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Some new perspectives on oxidation kinetics of SiAlON materials

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Abstract

The oxidation behavior of SiAlON materials has been investigated. The kinetic studies reported in literatures were also discussed. Based on the kinetic curves of the oxidation of SiAlON, a new model for predicting the oxidation weight gain as a function of temperature and other variables was established. The application of this new model to both experiment data of β-SiAlON ($z = 3.0$) powder and that of O′-SiAlON ($x = 0.18$) powder as well as that of β-SiAlON-Al_2O_3 pellet demonstrated that this new model could be used to predict the oxidation behavior and the calculated results agreed well with the experimental data, moreover, these formulae can not only be used to treat the oxidation for SiAlON materials but also can be applied to treat the problems of other non-metallic oxide materials due to similar mechanism.

Keywords: Oxidation; Kinetics; SiAlON materials; Thermogravimetry

1. Introduction

SiAlON material is a kind of compound consisting of silicon, aluminum, oxygen and nitrogen that has been found many applications such as engineering ceramics, cutting tools and refractory materials. Initially, it was found in the early 1970s[1–3] since then it had made a great progress and became a promising engineering material.

Similar to other nitrogen ceramics, SiAlON tends to be oxidized at high temperature when it is exposed to the atmosphere containing oxygen, therefore its application is limited in many aspects. In practice, the oxidation behavior may be slow due to the smaller interface area between gas and solid sample for the high dense body of SiAlON material.[4] Besides, the oxidation kinetics of SiAlON may also be influenced by the presence of dopants that was added to assist the densification process.[5,6] By contrast with Si_3N_4 and Si_2N_2O that have been investigated extensively,[7–11] the kinetic mechanism information of the oxidation processes of SiAlON materials is very limited. There are wide variations both in the observed reaction rates and in the morphology of the reaction products.[12] It is a general agreement that the reaction product is amorphous at the beginning of the oxidation and at a low temperature, but the product tends to crystallize after a longer time and at higher temperatures. However, there still remain unclear points regarding the oxidation kinetics of SiAlON materials.

The oxidation kinetics of SiAlON materials have previously been described by a parabolic rate law:

$$\left(\frac{\Delta w}{A}\right)^2 = kt + C$$

where $\frac{\Delta w}{A}$ was the oxidation mass change/unit area, k the reaction rate constant and c is numerical constant. Most researchers studied the oxidation kinetics of SiAlON materials using this formula.[13,14] The oxidation kinetics of β-SiAlON ($z = 2.45$) powder prepared by carbothermal synthesis was studied by isothermal thermogravimetry at 1100–1300 °C and was found that it followed satisfactorily a parabolic rate law with an activation enthalpy of 161 kJ/mol. It was suggested that the rate was controlled by the permeation of oxygen through the product layer developing on the grains.[13] MacKenzie et al. extended the powder oxidation study to O′-SiAlON and X-phase SiAlON, which was synthesized by the silicothermal method.[14] It was found that both materials followed the parabolic rate law with the activation enthalpy of 454 kJ/mol for O′-SiAlON powder (1000–1300 °C) and 250 kJ/mol for X-phase SiAlON powder

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Nomenclature

ΔE	apparent activation energy of oxidation
C_O^β	concentration of oxygen in β phase
C'^β_O	concentration of oxygen in the β phase at the gas/β side
C''^β_O	concentration of oxygen in the β phase at the α/β side
D_O^β	diffusion coefficient of oxygen in β phase
J_O^β	flux of oxygen in β phase
K	equilibrium constant
L_0	the original thickness of pellet
m_0	sample weight
Δm	the increment of sample weight
P_{O_2}	partial pressure of oxygen in gas phase
$P_{O_2}^{eq}$	oxygen partial pressure in equilibrium with oxide
r	radius of particle with original inorganic material
R	gas constant
R_0	radius of the original whole particle
t	time in s
T	absolute temperature in K
v_m	coefficient depending on substance and reaction
x	the thick of oxide layer in the particle $= R_0 - r$

Greek letters

α	original SiAlON material phase
β	oxide material phase
η	temperature-increasing rate
ξ	reacted fraction of oxidation

(900–1200 °C), respectively. However, Wang et al. had reported that it should follow the rate law of $(\Delta w/A)^n = kt + C$ where the exponent, n, changed from 1 to 6 during the oxidation[15]; therefore the parabolic rate law was too simple to describe the intrinsical oxidation mechanism and could not reach a consistent agreement.

Even though most oxidation processes have been interpreted with the parabolic rate law, there have been reported for β-SiAlON ceramics with the z value of 1, 2.5 and 3.8, which deviated from the parabolic rate law at temperatures above 1300 °C.[5] The kinetics was interpreted with the modified rate law:

$$\left(\frac{\Delta w}{A_0}\right) = a \arctan(bt)^{1/2} + c(t)^{1/2} + d$$

The rate law was derived by incorporation of a function $A(t)$, which described the decrease of the cross-section area of the amorphous phase available for oxygen diffusion. Further work should be still required to testify the validity of this model.

On the other hand, there are other rate formulae such as those of Carter formula,[16] Deal and Grove method,[17] which might treated solid–gas reaction more rigorously. However, this kind of treatments was unable to lead to an explicit analytic expression, and so they will be not easy for use as well as performing an intuitionistic quantitative discussion.

From the point of view of practical application it is desired to have a simpler and physical meaningful explicit analytic expression, which is not only convenient for use but also can still give a good prediction under an acceptable simplified assumption. The purpose of this paper was stressed on obtaining a simple formula to express the relation between the reacted fraction of oxidation and other related physical properties under a reasonable simplified assumption and that might not sacrifice too much calculation accuracy. This model had been successfully used in the systems of AlON and Si_3N_4.[18,19]

2. Experiment aspect

β-SiAlON (z = 3.0) powder used in the work was synthesized by reaction sintering at 1500 °C in flowing N_2 atmosphere for 5 h using fine Al_2O_3 (commercially pure), silicon (98 pct) and aluminum (98 pct) powders as raw materials. X-ray powder diffraction (XRD) analysis showed that monophase with z = 3.0 was predominated and a small amount of Al_2O_3 impurity also existed as shown in Fig. 1(a). The microstructure of β-SiAlON powder was presented in Fig. 1(b). The particle size distribution of the β-SiAlON powder determined by laser interferometer (MASTERSIZER 2000) was: 90% <11.6 μm, 50% <3.5 μm and 10% <0.99 μm.

The oxidation behavior of β-SiAlON (z = 3.0) powder was studied at a non-isothermal condition. It was carried out on a Nezsch STA409C (German) system. A schematic diagram of the apparatus is shown in Fig. 2. The balance of the unit had a detection limit of 1 μg. The system was fully controlled by IBM386PC (a trademark of International Business Machines Corp., Armonk, NY) through a TA controller 414/2.

In case of the non-isothermal oxidation of β-SiAlON, some experiments considering the effect of the heating rate as well as the particle sizes on the reaction were conducted. The experimental procedure was as follows. The samples (about 40.500 mg) were held in an alumina crucible that was placed in the heating furnace. Air was introduced into the reaction tube with fixed flow of 60 ml/min. The furnace was then heated from room temperature to the maximum temperature of 1450 °C with fixed heating rate. Blank trial runs with these heating rates were also performed and were used to correct the experimental data by subtracting a base line program in the instrument. At the end of the experiment, the reaction was arrested by replacing the air flow by argon, and the furnace was allowed to cool naturally.

Fig. 3 shows the experimental data of the thermogravimetric studies at heating rates with 5 and 15 K/min. The experimental results revealed that the oxidation started at around 927 °C and the rate increased rapidly after 1027 °C. The oxidation rate of the sample with the heating rate of 5 K/min was evidently faster than that of 15 K/min.

3. Model

3.1. Assumption and derivation for oxidation of powder

As reported in the literature, the oxidation of SiAlON material is a heterogeneous process. Its mechanism can be simply sum-

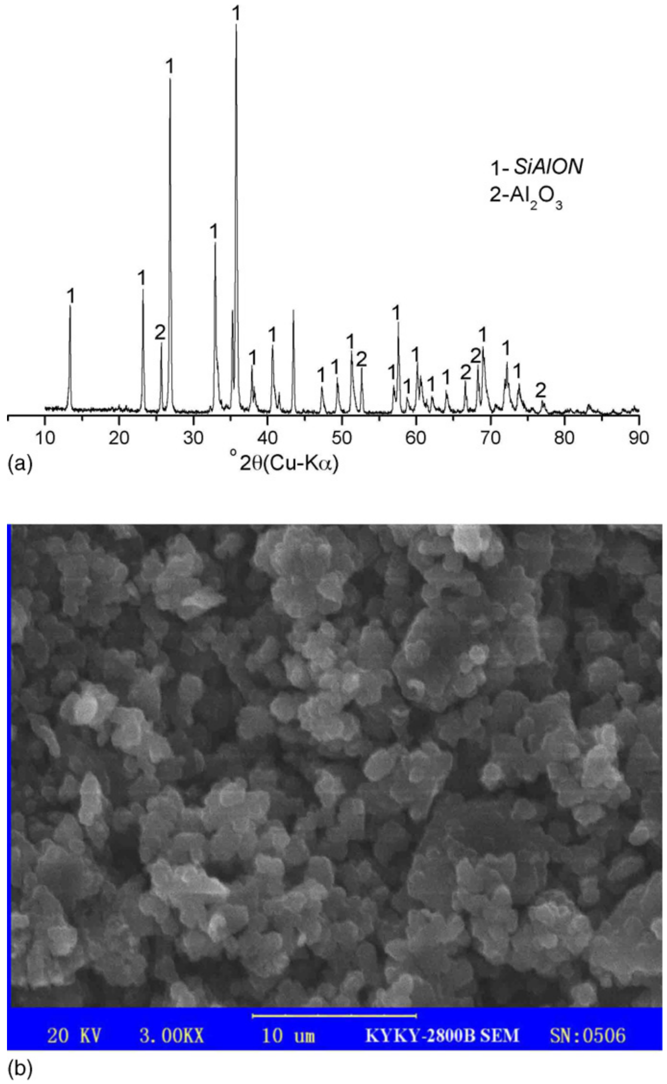

Fig. 1. (a) XRD pattern of β-SiAlON powder ($z = 3.0$); (b) SEM of β-SiAlON powder ($z = 3.0$).

marized as following steps: (1) oxygen transfer from the bulk of gas flow to the sample surface; (2) oxygen transfers from the surface to the interface by diffusion through the boundary layer between gas phase and solid phase; (3) After oxygen physisorption, chemisorption and surface penetration as well as oxygen diffusion through the oxide product layer, oxygen reacts with SiAlON to produce SiO_2, Al_2O_3 or mullite and N_2; (4) nitrogen transfers from interface to the sample surface; (5) nitrogen transfers from surface of SiAlON to the gas flow. In the most cases, the oxygen diffusion through the oxide layer will be the rate-controlling step. Therefore it is meaningful to study the oxygen diffusion as a controlling step.

For convenience, SiAlON powder was regarded as spherical balls with the same density and radius as shown in Fig. 4 where α represented SiAlON with radius of r, β was oxide layer with thickness of x. The whole particle was a ball of radius R_0.

Based on this idea, the oxidation formula of SiAlON powder for describing the reacted fraction ξ of oxidation with time t is

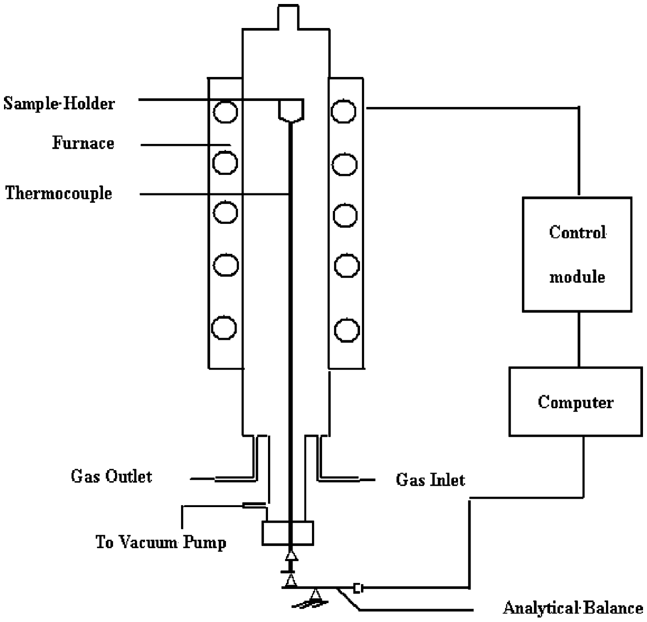

Fig. 2. Schematic diagram of the experiment assembly.

as follows[18]:

$$\xi = 1 - \left(1 - \sqrt{\frac{\exp(-\Delta E/RT)t}{B_T}}\right)^3 \tag{1}$$

where

$$B_T = \frac{1}{(2K_0^{\text{o}\beta} D_0^{\text{o}}/\upsilon_m)\left(\left(\sqrt{P_{\text{O}_2}} - \sqrt{P_{\text{O}_2}^{\text{eq}}}\right)/R_0^2\right)} \tag{2}$$

where ΔE represents the apparent activation energy, B_T a function of P_{O_2}, $P_{\text{O}_2}^{\text{eq}}$ and R_0, in which $P_{\text{O}_2}^{\text{eq}}$ is the oxygen partial pressure in equilibrium with oxide and should be related to temperature T. $K_0^{o\beta}$ and $D_0^{o\beta}$ are constant independent of temperature but relying on the material, υ_m a coefficient that depends on substance and reaction, and R_0 is the radius of the particle. If the

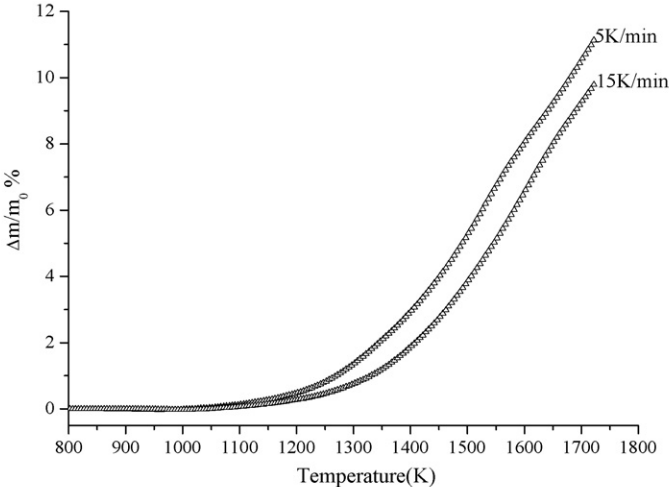

Fig. 3. The experiment data for non-isothermal oxidation behavior of β-SiAlON ($z = 3.0$) powder.

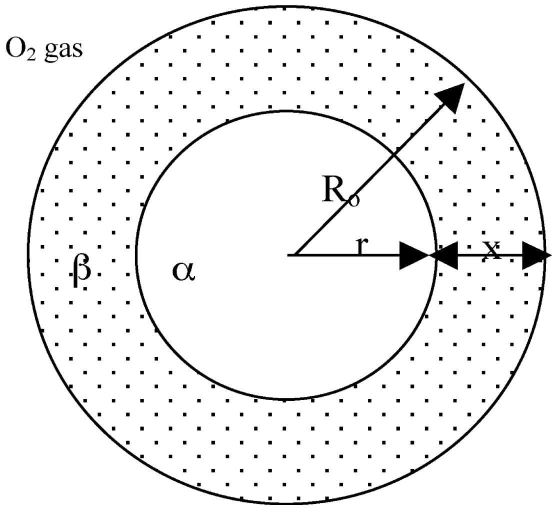

Fig. 4. Schematic diagram of oxidation of SiAlON particle.

value of $P_{O_2}^{eq}$ is very small or the temperature coefficient of $P_{O_2}^{eq}$ can be neglected, thus B_T would be constant if the particle radius and temperature are fixed.

Eq. (1) describes the relationship of reaction fraction with time at the constant temperature. When the temperature of furnace is heated up, the sample is in a condition with a certain temperature-increasing rate "η" where $\eta = \mathrm{d}T/\mathrm{d}t$. If the system is heated from room temperature T_0, thus the relation of temperature with time t should be

$$T = T_0 + \eta t \tag{3}$$

Therefore, the formula that describes the relation between reacted fraction of oxidation and temperature should be as follows:

$$\xi = 1 - \left(1 - \sqrt{\frac{1}{B_T} \exp\left(-\frac{\Delta E}{RT}\right) \frac{T - T_0}{\eta}}\right)^3 \tag{4}$$

Eqs. (1) and (4) are the general formulae expressing the reacted fraction ξ as the function of time t, temperature T and many other related parameters. These equations are explicit functions and are easy to use. The advantage of this kind of approximate treatment is that, one might find an explicit analytic solution just as we do here.

3.2. Assumption and derivation for oxidation of pellet

SiAlON materials have been paid much attention because of their practical applications as engineering ceramics, cutting tools and refractory materials. In practice, SiAlON materials were often manufactured in a certain shape of parts for application. In this section, a series of equations for fulfilling the pellet oxidation were derived.

Fig. 5 is a schematic plot for describing a pellet oxidation, in which α represents SiAlON with original thickness of L_0, β is oxide layer with thickness of x. As reported in the literature,[4–6,13,14] the stage of diffusion-controlled took most of time in the whole oxidation process.

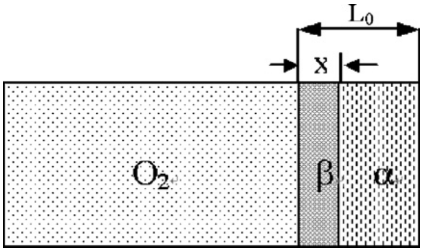

Fig. 5. Schematic plot of oxidation of a pellet under oxygen environment.

Based on this situation the oxidation formula of a SiAlON pellet could be deduced as follows and the deduced process in detail can also be referred to Ref. 18:

$$\xi = \sqrt{\frac{1}{\Theta_T} \exp\left(-\frac{\Delta E}{RT}\right) t} \tag{5}$$

where

$$\Theta_T = \frac{1}{(2K_0^{o\beta} D_0^{o}/v_m)\left(\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)/L_0^2\right)} \tag{6}$$

where ΔE represents the apparent activation energy, Θ_T a function of P_{O_2}, $P_{O_2}^{eq}$ and L_0, in which $P_{O_2}^{eq}$ is the oxygen partial pressure in equilibrium with oxide and should be related to temperature T, $K_0^{o\beta}$, $D_0^{o\beta}$ and v_m have the same meaning as in Eq. (2), and L_0 is the thickness of the pellet. If the value of $P_{O_2}^{eq}$ is very small or the temperature coefficient of $P_{O_2}^{eq}$ can be neglected, thus Θ_T would be a constant depending on the oxygen partial pressure and the thickness L_0 only.

Eq. (5) is the general formula expressing the reacted fraction ξ as the function of time t and many other related parameters at constant temperature. Similarly, the oxidation kinetics of pellet at variable temperature with a certain temperature-increasing rate "η" is as follows:

$$\xi = \sqrt{\frac{1}{\Theta_T} \exp\left(-\frac{\Delta E}{RT}\right) \frac{(T - T_0)}{\eta}} \tag{7}$$

These equations describe the calculation formulae of oxidation for both powder materials and pellet. These equations are an explicit function and are easy to be used. The advantage of this kind of approximate treatment is that, one might find an explicit analytic solution just as mentioned above. How accuracy of this kind of treatment can be judged from the application of this model in the practical examples that will be given in the latter sections.

4. Application of new model to practical systems

In this section, the model was first applied to the experimental data of β-SiAlON powder that we did recently and then to the oxidation kinetics of other SiAlON materials, namely O′-SiAlON powder and β-SiAlON-Al_2O_3 composite offered by literatures to compare the validity.

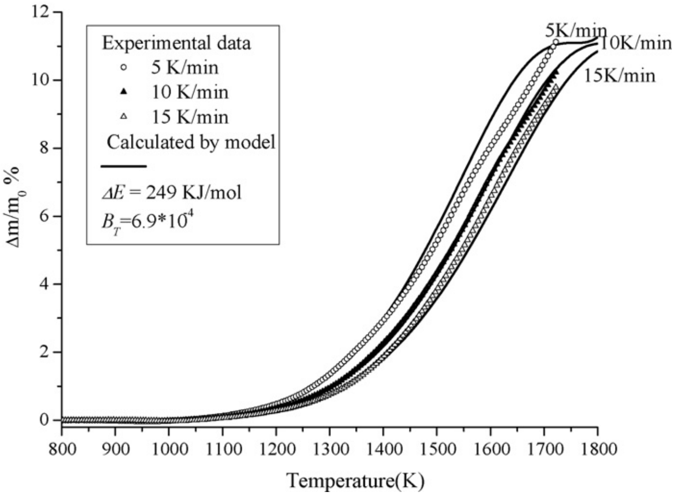

Fig. 6. A comparison of experimental data with model for oxidation of β-SiAlON (z = 3.0) powder with the corresponding temperature-increasing rate of 5 and 15 K/min.

4.1. Application of new model to oxidation of β-SiAlON (z = 3.0) powder

Fig. 2 shows the experimental data of the thermogravimetric studies at heating rates with 5 and 15 K/min. In order to compare the results of experimental data with theoretical calculation, the oxidation behavior at the heating rate of 5 and 15 K/min were also calculated by using the new model respectively that have been plotted in Fig. 6, from which it can be seen that the values predicted by this model were in good agreement with the experimental data. The activation energy calculated from Eq. (4) was 249 kJ/mol. Please note that, the curves corresponding to the heating rate of 10 K/min in Fig. 6 was completely obtained from theoretical prediction without using any experimental data. The coincidence of the theoretical calculation results with the experimental data indicates that this theory is reasonable.

4.2. Application of new model to oxidation of O′-SiAlON (x = 0.18) powder provided in literature

MacKenzie et al.[14] studied the oxidation behavior of O′-SiAlON powder (x = 0.18) that was prepared by silicothermal reaction of kaolinite (BDH "light"), silicon powder (Permascand 4D) and powder SiO_2 (Commercial Minerals superfine quartz). The particle size distribution of the O′-SiAlON determined by laser interferometer (Shimadzu Sald-2001) was: 100% <30 μm, 50% <3 μm and 10% <0.7 μm. The oxidation behavior was measured through isothermal thermogravimetry at 1000–1400 °C using a Cahn Model 2000 thermobalance and a Rheometrics STA 1500 thermoanalyser in flowing air at 50 ml/min. The oxidation data at 1333 °C were shown in Fig. 7. At present, our model, i.e., Eq. (1) was used to calculate the oxidation behavior and the obtained result was also listed in Fig. 7. It can be seen from these figures that the calculated results agreed well with the literature data.

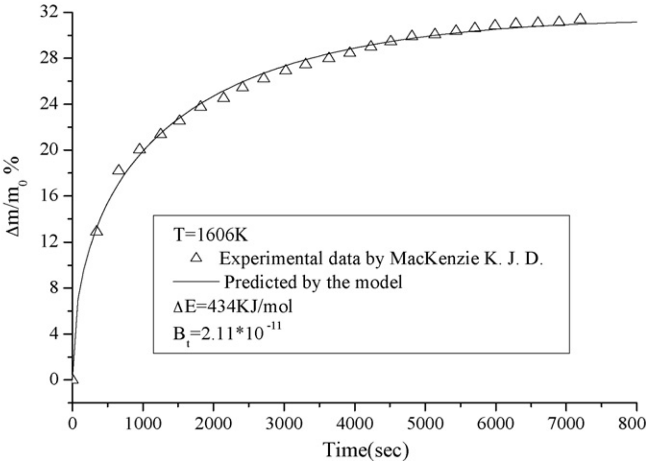

Fig. 7. A comparison of experimental data with model for oxidation of O′-SiAlON powder at 1333 °C.

4.3. Application of new model to oxidation of β-SiAlON-Al_2O_3 pellet provided in literature

Li et al.[20] have studied the oxidation behavior of β-SiAlON-Al_2O_3 pellet (ρ = 3670 kg/m^3) under non-isothermal condition from room temperature to 1427 °C with the heating rate of 15 K/min. The experiment results were listed in Fig. 8, from which it can be seen that the oxidation began at about 927 °C and increased apparently after 1277 °C.

At present, Eq. (7) has been used to fit the oxidation data of β-SiAlON-Al_2O_3 pellet. After substituting all related parameters into Eq. (7), we have

$$\frac{\Delta m}{A} = \sqrt{\frac{1}{1.6 \times 10^{-3}} \exp\left(-\frac{263000}{RT}\right) \frac{T - T_0}{(15/60)}} \tag{8}$$

where A represents the surface area of particle. The curve depicted by this formula was in accordance with experimental points very well as shown in the same figure.

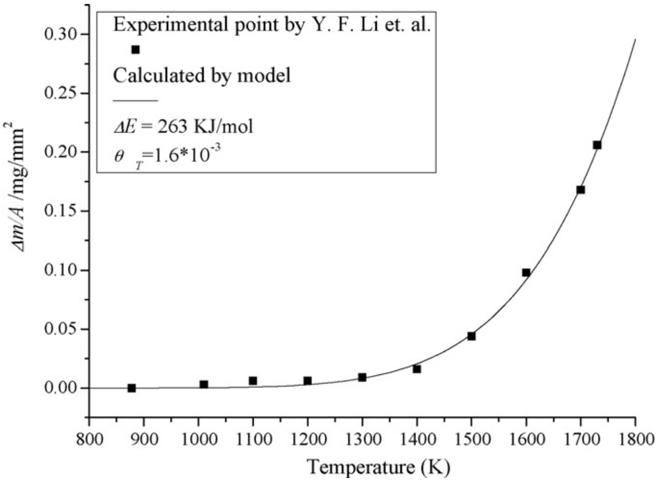

Fig. 8. A comparison of experimental data with model for oxidation of β-SiAlON-Al_2O_3 composite with the corresponding temperature-increasing rate of 15 K/min.

In sum, based on above examples, it may be seen that, the theoretical model presented in this paper can give a very good prediction no matter whether it was powder materials or pellet and no matter what kind of experimental condition was set, constant temperature or non-isotherm. More examples will be checked in future for a series of other formulae developed here based on other experiments.

5. Discussion

(1) As mentioned above, the oxidation reaction for SiAlON materials is a kind of complicated heterogeneous reaction; in principle, the mathematic treatment should be very complicated corresponding to solve a group of differential equations and it is difficult to obtain a simple solution that will prevent us from theoretical description of oxidation of SiAlON materials. The purpose of this paper was stressed on obtaining a simple formula to express the relation between the reacted fraction of oxidation of SiAlON and other related physical properties under a reasonable simplified assumption and that might not sacrifice too much calculation accuracy. As a result, they should be easy for use without using any complex numerical calculation; moreover, they can be used as theoretical analysis. The examples showed that our treatment was feasible. In this paper, the new model offers an explicit analytic expression of the oxidation fraction with time and temperature. It also describes the effect of particle size, pellet thickness and oxygen pressure, etc., on the oxidation kinetics quantitatively. The result will be reported in the future.

(2) Besides giving a simple formula to express the relation between the reacted fraction of oxidation and other related physical properties, the new model can predict the oxidation behavior using limited experimental data within the same oxidation mechanism. By comparison, the model reported in literature with the parabolic rate law was unable to express the reacted fraction as a function of temperature, oxygen partial pressure, particle size explicitly.

(3) In the derivation of our formulae, the variable used was the "reacted fraction" or "transferred fraction", ξ, however, many researchers prefer to use variable "increment of reaction", Δm, instead of ξ. In this case a transformation of variable had to be required prior for using our formulae.

(4) This new model actually is not limited in the application for treating the oxidation of SiAlON materials, they can also be used in dealing with problems of other material fields. Fig. 9 shows an example of using Eq. (3) to deal with the oxidation behavior of Si_3N_4 powder at different temperature. An excellent accordance between experiment data[19] and theoretical prediction demonstrated that the formulae derived here can also be used in the other field of materials science as long as they have a similar mechanism.

(5) In the above derivation of formulae, the premise of deduction was assuming that the diffusion of oxygen in oxide was the controlling step. The successful application to these examples demonstrates that this assumption was acceptable for many cases of oxidation of SiAlON materials. However, when the step of oxygen diffusion in oxide was not a dominant controlling step, the new model built in this paper does not agree with the experimental data well. Another treatment will be given in other future paper.

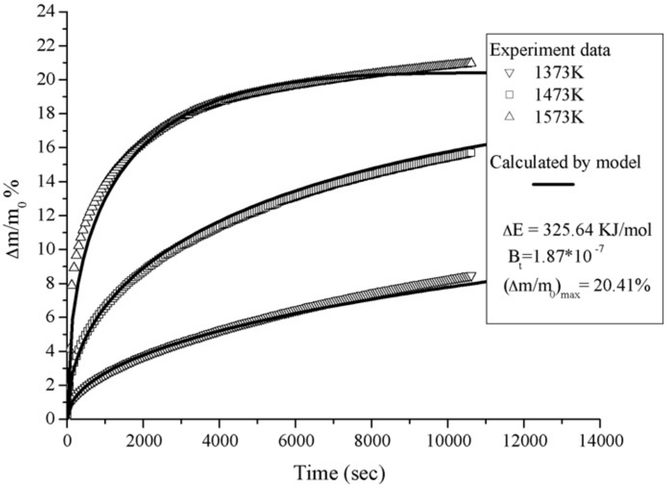

Fig. 9. A comparison of experimental data with model for oxidation of Si_3N_4 at temperature 1100, 1200 and 1300 °C, respectively.

6. Conclusion

(1) A new experiment was performed concerning the oxidation of β-SiAlON powder both in isothermal and non-isothermal, based on which, a new kinetics model was applied to calculate the oxidation behavior of SiAlON materials. The calculated results showed that both the theoretical calculation and the experimental data can reach a good agreement. The advantage of the new method was that it was easy to calculate and easy to perform a theoretical analysis and discussion due to its explicit expression.

(2) This method was then also applied to the system of β-SiAlON ($z = 3.0$) powder, O′-SiAlON ($x = 0.18$) powder and β-SiAlON-Al_2O_3 pellet offered from literatures. Calculated results agreed well with experimental data for these systems either.

(3) The paper gave a simple formula to express the relation between the reacted fraction of oxidation and other related physical properties explicitly and quantitatively. For example the effect of particle size, oxygen partial pressure and the thickness of pellet on the oxidation kinetics. Moreover, since most of oxidation processes of inorganic non-metallic materials had very similar mechanism with SiAlON oxidation, it might be expected that this new model would be suitable for the oxidation process of many other inorganic non-metallic systems. More results will be reported in near future.

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