ELSEVIER

Thermochimica Acta 390 (2002) 145–151

thermochimica acta

www.elsevier.com/locate/tca

Kinetics of reduction of magnesia with carbon

Li Rongti[a], Pan Wei[a,*], Masamichi Sano[b], Jianqiang Li[a]

[a]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China
[b]Department of Materials Process Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi-ken 464-8603, Japan

Received 26 November 2001; received in revised form 14 February 2002; accepted 20 February 2002

Abstract

Reduction kinetics of magnesia with carbon powder was studied using the thermal gravimetric technic in the temperature range of 1743–1883 K. The reduction ratio was determined as a function of time. The effects of compact-forming pressure, composition, partial pressure of CO, sample height, and temperature on reduction ratio were investigated. Experimental results revealed that the gas diffusion including Mg vapor, CO and CO_2 through the porous medium was the rate-determining step of the overall reduction process. Activation energy of the gas diffusion was estimated to be about 30.59 kJ mol^{-1}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Reduction kinetics; Magnesia and carbon; Thermal gravimetric technic; Diffusion

1. Introduction

MgO–C refractories bricks are widely used in steel-making industry as basic oxygen furnace (BOF) linings because of their good resistance both to slag corrosion and to thermal stresses [1]. However, a serious problem is that the reaction between magnesia and carbon takes place, and the strength and service life decrease when it is used under the steel-making condition at about 1600 °C for a long time [2]. Until now, little research work dealing with the reduction kinetics of magnesia with carbon has been reported.

Recently, the magnesium produced by the reduction of MgO with carbon attracts many researchers' interest owing to its strong chemical affinity to those non-metallic elements, such as oxygen, sulfur, phosphorous, and nitrogen, which can be used in steel-making industry to obtain high quality steels [3–7]. In our research group, the investigation on deoxidation [8] and desulfurization [9] of molten iron was carried out by using a porous immersion tube, the inside of which was charged with MgO–C pellets. Magnesia in the pellets was reduced by carbon to produce magnesium vapor, which was injected directly into the melt. It was found that the deoxidation and desulfurization rates and efficiency depend on the reduction rate of magnesia with carbon. Therefore, the kinetics of the reduction of magnesia with carbon is one key point in controlling the process of desulfurization and finding more efficient ways to improve the desulfurization rate and efficiency. Although, numerous studies have been conducted on carbothermic reduction of metal oxide [10–15], the mechanism of reduction of magnesia with carbon is not fully understood. The complexity of the

---

[*] Corresponding author. Tel.: +86-10-6277-2858; fax: +86-10-6277-1160.
E-mail address: panw@mail.tsinghua.edu.cn (P. Wei).

PII: S0040-6031(02)00128-4

reduction process makes it difficult to gain a clear insight of the various steps involved in the overall reduction reaction.

The purpose of the present study was to gain more understanding of the reduction kinetics of magnesia with carbon. Effects of compact-forming pressure, sample composition, CO partial pressure, sample height, and temperature on the reduction ratio would also be discussed.

2. Experimental

2.1. Specimen preparation

The magnesia powder (0.4 μm in average diameter, purity higher than 99.99%), graphite (fixed carbon 99.12%, ash 0.15%, water 0.4%, average diameter 3.9 μm, purity higher than 99.5%) and charcoal powder (44 μm in average diameter, purity higher than 99.5%) were used in this study as starting materials. These powders were supplied by the High Purity Chemical Institute of Japan.

Magnesia powder and graphite were mixed at molar ratios of 1:1 and 1:2, and magnesia powder and charcoal were mixed at a molar ratio of 1:1. The mixture was shaped into a 5 mm diameter pellet under sample-forming pressures of 100 and 150 MPa by using a cold isostatic press for 1 h. The size of the graphite crucible used in this study was 6.4 mm o.d., 5.8 mm i.d., and the height of the graphite crucible ranged from 4.2 to 7.3 mm.

2.2. Apparatus and experimental procedure

The reduction was carried out using a thermo-balance (NS95, Sinku-riko Incorporation of Japan), which was connected to a data acquisition and analysis system. The sample was put into the graphite crucible, which was placed on the top of the thermo-couple. A layer of graphite (about 3 mg) was put on the top of the sample in order to minimize the reoxidation of magnesium. The inert atmosphere was maintained by blowing argon at a flow rate of $1.67 \times 10^{-6}\ \mathrm{m^3\,s^{-1}}$. The air in the furnace was substituted with argon for 30 min, and then the sample was heated from room temperature to 773 K and kept at this temperature for 10 min to remove the absorbed gases and water from the sample. Then the temperature was raised to the experimental temperature at the heating rate of $50\ \mathrm{K\,min^{-1}}$ and this temperature was kept for 1 h. To correct the effect of the graphite crucible on the mass loss of the sample, blank experiments were carried out using the blank graphite crucible. The calibration runs were carried out under the same conditions as those for the samples.

3. Results and discussion

Based on our previous study, the interaction between magnesia and carbon can be represented by the following reactions:

Direct reduction:

$$\mathrm{MgO_{(s)} + C_{(s)} \rightarrow Mg_{(g)} + CO_{(g)}} \tag{1}$$

Indirect reduction:

$$\mathrm{MgO_{(g)} + CO_{(g)} \rightarrow Mg_{(g)} + CO_{2(g)}} \tag{2}$$

$$\mathrm{CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}} \tag{3}$$

The kinetics of a solid–solid reaction is influenced by many factors, such as sample composition, particle size and distribution, reaction products, compact-forming pressure, and heating rate. During the thermo-gravimetric reduction experiment, the mass loss of the sample is measured as a function of time. The reduction ratio α at a given instance is defined as:

$$\alpha = \frac{\Delta m}{m_0} \tag{4}$$

where m_0 and Δm represents the initial mass of magnesium in the sample and the magnesium mass change at a given instance, respectively.

3.1. Effect of compact-forming pressure

The effect of compact-forming pressure on the reduction ratio at the temperature 1848 K holding for 1 h is given in Fig. 1. It shows that the rate of reduction decreases significantly with the increment of compact-forming pressure. It is known that the contacting condition between magnesia and carbon particles would be improved with an increase of the sample compact-forming pressure. In our previous study on the reduction of magnesia with carbon under

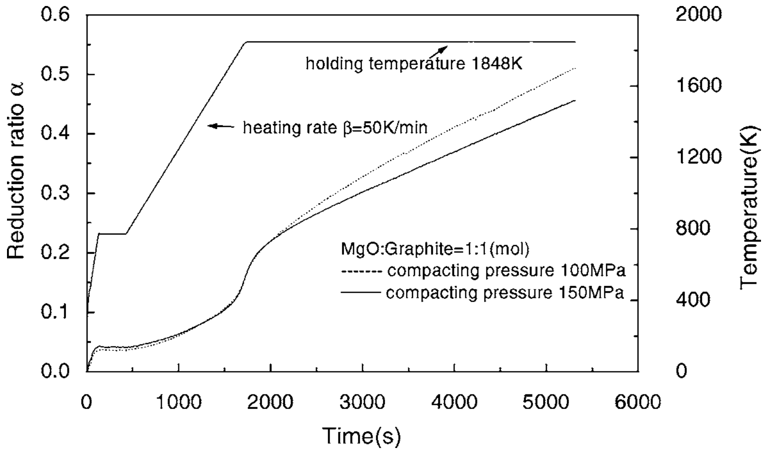

Fig. 1. Effect of sample-forming pressure on the reduction ratio at the temperature 1884 K holding for 1 h.

non-isothermal condition, the reaction rates are sensitive to the compact-forming pressure and the reduction rates increase with the increment of the contacting condition between particles. Therefore, the rate-determining step is changed at the present experimental condition. In this process, the possible rate-controlling step must be related to reactions between gas and solid or the gas diffusion including Mg vapor, CO and CO_2 through the porous media, because the path of gas diffusion becomes longer and more tortuous with the improvement of the contacting condition between magnesia and carbon particles, resulting in the decrease of the gas diffusion rate. The gas–solid surface reaction can usually be broken down into the following elementary steps:

(1) diffusion of the reactants to the surface;
(2) adsorption of reactants at the surface;
(3) chemical reactions on the surface;
(4) desorption of products from the surface;
(5) diffusion of products away from the surface.

Although, neither the diffusion rate of reactants to the solid surface nor the diffusion rate of products away from the solid surface seems to be directly rate-determining, the decrease of the gas diffusion rate leads to the decrease of the overall reduction rate.

3.2. *Effect of sample composition*

Fig. 2 shows the effect of the sample composition on the reduction ratio. It seems that changing of the sample composition has no significant effect on the reduction rate at the temperature 1848 K holding for 1 h. It is worth noticing that the reduction rate is much affected by the sample composition before the temperature reaches 1848 K, and the rate of the reaction between magnesia and graphite is slower than that of the reaction between magnesia and charcoal. In our previous study, it was found that at the initial stage of the reduction under the non-isothermal condition, the solid boundary reaction is the rate-determining step and its reaction rate is sensitive to the sample composition. The reaction activity of charcoal is higher than that of graphite, so the reaction between magnesia and charcoal is faster than that between magnesia and graphite before the temperature reaches 1848 K. But at the temperature holding step, their reaction rates are becoming very close. The only explanation for this phenomenon is that the reaction rate is independent of the sample composition and the possible rate-determining step is the gas diffusion including Mg vapor, CO and CO_2 through the porous media.

3.3. *Effect of CO partial pressure*

The effect of CO partial pressure on the reduction ratio is shown in Fig. 3. It indicates that the CO partial pressure has no evident effect on the reduction rate at 1848 K holding for 1 h. However, before the temperature reaches 1848 K, the reduction rate increases with the increase of the CO partial pressure. This result is in

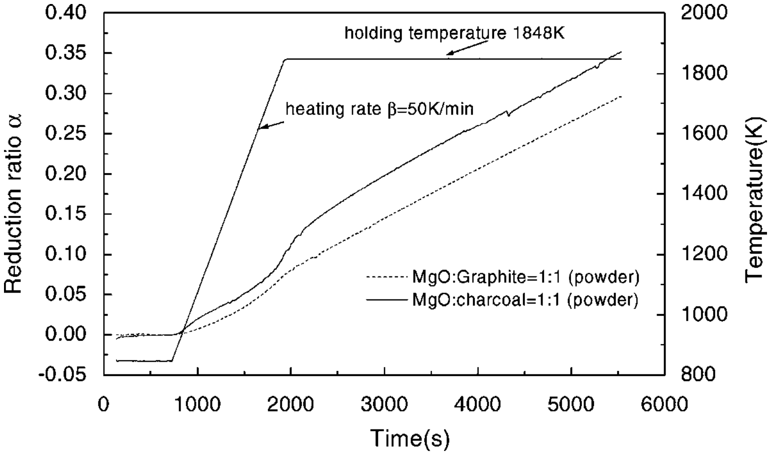

Fig. 2. Effect of composition on the reduction ratio at temperature 1884 K holding for 1 h.

a good agreement with our previous work. As we have stated, the possible rate-determining step is the gas diffusion including Mg vapor, CO and CO_2 through the porous media, therefore the effect of every possible factor on the gas diffusion coefficient must be taken into consideration. However, the effect of the CO partial pressure on the diffusion coefficient is so little that it can be neglected.

3.4. Effect of sample height

If the gas diffusion through the porous media is the rate-determining step, the reaction rate should be sensitive to the height of the sample. In order to prove this hypothesis, an experiment was designed by carrying out the reduction reaction at different sample heights. The schematic diagram of the experiment is shown in Fig. 4. Both the sample weight and sample height (δ) were changed (δ ranging from 0.5 to 3.5 mm) while h was kept constant (3.6 mm). Fig. 5 shows that the sample height has a significant effect on the reduction rate. When δ is in a range of 0.5 to 2.5 mm, the increase of the sample height reduces the reduction rate greatly. However, when δ is above 2.5 mm, the reduction rate is only changed slightly. The relation between the sample

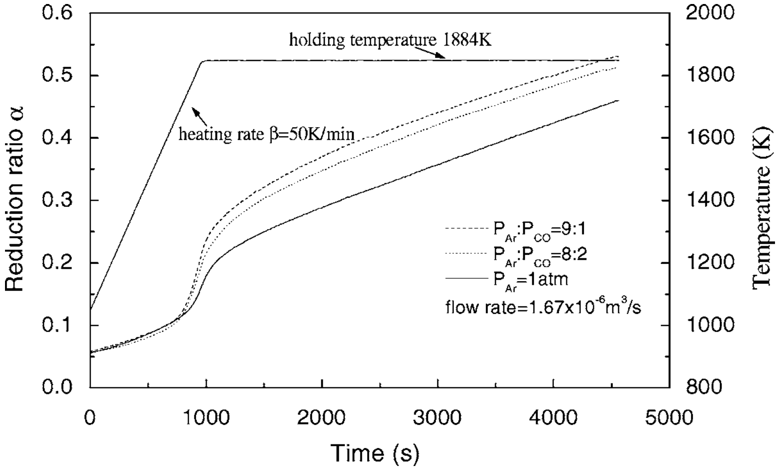

Fig. 3. Effect of pressure ratio of P_{Ar}/P_{CO} on the reduction ratio at 1848 K holding for 1 h.

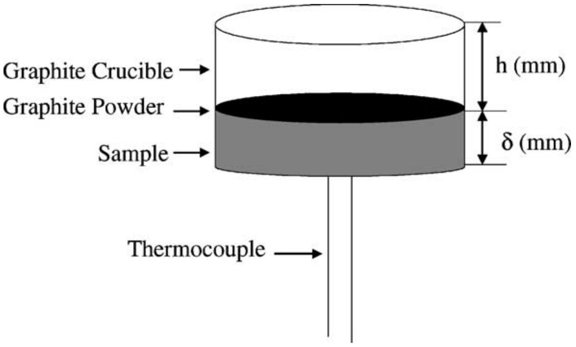

Fig. 4. The schematic diagram of the experiment.

height and the reduction rate can be expressed as following:

$$\frac{d\alpha}{dt} = (2.7 \times 10^{-5}) + (1.5 \times 10^{-4}) \exp(0.85 - 0.715\delta) \quad (5)$$

where δ (mm) is the sample height and $d\alpha/dt$ the reduction rate.

With the increment of the sample height, the total diffusion path of Mg, CO and CO_2 gases through the porous media is prolonged, so the molar flux of gases is decreased, resulting in the decrease of the reduction rate. This result is in a good agreement with the hypothesis that the gas diffusion through the porous media is the rate-determining step.

3.5. *Effect of temperature*

In order to investigate the influence of the reaction temperature on the reduction ratio, experiments were performed at 1743, 1773, 1813, 1848, and 1883 K, respectively. The results are shown in Fig. 6. It indicates that the reaction rate increases only slightly with the increase of temperature.In this experiment, the reduction rate is a constant. It can be expressed as:

$$\frac{d\alpha}{dt} = k \quad (6)$$

where $d\alpha/dt$ is the reaction rate and k the rate constant.

As the reaction rate is determined by the gas diffusion, the relationship between the reaction rate and the diffusion coefficient can be given as following:

$$\frac{d\alpha}{dt} = k = BD \quad (7)$$

where B is a constant and D the diffusion coefficient, whose relation with the temperature can be given by the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \quad (8)$$

where D_0 is the frequency factor and E the activation energy. Both D_0 and E are essentially constant over a wide temperature range.

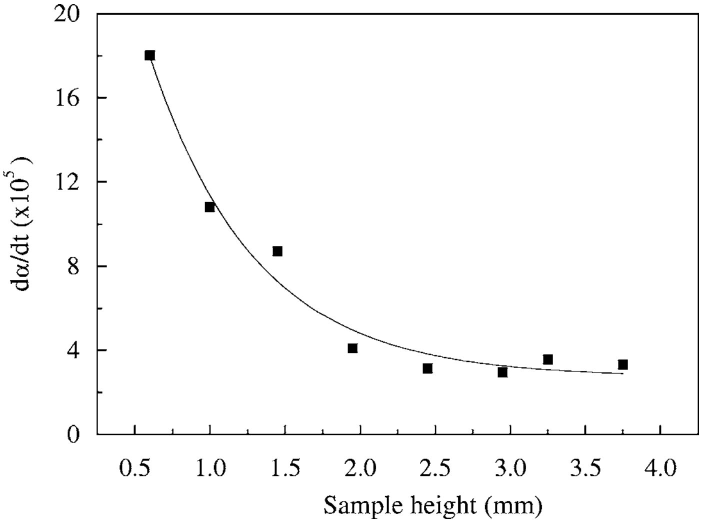

Fig. 5. Relationship between sample height and reduction rate at 1848 K holding for 1 h.

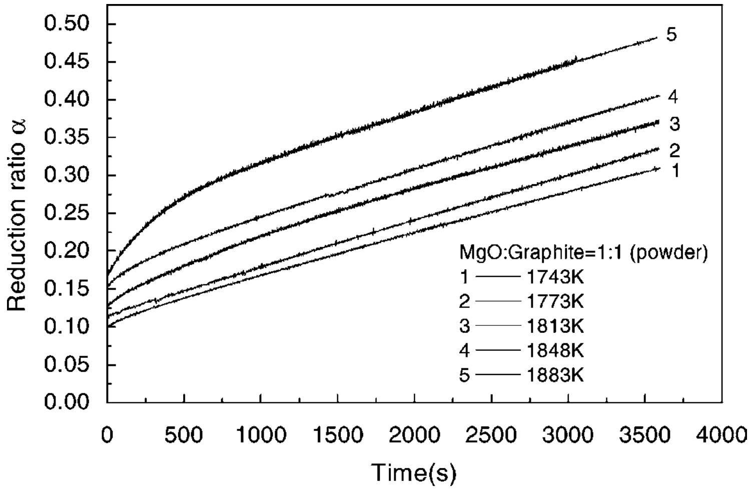

Fig. 6. Effect of the holding temperature on the reduction ratio.

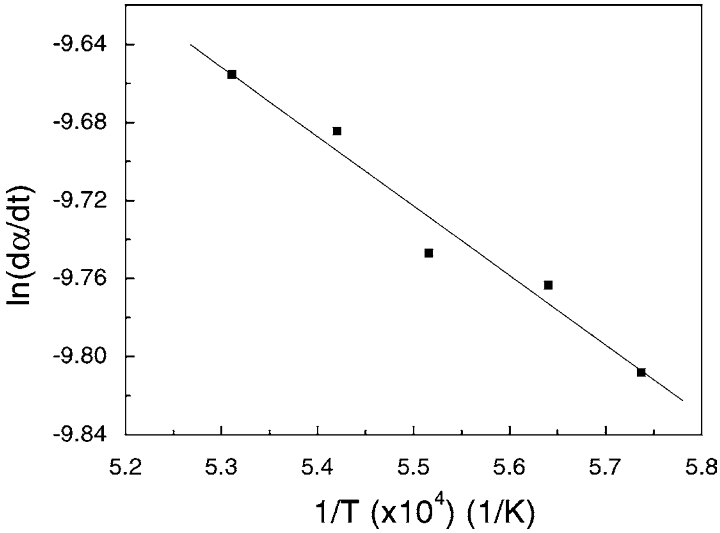

Fig. 7. Relation between reduction rate and temperature.

By substituting Eq. (8) into Eq. (7) and taking logarithms, the following equation can be obtained:

$$\ln\frac{d\alpha}{dt} = \ln BD_0 - \frac{E}{RT} \tag{9}$$

Eq. (9) indicates a linear relationship between ln(dα/dt) and 1/T. By plotting ln(dα/dt) versus 1/T (Fig. 7), the activation energy E is estimated to be 30.59 kJ mol^{-1}.

4. Conclusion

In the present work, reduction kinetics of mixtures of magnesia and carbon powder was investigated using the isothermal gravimetric technic in the temperature range of 1743–1883 K. It is found that the sample composition and CO partial pressure have no significant effect on the reduction rate, the reduction rate decreases with the increase of the compact-forming pressure, the reaction rate increases only slightly with the temperature, and the sample height has a strong effect on the reduction ratio. The gas diffusion (including Mg vapor, CO and CO_2) through the porous media is believed to be the rate-determining step in the overall reduction process.

References

[1] I. Peretz, B. Breany, Am. Ceram. Soc. Bull. 7 (1992) 1383.
[2] G.D. Picking, J.D. Batchelor, Am. Ceram. Soc. Bull. 50 (1971) 611.
[3] M. Ozawa, Y. Outsuka, R. Hori, R. Mori, The Report for Japan Society for the Promotion of Science, June, 1975.
[4] S. Yamaguchi, T. Uemura, H. Nashiwa, H. Sugita, Ironmaking Steelmaking 5 (1977) 276.
[5] W.H. Duquette, N.R. Griffing, T.W. Miller, Open Hearth Proc. 56 (1973) 79.
[6] W.G. Wilson, A. McLean, Desulfurization of Iron and Steel and Sulfide Shape Control, The Iron and Steel Society of AIME, 1980.
[7] P.J. Koros, R.G. Peirushka, R.G. Kerlin, Iron Steelmaker 4 (1977) 34.
[8] J. Yang, K. Okumura, M. Sano, in: Proceedings of the International Conference on Asia Steel, Vol. C, 2000, p. 80.
[9] J.Y. Shan, K. Okumura, M. Sano, in: Proceedings of the International Conference on Asia Steel, Vol. C, 2000, p. 94.
[10] D.J. Min, J.W. Han, W.S. Chung, Metall. Metal Trans. B 30 (1999) 215.
[11] M.A. Naiyang, N.A. Warner, Can. Metall. Quart. 38 (1999) 165.
[12] N.S. Sundar Murti, V. Seshadri, Trans. ISIJ 22 (1982) 926.
[13] Y.K. Rao, Chem. Eng. Sci. 29 (1974) 1435.
[14] Y.K. Rao, Metall. Trans. 2 (1971) 1439.
[15] L. Hong, K. Okumura, M. Sano, Metall. Metal Trans. B 30 (1999) 1003.