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# Effect of Oxidation-Induced Material Parameter Variation on the High Temperature Oxidation Behavior of Nickel**

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**ABSTRACT** In high temperature oxidation environment, the oxidation reaction will induce variations in material parameters, such as Young's modulus, thermal expansion coefficient (CTE), coefficient of oxygen diffusion (COD), etc. The oxidation-induced material parameter variations should be considered in high temperature mechanical analysis. In this paper, high temperature oxidation behavior of an oxide film/metal substrate system was investigated through a modified phase field approach. The oxidative stress and oxidation weight gain induced by high temperature oxidation were studied. Effects of Young's modulus, COD and CTE on oxidative stress in the oxide film were studied particularly. The simulation results showed that a better agreement with the experimental results could be obtained when considering the oxidation-induced material parameter variations in the high temperature mechanical analysis of oxide film/metal substrate system. The simulation results demonstrated that oxidative stress and oxidation weight gain were more sensitive to the variation of Young's modulus than to the variations of COD and CTE.

**KEY WORDS** high temperature oxidation, phase field simulation, material parameter variation, oxidative stress, oxidation weight gain

## I. Introduction

Hypersonic air vehicles are typically exposed to harsh, high temperature oxidative environments, which can lead to issues of structural integrity due to long-term oxidation and degradation. The oxidation reaction is one of the most important factors on the high temperature performance of metals[1]. It induces material property variations mainly on Young's modulus, coefficient of oxygen diffusion (COD), thermal expansion coefficient (CTE) and so on. As well known, the oxide film coating on metal substrate protects the metal substrate from oxidization[2]. However, it is also known that a significant mismatch in the CTE between the metal substrate and the oxide film causes great oxidative stress in the oxide film and the metal substrate/oxide film interface. The stress can induce a number of cracks in the oxide film which allow oxygen diffusion toward the metal substrate; and this diffusion degrades the metal substrate[3,4]. Therefore, to evaluate their integrity the knowledge of oxidative stress in the oxide film and metal substrate is essential, which however, has been poorly understood so far.

Generally speaking, the oxidation process of metal at high temperature has three steps: (a) oxygen atoms are adsorbed on the surface of the metal, and the reaction between metal and oxygen produces

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an oxide film; (b) oxygen diffuses though the oxide film to the surface of the metal substrate; (c) metal substrate is further oxidized and the oxide film thickness increases gradually[5]. It is well believed that the oxygen diffusion process at high temperature can be considered as a layer by layer distribution of oxygen molecules and oxide films, since the oxygen reaction speed is much greater than the oxygen diffusion speed[1, 2]. Therefore, understanding of the mechanism of oxygen diffusion in the oxide films is the key to investigate the oxidation process of metals at high temperature.

There have been a number of theoretical studies in the literature investigating the oxygen diffuses. Chou developed an oxygen diffusion model, and discussed the effects of temperature, oxygen pressure and particle size on the oxidization of cylinder and plate[5]. Feng discussed the mechanical-oxygen couple effect by combing the diffusion equation and the mechanical equilibrium equation[6, 7]. By applying the phase field model, Yao[8] simulated the oxygen concentration distribution in ZrB2/SiC with different porosity rates. Fang[9–12] analyzed the oxygen concentration distribution in nickel chromium alloy at high temperature by simultaneously considering the oxygen diffusion equation and the mechanical model, and discussed the oxygen-induced crack propagation in nickel chromium alloy. In these theoretical models, the objects were generally regarded with two components: the oxide film and the substrate. However, oxygen morphology and spectral analysis have shown that it is hard to identify the oxide film/substrate interface from the metal cross sections[13–18]. Actually, in the thickness direction from the oxide film surface to the metal substrate, the materials are composed of oxide and metal with the oxide volume fraction decreased[19–21]. Therefore, in theoretical models material parameter variations induced by material phase change should be considered. However, few studies have been carried out to investigate the effect of material phase change on the mechanical properties of metals during oxidization at high temperature.

The Phase Field Method (PFM) is believed to be an effective tool for the simulation of material phase change[22, 23]. Through this approach, people can get a deep understanding on the complicated mechanical-oxygen coupling effect by considering phase evolution and mechanical model together. In the work of Ma et al., hydrogen diffusion and hydride formation process near a blunt notch in zirconium was studied using PFM[8]. Yang et al. studied the oxidized growth stress and the localized oxidation caused by cracks of iron-based alloy using PFM[9–11]. Jia-Mian et al. investigated the influence of mechanical factors on magnetic domain switching in magnetic thin films using phase-field simulations[24]. Wang et al. discussed the $ZrO_2$ ceramic as thermal barrier coatings treated by shot peening using PFM[25]. In the current work, a novel modified phase field model is developed to simulate the oxidization of nickel at high temperature. In the phase field model, the oxidation-induced material property variations, such as elastic modulus, COD and CTE are considered. The oxidation weight gain and oxidative stress in the oxide film of nickel at 900 °C are calculated and compared with the experimental results. The effect of material phase change on oxidation weight gain and oxidative stress of nickel at different temperatures and pre-mechanical loadings are discussed.

## II. Phase Field Method

PFM based on the Landau phenomenological theory is a powerful approach in material simulation, and has been successfully applied in the simulation for solidification, domain switch, and hydrogenation. Since it is suitable for the simulation of microstructure evolution, PFM is developed to calculate oxidation. In the model of oxidation, the oxygen concentration $c$ is taken as the field variable. It is a conversed variable, which obeys the Cahn-Hilliard equation[22]:

$$\frac{\partial c(h,t)}{\partial t} = L_c \nabla^2 \frac{\delta E^{\text{total}}}{\delta c(h,t)} \tag{1}$$

where $E^{\text{total}}$ represents the overall energy. The right side of the equation is the variation of energy, which is the driving force of the field variable $c$. The microstructure evolution tends to reduce the overall energy to the lowest energy state. For the high temperature oxidation problem, the energy includes three components: chemical free energy, gradient energy and elastic energy[22].

$$E^{\text{total}} = \iiint (E^{\text{free}} + E^{\text{grads}} + E^{\text{elastic}}) \mathrm{d}h^3 \tag{2}$$