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A new treatment for kinetics of oxidation of silicon carbide

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Abstract

In this paper the oxidation kinetics of SiC has been studied as per both experimental and theoretical aspects based on current literatures, from which the shortcoming of theory has been discussed. A new model has been introduced that can express the oxidation weight gain as a function of temperature, oxygen partial pressure and the size of materials explicitly. Two examples, chemical vapor deposition (CVD) SiC pellet and ZrB_2–SiC pellet, have been selected to test our new model and the calculated results show that our new model can fit both isothermal and non-isothermal data very well. Therefore, it is expected that this new model could be used to predict the oxidation behavior of SiC materials based on limited experimental information.

Keywords: Oxidation; Mechanism; Kinetics; SiC

1. Introduction

SiC materials possess excellent properties of heat conductivity, hardness and high-temperature mechanical stability. Therefore, it has been widely used. For example, SiC materials have been manufactured in a certain shape of parts for the application of heating element, electrical resistors and a coating for environmental protection of high-temperature materials, etc. [1,2].

Especially, the good oxidation resistance for SiC ceramics is an important factor that is required for the application in high-temperature internal combustion engines. Intensive studies have been focused on the oxidation behavior of SiC materials experimentally [3–8]. There were some reports on the oxidation kinetics of SiC in the literatures [9,10]. Ogbuji and Opila studied the oxidation behavior of CVD SiC and compared with that of Si_3N_4 between 1473 K and 1773 K at 100 K interval [9]. It showed that the oxidation behavior of SiC and Si_3N_4 followed parabolic law and the activation energy of oxidation were determined to be 118 kJ mol^{-1} and 363 kJ mol^{-1} respectively. Tian et al. studied the oxidation kinetics of ZrB_2–SiC composites prepared by heat-press sintering using thermogravimetric analysis [10]. It was found that the ZrB_2–SiC composite had the best oxidation resistant when the sintering temperature was 2023 K and the mechanism of oxidation which followed parabolic rate law was investigated. However, due to the difficulty of experiments at elevated temperature and the large number of related systems, the theoretical study of oxidation kinetics of SiC is still scarce, especially in quantitative aspects. Thus, the measures of anti-oxidation are usually proposed from experience but not from scientific study. Along with the progress in science and technology, a new study was required to describe the oxidation process and based on which some new quantitative relations were established. These formulae are in analytic form expressing the reacted fraction as an explicit function of time, temperature, particle size, oxygen partial pressure etc., which have not been reported in the literatures before. The benefit of this method is that it is easy to make a calculation moreover easy to perform a theoretical analyses and discussion. These formulae have been proved to be suitable for the systems of Si–Al–O–N and Si_3N_4 very well [11,12]. In this paper, the method was used for treating the oxidation of SiC materials, from which one may expect to obtain some important message for directing us how to compare and improve the utilization of SiC materials.

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2. Model

2.1. General oxidation mechanism of SiC materials

It is well known that the oxidation of SiC material can be divided into two categories: active oxidation and passive oxidation [13]. The active oxidation of SiC is characterized by the loss in mass [14] according to

$$\mathrm{SiC(s)} + \mathrm{O_2(g)} = \mathrm{SiO(g)} + \mathrm{CO(g)} \tag{1}$$

By comparison, the conversion of SiC to SiO_2 results in a net mass increasing, which leads to SiC in passive oxidation [14] where

$$\mathrm{SiC(s)} + \tfrac{3}{2}\mathrm{O_2(g)} = \mathrm{SiO_2(s)} + \mathrm{CO(g)} \tag{2}$$

For a given temperature, the active oxidation region is the point where the partial pressure of oxygen (P_{O_2}) in the bulk gas is less than a critical pressure ($P_{O_{2(\max)}}$) and the passive oxidation region where $P_{O_2} > P_{O_{2(\max)}}$. In most cases, the oxidation behavior of SiC is passive and therefore, in this work, only the passive oxidation kinetics of SiC would be treated and the active oxidation of SiC will be reported in the future.

Numerous studies have been conducted on oxidation of SiC material. However, there are wide variation in the observed reaction rates and the morphology of the reaction products [15,16]. There is a general agreement that the reaction product was amorphous at the beginning of the oxidation and at low temperatures but tended to crystallize at longer times and at higher temperatures. However, there remains unclear regarding the oxidation mechanism of SiC material. Ogbuji and Opila [7,9] calculated the activation enthalpy for the oxidation of SiC and found that it was essentially the same as that for the oxidation of Si. This implied that the mechanism controlling the oxidation rate was probably the same for both materials, namely, the permeation of oxygen through silica oxidized phase (or layer). And the rate-limiting step does not change in the temperature range 1473–1773 K. By comparison, Luthra [5] provided new perspectives on the oxidation mechanism of SiC and pointed out that the oxidation of SiC should be mixed controlled, i.e., influenced both by an interface reaction and diffusion. Further, work is still required to testify the validity of this model.

Up to now though most of studies are concentrated on the experimental aspects, the theoretical studies on this topic are still not satisfactory comparing with the experiment work. 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 ξ with time t; how does the particle size affect the curve of reacted fraction ξ versus temperature T. All these questions have never been answered in the literatures before. In the following section, we will develop some new models for describing the oxidation rate of SiC material, which have already been successfully used in the systems of Si–Al–O–N and Si_3N_4 [11,12].

2.2. Assumption and derivation for oxidation of pellet

As mentioned above, the SiC materials have been manufactured in a certain shape of parts for the application. In this section, a series of equations that fulfill the pellet oxidation are given bellow.

Fig. 1 is a schematic plot for describing a pellet oxidation, in which α represents SiC with original thickness of L_0, β is oxide layer with thickness of x. As reported in the literatures [7–9], the stage of diffusion control occupied most of time in the whole oxidation process of SiC. Therefore, it is meaningful to study the oxygen diffusion as a controlling step.

Based on this idea, the formulae of oxidation of pellet for describing the reacted fraction ξ of oxidation of SiC with time t had been deduced as follows [12]:

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

where

$$\Theta_T = \frac{v_\mathrm{m} L_0^2}{2K_\mathrm{O}^{0\beta} D_\mathrm{O}^{0\beta}\left(\sqrt{P_{\mathrm{O_2}}} - \sqrt{P_{\mathrm{O_2}}^{\mathrm{eq}}}\right)} \tag{4}$$

where ΔE represents the apparent activation energy. Θ_T is 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; $K_O^{0\beta}$ and $D_O^{0\beta}$ are constant independent of temperature but relying on the material of the pellet. v_m is a coefficient that depends on substance and reaction 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. (3) is the general formula expressing the reacted fraction ξ as the function of time t and many other related parameters. It might be seen from Eq. (3) that the higher the temperature, the larger the reacted fraction ξ. It is in accordance with our common sense, as the higher the temperature, the faster the reaction rate. However, at most cases, the service temperature of SiC material is not constant but variable. For instance, SiC materials were used as refractory material at an elevated temperature. When the temperature of furnace was heated, the sample was in a condition with a certain temperature-increasing rate "η" where $\eta = dT/dt$. If the system was heated from room

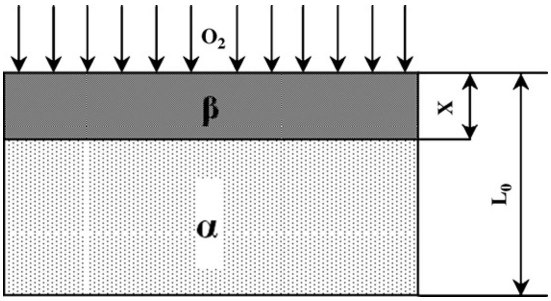

Fig. 1. Schematic plot of oxidation of a pellet under oxygen environment.

temperature T_0, thus the relation of temperature with time t should be

$$T = T_0 + \eta t \tag{5}$$

Therefore, the formula that described the relation of reacted fraction of oxidation with temperature was as follows:

$$\xi = \sqrt{\frac{1}{\Theta_T} \exp\left(-\frac{\Delta E}{RT}\right) \frac{(T - T_0)}{\eta}} \tag{6}$$

Eqs. (3) and (6) are the general formulae expressing the reacted fraction ξ as a function of time t and many other related parameters quantitatively. This Eq. (6) is 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 mentioned above. How accuracy of this kind of treatment can be judged from the application of this model to the practical examples that would be given in the latter sections.

3. Application of the new model to the practical system

3.1. The SiC pellet from CVD

Ogbuji and Opila had studied the oxidation kinetics of CVD SiC from 1473 K to 1773 K with 100 K interval [9]. The experiment was carried out in quartz tubes to ensure a clean oxidation environment because it had been reported that impurities in alumina tubes influenced both the oxidation kinetics and the oxide scale phase and microstructure [17]. The size of the samples were cut into 8 mm × 5 mm × 1 mm and the oxidation time was 5 h (18,000 s), 10 h (36,000 s), 25 h(90,000 s), 50 h(180,000 s), 75 h (270,000 s)and 100 h (360,000 s) respectively. After oxidation, the microstructure and the oxide thickness were measured respectively. The experiment showed that the oxidation rate was limited by permeation of oxygen through oxide layer and the oxidation activation energy was determined to be 118 kJ mol^{-1}. The oxidation behavior at different temperature is shown in Fig. 2. At present, let us use our model to fit these data. The obtained results are listed in the same Fig. 2, from which it may be seen that, it is a very good fitting, the theoretical curves are in good accordance with experimental data. The predicted activation energy is equal to ΔE = 118.1 kJ mol^{-1}, it is almost repeating the Ogbuji and Opila's result of 118 kJ mol^{-1}. Substituting these two parameters (another one Θ_T = 1050) into Eq. (3), we have the following equation

$$\zeta = 0.03086\sqrt{t}\exp\left(-\frac{7102.5}{T}\right) \tag{7}$$

Eq. (7) has successfully described a group of curves only with two parameters, this fact once again illustrates our theory is reliable from another point of view. Please note that, the ordinate of Fig. 2 is using thickness ζ instead of reacted fraction ξ. It is because there exists a proportional relation between increment of thickness and that of reacted amount.

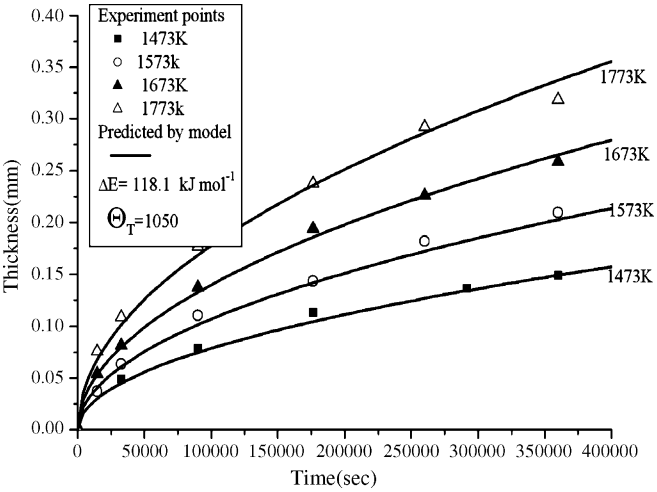

Fig. 2. Oxidation kinetics of CVD SiC at 1 atm oxygen.

3.2. The ZrB_2–SiC system

The ZrB_2–SiC composite is a new candidate for the coating material to protect the nose cap and wing leading edges on the space shuttle from oxidizing in the high-temperature air environment [2]. Therefore, it is necessary to study the oxidation behavior of ZrB_2–SiC material. Tian et al. had studied the oxidation of ZrB_2–SiC composites prepared by heat-pressing sintering in both non-isothermal and isothermal modes [10]. The oxidation reaction can be expressed as [10]

$$ZrB_2(s) + SiC(s) + 4O_2(g) = ZrO_2(s) + B_2O_3(s) + SiO_2(s) + CO(g) \tag{8}$$

The sample was cut into 3 mm × 4 mm × 15 mm and the weight change in air atmosphere was measured. It was found that the ZrB_2–SiC composite had the best oxidation resistant when the sintering temperature was 2023 K. In the isothermal mode, the oxidation kinetics was studied at 1273 K and 1573 K, respectively up to 40 h (144,000 s). The result showed that the oxidation behavior followed the parabolic rate law. The results of the sample sintered at 2023 K were shown in Figs. 3 and 4 respectively. Eqs. (3) and (6) are now used to calculate the oxidation behavior for both isothermal and non-isothermal modes as shown in Figs. 3 and 4, respectively. Eqs. (3) and (6) are selected to treat the oxidation problem of ZrB_2–SiC system, since these equations are the general form in dealing with the solid–gas reaction, which have already been proved very successful for describing the oxidation of Si_3N_4, Sialon etc., [11,12] as long as the oxidation process is in the diffusion control. It can be seen from these figures that the calculated results agreed well again with the literature data in the condition of non-isothermal oxidation (Fig. 3) [10]. For isothermal oxidation (Fig. 4), regarding the agreement between experimental data and theoretical calculation, the curve of 1273 K is better than that of 1573 K, basically both are fine if considering the experimental error and theoretical approximation. Two parameters extract from our fitting are equal to ΔE = 131 kJ mol^{-1} and Θ_T = 0.35, substituting these data into

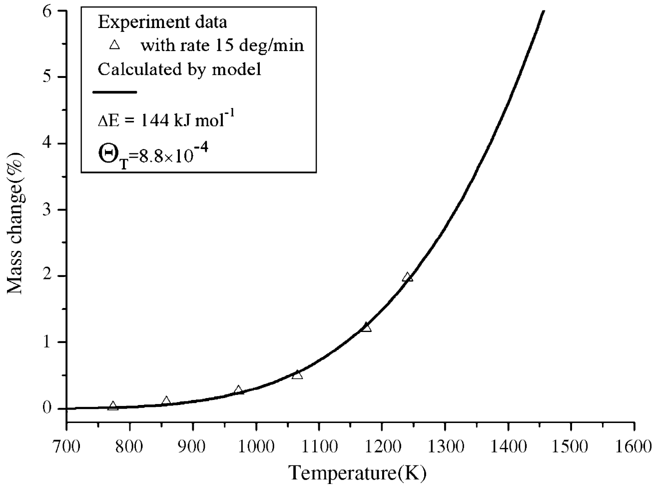

Fig. 3. Non-isothermal oxidation curves of ZrB_2–SiC sintered at 2073 K with the temperature increasing rate 15°min^{-1}.

Eq. (3) we have

$$\Delta m = 1.69\exp\left(-\frac{7878.3}{T}\right)\sqrt{t} \tag{9}$$

The dash lines of 1373 K and 1473 K in Fig. 4 are completely theoretical predicted values based on our limited information.

For the non-isothermal case, the fitting results are $\Delta E = 144$ kJ mol^{-1} and $\Theta_T = 8.8 \times 10^{-4}$ under the condition of $\eta = 15/60^{\circ}\mathrm{s}^{-1}$, substituting these data into Eq. (6), we have the following equation to describe the non-isothermal oxidation as

$$\Delta m = 67.42\sqrt{(T-298)}\exp\left(-\frac{8660}{T}\right) \tag{10}$$

It can be seen from Fig. 3 that the agreement between experimental data and theoretical calculation is very good. As mentioned above, the activation energy calculated from isothermal equation of Eq. (3) and the non-isothermal Eq. (6) are to be 144 kJ mol^{-1} and 131 kJ mol^{-1}, respectively. They are also very close. This fact demonstrates again that our theoretical models are acceptable from the other point of view.

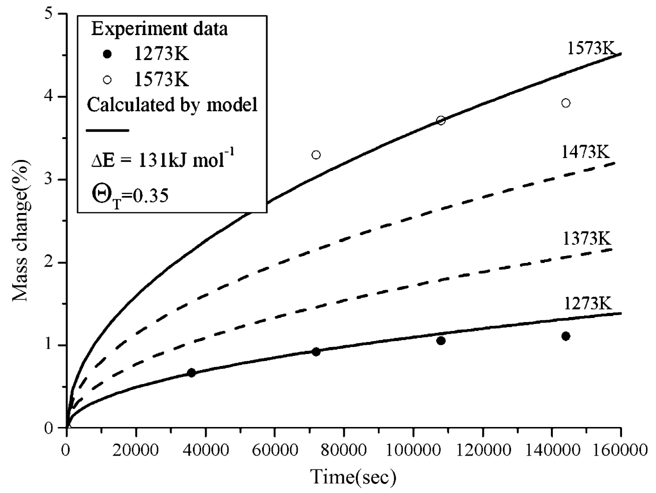

Fig. 4. Isothermal oxidation curves of ZrB_2–SiC at 1273 K and 1573 K.

Note that, the y-axis in the above experimental data is not the reacted fraction ξ but the Δm (Δm represents the increment of sample weight after oxidation at time t). In this case a transformation of variable has to be required prior to using our formulae.

4. Discussion

(1) The oxidation kinetics of SiC material has been studied in literature. However, the theoretical study is still unsatisfactory in comparison with the experimental study. It is because the oxidation process is very complicated. The mechanism of this process consisted of a series of sequential steps. Some researchers treated each step rigorously, that led to solve a group of differential or integral equations [3–7,9]. The situation was that these treatments were so complicated that could not offer an explicit analytic expression and give an intuitionistic quantitative discussion. On the other hand, some researchers studied the oxidation kinetics by simplifying the steps and concluded the oxidation behavior followed linear rate law initially and parabolic rate law later [8,10,14]. However, that treatment was too simple to study the intrinsical oxidation mechanism and could not provide scientific anti-oxidation measures for practical application.

(2) From the point of view of practical application it is desired to have a simpler and physical meaningful explicit analytic expression, which is convenient for use and can still give a good prediction under an acceptable simplified assumption. The purpose of this paper is 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. The new model was then applied to the systems of CVD SiC pellet and ZrB_2–SiC pellet. The calculated results show that it works very well.

(3) 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. In Fig. 4 the curves at 1373 K and 1473 K (dish line) actually came from the data of 1273 K and 1573 K. By comparison, the models reported in literature have not this function.

(4) In the derivation of our formulae, the variable used is the "reacted fraction" or "transferred fraction", ξ, however, many researchers like to use variable "increment of reaction", Δm, or "the oxide thickness", ζ, instead of ξ. In this case a transformation of variable has to be required prior to using our formulae.

(5) This new model is not limited actually in the application for treating the oxidation of SiC materials, but they can also be used in dealing with problems of other material fields, such

as hydrogen storage, Si–Al–O–N system and some metallurgical reactions. It is because, all these are related to the solid-gas reaction, and they should have the similar reaction mechanism. Therefore, it seems that this model should find more applications in the field of material science.

5. Conclusion

A new kinetics model was applied to calculate the oxidation behavior of SiC. The advantage of this method was that it is easy to calculate and easy to perform a theoretical analysis and discussion due to its explicit expression. This method was then applied to the system of CVD SiC and ZrB_2–SiC. Calculated results agreed well with experimental data for these systems.

Since most of oxidation processes of inorganic non-metallic materials had very similar mechanism, 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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Appendix A. Nomenclature

α	original SiC material phase
β	oxide material phase
ΔE	apparent activation energy of oxidation
ξ	reacted fraction of oxidation
ζ	thickness of oxide layer
$D_{\mathrm{O}}^{0\beta}$	a constant independent of temperature but relying on the material
$K_{\mathrm{O}}^{0\beta}$	a constant independent of temperature but relying on the material
η	temperature-increasing rate
P_{O_2}	partial pressure of oxygen in gas phase
$P_{\mathrm{o}_2}^{\mathrm{eq}}$	oxygen partial pressure in equilibrium with oxide
L_0	thickness of the original SiC
x	thickness of the oxide
R	gas constant
t	time in second
T	absolute temperature with K

Reference

[1] P. Krawiec, S. Kaskel, Thermal stability of high surface area silicon carbide materials, J. Solid State Chem. 179 (2006) 2281–2289.

[2] S.R. Levine, E.J. Opila, M.C. Halbig, et al., Evaluation of uitra-high temperature ceramics for aeropropulsion use, J. Eur. Ceram. Soc. 22 (2002) 2757–2767.

[3] E.J. Opila, Oxidation kinetics of chemically-vapor-deposited silicon carbide in wet oxygen, J. Am. Ceram. Soc. 77 (3) (1994) 730–736.

[4] Z. Zheng, R.E. Tressler, K.E. Spear, Oxidation of single-crystal silicon carbide, Part I: experimental studies, J. Electrochem. Soc. 137 (3) (1990) 850–855.

[5] K.L. Luthra, Some new perspectives on the oxidation of silicon carbide and silicon nitride, J. Am. Ceram. Soc. 74 (5) (1991) 1095–1103.

[6] E.J. Opila, R.E. Hann Jr., Paralinear oxidation of CVD SiC in water vapor, J. Am. Ceram. Soc. 80 (1) (1997) 197–205.

[7] E.J. Opila, Influnence fif alumina reaction tube impurities in the oxidation of chemically-vapor-deposited silicon carbide, J. Am. Ceram. Soc. 78 (4) (1995) 1107–1110.

[8] W.F. Du, H.N. Xiao, H.Q. Du, the oxidation of SiC-matrix multiphase ceramics at high temperature and its effect on strength, J. Chin. Ceram. Soc. 20 (5) (1992) 417–422.

[9] L.U.J.T. Ogbuji, E.J. Opila, A comparison of the oxidation kinetics of SiC and Si_3N_4, J. Electrochem. Soc. 142 (3) (1995) 925–930.

[10] T.Y. Tian, Y.J. Zhang, F. Sun, H.K. Wei, Study on oxidation resistance of ZrB2–SiC composite, Chinese Ceram. 5 (2006) 19–21 (in Chinese).

[11] X.M. Hou, K.C. Chou, X.J. Hu, H.L. Zhao, A new measurement and treatment for kinetics of isothermal oxidation of Si_3N_4, J. Alloy. Comp. 459 (2008) 123–129.

[12] K.C. Chou, A kinetic model for oxidation of Si–Al–O–N materials, J. Am. Ceram. Soc. 89 (5) (2006) 1568–1576.

[13] W.L. Vaughn, H.G. Maahs, Active-to-passive transition in the oxidation of silicon carbide and silicon nitride in air, J. Am. Ceram. Soc. 73 (6) (1990) 1540–1543.

[14] E.A. Gulbransen, K.F. Andrew, F.A. Brassart, the oxidation of silicon carbide at 1150 °C to 1400 °C and at 9×10^{-3} to 5×10^{-3} torr oxygen pressure, J. Electrochem. Soc. 113–1 (1–6) (1966) 1311–1314.

[15] J.A. Cotello, R.E. Tressler, Oxidation kinetics of silicon carbide crystals and ceramics-1: in dry oxygen, J. Am. Ceram. Soc. 69 (9) (1986) 674–681.

[16] H. Du, R.E. Tressler, K.E. Spear, Thermodynamics of the Si–N–O system and kinetic modeling of oxidation of Si_3N_4, J. Electrochem. Soc. 136 (1989) 3210–3215.

[17] Z. Zheng, R.E. Tressler, K.E. Spear, Effect of sodium contamination on the oxidation of single crystal carbide, Corros. Sci. 33 (4) (1992) 569–580.