

# Analytical Modeling of Unsteady Aluminum Depletion in Thermal Barrier Coatings

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## Abstract

The oxidation behavior of thermal barrier coatings (TBCs) in aircraft turbines is studied. A simple, unsteady and one-dimensional, diffusion model based on aluminum depletion from a bond-coat to form an oxide layer of  $Al_2O_3$  is introduced. The model is employed for a case study with currently available experimental data. The diffusion coefficient of the depleted aluminum in the alloy, the concentration profiles at different oxidation times, and the thickness of Al-depleted region are obtained. The results suggest that potential changes in the thermo-mechanical properties of the original alloy in the Al-depleted region may be partly responsible for the mechanical failure of TBC systems.

**Key Words:** thermal oxidation, thermal barrier coating, aluminum depletion, alumina, diffusion coefficient.

## Termal Bariyer Kaplamalarında Kararsız Alüminyum Transferinin Analitik Modeli

### Özet

Bu çalışmada uçak türbinlerinde kullanılan ısı bariyer kaplamalarının oksidasyon davranışları incelenmektedir. Bu amaçla zamana bağlı bir boyutlu bir kütle transfer modeli oluşturulmuştur. Model temel okside tabakası olan  $Al_2O_3$  oluşmasına sebep olan alüminyumun yapıştırıcı tabakadan transferini hareket noktası olarak almaktadır. Önerilen model ile difüzyon katsayısının, konsantrasyon profilinin ve alüminyum tüketilen bölge kalınlığının bulunabileceği, bir uygulama ile gösterilmektedir. Elde edilen sonuçlar kaplama ısı ve mekanik özelliklerinde değişim yaratacak seviyede alüminyum transferi olduğunu göstermektedir.

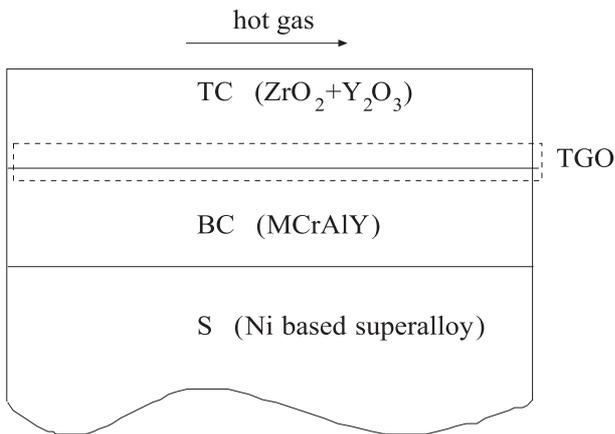
**Anahtar Sözcükler:** termal oksidasyon, ısı bariyer kaplamaları, alüminyum transferi, alüminyum oksit, difüzyon katsayısı.

### Introduction

Thermal barrier coatings (TBCs) are mainly used in aircraft applications for protecting hot components (i.e. vanes, blades) of gas turbines because of their outstanding thermomechanical properties. They suffer, however, from short operational life due to a thermally grown oxide (TGO) layer at high temperatures (900-1300 °C) (Evans and Taylor, 1997).

A conventional TBC system is shown in Figure 1, and basically includes two thin layers of coatings, bond-coat (BC) and top-coat (TC), on a Ni-based superalloy substrate (S). The bond-coat and top-coat are applied to the substrate by electron-beam physical vapor deposition or thermal spraying, but a wide variety of other choices in processing is possible as well (see review of Mortensen and Suresh, 1995). For this type of standard system, the top-

coat is a binary ceramic alloy with the base material of zirconia ( $ZrO_2$ ). Addition of yttria ( $Y_2O_3$ ) helps to increase the thermomechanical resistance of the coating. The critical value of the amount of yttria (7-8 wt%) for maximum resistance is well established (Stecura, 1985; Sacreu et al., 1993; Tawancy, 1993). Microstructural investigations of the top-coat has shown that at about this value of yttria, a zirconia-yttria system includes two-phases (cubic and tetragonal) and thus the material system is referred to as yttria-partially-stabilized zirconia (Scott, 1975; Miller et al., 1983). The bond-coat is a multi-component metallic alloy (MCrAlY), where M can usually be Ni, Co or their combinations. The small amount of yttrium (usually 0.5-2 wt% ) stands for improving the adherence strength of the bond coat (Prescott and Graham, 1992), whereas a relatively high amount of chromium (15-25 wt% ) promotes the formation of a protective  $\alpha-Al_2O_3$  oxide layer and prevents the internal oxidation of aluminum (Wood, 1970).



**Figure 1.** The schematic of a conventional thermal barrier coating system.

TBC systems with this precise choice of components can provide excellent protection for substrate from thermal attack. On the other hand, their tendency to form an oxide layer between the top-coat and bond-coat leads to significant stress increases in the system resulting in the mechanical failure (through spalling or buckling) of coatings (He et al., 1998).

In this paper, some of the main features of the overall oxidation phenomenon in TBC systems are described and a simple one-dimensional diffusion model based on the depletion of aluminum in the

bond coat is introduced. The model is tested with a currently available experimental study and found to be beneficial to predict some oxidation related parameters (i.e. growth rate, concentration profile in the bond coat, and depletion thickness).

### The Characteristic Features of the Oxidation Phenomenon in TBC Systems

In the oxidation of TBC systems, the major concern is in determining the rate of oxidation, which is measured by parabolic rate constants (either in thickness or in mass). The rate-constant in mass is usually defined as

$$k_{pm} = \frac{1}{t} \left( \frac{\Delta m(t)}{A} \right)^2 \quad (1)$$

where  $t$ ,  $\Delta m(t)$ , and  $A$  are, respectively, time (in s), mass gain (in g), and area perpendicular to diffusion flux (in  $cm^2$ ). Equation (1), at a specified temperature, refers to a constant value of  $k_{pm}$  since  $\Delta m$  is considered to be proportional to  $t^{1/2}$ . In practice, the value of  $k_{pm}$  sharply decreases with temperature (Sacreu et al., 1993) and with oxidation time (Brandl et al., 1996).

The chemical structure of the oxide scale is also of interest. In high-temperature oxidation of a MCrAlY alloy, the desired oxide layer is single crystal  $\alpha-Al_2O_3$  since it is highly stable, continuous and adherent. The formation of a thin layer  $\alpha-Al_2O_3$  may behave as a barrier to electron conduction, resulting in a slower rate of growth. In practice, however, the thermally grown oxide (TGO) includes some other phases of  $Al_2O_3$  (i.e.  $\beta$ ,  $\gamma$ ,  $\theta$ ) as well as other oxide phases (i.e.  $NiCr_2O_4$ ,  $NiO$ ,  $Cr_2O_3$ ). Thus, it is difficult to achieve a desired single-crystal and control the growth. These oxides, other than  $\alpha-Al_2O_3$ , are referred to as transition aluminas/oxides, and at higher temperatures transition aluminas can be converted to  $\alpha-Al_2O_3$  with or without applying heat treatment (Smialek and Gibala, 1983; Larsson et al., 1997). With the appropriate choice of components, NiCrAl ternary alloy appears to be the closest for satisfying the requirements of forming  $\alpha-Al_2O_3$ , (Stott et al., 1971). For NiCrAl ternary alloy, the transient oxides, such as  $Ni(Cr, Al)_2O_4$ ,  $NiO$ , and even  $Cr_2O_3$ , could be important only at the initial stage of the high temperature oxidation (Kear et al., 1971).

The mechanism involved in the initiation and evolution of alumina ( $\alpha-Al_2O_3$ ) growth has been studied extensively. The theory given by Wagner (1971) and

the electrical property measurements of the alumina scale (Sheasby and Jory, 1978; Abderrazik et al., 1985a) have shown that oxide growth is dominated by ionic species. Accordingly, the main difficulties in accurate modeling of oxidation phenomenon or alumina scale formation are in predicting the real location of where fresh oxide forms, and the transport properties of ions.

The growth of the oxide can be at one of the following locations: scale-gas interface (cation-dominated diffusion), alloy-scale interface (anion-dominated diffusion), and within the oxide layer (competing effect of cations and anions on ionic diffusion). There is substantial controversy in the literature in the sense that all possibilities have been reported by using different or similar methods under slightly different conditions (Prescott and Graham, 1992). The most complicated possibility, which assumes the growth of new oxide within the existing scale, seems to be valid according to the short-circuit diffusion explanation given by Stott et al. (1979) for FeCrAl and FeCrAlY alloys. This explanation is based on the transportation of ions (oxygen and aluminum ions) from different paths within the scale. Thus lateral scale-growth results in large residual stresses within the scale. Similar ideas have been found to be applicable for NiCrAl alloy (Kumar et al., 1974).

The lack of quantitative experimental data on the transport properties of the alumina scale is due to two main reasons. First, much of the available data have been taken at temperatures of  $T > 1500^\circ\text{C}$  (see for example Paladino and Kingery, 1962), whereas in most thermal oxidation problems the temperature range of interest is  $T = 900\text{--}1300^\circ\text{C}$ . Second, transport properties may vary with many competing factors, such as impurities (Wang and Kroeger, 1980; Abderrazik et al., 1985b), structural point defects (Gesmundo, 1987), and oxygen partial pressure (Wang and Kroger, 1980). This complex dependence of diffusion coefficients on so many factors requires tremendous experimental effort, and extrapolating data from one condition to another may lead to significant errors in calculations.

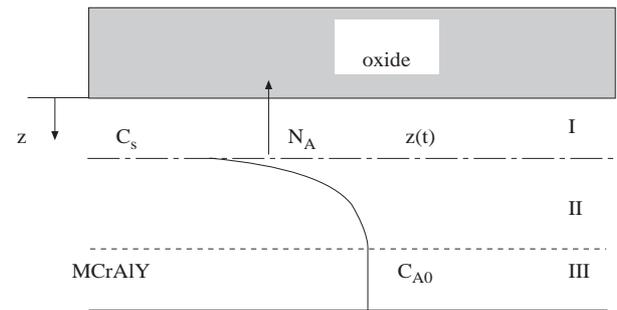
Much attention has been devoted recently to the investigation of the bond-coat. The majority of studies have tried to determine the contribution of bond-coat-related parameters on the overall oxidation phenomenon. Significant progress has been made in bond-coat design to ensure a better diffusion-barrier. The contouring of a bond-coat structure with a laser

(Schmitt-Thomas et al., 1997), the application of high-velocity-oxygen-fuel (HVOF) spray compared to chemical-vapor-deposition (CVD) (Brandl et al., 1997), the pre-aluminization of bond-coat material (Lih et al., 1992), and the inclusion of CVD- $\text{Al}_2\text{O}_3$  between top-coat and bond-coat (Sun et al., 1993) have all been suggested to diminish the rate of oxidation. Beele et al. (1997) have reported the improving effect of rhenium (Re) addition into the NiCr-CoAlY bond-coat for long-term oxidation behavior. Regardless of these improvements, the emphasis has still been on the depletion of Al near the oxide-alloy interface (Brandl et al., 1997; Lih et al., 1992; Sun et al., 1993; Beele et al., 1997).

The following section, therefore, introduces a simple diffusion model based on the depletion of a less noble metal (aluminum) in the bond-coat without invoking the complex kinetics, chemistry and microstructure of the oxide layer.

### Diffusion Model in a Bond-Coat

The schematic of the problem is given in Figure 2. The bond-coat is hypothetically divided into three different regions. Initially ( $t = 0$ ) molar concentration of aluminum is  $C_{A0}$  in all three regions. When the nucleation of oxide starts at  $z=0$ , a certain amount of Al is depleted from the region close to the interface (region I, the outer depletion region) leading to much lower concentrations of Al ( $C_s$ ). Depleted aluminum is replaced with some type of vacancy (most likely uncharged, i.e. voids, pores). A further stage of oxidation continues with Al supply from region II (inner depletion region) due to the concentration gradient ( $C_{A0} - C_s$ ) between its two interfaces.



**Figure 2.** The schematic of the oxidation model in the bond coat.

The interface between regions I and II moves with a velocity of  $v(t)$ , and its location is of interest for obtaining a solution. The original alloy-scale inter-

face,  $z(t = 0) = 0$ , is stationary because Al content in the alloy is usually less than 10 wt% and should not cause complete layer movement. Therefore, the appropriate modeling of the problem requires a reference frame that moves with the hypothetical interface (i.e.  $z(t>0)=0$  always represents that interface). The diffusion problem in region II can then be described as follows:

If Al is the only component that diffuses through the interface, the system can be reduced from multi-diffusion to a binary diffusion problem (A: Al and B: MCrAlY). The resulting diffusion equation for A species is given

$$\frac{\partial C_A}{\partial t} = -\frac{\partial N_A}{\partial z} \quad (2)$$

where  $C_A$  and  $N_A$  are the concentration and molar flux of species A, respectively. With the assumption of no-dependence of diffusion coefficient on position and composition ( $D_{AB} = D_{BA}$ ), molar flux in a binary system can be described as

$$N_A = -D_{AB} \frac{\partial C_A}{\partial z} + C_A v(t). \quad (3)$$

In equation (3),  $D_{AB}$  is diffusion coefficient of species A in B (i.e. aluminum in the alloy). The second term in (3) represents the diffusion of Al due to the moving coordinate. We define the following dimensionless parameters as

$$C(Z) = \frac{C_{A0} - C_A(Z)}{C_{A0} - C_S}, \quad (4)$$

$$Z(z, t) = \frac{z}{\sqrt{4D_{AB}t}}. \quad (5)$$

The solution of (2) is then fairly straightforward (see Arnold, 1944) and, with the boundary conditions of  $C(0)=1$  and  $C(\infty)=0$ , may be expressed as

$$C(Z) = \frac{1 - \operatorname{erf}(Z - \psi)}{1 + \operatorname{erf}(\psi)} \quad (6)$$

where  $\psi$  is a coefficient that accounts for the movement of the boundary (physically dimensionless molar velocity) and is given by

$$\psi = \frac{1}{\phi^{1/3} x_A} \sqrt{\frac{k_{pz}}{2D_{AB}}}. \quad (7)$$

In equation (7),  $\phi$  is the Pilling-Bedworth ratio,  $x_A$  is the atomic percentage of Al in the bond-coat,

and  $k_{pz}$  is the parabolic-scaling constant in thickness. In relating the depletion-model to the resulting oxide layer, we use the assumption of perfectly stoichiometric  $\text{Al}_2\text{O}_3$  and define the interface velocity accordingly as

$$\int v(t) dt \propto Z_{ox}(t) = \sqrt{2k_{pz}t} \quad (8)$$

$$v(t) = \left(\frac{k_{pz}}{2t}\right)^{1/2} \frac{1}{\phi^{1/3} x_A} \quad (9)$$

where  $Z_{ox}(t)$  is oxide thickness determined by parabolic-rate law as a function of time. In practical applications, the parabolic rate constant is usually given in terms of the mass increase of the specimen (see equation (1)). The relationship between these two parabolic rate constants, for a perfectly stoichiometric oxide layer ( $\text{Al}_2\text{O}_3$  here), is described with Wagner's notation (see Abderraziket al., 1985a and Birks and Meier, 1983) by

$$k_{pm} = k_{pz} \left( \frac{(3/2)\mu_{\text{O}_2}\rho_{\text{Al}_2\text{O}_3}}{\mu_{\text{Al}_2\text{O}_3}} \right)^2 \quad (10)$$

where  $\mu$  and  $\rho$  are molecular weight and density for the species  $\text{O}_2$  or  $\text{Al}_2\text{O}_3$ . The concentration profile determined in (6) can be used to calculate the rate of aluminum depletion from the bond coat as follows:

$$N_A|_{z=0} = -D_{AB} \left( \frac{\partial C_A}{\partial z} \right)_{z=0} \quad (11)$$

$$N_A|_{z=0} = \frac{(C_{A0} - C_S) \sqrt{\frac{D_{AB}}{\pi t}}}{1 + \operatorname{erf}(\psi)} \exp(-\psi^2). \quad (12)$$

The derivative is taken at  $z=0$  because the reference frame is attached to the moving interface. In order to determine the location of the reference frame at a particular time, the velocity given by (9) is used. The rate of Al depletion can now be used to predict either the oxide thickness or the mass gain of the specimen due to oxidation in terms of the bond-coat material parameters. For example, the oxide thickness is obtained as

$$Z_{OX}(t) = \phi^{1/3} \frac{\mu_A}{\rho_A} \int_0^t N_A dt \quad (13)$$

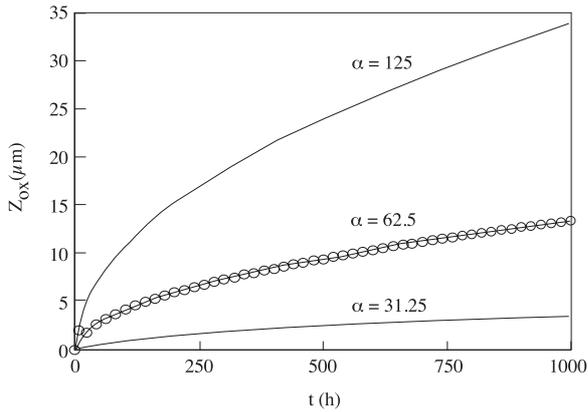
or in more explicit form,

$$Z_{OX}(t) = \frac{\phi^{1/3}(C_{A0} - C_S) \sqrt{\frac{4D_{AB}t}{\pi}}}{C_{A0}(1 + \operatorname{erf}(\psi))} \exp(-\psi^2). \quad (14)$$

**A parametric example**

The model presented above can be used for several purposes. For example let us consider the experimental parameters given by Lih et al. (1992) for a conventional Co-29Cr-6Al-1Y bond-coat ( $k_{pm} = 8.7 \times 10^{-13} \text{g}^2 \text{cm}^{-4} \text{s}^{-1}$  at  $T=1050\text{K}$ ). The calculations given below are performed under the assumption of  $C_{A0} \gg C_S$ .

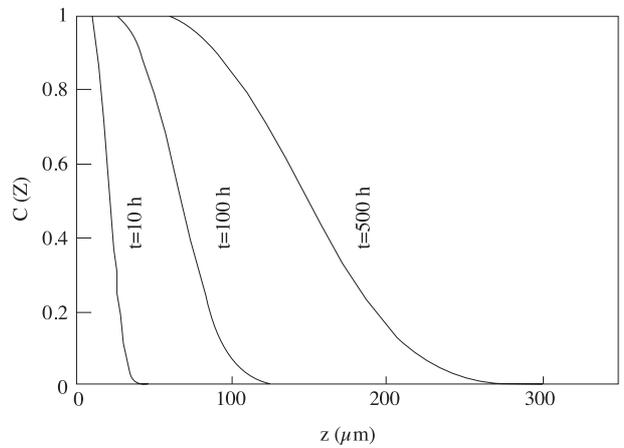
The time dependent oxide thicknesses for various  $\alpha$  values are given in Figure 3, where  $\alpha$  is equal to  $(D_{AB}/2k_{pz})$ . The solid lines are obtained by using equation (14). The symbols correspond to oxide thickness calculated from parabolic rate law, as given in equation (8). Thus equation (14) enables us to determine  $D_{AB}$  by using the matching value of  $\alpha$ . In other words, when either  $D_{AB}$  or  $k_{pz}$  is known, the other can be predicted by using equation (14). The predicted  $D_{AB}$  is  $7.828 \times 10^{-12} \text{cm}^2/\text{s}$  for  $\alpha=62.5$ . The experimental determination of  $D_{AB}$  is quite difficult. Thus equation (14) is very useful, even if it is used for this purpose only. The curves for  $\alpha=125$  and  $\alpha=31.25$  show the direct effect of  $\alpha$  on the oxidation rate.



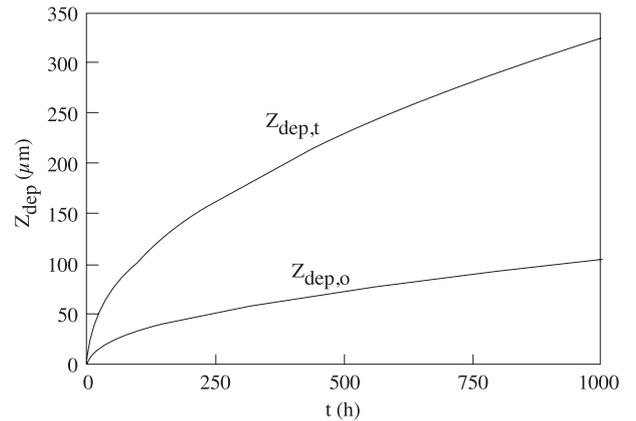
**Figure 3.** Variation of oxide thickness with time for selected values of  $\alpha = D_{AB}/2k_{pz}$  (Solid lines show calculations with equation (14) and symbols show calculations with parabolic rate law).

The normalized concentration profile of aluminum in the bond-coat are calculated with (6) and the results for selected oxidation times ( $t=10\text{h}$ ,  $100\text{h}$ , and  $500\text{h}$ ) are shown in Figure 4. The initial positions of the curves on the upper horizontal axis are different, as predicted by the model. These positions show the depth of the outer depletion region ( $Z_{dep,o}$ ) or the location of the moving interface from the original alloy surface. With increasing oxidation time, the

depth of the aluminum depleted region remarkably extends to the inner part of the bond-coat. This situation is shown more clearly in Figure 5. Both the thicknesses of outer ( $Z_{dep,o}$ ) and total depletion ( $Z_{dep,t}$ ) with oxidation time are plotted. The total depletion region is the sum of the outer depletion region and inner depletion (shown as Region I and Region II, respectively, in Figure 2). In the calculation made here, the inner depletion region is the distance between the locations of where  $C(Z)=1$  and  $C(Z)=0.1$ . This choice stems from the idea that it is almost impossible to detect less than 10% of changes on the original aluminum concentration in the bond coat (i.e. detecting nearly 1% aluminum in the global structure).



**Figure 4.** Normalized concentration profiles of aluminum in the bond coat for various oxidation times.



**Figure 5.** Variation of Al-depleted thicknesses with oxidation time.

## Concluding Remarks

The oxidation behavior of thermal barrier coatings (TBCs) in aircraft gas turbines is studied. A simple unsteady and one-dimensional, diffusion model based on aluminum depletion from a bond-coat to form an oxide layer of  $\text{Al}_2\text{O}_3$  is introduced. The model is applied to an example using currently available experimental data.

It is shown that by using the model, the diffusion coefficient of the depleted aluminum in the alloy, concentration profiles at different oxidation times, and the thickness of an Al-depleted region can be calculated. For the example considered here, significant values of depletion thickness seem to be possible at further stages of oxidation. This may change the

thermomechanical properties of the original alloy in the Al-depleted zone, and thus contribute to the mechanical failure of TBC systems.

The model presented in this study needs an experimentally determined transport property: either  $D_{ab}$  or  $k_{pz}$ . The theoretical calculation of  $k_{pz}$  and the effect of the depleted region on the thermomechanical properties of the bond-coat will be considered in later studies.

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