High-temperature oxidation of ceramic matrix composites dispersed with metallic particles

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Abstract

Oxidation behavior of ceramic matrix composites dispersed with metallic particles is discussed to establish materials design for high-temperature applications. Oxidation kinetics of ceramic matrix composites dispersed with metallic particles is understood from the viewpoint of the diffusion properties and defect chemistry of matrix oxides. High-temperature oxidation of Ni(p)/partially stabilized zirconia, Ni(p)/Al2O3 and Ni(p)/MgO was described as examples.

Keywords: High-temperature oxidation; Ceramic matrix composites; Metallic dispersoid; Diffusion; Defect chemistry

1. Introduction

New high-temperature materials are required to increase operation temperature for increasing conversion efficiency of thermal cycles such as gas turbine engines. Hybridization of different materials is an important concept of material design to develop new functional materials and high-performance materials. Ceramic matrix composites dispersed with metallic particles (referred to as M(p)–CMCs) are candidates for high-temperature structure materials as functionally graded materials (FGMs) or nano-composites. Their mechanical and physical properties have been studied as well as their production processes [1–4]. High-temperature oxidation/corrosion of M(p)–CMCs has, however, not been investigated in any details. High-temperature oxidation of thermal barrier coatings (TBCs) with a functionally graded structure has been reported briefly [5]. There are also a few phenomenological studies on the oxidation behavior of oxide ceramics with metals [4,6] or non-oxide ceramic dispersoid such as SiC or TiC [7–11].

At high temperatures, oxygen can pass through oxide matrix, and metallic dispersions will be oxidized in the matrix. The metallic dispersoid expands due to oxidation and stresses the matrix. The matrix is cracked when the stress generated by the oxidation of the metal dispersoid reaches to the fracture strength. Finally, the composite is fractured. Thus, to design FGMs and nano-composites for high-temperature applications, systematic understanding of oxidation/corrosion behavior M(p)–CMCs is required for estimation of their lifetime.

The author’s group has studied oxidation behavior of M(p)–CMCs at high temperatures, from the point of view with respect to diffusion properties of ceramic matrix. In this paper, the oxidation mode of M(p)–CMCs depending on diffusion properties of matrix is discussed for materials design of M(p)–CMCs with superior oxidation resistance.

2. Classification of oxidation behavior of ceramic matrix composites dispersed with metallic particles

Oxidation of metallic dispersoid in oxide matrix is dominated by not only diffusivity of ions of ceramic matrix, but also oxidation properties of itself. Luthra et al. [7] classified oxidation mode of oxide matrix composites dispersed with non-oxide dispersoid. A schematic illustration of the oxidation mode is shown in Fig. 1. Because engineering ceramics for high-temperature structure applications have high melting point and high Young’s modulus,
they have generally low diffusivities of component ions, except for oxide ions in zirconia and their related oxides. Almost M(p)–CMCs will show the mode II or III in the classification proposed by Luthra et al. In these modes, there are oxidized zones, which include oxidized metallic particles in the ceramic matrices. Oxidation behavior of real M(p)–CMCs is very complex because of the oxidation reaction between matrix and dispersoid and fracture of matrix due to the volume expansion of dispersoid by oxidation.

3. Diffusion in oxides

In order to discuss kinetics of oxidation of M(p)–CMCs at high temperatures, the steady-state diffusion through oxidized zone should be considered. Steady-state diffusion flux of substance i, $J_i$, is obtained by the following equation:

$$J_i = \frac{d n_i}{d t} = -D_i C_i \frac{d \mu_i}{R T} \frac{d x}{d x}$$  \hspace{1cm} (1)$$

where $D_i$, $C_i$ and $\mu_i$ are diffusion coefficient, concentration and chemical potential of substance i, respectively. Eq. (1) is well known as Fick’s First law.

Driving force for growth of oxidized zone is oxygen potential difference between the surrounding atmosphere and the oxidation front. In order to consider cation diffusion by using Eq. (1), chemical potential of M is derived from oxygen potential. Chemical potential of MO, $\mu_{MO}$ can be written by the following:

$$\mu_{MO} = \mu_M + \mu_O = \mu_M + \frac{1}{2} \mu_{O_2}$$  \hspace{1cm} (2)$$

Chemical potential of MO in the oxidized zone can be assumed to be constant during oxidation, hence

$$d\mu_{MO} = d\mu_M + d\mu_O = d\mu_M + \frac{1}{2} d\mu_{O_2} = 0.$$  \hspace{1cm} (3)$$

Difference in chemical potential of oxygen gives difference in chemical potential of M and leads to cation diffusion during oxidation.

Diffusion of ions in oxides occurs by migration of defects such as vacancies or interstitial ions. Defect concentration in oxide is a fundamental issue to discuss growth of oxidized zone of M(p)–CMCs. Because the ions are charged, the migration of ions will cause an electric field to be set up across the oxidized zone moving from the metallic particle to atmosphere. The net result of the migration of ions and electrons or electron-holes is therefore to be balanced for electrical neutrality condition. The defect with secondary fastest flux is the rate-controlling process on oxidation of metallic particles.

In this paper, oxidation of MO matrix composite dispersed with metal A (A/MO) is discussed to understand oxidation of M(p)–CMCs. Here the oxide of A, A$_2$O$_3$, is dissolved into MO. Fig. 2 shows the schematic drawing of diffusion in oxidized zone of A/MO. In the inside of A/MO, the oxygen potential is lower than the equilibrium between A and A$_2$O$_3$. Difference in oxygen potential between the surrounding atmosphere and the inside is the driving force for growth of oxidized zone. Defect chemistry of oxide MO doped with A$_2$O$_3$ should be considered as a function of oxygen partial pressure ($P_{O_2}$).

Defect chemistry of oxides can be expressed systematically by Brouwer diagram [12,13]. Fig. 3 shows the Brouwer diagrams of MO which forms predominantly the Schottky defects (a) and MO doped with a large mount of A$_2$O$_3$ (b). Oxide ceramics for high-temperature applications, such as Al$_2$O$_3$ and MgO, are typical insulators, that is, concentration of electrons or electron-holes are very small. Intrinsic formation of electron and electron-hole can

"Fig. 1. Schematic illustration of oxidation mode on ceramic matrix composites dispersed with metallic particles.

"Fig. 2. Schematic illustration of diffusion in oxidized zone during high-temperature oxidation of ceramic matrix composites dispersed with metallic particles."
be expressed as follows:

\[
\text{null} = e^l + h^i \quad (4)
\]

The equilibrium constant of Eq. (4), \( K_i \), is represented by:

\[
[e^l][h^i] = K_i \quad (5)
\]

The Schottky disorder is written as follows

\[
\text{null} = V_M^n + V_O^n \quad (6)
\]

then

\[
[V_M^n][V_O^n] = K_i \quad (7)
\]

The structural oxide ceramics has usually higher \( K_i \) than \( K_s \). Oxidized zone of A/\( \text{MO} \) consists of \( \text{MO} \) doped with a large amount of \( \text{A}_2\text{O}_3 \). As shown in Fig. 3(b), the concentration of cation vacancy is increased as seen in the following equation:

\[
\text{A}_2\text{O}_3 \rightarrow 2\text{A}^2+ + \text{V}_O^n + 3\text{O}_2^\cdot \quad (8)
\]

When \( P_{O_2} \) at the surface to the oxidation front (equilibrium between A and \( \text{A}_2\text{O}_3 \)) is located in the region in which \( [A_M^n] = 2[V_M^n] \) is the electrical neutrality condition, growth of oxidized zone is rate-controlled by outward diffusion of M with the vacancy diffusion mechanism. In this case, electrons move mainly to establish electronic neutrality under lower \( P_{O_2} \). With increasing \( P_{O_2} \), electron concentration decreases and electron-holes will migrate mainly for the electric neutrality. Since electrons and electron holes have much higher mobility than ions, the rate-controlling process of growth of oxidized zone will be the fastest ionic diffusion process.

4. Macroscopic defects in oxidized zone

Difference in diffusing ions during oxidation leads to difference in macroscopic defects in oxidized zone such as voids and cracks. Fig. 4 illustrates the macroscopic defects in oxidized zone of A/\( \text{MO} \). Almost metals will expand by oxidation. The ratio of volume change by oxidation is called as Pilling–Bedwarth ratio [14]. Inward diffusion of oxygen will give volume increase of dispersoid during oxidation. The matrix of oxidized zone will be fractured. On the other hand, outward diffusion of cations leads to develop new oxidized zone on the surface of the composite, as shown in Fig. 4(b). Volume change in the inside of oxidized zone will be negative. Voids will form in the inside of oxidized zone.

5. Growth kinetics of oxidized zone

Growth rate of oxidized zone of M(p)–CMCs with mode II or III can be estimated quantitatively from the diffusion flux of ions passing through oxidized zone. Oxidation kinetics of A/\( \text{MO} \) as shown in Fig. 2 is considered as an example. Diffusion flux in oxidized zone can be given by Eq. (1). Amount of metal A per area in dX can be obtained by

\[
dA = \frac{v_A}{v_{f}} dX \quad (9)
\]

where \( v_f \) and \( v_A \) are volume fraction and molar volume of metal A, respectively. Growth rate of oxidized zone, dX/dr, is given from the stoichiometric relationship of \( 3n_A = 2n_O \) in the oxidation reaction of metal A:

\[
\frac{dX}{dr} = \frac{v_A}{v_f} \frac{dn_A}{dr} = 2 \frac{v_A}{v_f} \frac{dn_O}{dr} \quad (10)
\]
When oxygen passing through the oxidized zone oxidizes metallic particles dispersed in the matrix and oxygen diffusion is the rate-controlling step, the growth rate can be expressed as follows:

\[
\frac{dX}{dt} = \frac{2}{3} \frac{v_A}{v_f} \frac{dn_O}{dt} = -\frac{2}{3} \frac{v_A}{v_f} \frac{D_O C_O \, d\mu_O}{RT \, dx} = -\frac{1}{3} \frac{v_A}{v_f} \frac{D_O C_O \, d\mu_O}{RT \, dx}
\]

(11)

Integration of Eq. (11) over the depth of the oxidized zone, \(X\), gives

\[
X = \frac{1}{3} \frac{v_A}{v_f} \int_{P_{O_2,S}}^{P_{O_2,OF}} D_O C_O \, d\ln P_{O_2}
\]

(12)

where subscripts of S and OF are surface and oxidation front, respectively. Finally, thickness of oxidized zone, \(X\), at oxidation time, \(t\), can be represented by:

\[
X^2 = -\frac{2}{3} \frac{v_A}{v_f} \left\{ \int_{P_{O_2,S}}^{P_{O_2,OF}} D_O C_O \, d\ln P_{O_2} \right\} t
\]

(13)

Growth of oxidized zone predominated by outward diffusion of cations can be expressed with the similar process as follows:

\[
X^2 = -\frac{2}{3} \frac{v_A}{v_f} \left\{ \int_{P_{O_2,S}}^{P_{O_2,OF}} D_M C_M \, d\ln P_{O_2} \right\} t
\]

(14)

These simple equations can estimate growth of oxidized zone of M(p)--CMCs. To estimate a parabolic constant for growth of oxidized zone, the product of diffusion coefficient--concentration is required as a function of oxygen partial pressure.

In the vacancy diffusion cases, the following relation between diffusion of species \(i\) and its vacancy should be established from the flux balance:

\[
D_i C_i = D_V C_V
\]

(15)

Since the vacancy concentration is generally quite low, \(C_i\) and \(D_V\) can be regarded to be constant. When diffusion coefficient, \(D_i\) under a fixed \(P_{O_2}\) is obtained and dependence of [\(V_i\)] on \(P_{O_2}\) is clarified as [\(V_i\)] \(\propto P_{O_2}^{1/n}\), diffusion coefficient of species \(i\) is given by:

\[
D_i = D_V \frac{C_V}{C_i} = D_V [V_i] = D_V P_{O_2}^{1/n}
\]

(16)

Thus, diffusion coefficient and defect chemistry are important for understanding oxidation properties of M(p)--CMCs at high temperatures. However, diffusion data and defect chemistry in engineering ceramics are not enough yet, in particular, on effects of impurities.

6. Case studies

Taking account of mechanical properties at high temperatures, Al2O3, MgO, zirconia and mullite are potential ceramics for matrix of M(p)--CMCs for high-temperature applications. Zirconia ceramics (stabilized zirconia) have been used for TBCs on metal parts such as gas turbine blades. Functional graded coatings are expected to reduce thermal expansion difference between TBCs and metal parts. Yoshida reported internal oxidation of TBCs for turbine blades [5]. Since this type of TBCs is usually porous, surrounding gas can pass into the inside of coating and oxidize the dispersed metallic particles. Nanko et al. [15,16] studied high-temperature oxidation of dense Ni-dispersed partially stabilized zirconia (PSZ). Ni is a base-metal for heat-resistant alloys. Fig. 5 shows the cross-section of Ni(p)/zirconia ceramics oxidized at 700 °C for 11 h in air. There is a cracked zone in the depth of 200 μm. The cracked zone grew proportionally with oxidation time. The oxidation of Ni/PSZ is different with the diffusion-controlled model described in Eqs. (13) and (14). Fig. 6 illustrates schematically a kinetic mechanism of high-temperature oxidation of Ni(p)/PSZ. Because PSZ is an oxide ion conductor, oxygen diffuses through zirconia matrix to the dispersed Ni particles in the beginning of oxidation. Ni particles are oxidized and then the matrix is fractured by volume expansion of Ni particles. The surrounding gas is supplied through the crack network in cracked zone. Ni particles below the cracks are oxidized by inward diffusion of oxide ions passing through zirconia ceramics again. The model gives a constant growth rate of cracked zone, which is obtained by dividing the average distance between Ni particles with a period to complete crack network between Ni particles.

In the case of Ni(p)/Al2O3 [17,18], voids were formed without any cracks in the oxidized zone. Fig. 7 shows the cross-section of Ni(p)/Al2O3 oxidized at 1300 °C in air.

![Fig. 5. Cross-section of partially stabilized zirconia composite dispersed with 2.5 vol% Ni particles oxidized at 700 °C for 11 h in air.](image-url)
The NiAl$_2$O$_4$ layer on the surface is observed. The product layer on the surface is also an evidence of outward diffusion of cations. Growth of the oxidized zone obeyed the parabolic law. Diffusion properties of Al$_2$O$_3$ ceramics are very complex and predominated by grain boundary diffusion. Both of oxide and cation can diffuse comparably in polycrystalline Al$_2$O$_3$. Wang at al. [19] reported phenomenological study on high-temperature oxidation of Ni(p)/Al$_2$O$_3$. Nanko et al. [18] reported high-temperature oxidation of nano-Ni(p)/Al$_2$O$_3$. Because of finer Al$_2$O$_3$ matrix, nano-Ni(p)/Al$_2$O$_3$ has faster oxidation rate than macro-Ni/Al$_2$O$_3$. High-temperature oxidation of Ni/MgO also followed the parabolic law [20]. In Ni/MgO, outward diffusion of cation is rate-controlling process and resulted in the formation of voids in the oxidized zone.

7. Summary

Oxidation behavior of ceramic matrix composites dispersed with metallic particles can be understood from the diffusion properties and defect chemistry of matrix oxides. High-temperature oxidation of Ni(p)/PSZ, Ni(p)/Al$_2$O$_3$ and Ni(p)/MgO was described as examples. In order to establish oxidation resistance of M(p)–CMCs, diffusion properties and defect chemistry of engineering ceramics should be studied, in particular, on influences of impurity doping.

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