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Diffusion and Stress Coupling Effect during Oxidation at High Temperature

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We report the diffusion and stress coupling effect during oxidation. An analytical model is developed for the stress and diffusion coupling effect based on equilibrium relationship and diffusion equation considering for the stress effect. Compressive stress will generate during the oxidation due to the growth strain. This growth stress can modify the diffusion coefficient; therefore, the oxidation kinetics is also affected. The coupling effect reduces both the oxidation rate and the stress. The proposed model is applied to predict the oxidation evolution for SiC and its consistence with the experimental data demonstrates the theoretical analysis.

I. Introduction

Superalloy or silicon carbide (SiC) is often exposed to high-temperature environment and its surface is oxidized seriously.[1–3] The stress generated in the oxide film during oxidation plays an important role for the performance and reliability of the structures based on these materials. When the stress exceeds the critical value σ_c, a crack will be induced and propagate in the oxide and cause the structure failure.[4–7] A variety of mechanisms have been proposed to explain the stress generation during oxidation such as the growth strain, thermal mismatch between the oxide film and substrate, phase transformation and so on.[8–10] As well, the film stresses resulting from the misfit strain or high temperature were analyzed extensively.[11–13] Recently, Dong *et al.*[14] reported the evolution of oxidation stress during oxidization. It has been observed that the stress can affect the oxidation rate in turn by modifying the diffusion of the reaction particles.[15,16] Therefore, the stress and diffusion coupling effect has to be considered to predict the stress evolution and the oxidation kinetics.

In this work, we propose a simple model to characterize the stress and diffusion coupling effect and predict the oxidation kinetics and stress evolution. Then, we compare the model prediction with the experimental data for SiC isothermal oxidation. This finding may provide a fundamental understanding for the stress effects on the oxidation at high temperature.

II. Stress-Diffusion Coupling Model

The oxidation process of the specimens at high temperature is determined by the diffusion rate of the moving O_2 (or ion) due to the fast reaction rate at the gas/oxide or oxide/substrate interface. For instance, the anions or cations transporting through the oxide scale controls the oxidation for metals, while the interstitial diffusion of O_2 through silica scale dominates the oxidation for silicon substrate or SiC. In most cases, the oxidation kinetics is described by the parabolic law as[17]:

$$\frac{dh_{ox}}{dt} = D\beta\frac{c_1 - c_2}{h_{ox}} \tag{1}$$

where h_{ox} is the thickness of the oxide film, t is time, D is the diffusion coefficient of O_2, β is a coefficient which is relative to substance and reaction, c_1 and c_2 represent the diffusion material concentration at the gas/oxide and oxide/substrate interface, respectively. During the oxidation, stress in the oxide would be generated owing to the thermal mismatch, phase transformation, or the oxide growth as shown in Fig. 1(a). One of the mechanisms that interpret the oxide growth strain is based on the assumption that the new oxide forms in the scale and proposes that the growth strain rate $\dot{\varepsilon}_g$ is proportional to the oxide growth rate, i.e., $\dot{\varepsilon}_g = D_{ox}\dot{h}_{ox}$, where D_{ox} is a coefficient dependent on the oxide microstructure.[18,19] This lateral growth strain of the oxide is constrained by the substrate, and a compressive stress is often observed. The stress companied with the oxidation process can affect the oxidation kinetics in turn by changing the diffusion coefficient as illustrated in Fig. 1(b). Barvosa-Carter *et al.*[15] referred this effect to strain-activated mobility, and the modified diffusion coefficient can be expressed as[20,21]

$$D = D_0\ exp\left(\frac{\alpha\Omega\sigma_{ox}}{RT}\right) \tag{2}$$

where D_0 is the diffusion coefficient independent on stress, Ω is the molar volume of the diffusion material, σ_{ox} represents the biaxial stress in the oxide, R is the gas constant, T is the absolute temperature, and α is a positive nondimensional coefficient. It can be seen that the tensile stress can increase oxidation rate while compressive stress will suppress it. Therefore, the coupling effect between stress and diffusion is important to the oxidation kinetics.

When the specimens are oxidized at high temperature, the grown oxide film and the specimens consist of thin film/substrate system, as shown in Fig. 1(a). H is the initial thickness of the specimens relative to the symmetry axis. The force equilibrium equation is given by:

$$\sigma_{ox}h_{ox} + \sigma_s(H - h_{ox}) = 0 \tag{3}$$

where σ_s is the biaxial stress in the substrate. The rate form of Eq. (3) is:

$$\dot{\sigma}_{ox}h_{ox} + \sigma_{ox}\dot{h}_{ox} + \dot{\sigma}_s(H - h_{ox}) - \sigma_s\dot{h}_{ox} = 0 \tag{4}$$

Based on the geometrical symmetry of the system, the strains in the oxide and substrate satisfy that $\dot{\varepsilon}_{ox} = \dot{\varepsilon}_s$, where

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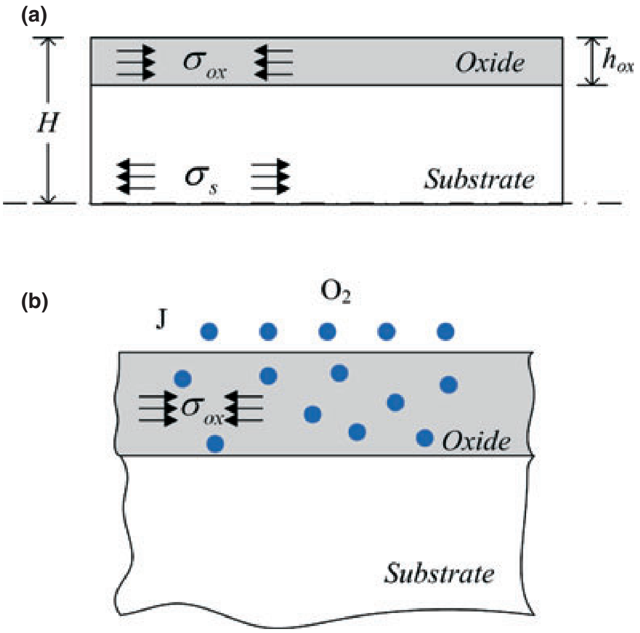

Fig. 1. Oxidation of the substrate with an initial thickness H, h_{ox} is the oxide thickness. (a) The force equilibrium of the oxide film/substrate system. (b) The stress effect on the diffusion of O_2.

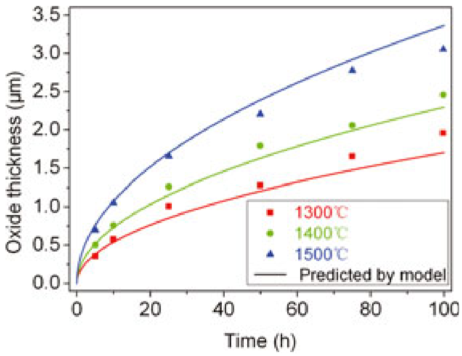

Fig. 2. Theoretical prediction by the present model compared with the experimental data (Ref. 22) for oxidation evolution of SiC at different temperatures.

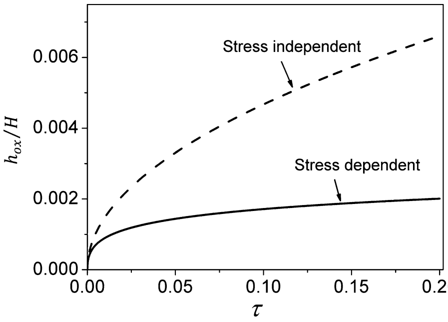

Fig. 3. The oxidation kinetics considering the stress and diffusion coupling effect. The solid line and dash line present the oxide nondimensional thickness versus oxidation time curve with stress effect and without stress effect, respectively. The parameters used for calculation are $\tilde{M} = 0.75$, $\tilde{A} = 400$, $\tilde{B} = 400$, $\tilde{\alpha} = 3$, and $\tilde{\beta} = 2.7 \times 10^{-7}$.

$\dot{\varepsilon}_{ox} = \dot{\sigma}_{ox}/M_{ox} + D_{ox}\dot{h}_{ox}$ and $\dot{\varepsilon}_s = \dot{\sigma}_s/M_s$ are the strain rate in the oxide and substrate, respectively, M_{ox} and M_s are the biaxial modulus of the oxide and substrate, respectively. Substitute Eqs. (1) and (2) into Eq. (4) and using the growth strain rate expression, the governing equation for the oxidation kinetics and stress evolution can be obtained. For simplicity, we show the governing equation in a nondimensional form:

$$\begin{cases} \left[\tilde{M}(1-\tilde{h}) + \tilde{h}\right]\frac{d\tilde{\sigma}}{d\tau} + \left[\tilde{A}(1-\tilde{h}) + \frac{1}{(1-\tilde{h})}\tilde{\sigma}\right]\frac{d\tilde{h}}{d\tau} = 0 \\ \frac{d\tilde{h}}{d\tau} = \frac{\tilde{B}\tilde{\beta}}{\tilde{h}}\exp\,(\tilde{\alpha}\tilde{\sigma}) \end{cases} \tag{5}$$

where $\tilde{M} = M_s/M_{ox}$, $\tilde{A} = M_s D_{ox} H/\sigma_c$, $\tilde{B} = R_s^2/H^2$, $\tilde{\alpha} = \alpha\,\Omega\,\sigma_c/RT$, and $\tilde{\beta} = \beta(c_1 - c_2)$, R_s is the radius of the substrate, $\tilde{\sigma} = \sigma_{ox}/\sigma_c$ and $\tilde{h} = h_{ox}/H$ represent the nondimensional stress and thickness of the oxide, respectively, and $\tau = D_0\,t/R_s^2$ is the nondimensional time. The initial conditions are $\tilde{\sigma} = 0$ and $\tilde{h} = 0$ at $\tau = 0$. Equation (5) shows a strong coupling effect between the stress and the oxide growth.

III. Discussion

To validate our model, we compare the oxide film thickness evolution predicted by the theoretical analysis with the experimental data reported by Ogbuji and Opila[22] for SiC oxidation. The bulk SiC sample fabricated by chemical vapor deposition was oxidized in a quartz tube to ensure a clean oxidation environment at different temperatures, and the oxide thickness was recorded during the experiment. The mechanical properties of SiC and silica and the physical parameters used for model calculation are obtained from Ref. 20, 22, and 23. From Fig. 2, we can see that the model prediction (solid line) is consistent to the experimental data for different temperatures, which demonstrates that the proposed model considering the stress-diffusion coupling effect could be applied to real system. However, for longer oxidation time, the model prediction deviates from experimental results. This may be caused by the creep of the silica during oxidation which would relax the stress in the oxide, and then, the diffusivity and the oxidation kinetics would be affected accordingly.

As aforementioned, not only would the oxidation induce stress in the oxide film but the oxidation kinetics may be affected by the induced stress. The growth strain generates due to the lateral growth of the oxide scale during oxidation that leads to growth stress. On the other hand, the stress could modify the diffusivity of the oxygen which would change the oxidation rate. To illustrate this coupling effect, we plot the oxidation kinetics versus time curve predicted by Eq. (5) with the results obtained from the conventional model which is stress-independent.

Figure 3 illustrates the nondimensional oxide thickness $\tilde{h}$ versus time τ with the stress effect (solid line) and without the stress effect (dash line). It is obvious that the compressive stress reduces the oxidation rate significantly. The nondimensional oxide thickness would reach 0.002 at τ = 0.2 considering the stress effect while it would exceed 0.006 at the same time without the stress effect. During the diffusional transport, O_2 or ions jump from one interstitial site to another, a tensile (compressive) stress can reduce (increases) the energy barrier that enhances (suppresses) the probability for this jump. Therefore, the stress in the oxide can affect the diffusion rate to a large extent. Recently, this effect has been observed in experiment that the externally applied tensile (compressive) stress increases (reduces) the oxidation rate of silicon.[23,24]

The stress evolution during oxidation is plotted in Fig. 4. We can see that the stress and diffusion coupling effect suppresses the stress increase, as the growth strain rate is proportional to the oxide growth rate. The stress would reach σ_c at a long time due to the coupling effect (solid line),

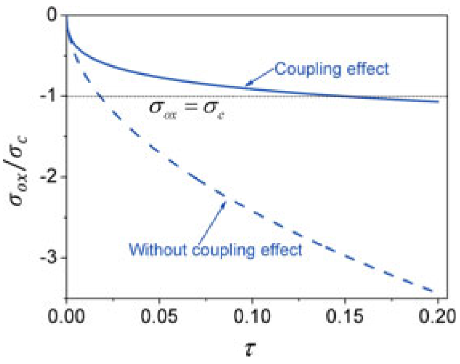

Fig. 4. The non-dimensional stress evolution during oxidation with coupling effect (solid line) and without coupling effect (dash line). The coupling effect inhibits the stress increase.

on the other hand it would exceed σ_c quickly without the coupling effect (dash line). However, σ_c can be achieved as long as the oxidation time is long enough, and a crack may be induced.

It should be noticed that, the present model is derived based on several assumptions. The premise of this analysis is assuming that the oxidation process is controlled by the diffusion of oxygen. As the reaction rate at the gas/oxide or oxide/substrate interface is quite faster than the diffusion rate, this condition is often satisfied in most cases. Other assumptions such as the growth strain rate is proportional to the oxide growth rate and the stress can modify the diffusivity of the oxygen have been observed in experiments. Therefore, our model is able to describe the oxidation kinetics for real system.

IV. Summary

We propose a simple model that characterizes the stress and diffusion coupling effect during oxidation at high temperature. The governing equation is derived based on equilibrium relationship and diffusion equation considering the stress effect. Compressive stress will generate during the oxidation as the growth strain is constrained by the substrate. This growth stress can modify the diffusion coefficient, therefore, the oxidation kinetics is also affected. Both the oxidation rate and the stress will be reduced by the stress-diffusion coupling effect. As the stress reaches the critical value, a crack would be observed in the oxide that will cause the oxide/substrate system failure. The proposed model is validated by the consistence of the theoretical calculation with the experimental data. Other stress generation mechanisms such as creep behavior and phase transformation in the oxide and substrate are not included in our model. We will investigate these in future work.

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