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# A new measurement and treatment for kinetics of isothermal oxidation of Si<sub>3</sub>N<sub>4</sub>

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#### Abstract

The kinetics of the oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder has been investigated in the temperature range from 1373 to 1573 K experimentally in the air by using thermogravimetry. The results show that the major oxidation product was crystalline SiO<sub>2</sub> and the oxidation reaction was mainly diffusion-controlled. Based on the experiment data, the new model for predicting the isothermal oxidation process of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder has been used, which offers an analytic form expressing the oxidation weight gain as a function of time and temperature explicitly. The comparison between experiment data and theoretical calculation shows that this new model works very well. Based on our model the activation energy for the oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> has been calculated to be 325.6 kJ/mol.

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Keywords: Oxidation; Isothermal kinetics; Nitride materials; Ceramics

#### 1. Introduction

Silicon nitride  $(Si_3N_4)$ -based ceramics has been studied extensively because of their excellent properties at both room temperature and high temperatures. In recent years,  $Si_3N_4$ ceramics has been used in the structural members of gas turbine, engines and other parts subjected to high-temperature conditions [1-4]. However, most actual applications for  $Si_3N_4$  materials required exposure to high temperatures, generally under oxidizing conditions.  $Si_3N_4$  is thermodynamically unstable with respect to oxidation under normal oxygen pressures. It is well known that the oxidation of  $Si_3N_4$  material can be divided into two categories: active oxidation and passive oxidation [5]. The active oxidation of  $Si_3N_4$  is characterized by the loss in mass according to

$$Si_3N_4(s) + 1.5O_2(g) = 3SiO(g) + 2N_2(g)$$
 (1)

Eq. (1) occurred under low oxygen pressures ( $10^3$  Pa at 1273 K). In most cases, the oxidation of Si<sub>3</sub>N<sub>4</sub> is in a net mass increasing by conversion of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub>, which leads to Si<sub>3</sub>N<sub>4</sub> in passive

0925-8388/\$ – see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.04.255 oxidation, where

 $Si_3N_4(s) + 3O_2(g) = 3SiO_2(s) + 2N_2(g)$  (2)

Eq. (2) occurred at most cases and passive oxidation has been extensively studied in literatures [6–14]. However, there are wide variation in the observed reaction rates and the morphology of the reaction products. Du et al. [7,8], Ogbuji and Bryan [9] and Ogbuji [10] have studied the oxidation behavior of Si<sub>3</sub>N<sub>4</sub> synthesized by chemical vapor deposition (CVD) at the temperature range from 1523 to 1673 K and found that the surface of Si<sub>3</sub>N<sub>4</sub> produced a protective oxide layer. They further verified that the oxidation process followed the parabolic rate law and the oxidation kinetic was controlled by the diffusion of oxygen. Weaver and Lucek [11] and Cubicciotti and Lau [12] studied the oxidation of Si<sub>3</sub>N<sub>4</sub> ceramic with additives, e.g. Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, etc., and found that the oxidation also followed the parabolic rate law but they reported that the oxide layer formed could not prevent Si<sub>3</sub>N<sub>4</sub> from being oxidized efficiently, implying that the rate-controlling step was not the outward diffusion of oxygen through the silicate film, but the outward diffusion of cations in the intergranular glass. Ogbuji and Bryan [9] and Ogbuji [10] also compared the oxidation rate of  $Si_3N_4$  (CVD) with SiC (CVD) in the temperature range from 1473 to 1773 K

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	Nomenclature		
	$D_{\Omega}^{\beta}$	diffusion coefficient of oxygen in $\beta$ phase	
	ĸ	equilibrium constant	
	т	sample weight	
	$\Delta m$	the increment of sample weight	
	$\Delta m_{\rm max}$	theoretical maximum increment after complete oxidation	
	$P_{O_2}$	partial pressure of oxygen in gas phase	
	$P_{\Omega_2}^{e\bar{q}}$	oxygen partial pressure in equilibrium with oxide	
	$r^{0}$	radius of particle with original Si <sub>3</sub> N <sub>4</sub> phase	
	R	gas constant	
	$R_0$	radius of the original whole particle	
	t	time in second	
	t <sub>c</sub>	characteristic oxidation time	
	Т	absolute temperature (K)	
	$v_{\rm m}$	coefficient depending on substance and reaction	
	x	the thick of oxide layer in the particle = $R_0 - r$	
Greek letters			
	α	original Si <sub>3</sub> N <sub>4</sub> phase	
	β	Si <sub>3</sub> N <sub>4</sub> phase (after oxidation)	
	$\Delta \varepsilon_{\mathrm{ap}}$	apparent activation energy of oxidation	
	ξ	reacted fraction of oxidation	

and found that  $Si_3N_4$  had more oxidation resistance than that of SiC. The activation energy of  $Si_3N_4$  was calculated to be 363 kJ/mol.

Up to now though most of studies are concentrated on the experimental aspects, it is still not enough. One needs more accurate experimental data, more rigorous experimental control and more experimental results under different kinds of conditions so as to establish a theoretical system for oxidation of Si<sub>3</sub>N<sub>4</sub>. On the other hand, comparing with the experiment work, the theoretical studies on this topic are still not satisfactory. It is because, in general, the oxidation of ceramics is a kind of heterogeneous reaction at an elevated temperature; one has to solve a group of differential equations to find a solution for the rate expression of oxidation of Si<sub>3</sub>N<sub>4</sub> ceramics. It is not easy and in the most of situations, what one can get is a numerical solution instead of an analytic solution. It is revealed that the overall reaction of oxidation is composed of several steps, involving oxygen dissociation and chemisorptions on the surface, surface penetration by oxygen atoms, oxygen diffusion in the oxide layer and motion of the oxide/Si<sub>3</sub>N<sub>4</sub> interface. If one of these steps is very slow, that one could become the rate-controlling step and the kinetics of the overall process can be described by simple rate expressions. The oxidation kinetics is greatly influenced by such factors as temperature, oxygen partial pressure, etc. As a result, various expressing equations were obtained and different interpretations were given in literatures [5,6].

However, there are still a couple of key problems that have not been theoretically solved yet, such as, what is the relationship of the reacted fraction of oxidation  $\xi$  with time *t*; how does the particle size affect the curve of reacted fraction  $\xi$  versus temperature *T*. All these questions have never been answered in the literatures before.

Recently we have developed some models for describing the oxidation rate of Si–Al–O–N materials, it is a general form that can be used for a series of solid–gas reaction system [14,15]. These formulae are analytic form expressing the reacted fraction as an explicit function of time, temperature, etc. It is expected that the application of this new model to the oxidation of  $Si_3N_4$  will lead us to get some important message to direct us how to compare and improve the utilization of  $Si_3N_4$  materials.

To our best knowledge, there are few reports available on  $Si_3N_4$  oxidation in theoretical analysis. At present, first of all, we like to investigate the oxidation of  $Si_3N_4$  experimentally that should be the base for this study.

#### 2. Experimental

There are several methods to produce Si<sub>3</sub>N<sub>4</sub> powder in literature [5,6], including direct nitridation of silicon powder, carbonthermic synthesis of silicon dioxide, silicon imide synthesis and decomposition as well as combustion synthesis (CS). Among the several methods, combustion synthesis possesses outstanding advantages such as low energy consumption, simplicity of equipment, high efficiency and purity of products. This method has been applied successfully by Ge et al. at the laboratory of USTB [16].  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder used in the work was synthesized by SHS method using Si powders ( $D_{50} = 17.2 \,\mu$ m), meanwhile, Si<sub>3</sub>N<sub>4</sub> ( $D_{50} = 2.2 \,\mu$ m) powder as an inert diluents reactant is also added for decreasing the reaction rate. The  $\alpha$ -phase content of the inert diluents Si<sub>3</sub>N<sub>4</sub> is more than 93%. The X-ray powder diffraction (XRD) analysis showed that the  $\alpha$  phase is predominated. The particle size distribution determined by laser interferometer (SEISHIN LMS-30) was: 90% < 6.465  $\mu$ m, 50% < 2.135  $\mu$ m and 10% < 0.819  $\mu$ m.

The oxidation behavior of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder was studied under isothermal conditions for 3 h at different temperatures ranging from 1373 to 1573 K with an interval of 100 K. It was carried out on a Nezsch STA409C (German) system. A schematic diagram of the apparatus is shown in Fig. 1. The balance of the unit had a detection limit of 1 µg. The system was fully controlled by an IBM 386PC (a trademark of International Business Machines Corp., Armonk, NY) through a TA controller 414/2. Since the experimental point with a small interval of time,



Fig. 1. A schematic diagram of the experiment assembly.

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Fig. 2. Procedure of cutting thin films from fine particles.

i.e. 1 point/min can be acquired by the equipment, the oxidation curves obtained will be smoother, which is in favor of the quantitative study of the oxidation kinetics.

The following procedure was adopted in the case of isothermal experiments. The sample about 16.600 mg was weighted carefully and held in an alumina crucible. The reaction tube was initially evacuated for 5 min and then flushed with purified argon gas (<5 ppm O<sub>2</sub>). The furnace was then heated to the oxidation temperature as quickly as possible in the flowing argon atmosphere. After the thermal equilibrium was established, the atmosphere was changed to air atmosphere (21 pct O<sub>2</sub>) with the flow-rate of 50 ml/min. The oxidation mass change was then monitored continuously for 3 h with 1 point/min. 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 run, the reaction was arrested by replacing the air flow by argon, and the furnace was allowed to cool naturally.

The crystalline phases formed after oxidation were identified by XRD analysis over the  $2\theta$  range from  $10^{\circ}$  to  $90^{\circ}$  using a Rigaku D/max-A diffractometer with Cu K $\alpha$  radiation.

#### 3. Results and discussion

#### 3.1. Oxidation products and kinetics

To understand the oxidation process of  $Si_3N_4$ , optical microscopy and XRD analysis were applied to the samples before and after oxidation. The specimens for optical microscopy were prepared by following method [17]. First, place a monolayer of fine particles on a polished metal strip (Fig. 2A). Then encapsulate the fine particles on the metal strip by ion deposition technique (Fig. 2B). Polish the surfaces of the encapsulated particle until the fine particles are sufficiently exposed for observation under optical microscopy (Fig. 2C). The cross-section of the particle after oxidation can be observed and some results are shown in Fig. 3. Fig. 3a is an optical photomicrograph of the cross-section of  $Si_3N_4$  fine particle, in which the grey area stands the metal strip and the darker points  $Si_3N_4$  particle. It may

oxidation as shown in Fig. 3a. The XRD result corresponding to this temperature range showed that  $Si_3N_4$  was the major components and the only detectable crystalline oxide phase was  $SiO_2$ , the intensity of which gradually increased with increasing oxidation temperature. Fig. 3d shows the oxidation condition at 1573 K. An obvious porous layer formed around  $Si_3N_4$  powder, which was probably caused by N<sub>2</sub> resulting from a rise in the partial pressure of nitrogen at the interface [18]. The components corresponding to this temperature showed that more amount of crystalline  $SiO_2$  was found. Therefore, the oxidation reactions of  $Si_3N_4$  powder in the experiment were passive behavior and could be described by Eq. (2).

From the oxidation curves of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders at 1373–1573 K for up to 3 h (as shown in Fig. 6), it showed that oxidation behavior followed a parabolic rate law, indicating that the step of diffusion of oxygen through the oxide product layer to the oxide/Si<sub>3</sub>N<sub>4</sub> interface is the rate-controlling step, which is in coincident with the results in literatures [7–13].

## 3.2. Kinetic model

In our experiment, the stage of diffusion may take a large portion of time in the whole process, which is similar to the kinetics of absorption and desorption of hydrogen in alloy powder [14]. Therefore, it is meaningful to study the oxygen diffusion as a controlling step. For convenience, the powder of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> was regarded as spherical balls with the same density and radius. Based on this assumption, the oxidation process can be described by the following schematic diagram (Fig. 4), where  $\alpha$  represents Si<sub>3</sub>N<sub>4</sub> with radius of *r*,  $\beta$  is oxide layer with thickness of *x*.

It can be seen from Fig. 4 that, first, oxygen diffuses in the gaseous phase, after reach the surface of particle, oxygen will be absorbed and then penetrates into oxide, i.e.  $\beta$  phase. After that oxygen will diffuse in the  $\beta$  phase. When oxygen reaches the interface between  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>  $\alpha$  and oxide  $\beta$ , a fast reaction occurs and the remaining steps are fast too.

$$O(in\beta phase) + \alpha = \beta(oxide)$$
(3)

Since both the mechanisms of the oxidation of  $Si_3N_4$  and the absorption and desorption of hydrogen in alloy powder are similar [14], the model for predicting the kinetics of absorption and desorption of hydrogen in alloy powder is expected to be suitable to the oxidation of  $Si_3N_4$ . Based on this idea we have developed a new model for describing the reacted fraction of oxidation of  $Si_3N_4$  ceramics  $\xi$  with time *t* as follows [15]:

$$\xi = 1 - \left(1 - \sqrt{\left(\frac{2K_{O}^{0\beta}D_{O}^{0}\left(\sqrt{P_{O_{2}}} - \sqrt{P_{O_{2}}^{eq}}\right)}{v_{m}}\exp\left(-\frac{\Delta\varepsilon_{ap}}{RT}\right)\right)}t\right)^{3}$$
(4)

be seen from Fig. 3a that the  $Si_3N_4$  particle consisted of many pores. Fig. 3b and c is at lower oxidation temperature, i.e. 1373 and 1473 K. The cross-section of  $Si_3N_4$  powder for Fig. 3b and c did not change much compared with that of the sample before where  $D_{\rm O}^0$  represents a constant related with diffusion of oxygen in the oxide but independent of temperature,  $K_{\rm O}^{0\beta}$  the constant independent of temperature,  $P_{\rm O_2}$  the oxygen partial pressure in gas phase and  $P_{\rm O_2}^{\rm eq}$  is the oxygen partial pressure in equilibrium with oxide in  $\alpha/\beta$  interface, i.e. oxide/Si<sub>3</sub>N<sub>4</sub> interface, that



Fig. 3. Optical microscopy images and XRD patterns of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder after oxidation at different temperatures.



Fig. 4. A schematic diagram of oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> particle.

will keep constant as temperature fixed.  $v_{\rm m}$  is a coefficient that depends on substance and reaction.  $\Delta \varepsilon_{\rm ap}$  represents the apparent activation energy. *R* and *T* are gas constant and temperature with Kelvin, respectively.

To simplify Eq. (4), a new concept of the "characteristic oxidation time" is introduced. It is expressed by the following equation:

$$t_{\rm c} = \frac{1}{(2K_{\rm O}^{0\beta}D_{\rm O}^{0\beta}/v_{\rm m})\left(\left(\sqrt{P_{\rm O_2}} - \sqrt{P_{\rm O_2}^{\rm eq}}\right)/R_0^2\right)\exp(-\Delta\varepsilon_{\rm ap}/RT)}$$
(5)

Substituting Eq. (5) into Eq. (4) yields

$$\xi = 1 - \left(1 - \sqrt{\frac{t}{t_{\rm c}}}\right)^3 \tag{6}$$

When  $t = t_c$ ,  $\xi = 1$ , therefore, the physical meaning of the "characteristic oxidation time" is that, it is the required time that the whole particle is completely oxidized. The smaller the  $t_c$ , the faster the oxidation reaction. From Eq. (5), it can be seen that the characteristic oxidation time should be a function of temperature *T*, oxygen partial pressure  $P_{O_2}$  and particle radius  $R_0$ .

When all parameters except for temperature are fixed, Eq. (4) can be simplified as the following form:

$$\xi = 1 - \left(1 - \sqrt{\frac{\exp(-\Delta\varepsilon_{\rm ap}/RT)t}{B_{\rm T}}}\right)^3 \tag{7}$$

where

$$B_{\rm T} = \frac{1}{(2K_{\rm O}^{0\beta}D_{\rm O}^{0}/v_{\rm m})\left(\left(\sqrt{P_{\rm O_{2}}} - \sqrt{P_{\rm O_{2}}^{\rm eq}}/R_{\rm O}^{2}\right)\right)} \tag{8}$$

B<sub>T</sub> is a function of  $P_{O_2}$ ,  $P_{O_2}^{eq}$  and  $R_0$ , in which  $P_{O_2}^{eq}$  is the oxygen partial pressure in equilibrium with oxide and should be related to temperature *T*. If the value of  $P_{O_2}^{eq}$  is very small or the temperature coefficient of  $P_{O_2}^{eq}$  can be neglected, thus  $B_T$  will be constant as the oxygen partial pressure and the particle radius are fixed.

It may be seen from Eq. (7) that the higher the temperature, the larger the reacted fraction  $\xi$ . It is in accordance with our



Fig. 5. A comparison of experimental data with model for oxidation of  $Si_3N_4$  at temperature 1573 K.

common sense since the higher the temperature the faster the reaction. From Eq. (4) it may be seen that the smaller the particle size, the fast the reaction. Since the particle size is not equal to constant but a distribution, therefore, the final calculated result should be corresponding to an "effective radius".

Eqs. (4) and (7) are the general formulae expressing the reacted fraction  $\xi$  as time *t* and many other related parameters. These equations are an explicit function that is easy to use. The advantage of this kind of approximate treatment is that, one might find an explicit analytic solution just as we did here. As to the validity of this kind of treatment, it can be seen from the application of this model to the practical examples that will be given in the latter sections.

# 3.3. Application of new model to oxidation of $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder

At present, let us use our experimental data of oxidation of  $Si_3N_4$  to check the theoretical model. According to Eq. (6), there is only one parameter  $t_c$  that is required to be fit. Fig. 5 shows the kinetic curves of  $Si_3N_4$  oxidized at 1573 K. After the data fitting, the only one parameter  $t_c$  is evaluated to be 12,500 s, thus one has

$$\xi = 1 - \left(1 - \sqrt{\frac{t}{12,500}}\right)^3 \tag{9}$$

The physical meaning of above equation means that, when the reaction time reaches 12,500 s, the oxidation will be completed. One may use this quantity as an index to compare different kind of nitride materials. It is evident that the smaller the  $t_c$ , the faster the oxidation rate. Please note, the *y*-axis in our experimental plot, Fig. 5, is not the reacted fraction  $\xi$  but the  $\Delta m/m$  (*m* denotes the sample weight and  $\Delta m$  denotes the increment of sample weight after oxidation at time *t*). The relation between  $\xi$  and  $\Delta m/m$  is that

$$\xi = \frac{\Delta m}{\Delta m_{\rm max}} \tag{10}$$

where  $\Delta m_{\text{max}}$  is the theoretical maximum increment after a complete oxidation.

For comparison the theoretical predicted line is also listed in the same figure. It may be seen that, an excellent agreement has been reached between the experimental data and theoretical prediction.

The oxidation kinetics of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder at different temperature can be predicted according to Eq. (7), when  $B_T$  and the apparent activation energy  $\Delta \varepsilon_{ap}$  are known. Based on our experimental data, these two parameters are easy to be extracted. The results are that  $\Delta \varepsilon_{ap}$  and  $B_T$  are 325.6 kJ/mol and  $1.87 \times 10^{-7}$ , respectively. Compared with the activation energy obtained by Ogbuji and Bryan [9] and Ogbuji [10], both are closed, Substituting the above  $\Delta \varepsilon_{ap}$  and  $B_T$  data into Eq. (7), one has the following equation to predict the oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.

$$\frac{\Delta m}{m_0} = 20.4 \left[ 1 - \left( 1 - \sqrt{\frac{t}{1.87 \times 10^{-7}}} \exp\left(\frac{-326,000}{RT}\right) \right)^3 \right]$$
(11)

The corresponding plots are shown in Fig. 6, where solid lines represent the theoretical calculation results. Comparing to the experimental data with calculated lines, it may be seen that both reach a good agreement. The relative coefficient for this curve fitting has reached 0.99. The fact that the theoretical calculation results are coincident with the experimental data indicates that this theory is reasonable and the rate-controlling step should be located in the oxygen diffusion range within the oxide layer.

One may doubt accuracy of the predicting curve of 1573 K since it looks that there is a little bit deviation between experiments and theoretical calculation near 3 h. That should be fine because the maximum weight increasing,  $\Delta m_{\text{max}}/m_0$ , is 0.2119 that is already very close to the experimental data at 3 h point (( $\Delta m_{\text{max}}/m_0$ ) = 0.204). There is also no so many room for change of  $\Delta m/m_0$ . Therefore, it is expected that, the curve of experiment and that of theoretical calculation should be closer and closer after 3 h.



Fig. 6. A comparison of experimental data with model for oxidation of  $Si_3N_4$  at temperature 1373, 1473 and 1573 K, respectively.



Fig. 7. The isothermal oxidation of  $Si_3N_4$  predicted by model at various temperatures.

Based on the parameters obtained from above curve fitting, a cluster of kinetics curves of oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder at temperature range from 1380 to 1560 K with an interval of 30 K have now been plotted in Fig. 7. They are all predicted without involving in any experimental data except for line at 1530 K that was listed for comparison. The coincidence of the theoretical calculation results with the experimental data indicates that this theory is reasonable.

# 4. Conclusion

- (1) An elaborate experiment has been performed for the oxidation of  $Si_3N_4$  in our new thermogravimetry equipment. The results obtained seem smoothly with a small interval of time collected by computer automatically.
- (2) The application of our new model to  $Si_3N_4$  systems shows that, a good agreement has been reached between experimental data and theoretical model. That means, assuming the diffusion as the controlling step is correct.
- (3) A simple and practical formula has been proposed to describe the oxidation of  $Si_3N_4$ . It is an explicit analytic function, therefore, that will be easy to use and has a clear physical meaning in the theoretical discussion. After using our new model to the  $Si_3N_4$  system, the apparent activation energy has been extracted to be 325.6 kJ/mol.
- (4) The "characteristic oxidation time" of materials is a new concept describing the kinetic property of oxidation of  $Si_3N_4$ . It is anticipated that this quantity just like the half-life of isotopes can be used for measuring and comparing the kinetic property for many silicon nitride ceramic materials. In the present sample the "characteristic oxidation time" for  $Si_3N_4$  at 1573 K is to be 12,500 s.
- (5) Since most of oxidation processes of inorganic non-metallic oxide materials have very similar mechanism, it might be expected that this new model will 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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