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Oxidation kinetics of TiN-containing composites

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Abstract

The oxidation of TiN-containing composites has been discussed from theoretical aspect based on the experimental data available in the literature. Although the experimental results show that the oxidation behavior is a complicated process involving different phases and oxidation mechanisms, it is diffusion controlled essentially. Therefore Chou's model has been employed to deal with the oxidation of TiN-containing composites. To describe more closely the oxidation behavior of TiN-containing composites, the factor of the sample shape has been taken into consideration. A good agreement has been found between the experimental results and theoretical calculation. In addition, a comparison of calculation errors has been given between our new model and the traditional model used in the literature.

Keywords: Ceramic-matrix composites; Oxidation kinetics; Sample shape

1. Introduction

The key features of non-oxide ceramic composites are considerable hardness, good strength and resistance to corrosion and wear. Therefore, they should be an important trend of development for structural or functional ceramics. For example, the addition of an electrically conductive secondary phase such as TiN, TiB_2 and TiC etc. to Si_3N_4 ceramics has been recognized as a promising candidate for specific applications in the field of high temperature heaters, igniters and heat exchangers [1–4]. There is also report that addition of the proper content of TiN can delay the decomposition of the γ-aluminum oxynitride (AlON) which is thermodynamically unstable below 1923 K [5–6]. Therefore, γ-AlON–TiN can find application as wear-resistant material. Since these ceramic composites are designed to work at high temperature, they tend to oxidize and lead to strength reduction and component failure. Therefore it is disadvantageous to use them in certain long-term or reusable applications. Thus the investigation of oxidation of the ceramic composites has increasingly attracted researchers' interest.

Whereas the studies and characterization of oxidation of ceramic composites have a relatively short history and are still a challenge. Several reasons are attributed to it. First, usually the composites are investigated in certain shape to contain all the phases, which leads to a complex oxidation kinetics involving different phases and oxidation mechanisms. Second, the theoretical studies were very limited up to date. Some researcher adopted other theories such as Wagner theory [7] to treat the oxidation behavior. Although Wagner theory is one of the simplest theories that takes diffusion of charged particles into account, it is still difficult for practical application. The main reasons are following. First there are couples of parameters that are unknown, for instance, the transport number for species of cation, anion and electron. Secondly, the equation is only used for one dimension calculation, if the sample is a ball or some other shape, it would not work. As a result, a lot of practical calculations go to parabolic rate model. i.e. parabolic rate law [8] or modification of the parabolic rate law by adding a correction factor. As discussed in our previous papers [9–11], the models used in the literature are far more enough not only because their unclear physical meaning of parameter "*k*" appearing in the traditional formulae, but also the larger error introduced when dealing with the oxidation. Although we have suggested an analytical solution to treat the oxidation of non-oxide ceramic in

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our previous work, it is only limited to the sample of single phase or with the shape of thin pellet [9–12]. In the practice, more shapes are presented, which require us to give some new suitable equations. It is also desired to have some accurate formulae to describe the kinetic curves in comparison with current traditional formulae. In this context, the oxidation behavior of the non-oxide ceramic composites will be systematically discussed from theoretical aspect based on the results in the literature.

2. Theoretical treatment

Oxidation of non-oxide ceramic composites is a complex process and can be divided into more than one regime. But the whole oxidation process can be considered as a gas–solid reaction and the process consists of the following steps:

1. Oxygen transfer from the bulk of gas flow through gas–solid boundary layer to the sample surface,
2. Oxygen transfer from the surface to the interface by diffusion through the oxide product layer,
3. Oxygen reacts with one phase of the ceramic composite to produce oxide product and nitrogen,
4. Nitrogen transfer from interface to the sample surface,
5. Nitrogen transfer from surface of the sample through gas–solid boundary layer to the gas flow.

When the oxidation reaction completes in one regime, the above steps take place repeatedly in another regime. Usually the composites are investigated in certain shape to contain all the phases, which leads to a complex oxidation kinetics involving different phases and oxidation mechanisms.

Fig. 1 shows a cuboid in the right-angle coordinates X, Y, Z system. When this cuboid (with L_0 depth M_0 wide and H_0 high) is placed in the oxygen gas flow, the surface of this cuboid should have the same concentration of oxygen C_0. The oxygen in the surface will enter into the inner of cuboid through diffusion and react with substance materials generating oxide. According to the first Fick's law, the oxygen flux j flowing into the cuboid per unit area from the surface can be calculated as,

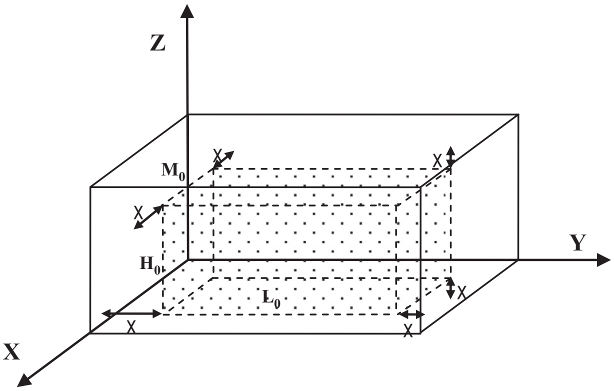

Fig. 1. Schematic plot of oxidation of a cubic ceramic composite under oxygen environment.

$$j=-D_O\frac{\partial C}{\partial \chi} \tag{1}$$

Where D_O represents the diffusion coefficient of oxygen and χ indicates the distance perpendicular to the surface of unit increment of cylinder surface. In an approximate treatment, it is assumed that the diffusion is isotropic and calculated based on one-dimension diffusion, therefore for a given time “t” the thickness of oxide layer χ should remain the same in all orientations of the cuboid. On the other hand, this oxygen flux will lead to a formation of oxides and the rate of oxide thickness should be proportional to the oxygen flux j, i.e.

$$\frac{dx}{dt}=\frac{j}{v_m} \tag{2}$$

where v_m is a coefficient related to the density of substance and oxide. For a general approximate treatment, the oxygen flux can approximately be expressed as the following form

$$j=-D_O\frac{C^{eq}-C_O}{\chi} \tag{3}$$

where C^{eq} is the oxygen concentration in equilibrium with the oxide at the interface between substance and oxide within cuboid. Substituting Eq. (3) into Eq. (2) yields

$$\frac{d\chi}{dt}=-\frac{D_O}{v_m}\frac{C^{eq}-C_O}{\chi} \tag{4}$$

Integrating Eq. (2) from $t=0,\chi=0$, to $t=\text{t},\chi=\chi$, one has the following equation,

$$\chi=\sqrt{2D_O(C_O-\frac{C^{eq})t}{v_m}} \tag{5}$$

On the other hand, the reacted fraction of this cuboid should be equal to the volume of oxide layer divided by the original cuboid volume, i.e. [13]. Since the samples were suspended in the furnace in the experiment [5,14], all the faces were exposed to the air. Therefore the oxidation reaction can be described as following:

$$\xi=1-\frac{(L_0-2\chi)(M_0-2\chi)(H_0-2\chi)}{L_0M_0H_0} \tag{6}$$

Substituting Eq. (5) into Eq. (6) generates

$$\xi=1-\left[1-\frac{2}{L_0}\sqrt{2D_0(C_0-\frac{C^{eq})}{v_m}t}\right]\left[1-\frac{2}{M_0}\sqrt{2D_0(C_0-\frac{C^{eq})}{v_m}t}\right]\left[1-\frac{2}{H_0}\sqrt{2D_0(C_0-\frac{C^{eq})}{v_m}t}\right] \tag{7}$$

It is well known that the diffusion coefficient of oxygen D_O should obey Arrhenius law

$$D_O=D_O^0\exp\left(-\frac{\Delta E}{RT}\right) \tag{8}$$

where D_O represents the diffusion coefficient of oxygen and D_O^0 a constant independent of temperature, ΔE activation energy. On the other hand, the oxygen concentration within the substance should obey the Sieverts' law, i.e.

$$C = k_0\sqrt{P_{O_2}} \tag{9}$$

where P_{O_2} represents oxygen partial pressure in the gas phase, k_0 Sieverts' constant depending on temperature (it can be derived from the thermodynamics based on an equilibrium $O_2(g) = 2O$). Substituting Eqs. (8) and (9) into Eq. (7) yields

$$\xi = 1 - \left[1 - \frac{2}{L_0}\sqrt{\frac{2D_O^0 k_O\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)}{v_m}t}\right]\left[1 - \frac{2}{M_0}\sqrt{\frac{2D_O^0 k_O\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)}{v_m}t}\right]\left[1 - \frac{2}{H_0}\sqrt{\frac{2D_O^0 k_O\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)}{v_m}t}\right] \tag{10}$$

In view of the oxidation of the sample in the shape of cube under isothermal condition, the effects of temperature and the sample shape on the reacted fraction versus time is as following:

$$\xi = 1 - \left[1 - \frac{2\exp(-\Delta E/2RT)}{M_0}\sqrt{\frac{t}{t_\varphi}}\right]\left[1 - \frac{2\exp(-\Delta E/2RT)}{L_0}\sqrt{\frac{t}{t_\varphi}}\right]\left[1 - \frac{2\exp(-\Delta E/2RT)}{H_0}\sqrt{\frac{t}{t_\varphi}}\right] \tag{11}$$

where $$t_\varphi = \frac{v_m}{2D_O^0 k_0\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)} \tag{12}$$

D_O^0 is a constant independent of temperature, k_0 is a constant depending on the temperature and can be derived from the thermodynamics based on an equilibrium $O_2(g) = 2O$, v_m is a coefficient related of the substance and oxide. If the value of $P_{O_2}^{eq}$ is very small or the temperature coefficient of $P_{O_2}^{eq}$ can be neglected, thus t_φ would be a constant depending on the oxygen partial pressure only.

For a large number of materials, their service temperature is not constant but variable. If the system is heated from room temperature T_0 to the experimental temperature T with a certain temperature-increasing rate "η" where $\eta = dT/dt$, the relation of temperature with time t should be

$$T = T_0 + \eta t \tag{13}$$

Substituting Eq. (13) into Eq. (11), an approximate relation of the reacted fraction with temperature will be obtained as follows:

$$\xi = 1 - \left[1 - \frac{2\exp(-\Delta E/2RT)}{M_0}\sqrt{\frac{T - T_0}{\eta t_\varphi}}\right]\left[1 - \frac{2\exp(-E/2RT)}{L_0}\sqrt{\frac{T - T_0}{\eta t_\varphi}}\right]\left[1 - \frac{2\exp(-E/2RT)}{H_0}\sqrt{\frac{T - T_0}{\eta t_\varphi}}\right] \tag{14}$$

In the following section, these equations will be employed to treat the oxidation kinetics of the TiN-containing ceramic composites from a quantitative point.

3. Application to oxidation of TiN-containing composites

3.1. Oxidation of Si_3N_4–TiN composites synthesized from HP process

Klein et. al. [14] has investigated the oxidation behavior of Si_3N_4–35 vol% TiN composites, which were synthesized from hot pressed (HP) and hipped process (HIP) respectively.

The oxidation tests were carried out on cubic samples with size of 4 mm × 4 mm × 4 mm in oxygen under both isothermal and non-isothermal condition. The weight gain was recorded with a SETARAM microbalance. The non-isothermal oxidation was carried out from room temperature up to 1673 K at the heating rate of 2 K/min with the oxygen flow rate of 5 l/h. In the case of isothermal experiments (temperature range 1273–1673 K for 24 h), the heating up stage was performed in argon atmosphere so that the sample inside the isothermal zone of the furnace can avoid preliminary oxidation. When the furnace reached the required temperature, the atmosphere was changed to oxygen and the weight gain was continuously recorded. Fig. 2a and b were the non-isothermal and isothermal oxidation results respectively for the sample synthesized from HP process. The non-isothermal oxidation results (Fig. 2a) showed that the oxidation obviously started above 1073 K and increased rapidly from 1473 K. In the isothermal experiments, the cross-sections of oxidized samples were analysized by X-ray diffraction (XRD). It showed that cristalline TiO_2 mainly existed below 1473 K, indicating that the oxidation was mainly governed by the oxidation of TiN in the temperature range of 1273 to 1473 K [14]. At above 1473 K, the phase of SiO_2 appeared in the XRD results, indicating oxidation of Si_3N_4 matrix took place. The whole oxidation behavior followed parabolic rate law throughout the experimental temperature range of 1273–1573 K (Fig. 2b). However, the oxidation mechanism changed at 1673 K because of the formation of liquid phase. Therefore, we only consider the oxidation behavior in the temperature range of 1273–1573 K. In view of the sample synthesized from HIP, the oxidation kinetics exhibited a paralinear shape up to 1373 K and became asymptotic above this temperature due to the formation of a compact silica sub-scale acting as an efficient diffusion barrier [14]. Its oxidation behavior was characterized by weight gains exhibiting negative temperature dependence. Because the oxidation behavior was abnormal from the view point of thermodynamics, we do not consider it in this work.

As to the experimental data of Si_3N_4–35 vol% TiN composites offered by Klein et. al. [14], Eqs. (11) and (14) can be used to investigate the oxidation quantitatively. Please note that, the ordinate of Fig. 2a is using the mass gain per unit area $\Delta m/A$

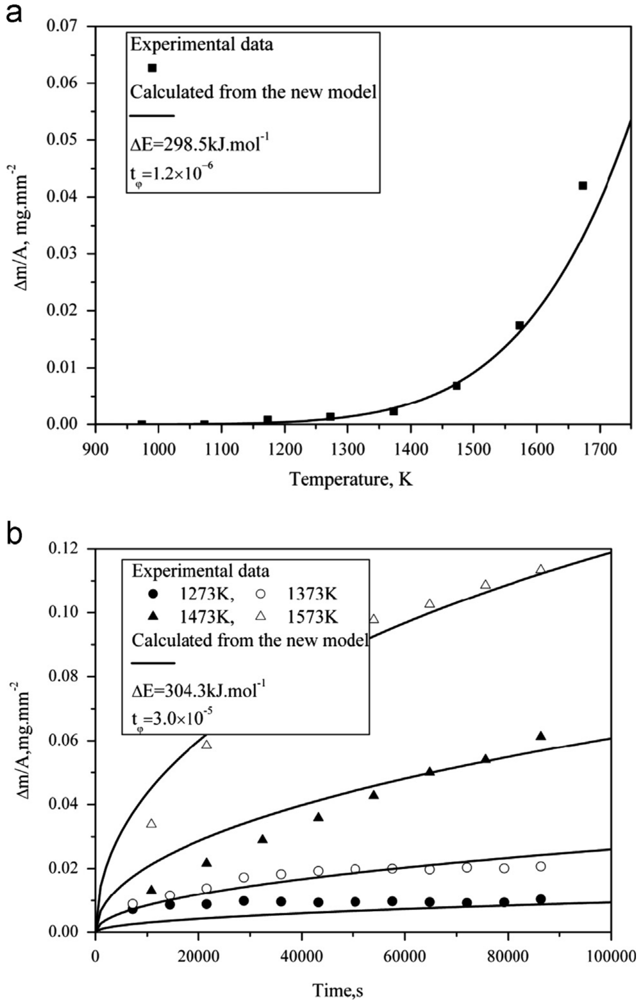

Fig. 2. Oxidation behavior of Si_3N_4–TiN composites synthesized from hot pressed (HP) process [14] (a) Non-isothermal oxidation and (b) Isothermal oxidation.

instead of reacted fraction ξ. A transformation of variable has to be required prior to using the formulae. According to these equations, there are two parameters, ΔE and t_φ that are requires to be determined by nonlinear regression fitting the experimental data. Substituting these two parameters into Eqs. (11) and (14) respectively, the models describing the non-isothermal and isothermal oxidation behavior of Si_3N_4–TiN composites are as follows:

Non-isothermal oxidation

$$\frac{\Delta m}{A}=0.402\left[1-\left(1-41.67\exp(-\frac{17951.7}{T})\sqrt{(T-298)}\right)^2\left(1-20.84\exp(-\frac{17951.7}{T})\sqrt{(T-298)}\right)\right] \tag{15}$$

Isothermal oxidation

$$\frac{\Delta m}{A}=0.23\left[1-\left(1-91.29\exp(-\frac{18300.6}{T})\sqrt{t}\right)^2(1-45.64\exp(-\frac{18300.6}{T})\sqrt{t})\right] \tag{16}$$

For comparison, these curves are drawn in the same plot of Fig. 2a and b. It may be seen that our theoretical calculation has given a good prediction though some errors exist. These small errors are inevitable as the high-temperature experimental conditions are hard to control. Some experiment conditions, such as the sizes of the sample… etc., are not exactly identical in different set of experiments. On the other hand, during our theoretical treatment, we apply an approximate method, i.e., a one-dimensional case, to treat the oxidation behavior of the cubic sample. Thus there should be some errors between experimental data and theoretical calculation.

In addition, the values of the parameter, ΔE calculated from Eqs. (11) and (14) is between that obtained in the literatures, i.e., 236 (1173–1473 K) and 362 kJ/mol (1473–1673 K). This is because ΔE in Eqs. (11) and (14) is an apparent activation energy which involves all the oxidation reactions of different phases.

Please note that the values of ΔE and t_φ obtained from Eqs. (15) and (16) are not in quite agreement to some degree. As shown in the experiments, the oxidation behavior followed parabolic rate law at the experimental temperature range of 1273 to 1573 K. The oxidation mechanism changed at 1673 K because of the formation of liquid phase [14]. While in the non-isothermal experimental temperature range from room temperature up to 1673 K, an approximate treatment i.e. diffusion-controlled model was adopted. This will lead to some diversion for the values of ΔE and t_φ obtained from Eqs. (15) and (16).

3.2. Oxidation of AlON–TiN composites

Zhang et. al.[5] researched the oxidation kinetics of AlON–15 wt%TiN composites with the size of 1 mm × 5 mm × 10 mm using thermogravimetry. Oxidation experiments have been carried out in air both in isothermal and non-isothermal modes. The non-isothermal oxidation was carried out from room temperature to a maximum temperature of 1773 K at a fixed rate of 20 K/min with the air flow rate of 800 ml/min. The results showed that the oxidation started at about 1273 K and the rates and degrees of oxidation increased with increasing temperature (Fig. 3a). Two distinct regimes of oxidation could be noticed in Fig. 3a and the second step started at about 1673 K due to the change of reaction mechanism. The isothermal studies were carried out in 1373 to 1573 K with 100 K interval and the results were shown in Fig. 3b. It indicated that the reaction rate was chemically controlled in the initial stages, followed by mixed chemical and diffusion control region in the middle stages, and then the diffusion-controlled stage. Among these, the diffusion-controlled stage occupied the large portion of the oxidation process [5].

Similarly, the oxidation of AlON–15 wt%TiN composites offered by Zhang et. al. [5] has also been investigated from quantitative point using Eqs. (11) and (14). In view of the non-isothermal oxidation, the two parameters, ΔE and t_φ are calculated to be 166.9 kJ/mol and 2.5×10^{-5} by regressing the experimental data. Substituting the two parameters into

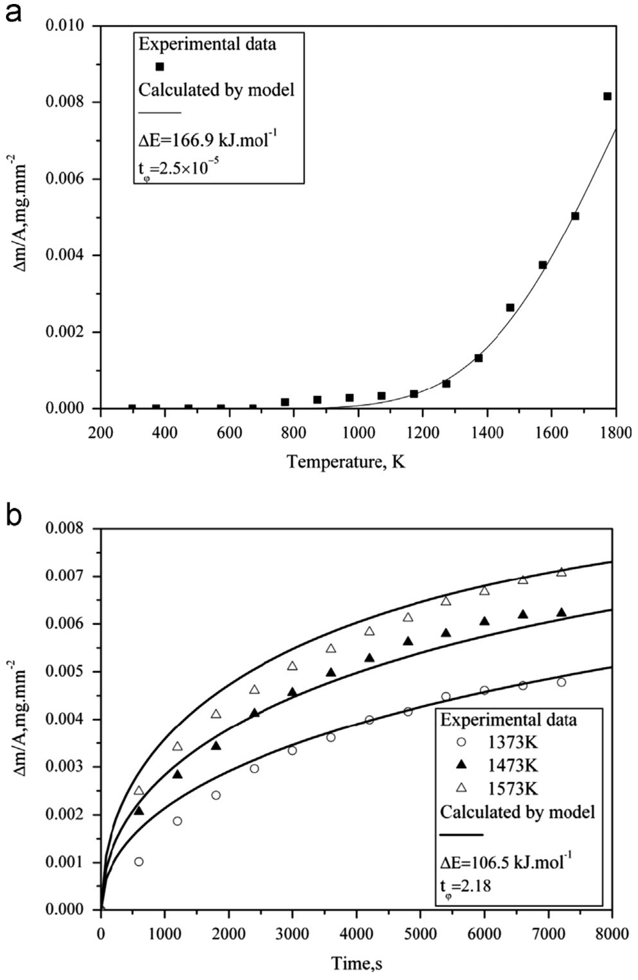

Fig. 3. Oxidation behavior of γ-AlON–TiN composites [5] (a) Non-isothermal oxidation (b) and Isothermal oxidation.

Eq. (14), one gets an explicit expression as following:

$$\frac{\Delta m}{A}=0.0082\left[1-\left(1-1.15\exp\left(-\frac{10037.3}{T}\right)\sqrt{(T-298)}\right)^{2}\left(1-5.77\exp\left(-\frac{10037.3}{T}\right)\sqrt{(T-298)}\right)\right] \tag{17}$$

Similarly, the oxidation equation under the isothermal condition is expressed as follows:

$$\frac{\Delta m}{A}=0.0072\left[1-\left(1-0.135\exp\left(-\frac{6404.86}{T}\right)\sqrt{t}\right)\left(1-0.271\exp\left(-\frac{6404.86}{T}\right)\sqrt{t}\right)\left(1-0.677\exp\left(-\frac{6404.86}{T}\right)\sqrt{t}\right)\right] \tag{18}$$

The curves obtained from the above equations are also shown in the same figure for comparison and a good agreement has been reached. The values of ΔE and t_φ obtained from Eqs. (17) and (18) are also not in quite agreement to some degree because of the similar reason point out in the section 3.1.

3.3. Compared with the previous oxidation kinetics studies

Eqs. (11) and (14) are general form in dealing with the solid–gas reaction under the condition of diffusion control. Although the oxidation process of TiN-containing composites is a complicated stage, their oxidation behavior belongs to solid–gas reaction and the controlling step is diffusion. Therefore we obtain a good curve fitting.

Based on the parameters obtained from the above formulae, one may further estimate the average relative error, Δ in terms of the following equation:

$$\Delta=\frac{1}{N}\sum_{i=1}^{N}\frac{|(\chi_n)_{mea}-(\chi_n)_{cal}|}{(\chi_n)_{mea}}\times 100\% \tag{19}$$

where $(\chi_n)_{mea}$ and $(\chi_n)_{cal}$ represent the transformed fractions of the measured and calculated values at a fixed time "t", respectively. N is the sum of experiment points. According to Eq. (19), the errors for the systems of Si_3N_4–TiN composite synthesized from HP process calculated by the new model is to be 15.1%. If one uses the pellet model instead of the cube model presented here, the average relative error will increase to 22.1%. One reason for deviation is probably caused by the shape of the sample, whose effect can be explained according to Eqs. (11) and (14). Another reason attributed to the error is that the oxidation process has been simplified to be one step, i.e., diffusion controlled. Actually there exist two steps, i.e., chemical reaction control and diffusion control during the oxidation process.

In view of the oxidation of AlON–15 wt%TiN composites, the errors calculated by the new model is to be 5.47%. If one uses the pellet model instead of the cube model presented here, the average relative error will increase to 17.2%.

On the other hand, compared with the treatment used by Zhang et. al. [5], i.e., three steps of rate-controlling method, all the parameters in our formulae have clear physical meaning, which is convenient for theoretical discussion and may guide the application of the material in practice.

A good agreement has been found between the experimental results and theoretical calculation by taking the factor of the sample shape into consideration. This new model actually is not limited in the application for treating the oxidation of cubic non-oxide ceramic materials, but they can also be used in dealing with problems of other shapes of materials, such as the material in shape of cylinder, just changing the size of the sample.

4. Conclusions

In this work, the system of TiN-containing composites has been selected to investigate the oxidation behavior of the non-oxide ceramic composites. The results in the literature showed that the oxidation behavior was a complicated process involving reaction of different phases. Whilst the oxidation mechanism was mainly diffusion controlled.

The oxidation kinetics has been investigated by adopting the Chou's model, in which the formulae concerning the relation of the reacted fraction of oxidation with various kinds of factors especially the sample shape under the conditions where diffusion controlled have been presented.

After applying our theoretical model to these experiments, good agreements have been found between the experimental results and theoretical calculation, validating the reasonability of the new model. Moreover, the factor of the sample shape has been taken into consideration in Chou's model. The calculated error is smaller compared with the models used in the literature.

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Appendices

ΔE	apparent activation energy of oxidation.
ξ	reacted fraction of oxidation.
D_0^o	diffusion coefficient of oxygen in oxide phase.
$\Delta m/A$	the increment of sample weight per area.
P_{O_2}	partial pressure of oxygen in gas phase.
$P_{O_2}^{eq}$	oxygen partial pressure in equilibrium with oxide.
M_0	the depth of the cubic sample.
L_0	the width of the cubic sample.
H_0	the height of the cubic sample.
η	the heating rate
R	gas constant.
t	time in second.
T	absolute temperature with K.
v_m	coefficient depending on substance and reaction.

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