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Quantitative investigation of the oxidation kinetics of magnesia/carbon composite

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The oxidation kinetics of magnesia/carbon (MgO/C) composite has been comprehensively investigated from both experimental and theoretical aspects based on current literatures, from which the shortcoming of theory has been discussed. A new kinetic model was developed to deal with the oxidation of MgO/C composite quantitatively. Effect of temperature and carbon content on the oxidation rate was especially discussed. Incorporation of the experimental data into the new model indicated that our new model could fit the experimental data very well. The kinetic parameter obtained from the new model was also compared with experimental values in literature. Besides the new model can perform a simple calculation, it can also reasonably predict the oxidation behavior based on limited experimental data.
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1. Introduction

Presence of carbon in MgO/C composite results in high slag corrosion resistance, thermal shock endurance, wettability reduction and diminished thermal expansion.[1)] Therefore, MgO/C materials have been widely used in the steelmaking industry. This leads to a demand for further improvements in their performance as a result of severe and diverse service conditions encountered in practice. Since oxidation of carbon in these materials produces a porous structure and causes the degradation of mechanical properties in service, one of the most important tasks to investigate the oxidation kinetics of MgO/C composite while used in high temperature and oxidizing conditions.

It has been confirmed that oxidation in MgO/C materials mainly takes place through two categories, i.e. direct and indirect mechanisms (Eqs. (1) and (2)). Although both mechanisms are important, but direct oxidation is considered as the main oxidation mechanism at low temperature up to 1673 K.[2)] Therefore, direct oxidation is the basis of comparison of the oxidation resistance between carbon containing materials.

(a) Direct oxidation of carbon with oxygen

$$2C(s) + O_2\,(g) = 2CO\,(g) \tag{1}$$

(b) Indirect oxidation of carbon with MgO particles

$$MgO(s) + C(s) = Mg\,(g) + CO\,(g) \tag{2}$$

The oxidation behavior of carbon in MgO/C materials has been investigated intensively since 1960s.[2)–11)] Komarek et al.,[5)] Carniglia[6)] and Tabata et al.[7)] have evaluated the overall oxidation rate of MgO/C materials at low oxygen partial pressures by measuring the mass change. Li et al.[8)] have used the atmospheric analysis method to study the oxidation kinetics in the range of 1273–1673 K in air. These studies, however, have been confined to temperatures above 1073 K. Sadrnezhaad et al.[9)] extended the experimental temperature range to 873–1523 K. The effect of temperature and grain size distribution on the oxidation rate was evaluated by a mathematical model. Three activation energies have been calculated: (a) 68 kJ·mol^{-1} for chemical adsorption of gas on the surface of the graphite flakes, (b) 22 kJ·mol^{-1} for pore diffusion of the gases within the decarburized layer, and (c) 140 kJ·mol^{-1} for internal diffusion of the reactants towards the active reaction sites.

In view of oxidation kinetics of MgO/C materials, many authors have previously developed mathematical models, such as, the well known shrinking core model (SCM). In this model, three mechanisms mainly control the reaction rate during oxidation, i.e., diffusion in gas phase; diffusion in oxide layer and chemical reaction. The total reaction time can be expressed by following equation:[11)]

$$t = \tau_g X + \tau_d\left[X + (1-X)\ln(1-X)\right] + \tau_{ch}\left[1-(1-X)^{\frac{1}{2}}\right] \tag{3}$$

Where τ_g, τ_d and τ_{ch} are time constants for gas layer, diffusion and chemical reaction mechanism, respectively. X is the fractional weight loss.

Since the diffusion mechanism has the most significant effect on the oxidation rate of MgO/C material,[11)] therefore Eq. (3) can be simplified as following:

$$t = \tau_d^*\left[X + (1-X)\ln(1-X)\right] \tag{4}$$

Where τ_d^* is the time constant when it is assumed that only diffusion mechanism is present. Most researchers have successfully treated oxidation of carbon-containing materials by employing Eqs. (3) and (4). However, since these models involve many complicated mathematical treatment, thus they are not convenient to use in practice.

Recently, Nemati and Moetakef[10)] have investigated oxidation of MgO/C composite using a kind of computational model, i.e., artificial neural network approach (ANN). The results showed

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that the kinetic parameters such as effective diffusion coefficient and diffusion activation energy of oxidation calculated from the model were in good agreement with the experimental data. However, this kind of calculation needs some special software. Besides this one, no other model had been reported to predict the oxidation behavior in literature.

From the point of practical application, it is desired to have a simple and physical meaningful explicit analytic expression. Therefore the model is convenient for use while can still give a good prediction under an acceptable simplified assumption. In the present work, a simple formula expressing the relationship between the reacted fraction of oxidation and other variables was developed. Then they were testified by the experimental data from the literature. Based on this, the obtained results were discussed from the quantitative point. Meanwhile, the model was also compared with the results reported in literature.

2. Theoretical aspects

As mentioned above, in most cases, the oxidation behavior of MgO/C is direct oxidation.[2] It is a complicated heterogeneous reaction. The following potential steps are considered to influence the oxidation rate:

(a) External mass transport of O_2 from the air flow bulk to the outer face of the oxidizing sample;

(b) Diffusion of O_2 through the pores in the decarbonized layer to reach the reaction interface;

(c) Chemical reaction between carbon and O_2 at the reaction interface to form CO;

(d) Diffusion of CO through the decarbonized layer to the outer face;

(e) Mass transfer of CO from the outer face into the surrounding atmosphere.

In the most cases, the oxygen diffusion through the oxide layer (b) will be the rate-controlling step. Therefore it is meaningful to study the oxygen diffusion as a controlling step.

MgO/C material has usually been manufactured in a certain shape for application. For convenience, the pellet model has been used in this paper to study the oxidation of MgO/C. The schematic model is shown in **Fig. 1**, in which α represents MgO/C material with original thickness of L_0, β is the oxide zone with thickness of x. Then the residual thickness of MgO/C material at time t will be L_0–x.

Based on the above idea and the Fick diffusion law, the formula describing the relation between the oxidation fraction ξ of MgO/C pellet and time t can be deduced. And this model has been proved that it worked very well in dealing with oxidation of Si–Al–O–N materials, hydrogen storage and nano-size materials[12)–15)] since they are related to the same oxidation mechanism, i.e., diffusion controlled during gas-solid reaction. The expression of the formula is as following:

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

$$\Theta_T = \frac{v_m L_0^2}{2k_0^{o\beta} D_0^{o\beta}\left(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}\right)} \tag{6}$$

where ΔE represents the apparent activation energy of oxidation. 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 the oxide, the value of which can be calculated from the reaction:. $\frac{1}{2}O_2 = [O]^{\beta}$. $K_0^{o\beta}$ and $D_0^{o\beta}$ are the reaction equilibrium constant coefficient and the diffusion coefficient, respectively, that relying on the properties of the particle material; v_m is a coefficient that is related to the density of reactant and product. L_0 is the thickness of the pellet. As seen from Eq. (6), if the value of $P_{O_2}^{eq}$ is very small or the temperature coefficient of $P_{O_2}^{eq}$ can be neglected, Θ_T would be a constant and its value depends on the oxygen partial pressure and the thickness L_0 only.

Equation (5) is the general formula expressing the reacted fraction ξ as the function of time t, temperature T and many other related parameters. It might be seen from Eq. (5) that the higher the temperature T, the larger the reacted fraction ξ. It is in accordance with our common sense, i.e., the higher the temperature, the faster the reaction rate. The advantage of this treatment is that, one might find an explicit analytic solution just as mentioned above. The accuracy of the model can be judged from the application to the practical examples in the latter sections.

3. Application of the new model to the practical system

Experimental data for evaluating the validity of our new model were obtained from Nemati and Moetakef's[10)] as well as Hashemi et al.'s[11)] recent work. Isothermal oxidation tests were carried out at various temperatures using thermogravimetery (TG) and the results were plotted as percent of weight loss versus time. As shown in **Figs. 2**, **3** and **4**, at a given oxidation time, the weight loss increased when carbon content increased. At all the oxidation temperature, the reaction rate increased quickly initially. While it decreased at longer time intervals, indicating that a diffusion step could be of importance in determining the rate of the reaction.[2)–11)]

As to the oxidation behavior of MgO/C material with different

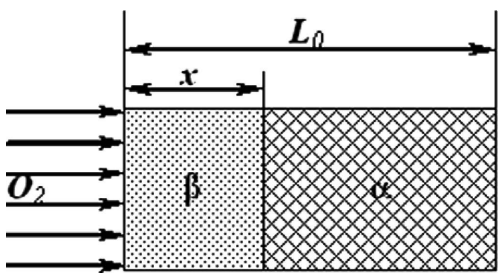

Fig. 1. Schematic plot of oxidation of a pellet under oxygen environment.

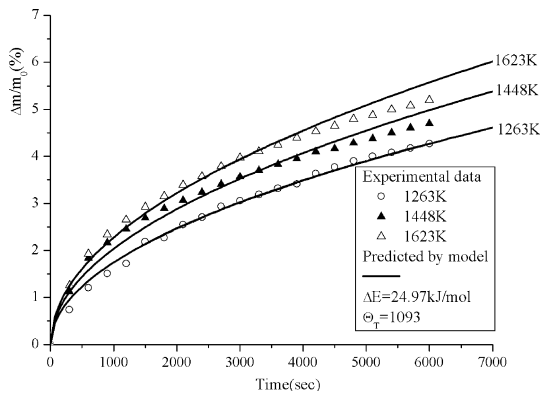

Fig. 2. Isothermal oxidation curves of MgO/C material with carbon content of 4.5 mass%.

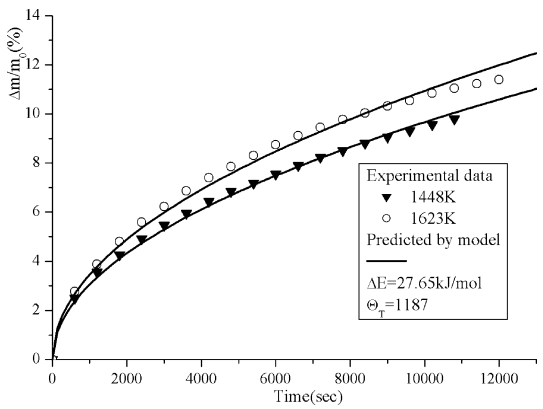

Fig. 3. Isothermal oxidation curves of MgO/C material with carbon content of 9 mass%.

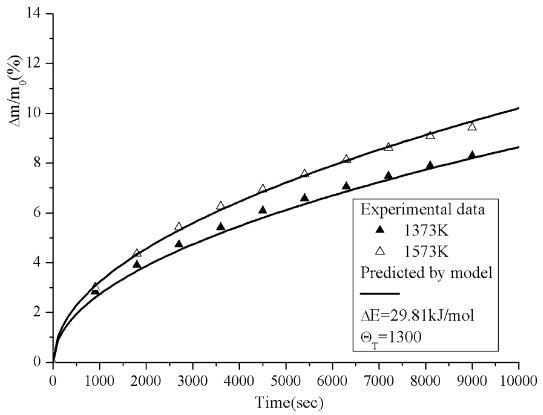

Fig. 4. Isothermal oxidation curves of MgO/C material with carbon content of 10 mass%.

carbon content as shown in Figs. 2, 3 and 4,[10),11)] Eq. (5) will be verified. Since the experimental data is the relationship between the dimensionless mass change, $\frac{\Delta m}{m_0}$ vs. time t, some conversions are needed before using Eq. (5). The relation between ξ and $\frac{\Delta m}{m_0}$ is

$$\xi = \frac{\frac{\Delta m}{m_0}}{\frac{\Delta m_{\max}}{m_0}} \tag{7}$$

Where m_0 represents the original sample mass and $\Delta m_{\max}$ is the theoretical maximum weight loss after a complete oxidation. In the experiments, resin was used as the carbon binder. Since it contained some amount carbon (1.5 mass%),[10),11)] the maximum weight loss of the sample included both the loss of carbon and resin.

According to Eq. (5), there are two parameters, i.e., ΔE and Θ_T, to be fixed to describe the oxidation behavior of MgO/C material. By fitting the experimental data, the values of ΔE and Θ_T for MgO/C material with carbon content of 4.5 mass% are 24.97 kJ/mol and 1093 by regression method. Substituting these data into Eq. (5), one obtains

$$\frac{\Delta m}{m_0} = 0.181\exp\left(\frac{-1501.4}{T}\right)\sqrt{t} \tag{8}$$

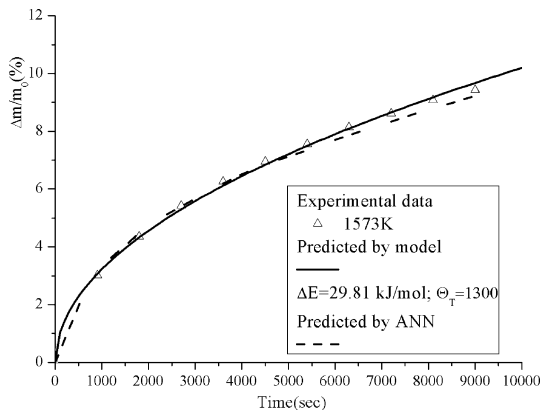

Fig. 5. Comparison of experimental data with the new model and ANN.

The theoretical curves of $\frac{\Delta m}{m_0}$ vs. t are also plotted in Fig. 2 (black line) for comparison. It can be seen that the theoretical results are in good agreement with the experimental data.

Similarly, the formulae for the oxidation of MgO/C material with carbon content of 9 and 10 mass% are as follows:
MgO/C material with carbon content of 9 mass%

$$\frac{\Delta m}{m_0} = 0.315\exp\left(\frac{-1742.7}{T}\right)\sqrt{t} \tag{9}$$

MgO/C material with carbon content of 10 mass%

$$\frac{\Delta m}{m_0} = 0.323\exp\left(\frac{-1813.2}{T}\right)\sqrt{t} \tag{10}$$

Based on the above equations, the theoretical curves of $\frac{\Delta m}{m_0}$ vs. t are also shown in Figs. 3 and 4 (black line). It can be seen that the theoretical results are in good agreement with the experimental data, demonstrating the validity of our new model.

4. Discussion

From above applications of the new model, it can be concluded that the model used in this paper can also quantitatively explain the effect of such factors as temperature and time on the oxidation behavior of MgO/C material because their oxidation mechanism is similar. Therefore a good agreement between the curves calculated from the model and the experimental data has been reached. This will greatly help us to consider the influence factors in a more comprehensive way and direct us to improve the property of the carbon-containing composite in practice.

Besides describing the oxidation behavior reasonably, the new model can also predict the oxidation behavior within the same oxidation mechanism using limited experimental data. The black line in **Fig. 5** is obtained from our new model. The dash line is predicted by ANN, which was used by Nemati and Moetakef.[10)] They are both in good agreement with the experimental data, indicating that our model can also reasonably predict the oxidation behavior.

In view of the reliability of the parameters obtained from the new model, the value of ΔE calculated from our new model is in the range of 24–30 kJ·mol^{-1}, which is comparable with the results reported in literature. For example, Sadrnezhaad et al.[9)] reported the value of ΔE to be 22 kJ·mol^{-1} for oxidation of MgO/

C (14.3 mass%) bricks in the temperature range of 1073–1523 K. In Nemati and Moetakef's work,[10] the value calculated by ANN is in the range of 29–37 kJ·mol^{-1}. The overall analysis shows that our new model is satisfactory.

Please note that, there exists some deviation between the experimental data and the calculated lines, especially at longer time intervals (as shown in Figs. 1, 2 and 3). This is possibly caused by the simplification treatment during the deduction of our model, i.e., we simplify the effect of the sample shape on oxidation behavior. This would cause some deviation between the experimental data and the calculated result from our model. A more comprehensive treatment will be done and the results will be reported in the future.

5. Conclusions

A new kinetics model was applied to calculate the oxidation behavior of MgO/C. The effect of temperature and carbon content on oxidation has been quantitatively discussed. The method was then applied to the systems of MgO/C with different carbon content. Calculated result agreed well with experimental data.

Besides describing the oxidation behavior reasonably, the new model can also predict the oxidation behavior within the same oxidation mechanism as well as ANN used in literature. Moreover, compared with the oxidation kinetics of MgO/C material reported in literature, our new model is not only easy to use and to perform a theoretical analysis and discussion, but also can give a good calculated result. Therefore, it will give us a guideline for reasonable application of carbon-containing materials in practice.

Appendix

Nomenclature

α : original MgO/C material phase
β : oxidized part of MgO/C material
ΔE : apparent activation energy of oxidation
ξ : reacted fraction of oxidation
$D_0^{o\beta}$: constant independent of temperature but relying on the material
$K_0^{o\beta}$: a constant independent of temperature but relying on the material
v_m : coefficient depending on substance and reaction
P_{O_2}: partial pressure of oxygen in gas phase
$P_{O_2}^{eq}$: oxygen partial pressure in equilibrium with oxide
L_0 : thickness of the original MgO/C material
x : thickness of the oxidized layer
R : gas constant
t : time in second
T : absolute temperature with K

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