Journal of Alloys and Compounds 509 (2011) 2395–2400

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Investigation of the effects of temperature and oxygen partial pressure on oxidation of zirconium carbide using different kinetics models

Xin-Mei Hou [a,b], Kuo-Chih Chou [a,c,*]

[a] Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China
[b] The Key Laboratory of Ecological and Recycle Metallurgy, Ministry of Education, University of Science and Technology Beijing, Beijing 100083, China
[c] Department of Materials Sciences and Engineering, Shanghai University, Shanghai 20072, China

ARTICLE INFO

Article history:
Received 6 June 2010
Received in revised form 3 November 2010
Accepted 4 November 2010
Available online 13 November 2010

Keywords:
Zirconium carbide
Oxidation
Kinetic model
Temperature
Oxygen partial pressure

ABSTRACT

The oxidation kinetics of ZrC materials is an important physicochenmical property for their practical application. Although the oxidation data have been extensively measured, the quantitative relationship of oxidation curves to various factors such as temperature and oxygen pressure is still limited. In this article, the oxidation kinetics of ZrC materials under the conditions of different rate-controlling steps existing has been investigated using two kinds of models (the model used in the literatures and Chou's model) based on the experimental data available in the literatures. The calculated results show that both models can fit the oxidation data well. Compared with the previous models used in the literatures, Chou's model can give a clear physical meaning in expressing all parameters. The most important thing is that Chou's model can give a more accurate performance in the theoretical analysis.

1. Introduction

Most of the transition metal carbides are refractory materials having good mechanical properties particularly useful for cutting tools and drilling heads. For example, zirconium carbide, ZrC is one of the most refractory materials with high melting point (3693 ± 20 K) and good mechanical properties especially a hardness that is comparable with the hardness of TiC [1]. Therefore, ZrC is an important high-temperature structural material and can be applied as a promising nuclear material [2–5]. By comparison, its chemical stability in air and at high temperature is quite poor, which restricts its range of applications. A systematical investigation of the oxidation kinetics for ZrC is essential.

Several studies on the oxidation of ZrC both as powder [6–9] and single crystal samples [1,5,10–13] have been reported. Various authors have identified that the oxidation of ZrC is affected by many factors such as temperature, oxygen partial pressure and phase of oxide product. Among these factors, the morphological development of oxide phase is a very important one because it changes the oxidation behavior of ZrC. Therefore, most current works have been focused on the reaction process based on morphological development and the results showed a complex picture. Bellucci et al. [1] investigated the oxidation behavior of three ZrC single crystals in Ar/O_2 mixtures using Auger Electron Spectroscopy (AES), Electron Probe Micro-Analysis (EPMA), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Raman techniques. The results identified carbon in amorphous state retention during the oxidation process and the presence of both the c-ZrO_2 and m-ZrO_2 phases. Shimada et al. [12,13] also confirmed the experimental fact during the oxidation of ZrC single crystal. Besides these, they carried out the oxidation experiments on ZrC powder by simultaneous thermogravimetry (TG), differential thermal analysis (DTA) and mass spectrometry (MS) at vious oxygen pressure between 0.5 and 40 kPa in the temperature range of 293–1273 K. It was pointed out that the oxidation of ZrC overshoots a degree of oxidation of 100% depending on temperature and oxygen pressure, which was due to the formation of carbon during oxidation.

For the application of ZrC material, it is important to foresee what damage is caused by high-temperature oxidation as well as to prevent it. Compared with the knowledge of the sequence of events that occur during the oxidation, theoretical investigation especially in quantitative aspect is far more enough. The current models used in the literatures such as the well known Jander's equation, the parabolic rate law and linear rate law. are usually expressed with a pre-exponential term *k* and an apparent enthalpy. However, the constant *k* does not have clear physical meaning and thus these expressions are only empirical fits and used for interpolating the available data. In addition, the current models used in literature are

---

* Corresponding author at: Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China. Tel.: +86 010 6233 2646; fax: +86 010 6233 2570.
E-mail addresses: kcc126@126.com, houxinmei@ustb.edu.cn (K.-C. Chou).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.028

Nomenclature

ξ	reacted fraction of oxidation
$D_0^{0\beta}$	constant independent of temperature
$K_0^{0\beta}$	constants independent of temperature
υ_m	coefficient related to the density of reactant and product
ΔE_d	the apparent activation energy of diffusion
ΔE_r	the apparent activation energy of chemical reaction
η	temperature-increasing rate
P_{O_2}	oxygen partial pressure in gas phase
$P_{O_2}^{eq}$	oxygen partial pressure in equilibrium with oxide
R_0	radius of the original whole particle
L_0	the original thickness of the pellet
k_0	a temperature-independent constant
R	gas constant
t	time in second
T	absolute temperature with K
k_0	temperature-independent constant
Δ	the average relative error
$(\chi_i)_{mea}$	experimental data
$(\chi_i)_{cal}$	the value calculated from the model
N	the number of experimental points

established on the following assumption, i.e., $d\xi/dt = k(T)f(\xi)$ where $f(\xi)$ is a function of reacted fraction ξ (some researcher called it as the reaction model) and $k(T)$ a function of temperature T, normally it can be expressed as an Arrhenius equation, $k(T) = A\exp(-\Delta E/RT)$. Apparently, the form of $k(T)/f(\xi)$ means that the variables ξ and T can be expressed separately in an expression, which actually is an important assumption for this kind of models. Therefore, the applicability of these models will depend on the reliability of this assumption. In general, this assumption might be acceptable. However big errors will be introduced under the conditions that the reaction is controlled by multiple steps or the sample shape is other than a sphere as pointed out in our previous paper [14].

Recently, Chou's model [14,15] has been used for the theoretical treatment, which is different from all current models used in the literatures because it is established on a real physical picture with certain size or shape of solid materials undergoing a real process of molecular and atom movement. Since these formulae express the reacted fraction as a function of time, temperature, sample shape, oxygen pressure, etc. in an explicit way, one can easily carry out a calculation and give a good theoretical discussion for practical problem, which has been successfully applied to treat the oxidation behavior of many non-oxide material systems, such as SiAlON and Si_3N_4. [14–16].

The aim of this paper is to prevent the oxidation behavior of ZrC material from a quantitative standpoint based on the reported data. The influence factors, especially temperature and oxygen pressure on the oxidation kinetics will be quantitatively investigated for the first time. The results obtained by our new model will be discussed and compared with those reported in the literatures, in terms of which to obtain some idea for the future application and development of ZrC materials.

2. Experimental

2.1. Oxidation of ZrC powder

Shimada and Ishii [7] have systematically investigated the oxidation of ZrC powder with the average particle size of 3.3 μm under both non-isothermal and isothermal conditions using an electro-microbalance. The isothermal oxidations were carried out at the temperature range of 653–823 K with different oxygen pressures and the results are shown in Fig. 1a–c. The oxide products were analysed by XRD and SEM. It showed that at lower temperature, i.e., below 743 K, the oxidation product is amorphous and above 743 K, c-ZrO_2 crystalline appeared and the resulting volume expansion growth stress cracks the grains, which led to the oxidation behavior change (Fig. 1b and c).

The oxidation kinetics was also investigated by Shimada and Ishii [7], who pointed out that the oxidation was controlled by diffusion and can be well described by the Jander's equation.

$$[1-(1-\xi)^{1/3}]^2 = kt \tag{1}$$

where ξ is the reacted fraction at time t and k is the rate constant that depends on temperature and pressure. Since at about 743 K, the oxidation mechanism changed because of the phase transition. Eq. (1) was well applied during the whole temperature range with different apparent activation energies, i.e., 138 kJ/mol below 743 K and 180 kJ/mol above that temperature.

Fig. 2a and b shows the effect of oxygen pressure on oxidation behavior under both non-isothermal and isothermal conditions. In view of the non-isothermal oxidation behavior of ZrC powder at different oxygen pressures, the oxidation rate increased with oxygen pressure increasing. While at all oxygen pressure, the oxidation reaction began at about 573 K and the rate increased from 700 K (shown in Fig. 2a). Fig. 2b shows the oxidation behavior at 753 K with different oxygen pressures, in which the oxidation rate was faster at higher oxygen pressure and was controlled by diffusion.

2.2. Oxidation of ZrC pellet

In practice, ZrC material is usually used in the form of compact and the application temperature is usually above 850 K. Kuriakose and Margrave [11] investigated the oxidation of ZrC pellet with the purity of 99.5% in the temperature range of 827–925 K (as shown in Fig. 3). The oxygen partial pressure used in the experiments was 9.8×10^4 Pa. The result showed that the oxidation followed a linear rate law with the activation energy of 70.1 kJ/mol.

3. Results and discussion

From the above experimental results, the oxidation of ZrC material is a complicate process and affected by many factors, such as temperature, oxygen pressure and the shape of ZrC material. A general mechanism of oxidation reaction for ZrC material can be described by a series of steps, i.e., (1) oxygen in the bulk gas phase transfer to the surface of ZrC material; (2) oxygen diffusion through the boundary layer between gas phase and solid phase; (3) physisorption of oxygen molecules; (4) dissociation of oxygen molecules and chemisorption; (5) surface penetration of oxygen atoms; (6) diffusion of oxygen through the oxide product layer to the oxide/ZrC interface; (7) nucleus formation and chemical reaction producing oxide product and gas; (8) gas diffusion through oxide product to the surface of ZrC material; and (9) gas diffusion through the gas/ZrC material boundary to the gas bulk. The nine steps are basically enough to describe the oxidation process of ZrC material. For the purpose of simplification and practical convenience, the rate of limited-step method is usually applied such as Jander's equation, the linear rate law and Chou's model.

In this section, the experimental data offered by Shimada and Ishii [7] and Kuriakose and Margrave [11] were used to investigate the oxidation kinetics of ZrC materials in terms of the models used in the literatures and Chou's model, respectively. The obtained results will be compared.

3.1. Application of the models used in the literature

3.1.1. Oxidation kinetics of ZrC powder

In case of the system of ZrC powder offered by Shimada and Ishii [7], Jander's equation is employed to treat its oxidation kinetics. The value of k can be calculated from the slope line for each temperature. The activation energy is obtained by linear regression of the plot of $\ln k$ versus of $1/T$, which was calculated to be 142 kJ/mol below 743 K and 175 kJ/mol above that temperature. The different values implied the change of oxidation kinetics caused by the phase transition. In addition, the values of the activation energy obtained are consistent with the results reported in the literatures [7], implying the reasonable of Jander' equation.

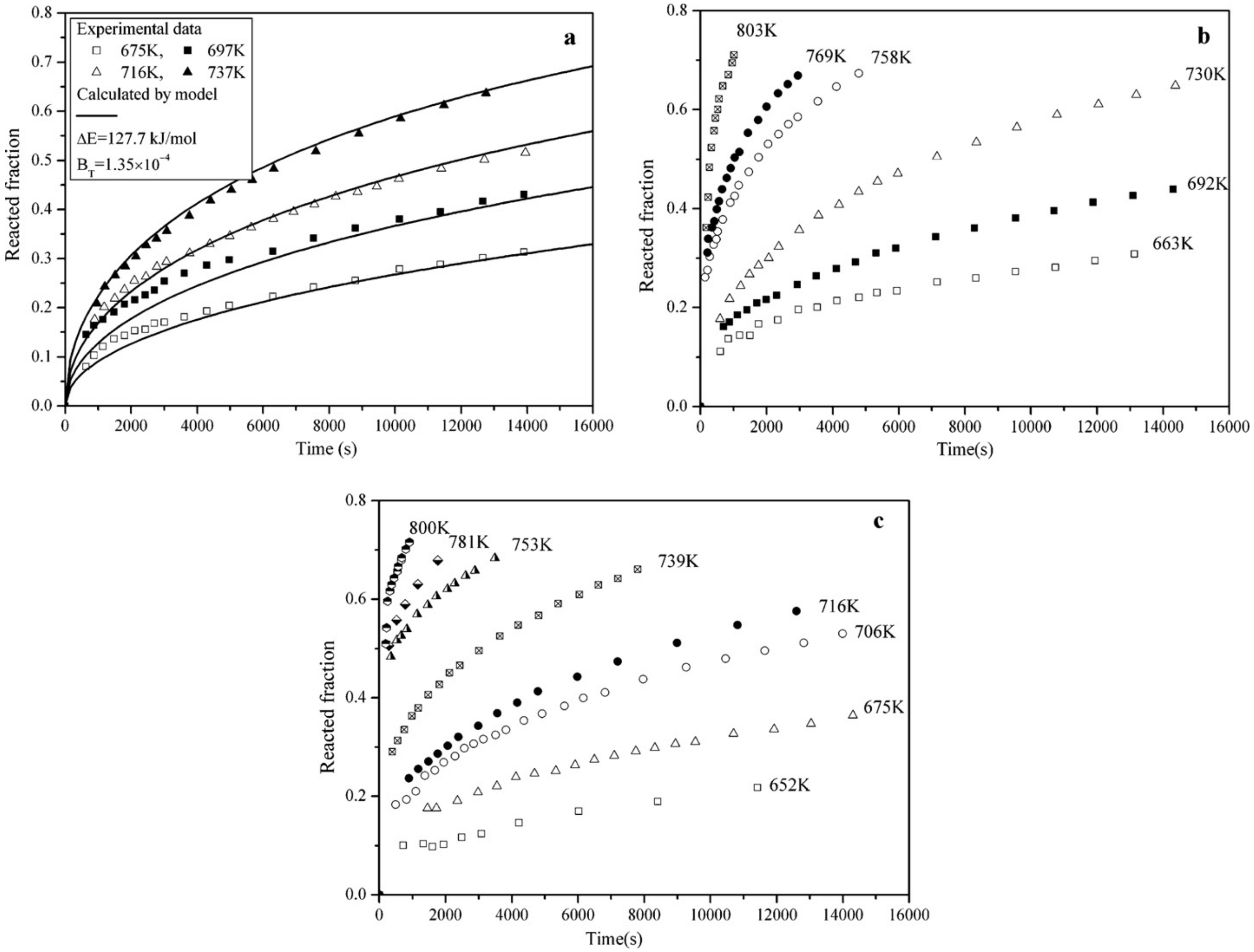

Fig. 1. The isothermal oxidation curves of ZrC powder at different oxygen pressures (a) 1.3×10^{-3} MPa, (b) 2.6×10^{-3} MPa, and (c) 7.9×10^{-3} MPa.

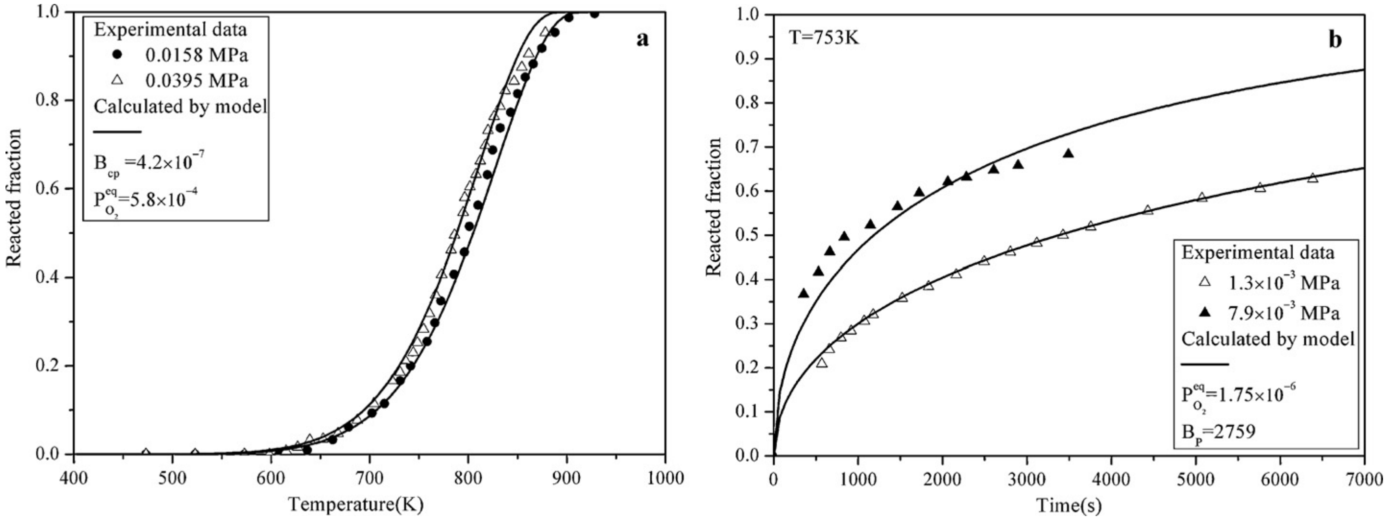

Fig. 2. Oxidation of ZrC powder at different oxygen pressures (a) non-isothermal oxidation and (b) isothermal oxidation.

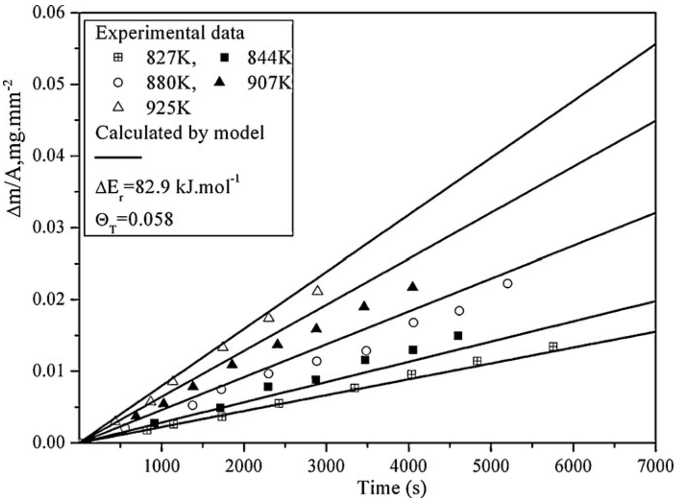

Fig. 3. The isothermal oxidation of ZrC pellet.

3.1.2. Oxidation kinetics of ZrC pellet

Since the oxidation of ZrC pellet investigated by Kuriakose and Margrave was controlled by chemical reaction [11], the linear rate law was employed and the result can be well fitted with the activation energy to be 72 kJ/mol.

3.2. Application of Chou model

3.2.1. Oxidation kinetics of ZrC powder

In view of the isothermal oxidation behavior of ZrC powder at the oxygen pressure of 1.3×10^{-3} MPa, its kinetics was controlled by diffusion [7]. One formulae of Chou's model can be employed to treat it, i.e.,

$$\xi = 1-\left(1-\sqrt{\frac{\exp(-\Delta E_d/RT)t}{B_{dT}}}\right)^3 \tag{2}$$

where

$$B_{dT} = \frac{1}{(2K_0^{0\beta}D_0^{0\beta}/v_m)((\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})/R_0^2)} \tag{3}$$

ΔE_d represents the apparent activation energy of diffusion; B_{dT} 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. $K_0^{0\beta}$ and $D_0^{0\beta}$ are constants independent of temperature but replying on the property of the material; v_m is a coefficient related to the density of reactant and product; R_0 is the radius of the particle. 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_{dT} will be constant as the oxygen partial pressure and the particle radius are fixed.

According to Eq. (2), two parameters, i.e., ΔE_d and B_{dT} should be extracted to describe the oxidation behavior, which could be fitted from the experimental data by regression method. Therefore, the oxidation kinetics formula can be described as follows:

$P_{O_2} = 1.3\times10^{-3}$ MPa (675–737 K)

$$\xi = 1-\left[1-86.07\exp\left(-\frac{7679.82}{T}\right)\sqrt{t}\right]^3 \tag{4}$$

Similarly, the isothermal oxidation behavior of ZrC powder at the oxygen pressure of 2.6×10^{-3} and 7.9×10^{-3} MPa, respectively can also be deduced. Because the oxidation mechanism changes at higher temperature, i.e., 743 K, thus the oxidation behavior should be treated, respectively. The equations are following:

$P_{O_2} = 2.6\times10^{-3}$ MPa

(a) 663–743 K

$$\xi = 1-\left[1-102.6\exp\left(-\frac{7679.82}{T}\right)\sqrt{t}\right]^3 \tag{5}$$

(b) 758–803 K

$$\xi = 1-\left[1-2582.0\exp\left(-\frac{9953.1}{T}\right)\sqrt{t}\right]^3 \tag{6}$$

$P_{O_2} = 7.9\times10^{-3}$ MPa

(a) 652–743 K

$$\xi = 1-\left[1-106.6\exp\left(-\frac{7679.82}{T}\right)\sqrt{t}\right]^3 \tag{7}$$

(b) 753–800 K

$$\xi = 1-\left[1-3162.3\exp\left(-\frac{9953.1}{T}\right)\sqrt{t}\right]^3 \tag{8}$$

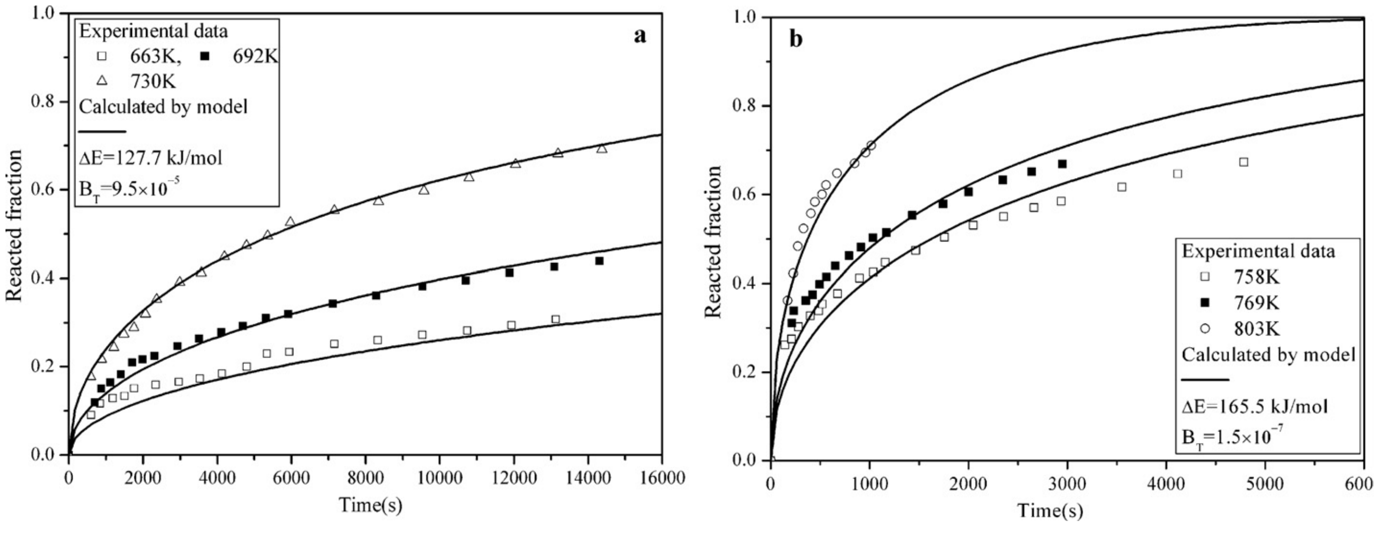

Fig. 4. A comparison of plots from Chou model and experimental data for isothermal oxidation of ZrC powder at an oxygen pressure of 2.6×10^{-3} MPa (a) 663–730 K and (b) 758–803 K.

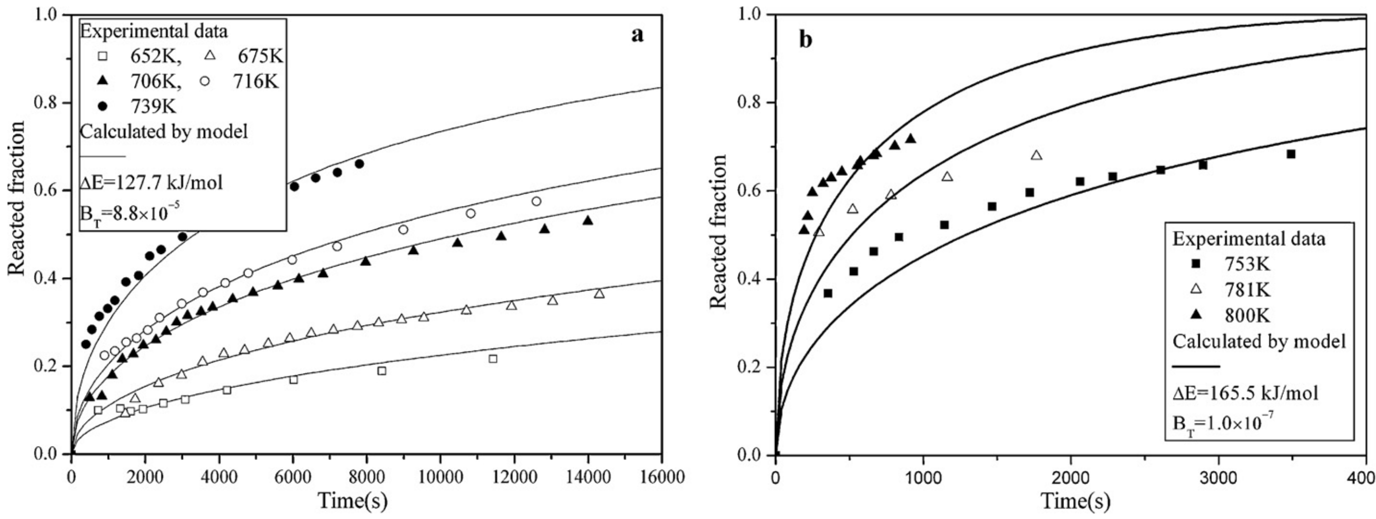

Fig. 5. A comparison of plots from Chou model and experimental data for isothermal oxidation of ZrC powder at an oxygen pressure of 7.9×10^{-3} MPa (a) 652–739 K and (b) 753–800 K.

The curves obtained from the above equations are also shown in the figures for comparison (as shown in Figs. 1a, 4a and b and 5a and b, respectively) and got a good agreement.

Shimada and Ishii [7] also investigated the oxygen pressure on oxidation of ZrC powder under both non-isothermal and isothermal conditions. Here the following equations are employed to treat the oxidation behavior, i.e.,

Isothermal oxidation:

$$\xi = 1 - \left(1 - \sqrt{\frac{(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}})t}{B_p}}\right)^3 \tag{9}$$

where

$$B_p = \frac{1}{(2K_0^{0\beta}D_0^{0\beta}/\upsilon_m)(\exp(-\Delta E_d/RT)/R_0^2)} \tag{10}$$

Non-isothermal oxidation:

$$\xi = 1 - \left(1 - \sqrt{\frac{(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}})\exp(-\Delta E_d/RT)}{B_{cp}}\frac{T - T_0}{\eta}}\right)^3 \tag{11}$$

where $B_{cp} = 1/(2K_0^{0\beta}/\upsilon_m D_0^{0\beta}/R_0^2)$ and η is temperature-increasing rate.

According to Eq. (11), the oxidation fraction of ZrC powder as a function of oxygen pressure and heating rate under non-isothermal condition is as follows:

$$\xi = 1 - \left[1 - 5345.2\exp\left(-\frac{9766.7}{T}\right)\sqrt{(T - 298)(\sqrt{P_{O_2}} - 0.0241)}\right]^3 \tag{12}$$

To compare with the experimental data, the results calculated at the oxygen pressure of 1.58×10^{-2} and 3.95×10^{-2} MPa are listed in Fig. 2a. The coincidence of the theoretical calculation results with the experimental data indicates that this theory is reasonable.

The effect of oxygen pressure on oxidation under isothermal condition can also be quantitatively discussed using Eq. (9). The experimental oxidation data at 753 K with the oxygen pressure of 1.3×10^{-3} and 7.9×10^{-3} MPa were used to testify Eq. (9) and the result showed that a good agreement was obtained (Fig. 2b). The formula is as follows:

$$\xi = 1 - \left[1 - 0.019\sqrt{(\sqrt{P_{O_2}} - 0.00132)t}\right]^3 \tag{13}$$

3.2.2. Oxidation kinetics of ZrC pellet

In view of the oxidation of ZrC pellet, its oxidation was controlled by chemical reaction [11]. Chou's model has also developed a series of formulae to deal with this condition as following:

$$\xi = \frac{1}{\Theta_T}\exp\left(-\frac{\Delta E_r}{RT}\right)t \tag{14}$$

where

$$\Theta_T = \frac{\upsilon_m L_0}{k_0(\sqrt{p_{O_2}} - \sqrt{p_{O_2}^{eq}})} \tag{15}$$

and ΔE_r represents the apparent activation energy of chemical reaction, $P_{O_2}^{eq}$ is oxygen partial pressure equilibrium with oxide, k_0 is a temperature-independent constant; υ_m is a coefficient related to the density of reactant and product, L_0 is the original thickness of the pellet. If all these parameters are known, of course, one can find the relation between reacted fractions ξ with time t. In some particular cases, one can combine part of these parameters to construct an auxiliary function like Θ_T (see Eq. (15)) that can be found through curve fitting.

Eq. (14) is employed to deal with the oxidation behavior of ZrC pellet and the isothermal oxidation equation is given as follows:

$$\frac{\Delta m}{A} = 0.379\exp\left(-\frac{9965.12}{T}\right)t \tag{16}$$

Based on the above formulae, a set of theoretical oxidation curves for ZrC pellet is also plotted in Fig. 3 for comparison. A fair agreement has been gotten and the corresponding activation energy is 82.9 kJ/mol.

3.2.3. Comparison with previous oxidation studies of ZrC

The experimental data offered by Shimada and Ishii [7] and Kuriakose et al. [11] showed that the oxidation mechanism of ZrC powder seems not a simple one. The effects of temperature and oxygen pressure on the oxidation behavior of ZrC were evident.

As mentioned above, the oxidation reaction of ZrC is a kind of complicated heterogenous reaction. Most researchers studied the

Table 1
Comparison of the calculation error from the model used in the literature and the new model.

Data	Δ (average relative error)	
	Calculated from the models used in the literature (%)	Calculated from Chou model (%)
Oxidation of ZrC offered by Shimada and Ishii [7]		
Oxidized with the oxygen pressure of 1.3×10^{-3} MPa	13.9	6.7
Oxidized with the oxygen pressure of 2.6×10^{-3} MPa		
663–743 K	15.8	8.1
758–803 K	22.9	7.6
Oxidized with the oxygen pressure of 7.9×10^{-3} MPa		
652–743 K	12.5	7.3
753–800 K	24.0	10.7
Oxidation of ZrC pellet offered by Kuriakose and Margrave [11]	9.5	7.2

oxidation kinetics of ZrC materials using the linear rate law or Jander's equation. The major difference between Chou's model and the models used in the literatures is that, firstly, Chou's model can express the relation between reacted fraction and temperature, oxygen partial pressure and many other variables explicitly. Secondly, Chou's model has revealed the physical meaning of the parameter "k" of the models used in the literature, which can be expressed as a function of temperature T, particle size R_0, oxygen pressure P_{O_2}, etc. All these parameters appearing in Chou's model have clear physical meaning because the model has been derived based on a real physical picture without vagueness assumption. Therefore, it is impossible to assign an arbitrary value to them if that does not meet the requirement of physical meaning. Then from the view of mathematical treatment, Chou's model is much better than the models used in the literatures in extracting the activation energy because it only needs to perform regression just once. Therefore, the calculated error from Chou's model should be smaller. The calculated error from the new model and the model used in the literatures can be obtained by the following equation:

$$\Delta = \frac{1}{N}\sum_{i=1}^{N}\frac{|(\chi_i)_{\text{mea}} - (\chi_i)_{\text{cal}}|}{|(\chi_i)_{\text{mea}}|} \times 100\% \qquad (17)$$

where Δ is the average relative error, $(\chi_i)_{\text{mea}}$ is experimental data, $(\chi_i)_{\text{cal}}$ is the value calculated from the model and N is the number of experimental points. Table 1 shows the calculation results from the model used in the literatures and the new model presented here in treating the oxidation of ZrC materials from which it can be seen that the error calculated by Chou's model is smaller than that calculated by the model used in the literatures. Therefore it makes us feel more comfortable to add some predicted lines within the same reaction mechanism that might be interested in application.

4. Conclusion

The effects of temperature and oxygen pressure on oxidation behavior of ZrC materials have been studied from theoretical aspect based on the experimental data. The experimental results showed that the effect of temperature and oxygen pressure on the oxidation behavior of ZrC was evident.

Two sets of experimental data were used in this analysis: Shimada et al. and Kuriakose et al. For Shimada's data, although the oxidation kinetics was diffusion controlled during the whole experimental temperature range, the activation energy was different because of the phase transition. The oxidation behavior should be described by different equations, i.e., Eqs. (4)–(8).

In view of the effect of oxygen pressure on oxidation behavior under non-isothermal and isothermal conditions, we also deduced two quantitative formulae, Eqs. (12) and (13) and got a good agreement with experimental data.

Concerning the oxidation of ZrC pellet investigated by Kuriakose et al., the oxidation behavior followed a linear rate law and the oxidation kinetics can be expressed as follows:

$$\frac{\Delta m}{A} = 0.379 \exp\left(-\frac{9965.12}{T}\right) t$$

Based on the error analysis, it is clear that Chou's model can give more accurate results than that offered by the traditional models used in the literature.

Acknowledgements

The authors sincerely thank the support from Key Lab. of Ecologic & Recycle Metallurgy, Ministry of Education, University of Science and Technology Beijing. The authors also would like to express their thanks to the National Natural Science Foundation of China (Nos. 50974084 and 50874013).

References

[1] A. Bellucci, D. Gozzi, T. Kimura, T. Noda, S. Otani, Surf. Coat. Technol. 197 (2005) 294–302.
[2] D. Ferro, S.M. Barinov, J.V. Rau, A. Latini, R. Scandurra, B. Brunetti, Surf. Coat. Technol. 200 (2006) 4701–4707.
[3] Y. Ozaki, R.H. Zee, Mater. Sci. Eng. A 202 (1995) 134–141.
[4] C. Kral, W. Lengauer, D. Rafaja, P. Ettmayer, J. Alloys Compd. 265 (1998) 215–233.
[5] S. Shimada, M. Nishisako, M. Inagaki, K. Yamamoto, J. Am. Ceram. Soc. 78 (1995) 41–48.
[6] R.W. Bartlett, M.E. Wadsworth, I.B. Cutler, AIME Trans. Metall. Soc. 227 (1963) 467–472.
[7] S. Shimada, T. Ishii, J. Am. Ceram. Soc. 73 (1990) 2804–2808.
[8] G.A. Rama Rao, V. Venugopal, J. Alloys Compd. 206 (1994) 237–242.
[9] S. Shimada, Solid State Ionics 149 (2002) 319–326.
[10] S. Shimada, M. Inagaki, M. Suzuki, J. Mater. Res. 11 (1996) 2594–2597.
[11] A.K. Kuriakose, J.L. Margrave, J. Electrochem. Soc. 111 (1964) 827–831.
[12] S. Shimada, Solid State Ionics 101–103 (1997) 749–753.
[13] S. Shimada, Solid State Ionics 141–142 (2001) 99–104.
[14] K.C. Chou, X.M. Hou, J. Am. Ceram. Soc. 92 (2009) 585–594.
[15] K.C. Chou, J. Am. Ceram. Soc. 89 (2006) 1568–1576.
[16] X.M. Hou, K.C. Chou, X.J. Hu, H.L. Zhao, J. Alloys Compd. 459 (2008) 123–129.