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Kinetics of non-isothermal oxidation of AlN powder

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Abstract

The non-isothermal oxidation of AlN powder has been studied, based on which a new formula has been suggested to express the reacted fraction of the oxidation as a function of oxidation time, oxygen partial pressure, the particle size, as well as the temperature increasing rate explicitly. The application of this new model to the oxidation of AlN powder shows that this new model can give a more accurate and reasonable result. The diffusion activation energy of AlN powder is extracted to be 356.3 kJ/mol.

Keywords: Non-isothermal; Partial pressure; Reacted fraction; Diffusion; Oxidation

1. Introduction

AlN has been used extensively as electronic substrates, heat radiation fins and refractory materials because of its 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] However, the oxidation of AlN seriously influences the intensity and function of materials especially at an elevated temperature. Understanding the oxidation behavior of AlN is a critical part of learning to deal with the practical applications, recently, various oxidation kinetic models (linear or parabolic) have been proposed to describe the oxidation mechanism of AlN powder.[4–7] It is well known that in many cases, AlN is not used in an isothermal environment but in a non-isothermal manner. Consequently, it is necessary to further investigate the kinetics of non-isothermal oxidation of AlN. Nevertheless, the study in this aspect is very limited. Besides, the effects of many factors such as particle size, oxygen partial pressure on the oxidation process have not been fully investigated yet. It is well known that the oxidation rate of AlN will increase with the increase of oxygen partial pressure, P_{O_2}, whereas it is still not clear how the oxygen partial pressure affects the oxidation rate quantitatively. Therefore, it is meaningful for us to study the relation between the reacted fraction ξ and time t quantitatively for both practical applications and theoretical analyses in a non-isothermal oxidation process, based on which the influence of oxygen partial pressure on the AlN oxidation process will be further clarified.

2. Derivation of formulae

For a gas–solid reaction, the mechanism of reaction involves many steps, they are, diffusions in both bulk gas phase and the boundary of interface, the physisorption of gas molecule on the solid surface, the chemisorption, the diffusion of gas atoms through solid product as well as the chemical reaction and so forth. When the rate of one of these steps is much slower than that of others, this step will become the controlling step and the reaction rate of the whole oxidation process can be approximately described in terms of the kinetic formula of this controlling step.

A general mechanism of oxidation reaction for AlN powder can be described as follows:

(i) Oxygen in the bulk gas phase transfers to the surface of AlN particle.
(ii) Oxygen diffusion through the boundary between the gas phase and the surface of AlN particle.
(iii) Physisorption of oxygen molecules on the surface of AlN particle.
(iv) Dissociation of oxygen molecules and chemisorption.
(v) Surface penetration of oxygen atoms.
(vi) Diffusion of oxygen atoms from the surface of particle through the oxide product layer to the Al_2O_3/AlN interface.

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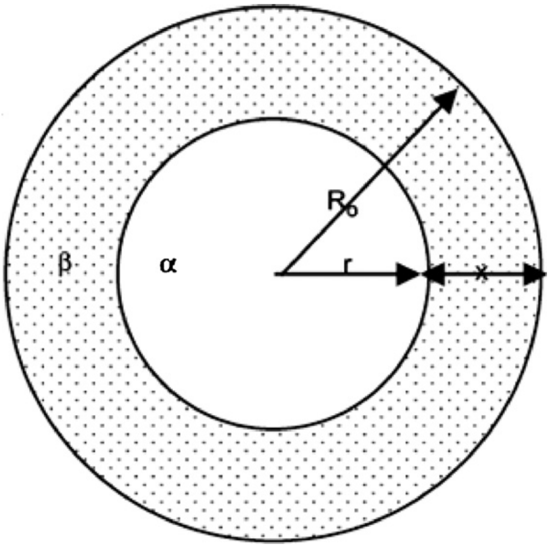

Fig. 1. Schematic diagram of mechanism of oxidation reaction of AlN.

(vii) Nucleus formation and chemical reaction producing oxide product and gas.

Of course, if needed, more intermediate steps can be given, however, the above seven steps are basically enough to describe this kind of mechanism. In general, at an elevated temperature, the controlling step of the AlN oxidation reaction is in the step (vi),[4,6,8,9] based on which a new kinetic formulae has been derived as follows.

First let us assume that, powder of materials can be regarded as spherical balls with the same density ρ and radius R_0 as shown in Fig. 1, where α represents AlN phase with a radius of r, β the oxide layer with thickness of x. It is further assumed that the change of thickness before and after oxidation is neglected.

It can be seen from Fig. 1 that the reacted fraction ξ of oxidation of AlN at time t and radius r can be calculated in terms of the following equation:

$$\xi = 1 - \frac{r^3}{R^3} \tag{1}$$

Differentiating Eq. (1) with respect to time t, one obtains:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -\frac{3r^2}{R^3}\frac{\mathrm{d}r}{\mathrm{d}t} \tag{2}$$

On the other hand, the time derivative of radius r is proportional to the rate of oxidation reaction, *i.e.*:

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{V}{\upsilon_\mathrm{m}} \tag{3}$$

where V is the reaction rate and υ_m is a constant coefficient that depends on density of AlN and oxidation product.

In order to find a simple analytical solution, one may approximately assume that the diffusion rate V for oxygen atom at steady state obeys the following equation[10,11]:

$$V = \frac{D}{R-r}[C_\mathrm{O} - C_\mathrm{O}^\mathrm{eq}] \tag{4}$$

where C_O represents the concentration of oxygen atom at the particle surface; C_O^eq is the equilibrium concentration of oxygen atom at the interface between Al_2O_3 and AlN; D is the diffusion coefficient of oxygen atom in the oxidation layer. Here, it is approximately assumed that $C_\mathrm{O}^\mathrm{eq} \approx 0$ due to a very small value. Therefore:

$$V = \frac{D}{R-r}C_\mathrm{O} \tag{5}$$

Based on the Sevart's law, the relationship between oxygen atom concentration C_O and oxygen partial pressure P_{O_2} is:

$$C_\mathrm{O} = k\sqrt{P_{\mathrm{O}_2}} \tag{6}$$

Substituting Eq. (6) into Eq. (5) yields:

$$V = \frac{Dk}{R-r}\sqrt{P_{\mathrm{O}_2}} \tag{7}$$

where k is the rate constant depending on temperature.

Combining Eqs. ((1)–(3)) and (7) and rearranging it, one obtains:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{Dk\sqrt{P_{\mathrm{O}_2}}}{R^2\upsilon_\mathrm{m}}\frac{3(1-\xi)^{2/3}}{1-(1-\xi)^{1/3}} \tag{8}$$

Integrating Eq. (8) with the initial condition, $t = t_0$ (or $T = T_0$), $\xi = \xi_0$, one obtains:

$$\int_{\xi_0}^{\xi}((1-\xi)^{-2/3} - (1-\xi)^{-1/3})\,\mathrm{d}\xi = \int_{t_0}^{t}\frac{3Dk\sqrt{P_{\mathrm{O}_2}}}{R^2\upsilon_\mathrm{m}}\,\mathrm{d}t \tag{9}$$

According to Arrhenius law, the temperature dependences of both diffusion coefficient D and equilibrium constant k can be expressed as:

$$D = D_0\exp\left(-\frac{\Delta E_\mathrm{d}}{RT}\right) \tag{10}$$

$$k = k_0\exp\left(-\frac{\Delta E_\mathrm{k}}{RT}\right) \tag{11}$$

where ΔE_d and ΔE_k represent the activation energy of diffusion of the oxygen atom in the oxidation layer and the chemical reaction of the oxygen molecule dissociation, respectively; D_0 and k_0 are constant independent of temperature, thus Eq. (9) becomes:

$$\int_{\xi_0}^{\xi}((1-\xi)^{-2/3} - (1-\xi)^{-1/3})\,\mathrm{d}\xi = \int_{t_0}^{t}\frac{3D_0k_0\sqrt{P_{\mathrm{O}_2}}}{R^2\upsilon_\mathrm{m}} \times\exp\left(-\frac{\Delta E_\mathrm{d}+\Delta E_\mathrm{k}}{RT}\right)\mathrm{d}t = \int_{t_0}^{t}\frac{3D_0k_0\sqrt{P_{\mathrm{O}_2}}}{R^2\upsilon_\mathrm{m}}\exp(-\frac{\Delta E}{RT})\,\mathrm{d}t \tag{12}$$

where ΔE is the apparent activation energy that is equal to the sum of two parts of activation energy, $(\Delta E_\mathrm{d} + \Delta E_\mathrm{k})$. If $\eta = (T - T_0)/t$ represent the heating rate, one obtains:

$$(1-(1-\xi)^{1/3})^2 = \int_{T_0}^{T}\frac{\sqrt{P_{\mathrm{O}^2}}}{B_\mathrm{CP}}\exp\left(-\frac{\Delta E}{RT}\right)\mathrm{d}T + (1-(1-\xi_0)^{1/3})^2 \tag{13}$$

or:

$$\xi=1-\left(1-\sqrt{\frac{\sqrt{P_{O_2}}}{B_{CP}}\int_{T_0}^{T}\exp\left(-\frac{\Delta E}{RT}\right)\,\mathrm{d}T+(1-(1-\xi_0)^{1/3})^2}\right)^3 \tag{14}$$

where $B_{CP}=(R^2 v_m \eta)/(2D_0 k_0)$, determined by radius of particle.

Define:

$$f(\xi)=(1-(1-\xi)^{1/3})^2 \tag{15}$$

Combining Eqs. (13) and (15), one obtains:

$$\frac{\mathrm{d}f(\xi)}{\mathrm{d}t}=\frac{\sqrt{P_{O_2}}}{B_{CP}}\exp\left(-\frac{\Delta E}{RT}\right) \tag{16}$$

or:

$$\ln\frac{\mathrm{d}f(\xi)}{\mathrm{d}T}=\ln\left(\frac{\sqrt{P_{O_2}}}{B_{CP}}\right)-\frac{\Delta E}{RT} \tag{17}$$

According to Eq. (17), parameters of B_{CP} and ΔE could be extracted through a regression analysis of the experimental data.

3. Application to oxidation of AlN powder

Hou et al.[12] had measured the non-isothermal oxidation of AlN powder under different oxygen partial pressures with a heating rate of 10K/min, which has been plotted in Fig. 2. In this study, the relevant data have been adopted starting from 1215K, since the oxidation of AlN exhibited evidently at this temperature. As discussed in the previous paragraph, the controlling step of AlN oxidation was in the diffusion step of oxygen through the oxide layer. Therefore the theoretical formula presented in this paper can be used to describe the behavior of oxidation kinetics of AlN.

It is noted that the y-axis in the experimental plot of Fig. 2 is not the reacted fraction ξ but $\Delta m/m_0$ (m_0 denotes the sample original weight and Δm the increment of sample weight at time t after oxidation). In this case a transformation of variable must be made prior to use our formulae. The relation between ξ and $\Delta m/m_0$ is:

$$\xi=\frac{\Delta m}{\Delta m_{\max}} \tag{18}$$

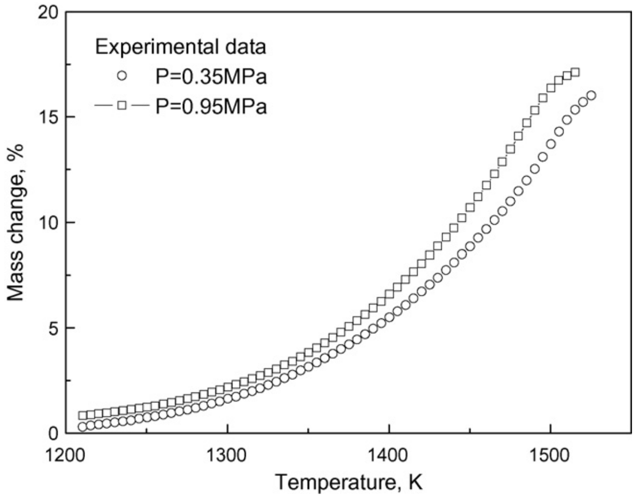

Fig. 2. Oxidation curves under non-isothermal condition with different oxygen partial pressure.

where $\Delta m_{\max}$ is the theoretical maximum increment after a complete oxidation. Therefore, one has the following equation:

$$\frac{\Delta m}{m_0}=\frac{\Delta m_{\max}}{m_0}\xi \tag{19}$$

The reaction of AlN and O_2 is:

$$4\mathrm{AlN}+3\mathrm{O_2}=2\mathrm{Al_2O_3}+2\mathrm{N_2} \tag{20}$$

From Eq. (20), $\Delta m_{\max}/m_0=24.4\%$, therefore:

$$\frac{\Delta m}{m_0}=24.4\%\,\xi \tag{21}$$

The apparent activation energy ΔE and the parameter B_{CP} of Eqs. (14) and (17) can be calculated to be 356.3 kJ/mol and 1.893×10^{-10} respectively by regressing the experimental data.

Substituting B_{CP} and ΔE into Eq. (14), the expressions for describing the behavior of oxidation kinetics with the oxygen partial pressure of 0.35 and 0.95 Mpa are obtained as follows:

$$\frac{\Delta m}{m_0}=24.4\%\times\left(1-\left(1-\sqrt{5.282\times10^9\times\sqrt{0.35}\times\int_{1215}^{T}\exp\left(-\frac{3.563\times10^5}{RT}\right)\mathrm{d}T+2.44\times10^{-5}}\right)^3\right) \tag{22}$$

$$\frac{\Delta m}{m_0}=24.4\%\times\left(1-\left(1-\sqrt{5.282\times10^9\times\sqrt{0.95}\times\int_{1215}^{T}\exp\left(-\frac{3.563\times10^5}{RT}\right)\mathrm{d}T+1.46\times10^{-4}}\right)^3\right) \tag{23}$$

Fig. 3 shows a comparison between experimental data and theoretical calculations, from which it can be seen that the theoretical expression can give a very good description for the non-isothermal oxidation of AlN under different oxygen partial pressures.

4. Discussion

(1) In our previous paper,[11] a formula for describing the oxidation behavior of non-metal materials in a non-isothermal

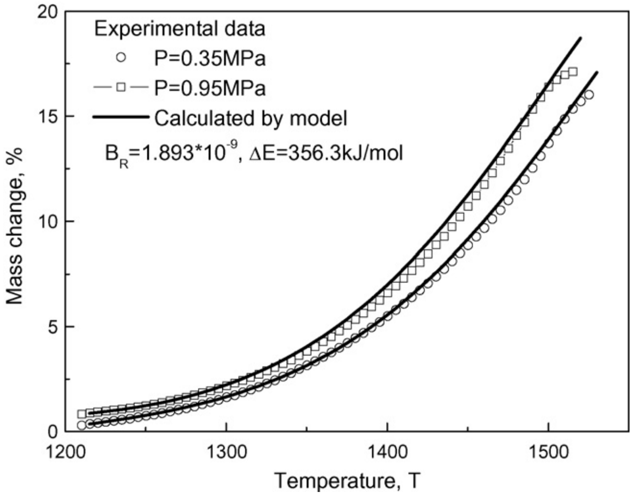

Fig. 3. A comparison of experimental data with model calculated value for non-isothermal oxidation with different oxygen partial pressure.

case has been presented:

$$\xi=1-\left(1-\sqrt{\frac{\sqrt{P_{\mathrm{O}_2}}-\sqrt{P_{\mathrm{O}_2}^{\mathrm{eq}}}}{B_{\mathrm{CP}}}\exp\left(-\frac{\Delta E}{RT}\right)(T-T_0)}\right)^3 \tag{24}$$

The difference between Eqs. (24) and (14) is that, the former one gives a theoretical maximum oxidation result. It is a limiting value for a non-isothermal oxidation and no oxidation curve could be faster than that one. The advantage of Eq. (24) is simple to use without performing integrations, while the formula presented in this paper can give a more accurate result. However, the difference calculated from these two equations will be getting smaller as the temperature increasing rate η decreases.

(2) The diffusion activation energy of AlN is calculated to be 3.563×10^5 J/mol through Eq. (14), while it is 3.7×10^5 J/mol through our previous formula Eq. (24). The relative error between them is 3.7%.

(3) The calculation procedure by using Eq. (14) can be described as follows:

Firstly, apply the general equation to determinate the constants ΔE and A:

$$\ln\frac{\mathrm{d}f(\xi)}{\mathrm{d}T}=\ln A-\frac{\Delta E}{RT} \tag{25}$$

where $f(\xi)$ is a function of reacted fraction, which is different depending on different reaction mechanisms, in this paper it is given by Eq. (15); A is a pre-exponential factor; ΔE is the activation energy; T is the absolute temperature and R is gas constant. When plotting $\ln \mathrm{d}f(\xi)/\mathrm{d}T$ with $1/T$, one can find parameters A and ΔE by regressing the experimental data.

Secondly, substituting the values of parameters ΔE and A into Eq. (25), the relationship between the reacted fraction ξ and time t can be obtained.

The Jander's model[13] and Ginstling–Brounshtein's model[14] are also widely used to deal with the diffusion problems. In these cases, $f(\xi)$ should have the following forms:

(a) Jander's model $f(\xi)=(1-(1-\xi)^{1/3})^2$, which is similar to our expression. However, in the Jander's equation, the oxygen partial pressure is not included. Therefore, it is impossible to discuss the influence of different oxygen partial pressures on the kinetics of the oxidation of AlN

(b) Ginstling–Brounshtein's model $f(\xi)=(1-2/3\xi-(1-\xi)^{2/3})$. It is also impossible to discuss the influence of oxygen partial pressure on the oxidation kinetics of AlN due to without the parameter of oxygen partial pressure appearing in the Ginstling–Brounshtein's expression.

(4) Eq. (14) is an approximate formula due to the approximate expression of reaction rate of Eq. (4). One can have a more accurate rate formula as follows[15]:

$$V=\frac{RD(C_{\mathrm{O}}-C_{\mathrm{O}}^{\mathrm{eq}})}{r(R-r)} \tag{26}$$

Nevertheless, if the Eq. (26) is adopted, one will never obtain an analytical equation to express the reacted fraction as a function of oxidation time, temperature, atmosphere as well as the temperature increasing rate, explicitly. Thus, the treatment of the oxidation of AlN will become more complicated. This case will be discussed in our future work.

(5) The derived formulae for the oxidation of AlN powder mentioned above might also be applied to the oxidation of other N/C based refractory materials due to a very similar oxidation mechanism.

5. Conclusions

There are two formulae developed by us to describe the AlN oxidation under non-isothermal condition: one is approximate; another more accurate. Though the formula developed in this paper includes an integration procedure, the calculated result will be more accurate than that of the former one. It is expected both methods will approach to a real curve of the reacted fraction vs time, when the temperature increasing rate η is getting slower.

The application of this model to the oxidation of AlN powder shows that this model works well. The diffusion activation energy of the oxygen atom passing through the oxide layer is calculated to be 356.3 kJ/mol in an AlN oxidation process.

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