# Coupled mechanical-oxidation modeling during oxidation of thermal barrier coatings

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## ARTICLE INFO

## ABSTRACT

The durability of thermal barrier coatings (TBCs) is controlled by the thermally grown oxide (TGO) growth, which is sustained by continuous diffusion of oxygen in TBCs. At the same time, stresses are induced due to volumetric change when TBCs are oxidized. Such stress may in return affect the diffusion of oxygen in the TGO layer, thus changing the TGO growth kinetics. In the present research, a continuum thermodynamic model is developed to account for such stress–diffusion interaction in the oxidation of TBCs. Then we numerically implement our chemo-mechanically-coupled constitutive theory into the widely used finite element software to simulate the oxidation behavior of TBCs. The results demonstrate that the maximum tensile stresses locate at the peak regions of bond coating (BC) layer and the valley region of top coating, respectively. It implies that the failure of the TBCs may occur at the peak of BC/TGO and the valley of TC/TGO interface, which is consistent with the experimental observations. It is also found the stress significantly slows down the rate of oxidation. Consequently, the TGO growth kinetic is not strictly parabolic.

## 1. Introduction

Thermal barrier coating system (TBCs) are widely used in modern gas turbine engine to improve the turbine inlet gas temperature, therefore improves the efficiency of aircraft engine. A typical TBCs are comprised of three key layers: an oxidation resistant bond coat (BC) such as diffusion aluminide or overlay MCrAlY bond coating, a ceramic top layer (TC), typically 7–8 wt% $Y_2O_3$-stabilized $ZrO_2$ (7YSZ), to reduce the heat flux into the component, and a thin thermally grown oxide (TGO) layer [1–3]. TGO layer grows at TC/BC interface at high temperature. On one hand, it acts as an oxidation barrier coating which suppresses the formation of other detrimental oxides during extended thermal exposure in service [4,5]. On the other hand, out-of-plane stress which typically develop at BC-TC interface undulations, increase as the TGO thickens [6,7]. The stress leads to cracking within the brittle ceramic coatings and fracture at the interfaces. As emphasized by Evans [8], the growth of TGO has a major influence on the TBCs durability. In recent years, a significant amount of work has been done on the

analysis of TBCs failure mechanisms associated with TGO growth [1,8–13]. However, it is still essential and urgent to investigate the TGO growth behavior and stress development during the service of TBCs.

Due to the diversity of diffusion-reaction mechanism at elevated temperature, the oxidation behavior of TBCs is extremely complicated. Generally, the average thickness of TGO proceeds in an approximate parabolic manner with time and it varies remarkable at the TC/BC interface [14–20]. The TGO layer is thicker in the peak regions, while it is thinner in the valley areas, than the average thickness. With the growth of TGO layer, large residual compressive stress is developed in this thin layer because of growth and thermal expansion misfit, causing cracking in the TC/BC interfacial region, which eventually leads to spallation of TC layer. During the last decades, many researchers have been performed to investigate the stress distribution and crack propagation in the TBCs with different thickness and morphology of the TGO layers [7,21–23]. It has been found that the stress intensity in TBCs increases with TGO layer growing. Interface roughness has also been found to have obvious effect on the TGO residual stress and the lifetime of TBCs

[24–28]. Recently, the stress is analyzed based on the real interface morphology extracted from the cross-section micrographs, which can provide the more accurate stress state of the TBCs [25,29–31]. Gupta et al. [31] adopted this modeling method to investigate the TGO growth and stress evolution in TBCs, and the results revealed that the TGO growth was uneven and the stress distribution was not uniform. What is important is that the local stress change significantly owing to the uneven growth of TGO. As reported by Che et al. [20], the uneven TGO leads to 200% increase in the highest out-of-plane stresses and 60% decrease in the maximum tensile stresses along the TGO/TC interface. However, the interrelationship between stress distribution and uneven growth of TGO is still not understood.

Oxidation-induced volumetric change can lead to mechanical stress in the constrained solid. These stresses accompanying the growth of the oxide have been of great interest for many years due to their importance in the design of TBCs [1,8]. The physical origins of these stresses and stress distributions are still not fully understood, though different mechanisms have been reported as possible explanations [8,10–12,32–34]. The most popular among these is the explanation offered by Clark [33], who proposed that the growth strain rate is proportional to the oxide growth rate. This explanation has been acknowledged and widely used by many researchers [35–38]. However, the stress effect on oxidation reaction is not considered in above researches. In recent years, it has been reported that the stress can strikingly influence the chemical reaction [36,39–44]. So the stress and chemical reaction coupling effects must be considered to predict the stress distribution and the chemical field evolution while the materials are in service at chemo-mechanical coupled environment. Most of these studies are forced on the Li-ion battery [41,43,44], and the researches about oxidation are just limited to metal oxidation [36,39]. To the best of my knowledge, the study on the TBCs oxidation considering the coupling effect has not been reported until now. However a mathematical model is developed by Hille to simulate the TGO growth [24]. In this paper, we improve the TGO growth model based on the Hille's model, and then we investigate the interactive of stress distribution and TGO evolution by finite element method.

In the present research, we firstly develop the chemo-mechanical coupled framework to gain the governing equations including equilibrium equations, constitutive equation and boundary conditions of research problem, and then the weak forms of above equations are implemented in COMSOL Multiphysics to simulate TGO growth and stress evolution simultaneously (Section 2). Finally, the results and discussion are presented in detail for TGO growth, growth stress distribution, and the coupling effect between them (Section 3). The purpose of this work is to clarify the coupling effect of stress and chemical reaction during the oxidation of TBCs.

## 2. Chemo-mechanical coupled framework of TBCs oxidation

### 2.1. Governing equations of chemo-mechanical coupled model

Since the process of atomic diffusion in solids is much slower than elastic deformation, and the established process of mechanical equilibrium is much faster than that of diffusion, mechanical equilibrium can be treated as a static equilibrium problem. The deformation of a solid is described by the following equilibrium equation:

$$\sigma_{ij,i} + f_j = 0, \tag{1}$$

where $\sigma_{ij}$ are the stress components, $f_j$ denote the components of body forces $\mathbf{f}$, and the comma indicates differentiation with respect to the spatial variables.

The total strain $\varepsilon_{ij}$ caused by the concentration change and applied load can be written as

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) = \varepsilon_{ij}^e + \varepsilon_{ij}^c, \tag{2}$$

where $u_{i,j}$ is the displacement, $\varepsilon_{ij}^e$ is the elastic strain and $\varepsilon_{ij}^c$ is the chemical strain. Assuming that the solid is linear elastic, so the constitutive equation with the effect of concentration can be expressed as

$$\varepsilon_{ij} = \frac{1}{E}[(1 + v)\sigma_{ij} - v\sigma_{kk}\delta_{ij}] + \beta(c - c_0)\delta_{ij}, \tag{3}$$

where $c$ is the concentration with dimension mol/m$^3$, $c_0$ is the reference concentration which is equal 0 in present study, $\beta$ is coefficient of compositional expansion which is a material property that characterizes the linear measure of the volumetric change due to the unit change of the composition, the $E$ and $v$ are the Young's modulus and Poisson's ration of the material, respectively, and $\delta_{ij}$ is the Kronecker delta.

By assuming small strain and concentration-independent isotropic elasticity, the chemo-mechanical potential $\mu$ in an ideal solid solution takes the following form by ignoring the drift terms based on the thermodynamics

$$\mu = \mu_0 + RT\ln c - \Omega\sigma_m, \tag{4}$$

where $\mu$ is the diffusion chemical potential (J/mol), $\mu_0$ is the standard chemical potential independent of stress, $R$ is the gas constant, $T$ is the absolute temperature, $\Omega$ is molar volume (m$^3$/mol) which is constant and independent of concentration and $\sigma_m$ is the mean stress. Eq. (4) accommodates the important physical effects associated with the concentration and stresses.

The thickness of the oxide scale is controlled by the diffusion and reaction. The chemical potential is regarded as the driving force which drives oxygen diffusion through the oxide film. Moreover, in the near equilibrium state, the relationship between the vector of the diffusion flux $\mathbf{J}$ and the gradient of chemical potential satisfy $\mathbf{J} = -Mc\nabla\mu$, where $M$ is the solute mobility which is independent of time. In terms of Eq. (4), the diffusion flux in the stressed solid can be expressed as

$$J = -Mc\nabla\mu = -D_0\left(\nabla c - \frac{\Omega c}{RT}\nabla\sigma_m\right), \tag{5}$$

where $D_0 = MRT$ is the diffusion coefficient in a stress-free state (m$^2$/s).

The TGO layer formation is due to the reactants, i.e., the free (mobile) oxygen and aluminum. Although the diffusions of both the oxygen (inward through the TGO) and the aluminum (outward through the TGO) are contributed to the growth of the alumina scale, it is generally accepted that the inward diffusion of oxygen is the predominant step and the oxidation reaction occurs primarily at the BC/TGO interface, which is in order of magnitude larger than the diffusivity of aluminum in the TGO layer because of the diffusivity of oxygen. Fig. 1(a) displays microstructure of TBCs, which can be found that the uneven TGO thickness distribution around the interface. TGO thickness at the peak of interface is obviously larger than valley. Fig. 1(b) shows the oxidation mechanism, the oxygen diffuses through the TC to the BC, while the aluminum is contained in the BC. The distribution of concentration of free oxygen $c$ is governed by the diffusion–reaction equation. The growth of the TGO layer is described by the volume fractions of the TGO layer. During the oxidation process, the volume fraction varies from $n = 0$ (pure BC material) to $n = 1$ (pure TGO material), which is similar to the order parameter in the phase field model. In fact, some researchers [45,46] have used the phase field model to study the microstructure evolution under the high temperature oxidation.

The model developed by Hille [24] is adopted in this paper for oxidation growth. The concentration of mobile oxygen $c$ and the volume fraction of TGO $n$ can be determined by solving the following equations:

$$\frac{\partial c}{\partial t} + \nabla\cdot(\mathbf{J}) = -L\eta(1-n)c, \tag{6}$$

$$\frac{\partial n}{\partial t} = \eta(1-n)c \tag{7}$$

where $L$ is the ratio of confined oxygen atoms to formed TGO volume,