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Influence of the density of oxide on oxidation kinetics

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ABSTRACT

A new kinetic model is proposed to describe the isothermal oxidation of metals and alloys in the form of sphere, flat plate and fiber shape with considering oxidation induced volume change or Pilling–Bedworth Ratio. The effects of temperature, oxygen partial pressure, particle size, sample shape on the oxidation reaction fraction are analyzed in the model through a physical meaning explicit function. The oxidation experimental data of zinc powders and plates were used to check the model. The results show that the calculated curves agree well with the experimental data and the model can give a good theoretical prediction. All of these will be useful for studying the oxidation of intermetallics either.

1. Introduction

The oxidation of metal and alloy is a very important issue for material sciences, especially for the high temperature materials [1,2]. The oxidation of functional materials even caused more serious accident. In space era the destruction of some aircraft and space vehicle might be directly attributed to oxidation. Therefore, much attention has been focused on the oxidation resistance of high temperature materials. The subject of the high-temperature oxidation of metals receives extensive investigation and theoretical treatment. However, the oxidation experiments are time consuming and expensive. In order to reduce the time and cost of these experiments, lots of scholars developed kinetic models for oxidation, such as Tammann–Pilling–Bedworth (TPB) parabolic rate law [3,4], Wagner theory [5,6], Cabrera–Mott theory [7], Gulbransen theory [8], Jost–Hoar–Price model [9,10] and the non-parabolic kinetic equations [11–15]. In our previous papers [16–18] we have systematically studied the gas–solid reaction and discussed the influence of temperature, oxygen partial pressure, sample shape and size on the oxidation rate and the effect of non-isothermal condition on the reacted fraction. However, all of these were established on the basis that the volume of oxide layer is the same as that of the matrix itself. This assumption is correct only upon the situation where the volumes between matrix and oxide layer is the same. Otherwise a big error would be introduced. Actually, the volume of metal will expand or shrink after oxidation. The technique word of “the difference between the volumes of matrix and oxide layer” can be expressed as the Pilling–Bedworth Ratio (PBR) [4], which was firstly noticed by Pilling and Bedworth in 1923.

In this paper, an effort will be made to solve these problems, i.e., (i) considering the PBR parameter, how do the temperature, oxygen partial pressure, powder size affect the reaction fraction of powder; (ii) the factors mentioned above how to affect the thin plate plane oxidation; (iii) the fiber oxidation is a very important issue for composite, how do the above factors affect the fiber oxidation under different PBR parameter. All these questions have never been addressed in the literature before. In the light of this idea, a series of new functions will be proposed to solve the above question quantitatively. In addition, the oxidation behaviors of zinc powders and pellet are presented as example to confirm the validity of the new model.

2. Derivation of formulae

2.1. Sphere ball

Fig. 1(a) shows a sphere particle exposing in the oxygen environment, the flux of oxygen can be calculated according to the following equation

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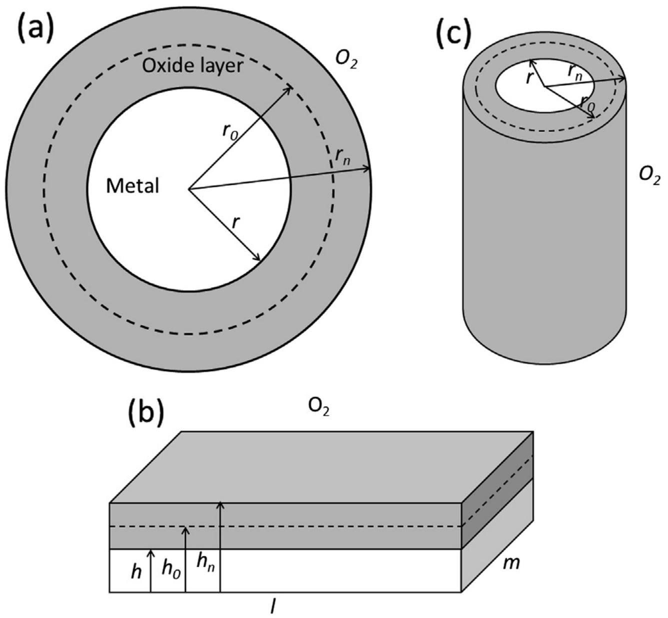

Fig. 1. The schematic diagrams of the oxidation of metal: (a) sphere particle, (b) flat thin plate and (c) fiber.

$$j = -D_O \frac{\partial C}{\partial r} = -D_O \frac{C_0 - C_{eq}}{r_n - r} \tag{1}$$

where r_n represents the radius of the particle from the center to the outside oxide layer, r is the radius of the matrix metal, C_0 and C_{eq} are the oxygen concentration at the gas/oxide interface and oxide/metal interface respectively, the later one is in equilibrium with oxide, D_O is the diffusion coefficient of oxygen and j is the flux of oxygen per unit area. The relation between "j" and the growing radius should be

$$\frac{\mathrm{d}r}{\mathrm{d}t} = j\frac{M}{\rho} \tag{2}$$

where M and ρ are the molecule weight of metal and density of metal, respectively. Substituting Eq. (1) into Eq. (2) and rearranging it yields

$$\frac{\mathrm{d}\frac{r}{r_0}}{\mathrm{d}t} = -\frac{D_O M}{\rho r_0^2} \frac{C_0 - C_{eq}}{\frac{r_n}{r_0} - \frac{r}{r_0}} \tag{3}$$

On the other hand, since the Pilling–Bedworth ratio β is equal to the ratio of oxide volume to metal volume, i.e

$$\beta = \frac{r_n^3 - r^3}{r_0^3 - r^3} \tag{4}$$

or

$$\frac{r_n}{r_0} = \left[\beta - (\beta - 1)\left(\frac{r}{r_0}\right)^3\right]^{\frac{1}{3}} \tag{5}$$

Combining Eq. (3) and Eq. (5) and rearranging it yields

$$\left\{\left[\beta - (\beta - 1)\left(\frac{r}{r_0}\right)^3\right]^{\frac{1}{3}} - \frac{r}{r_0}\right\}\mathrm{d}\frac{r}{r_0} = -\frac{D_O M (C_0 - C_{eq})}{\rho r_0^2}\mathrm{d}t \tag{6}$$

Integrating Eq. (6) one can find the relation between the particle radius and time. Since the reaction fraction of oxidation ξ is

$$\xi = 1 - \left(\frac{r}{r_0}\right)^3 \tag{7}$$

Combining Eq. (6) and Eq. (7) and rearranging it yields

$$\frac{[\beta - (\beta - 1)(1 - \xi)]^{\frac{1}{3}} - (1 - \xi)^{\frac{1}{3}}}{3(1 - \xi)^{\frac{2}{3}}}\mathrm{d}\xi = \frac{D_O M (C_0 - C_{eq})}{\rho r_0^2}\mathrm{d}t \tag{8}$$

Integrating it from $t = 0$, $\xi = 0$ to $t = t$, $\xi = \xi$ yields

$$\int_0^{\xi} \frac{[\beta - (\beta - 1)(1 - \xi)]^{\frac{1}{3}} - (1 - \xi)^{\frac{1}{3}}}{3(1 - \xi)^{\frac{2}{3}}}\mathrm{d}\xi = \frac{D_O M (C_0 - C_{eq})}{\rho r_0^2} t \tag{9}$$

This integration doesn't have analytical solution but numerical solution.

2.2. Flat thin plane

The flat thin plane has a simpler situation. As shown in Fig. 1(b) the size of flat thin plane with a dimension of "l" length, "m" wide and "h_0" high. The oxygen flux per unit area should be

$$j = -D_O \frac{\partial C}{\partial r} = -D_O \frac{C_0 - C_{eq}}{h_n - h} \tag{10}$$

The Eq. (2) now should become

$$\frac{\mathrm{d}h}{\mathrm{d}t} = -\frac{D_O M}{\rho} \frac{C_0 - C_{eq}}{h_n - h} \tag{11}$$

According to the definition of PBR, the β for a flat thin plane should be

$$\frac{h_n}{h_0} = \left[\beta - (\beta - 1)\frac{h}{h_0}\right] \tag{12}$$

Substituting Eq. (12) into Eq. (11) yields

$$\beta\left(1 - \frac{h}{h_0}\right)\mathrm{d}\frac{h}{h_0} = -\frac{D_O M}{\rho h_0^2}(C_0 - C_{eq})\mathrm{d}t \tag{13}$$

Since the reaction fraction ξ for a flat thin plane is

$$\xi = 1 - \left(\frac{h}{h_0}\right) \tag{14}$$

Substituting Eq. (14) into Eq. (13) yields

$$\beta\xi\mathrm{d}\xi = \frac{D_O M}{\rho h_0^2}(C_0 - C_{eq})\mathrm{d}t \tag{15}$$

Integrating Eq. (15) from $t = 0$, $\xi = 0$ to $t = t$, $\xi = \xi$, one has

$$\xi = \sqrt{\frac{D_O M (C_0 - C_{eq})}{\beta \rho h_0^2} t} \tag{16}$$

It is the result for the thin flat plane.

2.3. Fiber oxidation

Fibers have been widely used as reinforced materials in composite materials, which suffered the problem of oxidation. Therefore it is meaningful to study fiber oxidation. Fibers can be seen as a long cylinder with a small radius of r_0 and long length "l" as shown