (also known as the diffusive-interface method) may constitute a suitable alternative to the sharp-interface approach for the highly coupled problem of oxidation and growth stresses. Furthermore, once a phase field model for oxidation and stress is built, simulation of crack patterning in the oxide scale can be feasible provided that a coupling with another phase field model incorporating constitutive equations for damage is integrated. Only a few phase models of oxidation can be found in the literature, which were only developed during the last decade. For instance, Ammar et al. [71] developed a phase field model to study the oxidation kinetics of zirconium exposed to high temperatures. However, these authors presented simplified models that did not consider the generation of stresses.

In this paper, we developed a phase field model capable of computing the thickening rate of the TGO grown over metals under the effect of growth stresses generated in both the metal and TGO. This initial framework had to first couple oxidation and stresses under a simplified approach relying on the PB ratio. The model can, however, be easily modified to incorporate more robust mechanisms for stress generation. The phase field model assumes that stress is only generated by the compositional deviation from the equilibrium values across the interfaces and inside the metal and oxide phases. The governing evolution equations of phase field variables are derived by minimizing the total free energy of the system considering diffusion of species. These governing equations are coupled to mechanical equilibrium equations to determine the induced stresses and their effects on composition depth profile of the oxygen in the oxide layer and in the metallic substrate. To solve the governing equations of the problem a finite element model which was initially developed by Asle Zaeem and Mesarovic [72,73] and applied for studying phase transformation in binary alloy systems [74–77], is used to compute the thickening rates of the oxide scale and the stress profiles developed upon the oxidation of Zircaloy-4.

2. Phase field model of oxidation

For deriving the governing equations of the phase field model, one conserved and one non-conserved phase field variables are used. The conserved phase field variable, $c(\mathbf{x}, t)$, is considered for the concentration of oxygen in spatial (\mathbf{x}) and time domains (t). A non-conserved phase field variable, so called order parameter, $\phi(\mathbf{x}, t)$, is considered as the marker of different phases, which takes values $\phi_m = 0$ in the metal, $\phi_o = 1/2$ in the oxide, and $\phi_f = 1$ in the fluid.

The inclusion of the fluid phase enables capturing the case of cationic mechanism of oxidation, which would cause an outward growth of the oxide scale. Generally, oxidation proceeds under both cationic and anionic mechanisms, the latter promoting inward growth of the scale. However, in practice, either case predominates. In Zircaloy for instance, the diffusion of zirconium is much slower than that of oxygen in the oxide layer, so oxidation is essentially anionic as the new oxide molecule predominantly forms at the metal/oxide interface. Some existing models, such as the one developed by Ammar et al. [71], do not consider a fluid phase therefore are not capable of capturing the outward growth of the oxide scale. Thus, they may overlook the effect of the kinetics and thermodynamics related to oxygen generation and absorption at oxide–fluid interface. This is known to be the case in nuclear reactors where the corrosive environment is water vapor, which also generates hydrogen. The total free energy of a system including a metal phase (m), an oxide phase (o) and a fluid phase (f) can be written as:

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