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Modeling of growth stress gradient effect on the oxidation rate at high temperature*

Fan YANG[1], Bin LIU[1], Dai-ning FANG[†‡1,2]

([1]*Applied Mechanics Laboratory, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China*)

([2]*State Key Laboratory for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing 100871, China*)

[†]E-mail: fangdn@mail.tsinghua.edu.cn

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Abstract: A new oxidation kinetics model is established for high-temperature oxidation. We assume that the interface reaction is fast enough and the oxidation rate is controlled by diffusion process at high temperature. By introducing the growth stress gradient we modify the classical oxidation parabolic law. The modified factor of the oxidation rate constant is a function of growth strain, environment oxygen concentration, and temperature. The modeling results show that the stress gradient effect on the oxidation rate cannot be ignored. Growth strain will dominate whether the stress gradient effect promotes or slows down the oxidation process. The stress gradient effect becomes weaker at higher temperature. This effect is amplified at higher concentrations of environmental oxygen. Applied mechanical loads do not affect the oxidation rate. This model is available for high temperature oxidation of metals and alloys.

Key words: High temperature, Modeling, Growth stress gradient, Oxidation rate
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1 Introduction

With progress in the aerospace industry, especially with supersonic aircraft, the manufacture of thermal protection materials has become a key technology. The materials are required to possess outstanding mechanical properties under harsh mechanical and thermal loads. A huge challenge for these high-temperature materials is oxidation corrosion. Therefore, oxidation resistance is an important property for evaluating thermal protection materials. Normally, the thermogravimetric analysis experiment is carried out to investigate this property (El-Dahshan *et al*., 1975; Opeka *et al*., 1999; Hashemi *et al*., 2006; Han *et al*., 2008; Guo *et al*., 2009). However, the experiment is time-consuming and expensive, and some working temperatures in application cannot even be reached in the experiment. To save time and reduce the cost of these experiments, numerous researchers have developed kinetics models for oxidation for which only several parameters are needed and can be extracted from isothermal oxidation experiments.

Among these works, Wagner (1933) obtained a parabolic law by considering ionic diffusion through the oxide layer. Wolf and Grochowski (1975) established an isothermal oxidation model, called the W-G model. Markworth (1977) modified the parabolic rate law and derived an anisothermal oxidation model which can describe the oxidation when temperature rises linearly with time. Some have suggested multiple-law models (Nickel, 2005). For powders, fibers, and pellets, many researches established a series of oxidation models in which parameters have definite physical meanings (Chou, 2006; Hou *et al*., 2008; Chou and Hou, 2009; Hou and Chou, 2009),

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[‡] Corresponding author

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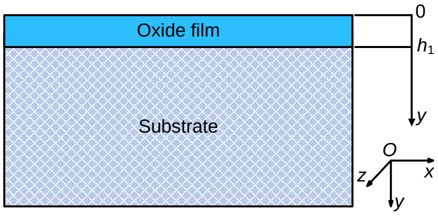
and the effects of temperature-increasing rate, oxygen partial pressure, and particle size on the reacted fraction of oxidation are involved.

Some recent reports have shown that in the oxidation process large growth stress and stress gradients are generated due to the crystalline lattice mismatch between the oxide scale and the substrate material (Hou *et al*., 2007; Kemdehoundja *et al*., 2007; Reddy *et al*., 2007). The oxidation process includes three steps: oxidant transport from gas phase to oxide surface, ionic diffusion through the oxide scale, and reaction at oxide/substrate interface. The stress will affect the oxidation rate by influencing the above steps. At low temperatures, the oxidation rate is controlled by both the diffusion process and the interface reaction. Some previous oxidation models have introduced the stress effect by adding it to activation energy to describe the stress effect on the low temperature oxidation of silicon (Kao *et al*., 1987; 1988). At high temperatures, the interface reaction rate is high and the oxidation rate is mainly dominated by the diffusion process. The stress gradient will affect the oxidation rate by accelerating or slowing down the speed of ionic diffusion (Aifantis, 1980). Here, we develop an oxidation model considering the stress gradient effect on ionic diffusion to modify the oxidation rate constant for high temperature oxidation.

2 Oxidation kinetics modeling

The oxide film/substrate system is illustrated in Fig. 1. The parameters used in calculation are listed in Table 1.

Firstly, we use a simple model to obtain the growth stress in the oxide scale. As shown in Fig. 2, three steps should allow one to obtain the elastic stress in oxide film involving the applied mechanical load.

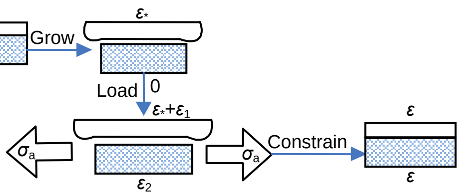


h_1: thickness of the oxide film

Fig. 1 Schematic diagram of oxide film/substrate system

Table 1 Parameters used in analysis

Parameter	Value
Young's modulus (GPa)	160
Ideal gas constant (J/(mol·K))	8.31
Gas mole volume (m^3/mol)	16.7×10^{-7}
Temperature (K)	900
Pilling-Bedworth ratio (PBR)	1.1
Relaxation factor (%)	18
Growth strain (%)	0.6
Environment oxygen concentration	1.0



ε_*: stress free strain; ε_1: elastic deformation of oxide film; ε_2: elastic deformation of substrate; σ_a: applied stress

Fig. 2 Schematic diagram of elastic modeling

Step 1: The oxide film is removed from the substrate and is allowed to grow freely. In this step, a stress free strain is generated in the oxide film.

Step 2: Both oxide film and substrate are loaded by uniform stress σ_a. Oxide film and substrate deform separately according to their own elastic properties. The elastic deformations of oxide film and substrate are ε_1 and ε_2, respectively.

Step 3: Glue the oxide film and the substrate together. Suppose their strains in the thickness directions are the same. The mismatch between them leads to the generation of growth stress. As the film is quite thin compared to the transverse size and substrate's thickness, it is assumed that strains vary only along the thickness direction and that the strain in the substrate is uniform. The isotropy constitutive relation for the oxide and the substrate is

$$\sigma_1^x = E_1(\varepsilon - \varepsilon_*), \quad \sigma_2^x = E_2\varepsilon, \tag{1}$$

where σ^x represents the transverse stress, and ε represents transverse strain, ε_* is the stress free strain, E is Young's modulus, and subscripts "1" and "2" represent oxide film and substrate, respectively. The equilibrium equation is

$$\int_0^{h_1} \sigma_1 \mathrm{d}y + \sigma_2 h_2 = \sigma_a(h_1 + h_2), \tag{2}$$

where σ_a represents the applied stress, h_1 and h_2 are the thickness of oxide film and substrate, respectively.

According to Larche and Cahn (1985)'s theory, the stress free strain is proportional to the concentration of gas:

$$\varepsilon_* = \varepsilon_0 (c - c_{\text{ref}}), \tag{3}$$

where ε_0 is the growth strain of totally oxidized material and is a constant, c is the oxygen concentration, and c_{ref} is the reference concentration. Growth strain can be expressed by the Pilling-Bedworth ratio (PBR) according to Huntz (1995):

$$\varepsilon_0 = \omega(\text{PBR}^{1/3} - 1), \tag{4}$$

where PBR is defined as the volume after oxidation divided by the corresponding volume before oxidation, and ω is the relaxation factor.

According to the above equations, the stress in the oxide scale can be obtained as follows:

$$\begin{aligned}\sigma_1 = E_1 \Bigg\{ & \frac{1}{E_1 h_1 + E_2 h_2} [\sigma_a (h_1 + h_2) \\ & + E_1 \varepsilon_* \int_0^{h_1} c(y) \mathrm{d}y] - c(y)\varepsilon_0 \Bigg\}.\end{aligned} \tag{5}$$

The generalized Fick's second law involving stress effect on diffusion can be expressed as follows:

$$J = -D\left(\nabla c - \frac{cV}{RT}\nabla\sigma\right), \tag{6}$$

where J is the oxygen flux, D is the diffusion coefficient, V is the molar volume of oxygen in solid solution, and σ represents the trace of stress tensor.

Substituting the stress expression into Fick's law, we have:

$$J = -D\left(\nabla c + \frac{cVE_1\varepsilon_0}{RT}\nabla c\right) = -D\nabla c\left(1 + \frac{cVE_1\varepsilon_0}{RT}\right). \tag{7}$$

Under high temperatures, the oxidative reaction process is so rapid that the oxidation rate is mainly controlled by the diffusion process. The oxidation rate is proportional to the flux oxygen on the matrix/oxide interface (Chou, 2006). Thus, the kinetics governing equation is

$$\frac{\mathrm{d}h_1}{\mathrm{d}t} = \beta J = -\beta D\nabla c\left(1 + \frac{cVE_1\varepsilon_0}{RT}\right), \tag{8}$$

where t is time, and β is the proportionality coefficient.

When the reaction is in a quasi-steady state, the oxygen concentration on the two interfaces remains constant. Therefore, the derivation in the above equations can be approximately replaced by the difference (Chou, 2006) as

$$\frac{\mathrm{d}h_1}{\mathrm{d}t} = \beta J = -\beta D\frac{c_o^2 - c_o^1}{h_1}\left(1 + \frac{cVE_1\varepsilon_0}{RT}\right), \tag{9}$$

where c_o^1 and c_o^2 represent the oxygen concentrations at the gas/oxide interface and the oxide/substrate interface, respectively.

Integrating the above equation, the relationship between oxide film thickness h_1 and time t can be obtained:

$$h_1^2 = 2\beta D(c_o^1 - c_o^2)\left(1 + \frac{cVE_1\varepsilon_0}{RT}\right)t. \tag{10}$$

This is a modified form of the classical parabolic law for metal and alloy oxidation. Oxidation rate constant k can be expressed as follows according to its definition:

$$k = \frac{h_1^2}{t} = 2\beta D(c_o^1 - c_o^2)\left(1 + \frac{cVE_1\varepsilon_0}{RT}\right). \tag{11}$$

If the stress gradient is not considered, the kinetics governing equation is

$$\frac{\mathrm{d}h_1}{\mathrm{d}t} = \beta J = -\beta D\nabla c. \tag{12}$$

For the classical parabolic law, the oxidation rate constant k_0 can be expressed as

$$k_0 = 2\beta D(c_o^1 - c_o^2). \tag{13}$$

Therefore, the modified factor for stress affected oxidation rate is

$$\alpha = \frac{k}{k_0} = 1 + \frac{cVE_1\varepsilon_0}{RT}. \tag{14}$$

3 Results and discussion

We compare our theoretical results with the experiment data of Fei *et al*. (2004) in Fig. 3.

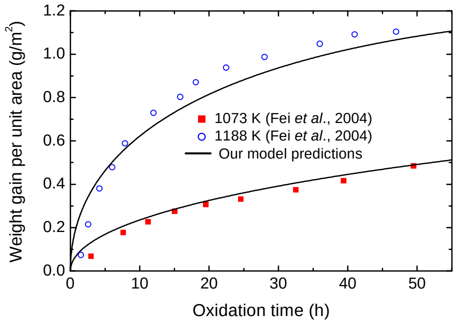


Fig. 3 Thermogravimetric curves of Fe-Cr-Al-Y alloy under different temperatures of our model compared with experiment data of Fei *et al*. (2004)

This shows that our modeling results agree with the experiment very well at two different temperatures. The relationship between oxide growth strain and modified factor for the oxidation rate constant is plotted in Fig. 4, indicating that the growth strain significantly affects the oxidation rate. If the growth strain value is positive, which means the oxide expands compared to the substrate, the stress gradient will accelerate the diffusion process, as shown in Eq. (7), and the oxidation rate is accelerated by the existence of the growth stress gradient. On the contrary, if the growth strain value is negative, which means the oxide shrinks compared to the substrate, the oxidation rate is slowed down by the existence of the growth stress gradient.

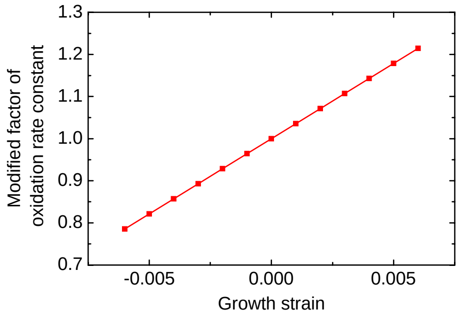


Fig. 4 Growth strain-modified factor curve

Fig. 5 demonstrates the linear relationship between the environment oxygen concentration and the modified factor. This shows that a larger outside oxygen concentration will amplify the stress gradient effect, because the stress gradient is proportional to the oxidation degree, which depends on the outside oxygen concentration.

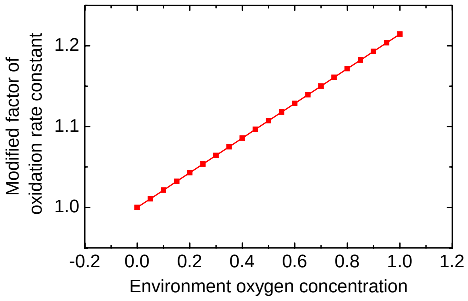


Fig. 5 Oxygen concentration-modified factor curve

Fig. 6 shows the modified factors under different temperatures. It can be seen that higher temperatures minimize the stress gradient effect on oxidation rate. At high temperatures, the ionic diffusion speed is so rapid that they can remove the stress effect more easily.

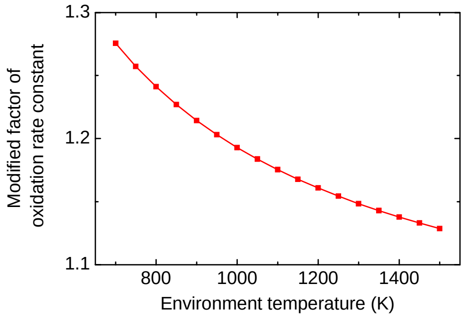


Fig. 6 Temperature dependence of modified factor

In our model, stress gradient and concentration gradient are the driving forces for ionic diffusion. However, applied mechanical load does not affect either of them. The stress gradient is mainly generalized by the non-uniform oxygen concentration distribution.

This kind of non-uniform distribution leads to the heterogeneous stress free strain in the oxide scale, and the heterogeneous stress free strain results in the stress gradient.

4 Conclusions

We develop a new oxidation kinetics model to involve the growth stress gradient effect on the oxidation rate for high-temperature materials. In this model, we assume the reaction rate is fast, and the oxidation rate is dominated mainly by the ionic diffusion process. The model is available for high-temperature metals and alloys. By introducing the growth stress gradient into Fick's law, we modified the classical parabolic oxidation law. The modified oxidation rate constant is analytically obtained. The analysis results show that the stress gradient effect on oxidation rate cannot be ignored. Whether the growth stress gradient accelerates or slows down the oxidation process depends on the sign of the oxide growth strain. A greater environment oxygen concentration helps amplify the stress gradient effect. High temperatures will minify the stress gradient effect on oxidation rate. Applied mechanical load does not, however, affect the ionic diffusion process.

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