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Investigation of isothermal oxidation of AlN ceramics using different kinetic model

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ABSTRACT

The oxidation kinetics of AlN ceramics under the conditions of different rate-controlling steps existing has been discussed using two kinds of models (the model used in the literature and Chou model) based on the results reported in literatures. The analysis shows that though both models can be used to describe the oxidation behavior of AlN ceramics, Chou model is preferred. It is because, not only Chou model can give a clear physical meaning in expressing all parameters that will be convenient for theoretical discussion, but also it will perform a simple calculation. The most important thing is that the new model will lead to a more accurate calculation result.

1. Introduction

Aluminum nitride (AlN) ceramics as bulk materials has been received considerable attention for various industrial applications because of their excellent physical properties such as high thermal conductivity (3.2 W/cm K), low coefficient of thermal expansion ($4.03–6.0 \times 10^{-6}$/K) and high electrical resistivity ($>4 \times 10^{8}\ \Omega$ cm) [1–3]. For example, AlN ceramics find large applications as electronic substrates and heat radiation fins [4]. However, many AlN materials are usually designed to work in a condition with high-temperature, it is important to determine their high-temperature corrosion resistance. Strictly speaking, high-temperature oxidation is one type of the most important high-temperature corrosion reaction.

Compared with the experimental aspects, theoretical investigations on oxidation kinetics of AlN ceramics are far more enough. Since the oxidation of AlN ceramics is a kind of gas–solid reaction, it is very complicated and a group of differential equations are required to be solved if it is treated rigorously. Even that it is still difficult to get an analytic solution. It has been found from the experiments that the oxidation of AlN materials is basically controlled by the chemical reaction or the diffusion step [5–8]. To simplify the calculation, the rate of limited-step method was applied, such as the well-known the linear rate, the parabolic rate law, etc. However, these formulae have their own defects, i.e., the parameter "k" appearing in these formulae contains so many factors, such as temperature, oxygen partial pressure, etc. that it does not has clear physical meaning and thus it is difficult to perform a theoretical analysis and make the calculation complicated. Therefore, the calculation results based on these methods were not accurate.

Recently, Chou [9,10] has developed a series of formulae that can explicitly describe the oxidation reaction under the condition where all kinds of possible controlling steps exist. They have been developed on the basis of some approximate but reasonable assumptions. Since these formulae analytically express the reacted fraction as a function of oxidation time, temperature, pellet size and oxygen partial pressure, one can perform a calculation easily and give a good theoretical discussion for practical problem. Besides, the most attractive point is that one might get a more accurate calculation result in comparison with the method mentioned above. These formulae have been successfully applied to treat the oxidation behavior of SiC, Si_3N_4 and SiAlON materials [11–14]. Since the oxidation of AlN materials is similar to these materials, i.e., belonging to gas–solid reaction, these formulae can also be expected to treat the oxidation of AlN.

In this paper, the oxidation kinetics of AlN pellets has been theoretical investigated using the model used in literatures and Chou model, respectively, based on the experimental data available in literatures. A series of comparison of the two kinds of models will be given, expecting to provide a more convenient and accurate method to study the oxidation behavior of AlN pellets.

2. Kinetic models

A general mechanism of oxidation reaction for AlN pellet can be described as the following steps, they are:

(i) Oxygen in the bulk gas phase transfer to the surface of AlN ceramics.

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(ii) Oxygen diffusion through the boundary layer between gas phase and solid phase.
(iii) Physisorption of oxygen molecules.
(iv) Dissociation of oxygen molecules and chemisorption.
(v) Surface penetration of oxygen atoms.
(vi) Diffusion of oxygen through the oxide product layer to the oxide/nitride interface.
(vii) Nucleus formation and chemical reaction producing oxide product and gas.
(viii) Gas diffusion through oxide product to the surface of nitride ceramics.
(ix) Gas diffusion through the gas/pellet boundary to the gas bulk.

Of course, if needed, one may give more intermediate steps, however, the above nine steps are basically enough to describe this kind of mechanism. In most cases, the step (vi) and (vii) will be the rate-controlling step. In the following section, the kinetic model under these two cases will be discussed.

2.1. Kinetic models used in the literature

As reported in the literature, linear kinetic model has been developed to treat the oxidation behavior when chemical reaction is the rate-controlling step [7]. Its expression is as following:

$$\xi = k_r t \tag{1}$$

where k_r is the linear rate constant (1/s). The oxidation rate follows Arrhenius' law, thus k_r increases exponentially with temperature

$$k_r = k_0 \exp\left(-\frac{\Delta E_r}{RT}\right) \tag{2}$$

where k_0 is a temperature–independent constant (1/s), R is the gas constant (J/(mol K)), and ΔE_r is the activation energy (J/mol).

The parabolic rate law was developed under the assumption that the rate-controlling step is diffusion [7,8]. The expression of the formula can be written in the following form

$$(\Delta m)^2 = kt + c \tag{3}$$

where Δm was the mass change of oxidation (mg), k was the rate constant of reaction and c was a numerical constant (mg^2/s). Similarly the oxidation rate constant k also follows Arrhenius' law.

Although these two above models have been extensively used to investigate the oxidation behavior of AlN ceramics [7,8], the physical meaning of the parameter "k" in both the linear rate law and the parabolic rate law does not has clear physical meaning and thus they are difficult to perform a theoretical analysis and make the calculation complicated.

2.2. Chou model

Chou et al. [9] have proposed a method to explicitly express the reacted fraction of reactions as an explicit function of time t, temperature T and pellet size L, etc. under the conditions of different rate-controlling steps existing. For the case where the chemical reaction is the controlling step, the relation of the reacted fraction ξ and time t is given by

$$\xi = \frac{1}{B_T} \exp\left(-\frac{\Delta E_r}{RT}\right) t \tag{4}$$

where

$$B_T = \frac{\upsilon_m L_0}{k_0\left(\sqrt{p_{O_2}} - \sqrt{p_{O_2}^{eq}}\right)} \tag{5}$$

and ΔE_r represents the apparent activation energy of chemical reaction (J/mol), $P_{O_2}^{eq}$ is oxygen partial pressure equilibrium with oxide (Pa), k_0 is a temperature-independent constant; υ_m is a coefficient related to the density of reactant and product, L_0 is the original thickness of the pellet (mm). If all these parameters are known, of course, one can find the relation between reacted fraction ξ with time t (s). In some particular cases, one can combine part of these parameters to construct an auxiliary function like B_T (see Eq. (5)).

In case of diffusion controlling the oxidation process, Chou et al. [12] has also proposed a model under this condition, in which the reacted fraction ξ has been expressed as a function of time t, temperature T, oxygen partial pressure P_{O2} and particle radius R_0, etc. The relation of the reacted fraction ξ and time t is given by

$$\xi = \sqrt{\frac{1}{\Theta_T} \exp\left(-\frac{\Delta E_d}{RT}\right) t} \tag{6}$$

where

$$\Theta_T = \frac{\upsilon_m L_0^2}{2K_0^{0\beta} D_0^{0\beta}\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)} \tag{7}$$

and ΔE_d represents the apparent activation energy (J/mol), $P_{O_2}^{eq}$ is oxygen partial pressure equilibrium with oxide (Pa), $K_0^{O\beta}$ and $D_0^{O\beta}$ are equilibrium constant of oxidation reaction and diffusion coefficient of oxygen that is relied on the particle material; υ_m is a coefficient related to the density of reactant and product. In some particular cases, one can combine part of these parameters to construct an auxiliary function like Θ_T (see Eq. (7)) and thus the formula has a simple expression. From Eq. (7), Θ_T is a function of oxygen pressure P_{O_2} (Pa) and the pellet size L_0 (mm).

Eqs. (4) and (6) are the general formula expressing the reacted fraction ξ as the function of time t, temperature T and many other related parameters under the conditions of different rate-controlling steps existing. One can use these to quantitatively discuss the oxidation kinetics of AlN pellet.

3. Experimental facts

Bellosi et al. [7] investigated the thermal stability of AlN ceramics in air at 873–1673 K. Two kinds of samples were used in the experiment, i.e., one without additives added and the other using CaC$_2$ as sintering aids. The oxidation tests were carried out in isothermal condition using a TG apparatus (P.L. Thermal Sciences, UK). The result showed that the oxidation of both two kinds of AlN ceramics became obvious from 1273 K. Fig. 1a and b showed the oxidation behavior of AlN specimens without additives added and that with CaC$_2$ added as sintering aids, respectively, at the temperature range of 1373–1673 K. The results showed that the oxidation behavior of AlN ceramics without additives added was governed by a surface reaction and followed the linear rate law at 1373–1673 K. By comparison, the oxidation behavior of AlN ceramics changed when CaC$_2$, used as sintering aids additives, was added. It followed the linear rate law at lower temperature, i.e., 1373–1473 K and changed to be controlled by diffusion at the temperature range of 1523–1673 K.

Osborne et al. [8] researched the oxidation kinetics of polycrystalline AlN pellet in air at temperature range of 1423–2023 K by measuring the weight increase. The result showed that at higher temperature, i.e., 1623–2023 K, the sample was covered with a dense oxide layer and the oxidation behavior followed a parabolic rate law (Fig. 2). The activation energy of oxidation during the temperature range was calculated to be 395 kJ/mol.

4. Results

In this section the experimental data offered by Bellosi et al. [7] and Osborne et al. [8] were used to study the oxidation kinetics of