



Stress–diffusion interaction during oxidation at high temperature



Xuelin Dong^{a,b,c}, Xue Feng^{a,b,*}, Keh-Chih Hwang^{a,b}

^a AML, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China

^b Center for Mechanics and Materials, Tsinghua University, Beijing 100084, China

^c Key Laboratory of Petroleum Engineering, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

Article history:

Received 6 August 2014

In final form 4 September 2014

Available online 16 September 2014

ABSTRACT

Superalloy or other thermal protective materials are often oxidized seriously at high temperature. For most materials diffusion is the controlling step of oxidation. During oxidation, stress would be induced by growth strain and it can affect the diffusion process through chemical potential and diffusivity. Governing equation for diffusion is derived considering chemo-mechanical potential and diffusivity affected by stress. Oxidation kinetics is obtained to interpret the stress–diffusion coupling effects. The stress and its gradient influences on oxidation are also discussed.

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It has been observed that significant mechanical stress may generate in oxide film caused by the scale growth for superalloy or other thermal protective materials during oxidation [1–5]. Stress is crucial to the performance and reliability of the structures based on these materials [1,6,7]. Growth strain is one of the mechanisms to explain the stress generation, and it is related to the oxidation kinetics [8–11]. For most materials the oxygen diffusion through the grown oxide film is the control step of oxidation [3,12]. Hence the oxide stress is determined by oxygen diffusion process. In return, it has been demonstrated that the stress can affect the diffusion [13–16]. The applied tensile stress would accelerate the oxidation rate since it may increase the diffusivity [13]. Meanwhile, stress in the oxide can change the oxygen potential gradient which is the driven force for diffusion [17–19]. Therefore, it is necessary to consider the stress–diffusion coupling effects to analyze the stress evolution and oxidation kinetics. In this letter, we derive a governing equation for diffusion considering the growth stress, stress-dependent diffusivity as well as the chemo-mechanical potential. The oxidation kinetics is predicted by the proposed model and compared with the experimental results. Then we investigate the stress and its gradient effects on diffusion for oxidation kinetics. This finding is useful for interpreting the mechanical behavior of oxide film/substrate structure during oxidation.

Generally, the oxide scale formation involves a sequence of events including the adsorption of atomic oxygen at the substrate surface at first stage. Then nucleation and growth occurs and a thin oxide film forms until it covers the substrate surface at second stage. The substrate is oxidized further and oxide scale thickens with growth stress generated at third stage. Since the oxidation reaction rate is faster than oxygen diffusion for most materials, oxidation kinetics is dependent on oxygen diffusion at the third stage. Therefore, we focus on the diffusion process and analyze the stress–diffusion coupling effects during oxide film growth, *i.e.* the third stage.

The oxide/substrate structure can be modeled as a thin film/substrate system with a migrating interface as illustrated in Figure 1. For simplicity only half of the system is shown due to symmetry. The origin of the axis Z is set at the center on the top surface of the oxide. h_{ox} and H represent the thickness of the oxide film and the system, respectively. During oxidation the oxide film would grow laterally and it can be viewed as a path for oxygen diffusion. Growth strain would be generated in the oxide since the lateral growth is constrained by the substrate. As the oxide film is quite thin the stress in the oxide is equi-biaxial and can be expressed as $\sigma_{ox} = M_{ox}(\varepsilon_{ox}^e - \varepsilon_g)$, where σ_{ox} is the oxide stress, ε_{ox}^e and ε_g represent the elastic strain and growth strain, respectively, $M_{ox} = E_{ox}/(1 - \nu_{ox})$ is the biaxial modulus of the oxide, E_{ox} and ν_{ox} are the Young's modulus and Poisson's ratio of the oxide, respectively [20]. According to Larche and Cahn's theory [21] the growth strain is related to the oxygen concentration and Pilling-Bedworth's ratio (PBR) as $\varepsilon_g = \omega(PBR^{1/3} - 1)[c(z) - c_{ref}]$, where ω is the relaxation factor, c and c_{ref} are the oxygen concentration and reference concentration respectively. The stress in the substrate σ_s

* Corresponding author at: AML, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China.

E-mail addresses: fengxue@tsinghua.edu.cn, xfeng9@gmail.com (X. Feng).

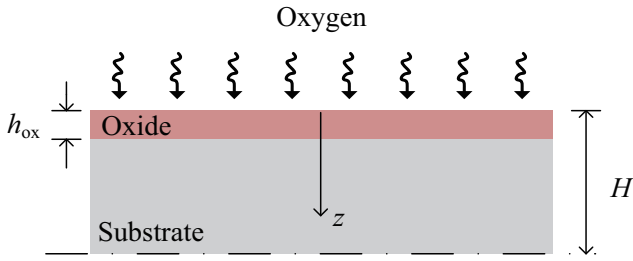


Figure 1. Schematic of the oxide film/substrate system during oxidation.

can be estimated as $\sigma_s = M_s \varepsilon_s^e$, where ε_s^e is its elastic strain and $M_s = E_s / (1 - \nu_s)$ is the biaxial modulus of the substrate, E_s and ν_s are the Young's modulus and Poisson's ratio of the substrate, respectively. The force balance of the system requires that:

$$\int_0^{h_{ox}} \sigma_{ox} dz + \sigma_s (H - h_{ox}) = 0 \quad (1)$$

The deformation continuity between the substrate and oxide film leads to $\varepsilon_{ox}^e = \varepsilon_s^e$. Substitute the growth strain and stress expressions into Eq. (1), the oxide stress is obtained as:

$$\sigma_{ox} = \frac{M_{ox}^2 \varepsilon_0 \int_0^{h_{ox}} c(z) dz}{M_{ox} h_{ox} + M_s (H - h_{ox})} - M_{ox} \varepsilon_0 \left[c(z) - \frac{M_s (H - h_{ox})}{M_{ox} h_{ox} + M_s (H - h_{ox})} c_{ref} \right] \quad (2)$$

Eq. (2) shows that the stress is proportional to the oxygen concentration.

It can be seen that the stress in the oxide is induced by the oxygen diffusion during oxidation from Eq. (2). For most metal or ceramic materials, the oxygen diffusion controls the oxidation kinetics since the reaction rate at the oxide film/substrate interface is very fast. Based on Fick's law the oxygen diffusion through the oxide scale can be described as [12]:

$$\frac{\partial c}{\partial t} + \nabla \cdot J = 0 \quad (3)$$

where t represents the oxidation time, and J is the oxygen flux that is given by:

$$J = -\frac{Dc}{RT} \nabla \mu \quad (4)$$

where D is the diffusion coefficient (diffusivity), R is the gas constant, T is the absolute temperature, and μ represents the chemical potential of the oxygen.

The stress effects on the oxygen diffusion reflect in the chemical potential and diffusion coefficient. When an oxygen atom in the oxide is subjected to stress, its chemical potential incorporates both chemical and mechanical energies, which is also referred to as chemo-mechanical potential. Considering the stress in the oxide, this chemo-mechanical potential is expressed in terms of the chemical potential μ_0 , the partial volume Ω , concentration of oxygen, and the hydrostatic stress σ_h as [17,19]:

$$\mu = \mu_0 + RT \ln c - \sigma_h \Omega \quad (5)$$

For current stress state in the oxide $\sigma_h = 2\sigma_{ox}/3$. Eq. (5) is consistent with the experimental observation that the chemical potential increases when the material is under compression and *vice versa*. It should be noted that it is the stress gradient along the oxide thickness that will affect oxygen diffusion based on Eqs. (4) and (5). In other words, uniform stress would not have any influence on oxidation since it could not change the oxygen chemical potential gradient.

Diffusivity is another important factor to the diffusion process according to Eq. (4), which would be modified by the stress in the oxide as [14,15]:

$$D = D_0 \exp \left(\frac{\alpha \Omega \sigma_{ox}}{RT} \right) \quad (6)$$

where D_0 is the stress-free diffusivity, α is a positive dimensionless coefficient. It can be inferred that the diffusivity would increase (decrease) when the oxide is under tension (compression) based on Eq. (6). Therefore, the stress effects on diffusion reflect in two aspects: the chemo-mechanical potential and the diffusivity.

The stress in the oxide, chemo-mechanical potential and the modified diffusivity are given by Eqs. (2), (5) and (6), respectively. With Eqs. (3) and (4), the governing equation for oxygen diffusion is developed as:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left\{ D_0 \exp \left[\frac{\alpha \Omega M_{ox} \varepsilon_0}{RT} \left(\frac{M_{ox} \int_0^{h_{ox}} c(z) dz}{M_{ox} h_{ox} + M_s (H - h_{ox})} - c(z) \right) \right] \right. \\ \left. \times \left(1 + \frac{2M_{ox} \Omega \varepsilon_0}{3RT} c(z) \right) \frac{\partial c}{\partial z} \right\} \quad (7)$$

Then the oxidation kinetics can be determined by:

$$\frac{dh_{ox}}{dt} = \beta J \quad (8)$$

where β is a coefficient related to substance and reaction [12]. From the above analysis, the governing equations for diffusion, oxidation kinetics and stress evolution are presented in Eqs. (7), (8) and (2), respectively.

Let $\tilde{c} = c/c_0$ (c_0 is the oxygen concentration at the oxide outer surface), $\tilde{z} = z/H$, $\tilde{h} = h_{ox}/H$, $\tilde{M} = M_s/M_{ox}$, $\lambda_1 = \alpha \Omega M_{ox} \varepsilon_0 c_0 / RT$, $\lambda_2 = 2\Omega M_{ox} \varepsilon_0 c_0 / 3RT$, $\tilde{c}_{avg} = \int_0^{h_{ox}} c(z)/c_0 dz / h_{ox}$, and $\tau = D_0 t / H^2$. Then, the diffusion governing equation can be cast into dimensionless form:

$$\frac{\partial \tilde{c}}{\partial \tau} = \frac{\partial}{\partial \tilde{z}} \left\{ \exp \left[\lambda_1 \left(\frac{\tilde{c}_{avg}}{1 + \tilde{M}(\tilde{h} - 1)} - \tilde{c} \right) \right] (1 + \lambda_2 \tilde{c}) \frac{\partial \tilde{c}}{\partial \tilde{z}} \right\} \quad (9)$$

where τ is the non-dimensional oxidation time as defined. Assume that the oxygen concentration is steady by constant supply of oxygen at the scale outer surface, and no oxygen can cross the interface into the substrate that means the oxygen flux must cease at the oxide/substrate surface [19,22,23]. Then the boundary conditions for the above equation are:

$$\begin{cases} \tilde{c} = 1, & \tilde{z} = 0 \\ \tilde{J} = 0, & \tilde{z} = \tilde{h} \end{cases} \quad (10)$$

where \tilde{J} is the non-dimensional oxygen flux at the oxide film/substrate interface. The oxide and substrate phases are also separated by this migrating interface.

In this letter, the governing equation is solved by numerical method and the material properties and geometry parameters for simulation are obtained from reference [15,24]. The oxide thickness predicted by the current model is plotted as the solid line in Figure 2. For comparison purpose, the experimental results by Lakshmi et al. [24] are also shown as the triangle symbols. It can be seen that the model prediction is consistent with the experimental data during oxidation, and the solid curve is fitted well to parabolic law.

The dimensionless oxygen concentration distribution across the oxide thickness at different oxidation time is illustrated in Figure 3. It shows that the oxygen concentration is highest at the outer surface of the oxide due to the prescribed constant surface supply of oxygen. On the other hand, there is nearly non-oxygen at the oxide

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