

# Smelting reduction of MgO in molten slag by liquid ferrosilicon

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Submitted: 25 May 2015; Accepted: 16 January 2016; Available On-line: 21 June 2016

**ABSTRACT:** The smelting reduction of magnesium oxide was researched in this paper. The effect of molten slag composition and reduction temperature on percent reduction of magnesium oxide were discussed, and kinetics of smelting reduction of magnesium oxide in molten slag was studied. The results showed that the reduction extent of magnesium oxide increased by increasing either one of the following factors: the initial mass ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$ , the addition of  $\text{CaF}_2$ , the initial molar ratio of  $\text{Si}/2\text{MgO}$ , and reaction temperature. The overall smelting reduction was controlled by mass transfer in slag with an apparent activation energy  $586 \text{ kJ mol}^{-1}$ .

**KEYWORDS:** Kinetic; MgO; Slag; Smelting reduction

**Citation / Cómo citar este artículo:** Tang, Q., Gao, J., Chen, X., Wei, X. (2016) "Smelting reduction of MgO in molten slag by liquid ferrosilicon". *Rev. Metal.* 52 (2): e065. doi: <http://dx.doi.org/10.3989/revmetalm.065>.

**RESUMEN:** *Reducción de MgO en escorias fundidas por ferrosilicio líquido.* En este trabajo se estudia la reducción de óxido de magnesio. La influencia de la composición de las escorias y de la temperatura de reducción sobre el porcentaje de reducción de óxido de magnesio han sido discutidas, y asimismo se ha estudiado la cinética de la reducción del óxido de magnesio en escorias fundidas. Los resultados muestran que la reducción se incrementa al aumentar alguno de los siguientes factores: la proporción de  $\text{Al}_2\text{O}_3/\text{SiO}_2$ , la adición de  $\text{CaF}_2$ , la proporción molar de  $\text{Si}/2\text{MgO}$  y la temperatura de reacción. En general la reducción fue controlada por la transferencia de masa en la escoria con una energía aparente de  $586 \text{ kJ mol}^{-1}$ .

**PALABRAS CLAVE:** Cinética; Escoria; MgO; Reducción de fundición

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## 1. INTRODUCTION

Magnesium is well known for its good capability and widely used in the fields of aviation, aerospace, automotive, electronics, metallurgy and chemical engineering, etc (Friedrich and Schumann, 2001; Mordike and Ebert, 2001). Two processes currently are used in magnesium production-electrolytic reduction of magnesium chloride and thermal reduction of dolomite. In order to promote the further development of magnesium production, it is necessary to carry on fundamental studies as to provide theoretical base.

Several research investigations on kinetic of thermal reduction have been carried out. Morsi *et al.* (2002) indicated that the silicothermic reduction process under inter atmosphere was controlled by diffusion of reacted species and the apparent activation energy of the reduction process was about  $306 \text{ kJ mol}^{-1}$ . Barua and Wynnyckyj (1981) carried out relevant research in flowing argon and hydrogen atmosphere, respectively. Some researcher also studied the kinetics of thermal reduction by other reactants, such as Fe-Si-Al alloy, aluminum and carbon (Lan *et al.*, 1999; Li *et al.*, 2002; Lan *et al.*, 2003; Fu *et al.*, 2014). Most information on reduction

kinetic of magnesium production focused on solid-solid reaction, while the kinetic of thermal reduction which takes place in liquid phases was seldom studied.

In this present work, the kinetics of smelting reduction of MgO in molten slag by liquid ferrosilicon was investigated at high temperature. Effects of reaction temperature, addition of CaF<sub>2</sub>, primary slag composition and MgO/Si molar ratio were discussed.

## 2. MATERIALS AND METHODS

Calcined dolomite (CaO·MgO) powder supplied by the Chongqing Haibo magnesium smelting Co., Ltd and reagent grade chemical powders (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaF<sub>2</sub>) were used to prepare the experimental primary slag. Ferrosilicon (75% Si) powder was used as reductant. All of powders passed through the 200-mesh sieve.

The mixture was prepared by weighing and mixing, and the pellets were compacted into 10 mm-diameter and 30 mm-height. About 150 g pellets charged in graphite crucible. The smelting reduction was carried out in the high-temperature vacuum furnace which was internally heated by using a regulated graphite resistance and had a maximum temperature of 1873 K and a limit vacuum 0.01 Pa. The reduction process was controlled under 4~40 Pa. From previous study (Tang *et al.*, 2013), in order to forming molten slag at 1500~1600 °C, the composition of primary slag was about 55% calcined dolomite (32.0% CaO and 23.0% MgO) and 45% additive (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>). So the primary slag composition and the relevant experimental conditions were list in Table 1. After reduction, the residue slag in graphite crucible was cooled to room temperature and pulverized to powder which passed through the 200-mesh sieve. Chemical compositions of the residue were measured by X-ray fluorescence (XRF-1800). The reduction extent of MgO in slag was defined by the Eq. (1):

$$\eta = [1 - W_{(\text{MgO})t} / W_{(\text{MgO})0}] \times 100\% \quad (1)$$

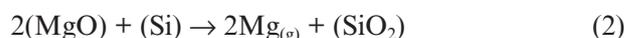
where  $W_{(\text{MgO})t}$  is the weight of MgO in the slag at any time,  $t$  and  $W_{(\text{MgO})0}$  is the weight of MgO in the slag at  $t=0$ , respectively.

## 3. RESULTS

### 3.1. Effect of primary slag composition

Reduction experiments for primary slag with different compositions were carried out at 1550 °C for 1X Si ( $n_{(\text{Si})} / n_{(2\text{MgO})} = 1.0$ ), and the results were shown in Fig. 1. It can be seen from Fig. 1 that the more the mass of SiO<sub>2</sub> in primary slag, the lower the reduction extent of MgO.

In smelting reduction of MgO by ferrosilicon, the reaction was described as follow:



From Eq. (2), it could be found that SiO<sub>2</sub> produced in reduction. When the mass of SiO<sub>2</sub> in slag was little, SiO<sub>2</sub> diffused away from reaction interface easily and the Eq. (2) favored a move to the right-hand side. Increasing the mass of SiO<sub>2</sub> in primary slag, both of the viscosity of slag and SiO<sub>2</sub> concentration near reaction interface improved. Hence, it was difficult for SiO<sub>2</sub> produced in reduction reaction to remove away from reaction interface, which hindered the reduction reaction processing, so the reduction extent of MgO decreased.

### 3.2. Effect of calcium fluoride

In the process of magnesium production by solid-solid reaction, CaF<sub>2</sub> was a common additive as catalyst and could greatly improve the reduction extent of MgO (Tian *et al.*, 2012). In present work, the influence of CaF<sub>2</sub> on the reduction extent of MgO was investigated. The experimental results were shown in Fig. 2, indicated that the reduction

TABLE 1. Values of experimental condition variables

Number	Temperature (°C)	Composition of primary slag (%)					$n_{(\text{Si})} : n_{(2\text{MgO})}$
		CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaF <sub>2</sub>	
1	1550	31.0	22.3	34.0	9.7	3.0	1.0
2	1550	31.0	22.3	21.8	21.9	3.0	1.0
3	1550	31.0	22.3	9.7	34.0	3.0	1.0
4	1550	32.0	23.0	35.0	10.0	0	1.0
5	1550	29.1	20.9	31.9	9.1	9.0	1.0
6	1550	31.0	22.3	34.0	9.7	3.0	0.6
7	1550	31.0	22.3	34.0	9.7	3.0	0.8
8	1550	31.0	22.3	34.0	9.7	3.0	1.2
9	1600	31.0	22.3	34.0	9.7	3.0	1.0

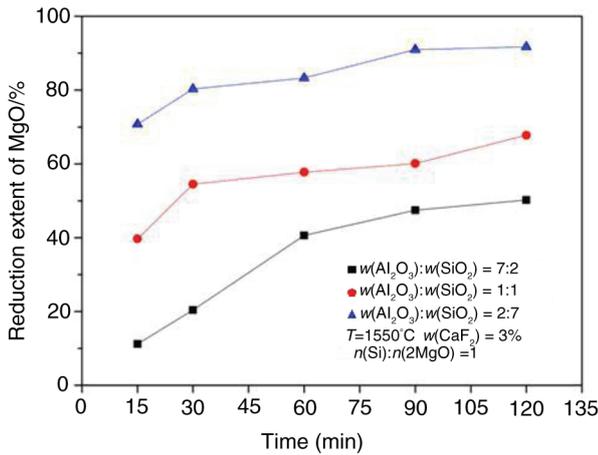


FIGURE 1. Effect of slag composition on reduction extent of MgO.

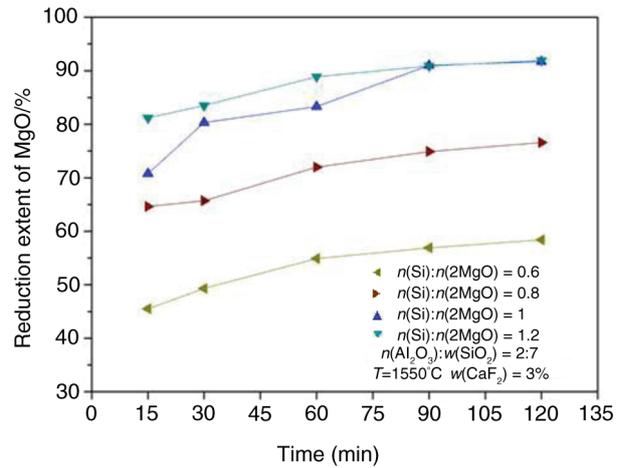


FIGURE 3. Effect of silicon stoichiometry on reduction extent of MgO.

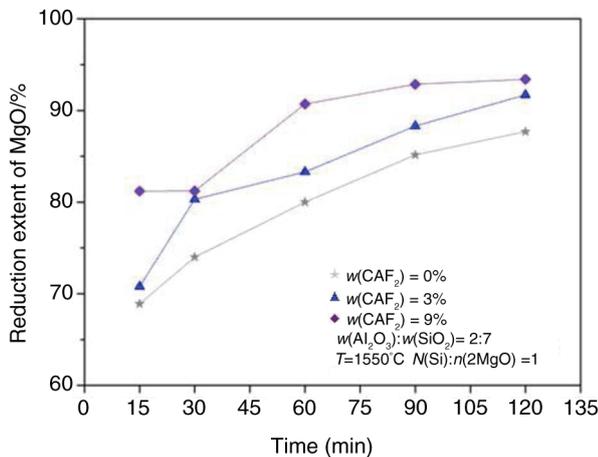


FIGURE 2. Effect of  $\text{CaF}_2$  on reduction extent of MgO.

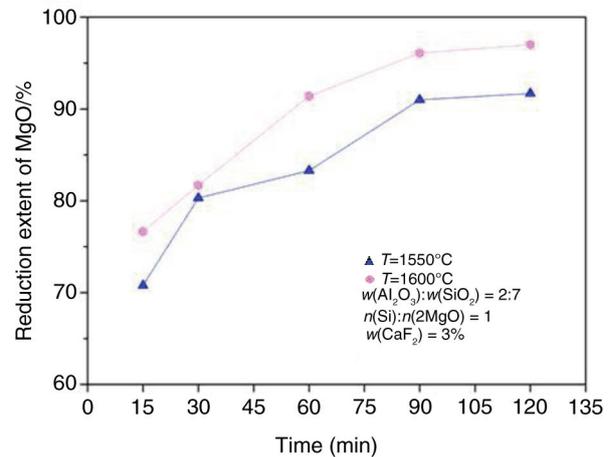


FIGURE 4. Effect of reaction temperature on reduction extent of MgO.

extent of MgO just increased a little with adding  $\text{CaF}_2$ . Compared with solid-solid reaction,  $\text{CaF}_2$  had not significant effect on the reduction extent of MgO in smelting reduction. In smelting reduction, the reaction rate was very fast due to reduction taking place in liquid state, so the catalysis influence of  $\text{CaF}_2$  did not play an important role.

### 3.3. Effect of silicon stoichiometry

The experiments of smelting reduction with different initial molar ratio of  $\text{Si}/2\text{MgO}$  were carried out and the results of this series of experiments were shown in Fig. 3. When the initial molar ratio of  $\text{Si}/2\text{MgO}$  was less than 1.0, the reduction extent of MgO improved significantly with increasing silicon stoichiometry. Under this condition, a high Si content in the charge provided more active Si and surface area for reaction, which could promote the

reaction moving to right-hand side. When the initial molar ratio of  $\text{Si}/2\text{MgO}$  increased from 1.0 to 1.2, the reaction rate had only a small amount of increase.

### 3.4. Effect of reaction temperature

The melting point of experimental primary was above  $1500^\circ\text{C}$ , so experiments were conducted at  $1550^\circ\text{C}$  and  $1600^\circ\text{C}$  due to the limitations of the maximum operating temperature of the furnace. The results were shown in Fig. 4 and indicated that the higher the temperature, the faster the reaction. The final reduction ratio was 97% at  $1600^\circ\text{C}$  for 2 hours. With increasing reaction temperature, the viscosity of slag was decreased, mass transfer became easier. Thus, the reaction rate accelerated the reduction extent of MgO.

### 3.5. Reaction kinetic

#### 3.5.1. Reaction order

Before the start of smelting reduction, the slag and metal layer were formed after the melting of mixture charge. Therefore, the reaction rate of smelting reduction could be expressed by Eq. (3)

$$\frac{dC_{\text{MgO}}}{dt} = k(C_{\text{MgO}})^n \quad (3)$$

where  $K$  was apparent rate constant,  $t$  was reaction time,  $C_{\text{MgO}}$  was MgO content (weight percent) in slag at time  $t$ , and  $n$  was reaction order. Integration of Eq. (3) gave:

$$\int_{C_0}^{C_t} \frac{dC_{\text{MgO}}}{(C_{\text{MgO}})^n} = \int_0^t K dt \quad (4)$$

when  $n=1$  and 2, the Eq. (4) became:

$$-(\ln C_t - \ln C_0) = Kt \quad n=1 \quad (5)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = Kt \quad n=2 \quad (6)$$

According to the Eq. (5) and Eq. (6), the reaction order could be determined by the relationship between  $C_t$  and  $t$  in smelting reduction. By dealing with some group data, it was found that the linear relationship between  $1/C_t$  and  $t$  was well maintained from Fig. 5. The value of apparent rate constant  $K$  and the correlation coefficient  $r$  of fitted line at different condition were list Table 2. The correlation coefficient  $r$  of fitting line was in the range

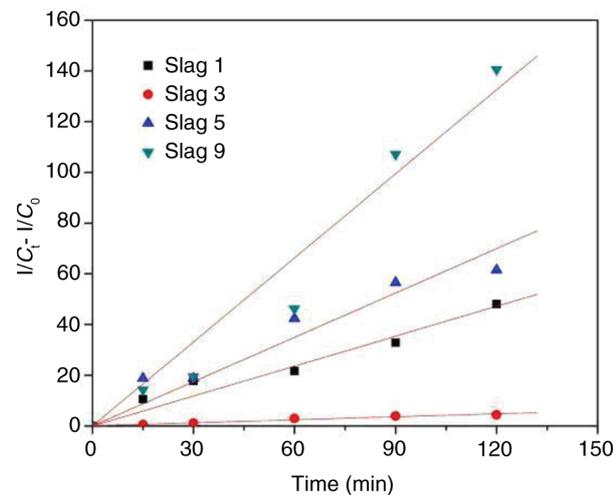


FIGURE 5. The relationship between  $\frac{1}{C_t} - \frac{1}{C_0}$  and  $t$  at different condition.

TABLE 2. Value of apparent rate constant  $K$  and correlation coefficient  $r$  of fitted line at different condition

Number	$K$	$r$
1	0.39333	-0.9833
3	0.04039	-0.9827
5	0.58262	-0.9733
9	1.10489	-0.9830

$-0.99 < r < -0.97$  with an average value of  $-0.981$ . Therefore, it could be considered that the reduction of MgO in molten slag was the second order reaction and the reaction rate could be expressed by Eq. (7)

$$\frac{dC_{\text{MgO}}}{dt} = K(C_{\text{MgO}})^2 \quad (7)$$

#### 3.5.2. Apparent activation energy

The relationship between apparent rate constant  $K$  and reaction temperature  $T$  could be expressed by Arrhenius equation as follow:

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

where  $A$  was frequency factor,  $E$  was apparent activation energy,  $R$  was gas constant. Logarithming of Eq. (8) gave:

$$\ln K = -\frac{E}{R} \frac{1}{T} + \ln A \quad (9)$$

Due to the limitation of the maximum operating temperature of the furnace, the experimental temperature was carried at 1550 °C and 1600 °C with the same composition mixture charge (slag 1 and slag 9). The relationship between  $\ln K$  and  $T^{-1}$  was shown in Fig. 6.

By calculation, the relationship between apparent rate constant  $K$  and reaction temperature  $T$  was depicted as follow:

$$K = 2.5997 \times 10^{16} \exp\left(-\frac{586129}{RT}\right) \quad (10)$$

From Eq. (9), it was well known that the apparent activation energy of smelting reduction was 586 kJ mol<sup>-1</sup>.

#### 3.5.3. Reaction mechanism

At high temperature, the reduction of MgO in molten by ferrosilicon was liquid-liquid state reaction. The preceding of settling reaction could be summarized as follows:

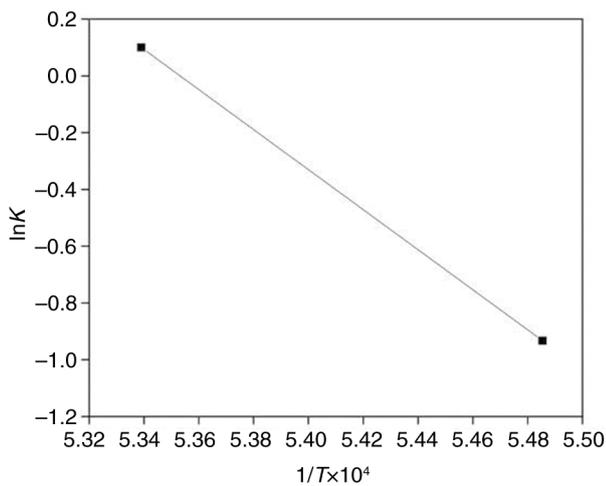


FIGURE 6. The relationship between  $\ln K$  and  $1/T$  at 1550 and 1600 °C.

1. Mass transfer of MgO in slag towarded the metal/slag interface;
2. Mass transfer of Si in liquid ferrosilicon towarded the metal/slag interface;
3. Reaction took place on the metal/slag interface;
4. Mass transfer of SiO<sub>2</sub> towarded slag from metal/slag interface;
5. Mg vapor leaved the metal/slag interface and diffused through the slag.

The smelting reduction was carried at high temperature, the chemical reaction took place on the metal/slag interface fast. Hence, it was generally considered that chemical reaction was not the controlling step. In this work, the reducing agent was 75% Si-alloy which had about 67% Si and 23% FeSi<sub>2</sub>. The activity of Si  $a_{Si}$  was near 1 and the viscosity of Si-alloy was low, which made the mass transfer of Si in liquid ferrosilicon easy, so the overall process was not controlled by step (2). The smelting reduction took place under vacuum, Mg vapor diffused through the slag very rapidly. Therefore the process was not controlled by step (5) either. From the above discussion, the step (1) and/or step (4) might be the rate limiting step. The diffusion activation energy of MgO and SiO<sub>2</sub> in slag had the same order of magnitude, so the total process might be controlled by mass transfer in slag.

Assumed that the overall process was controlled by mass transfer in slag, the rate of mass transfer in slag might be expressed as:

$$\frac{dC_{MgO}}{dt} = \frac{D S}{\delta V} (C_{MgO} - C_{MgO}^*) \quad (11)$$

where  $D$  was the diffusion coefficient of MgO in slag,  $\delta$  was the effective boundary layer thickness of slag,  $S$  was the area of metal/slag interface,  $V$  was the volume of slag, and  $C_{MgO}$  and  $C_{MgO}^*$  were MgO content

(weight percent) in slag and at the metal/slag interface, respectively. During the overall process,  $C_{MgO}$  was much larger than  $C_{MgO}^*$ . Thus, the Eq. (11) could be expressed as:

$$\frac{dC_{MgO}}{dt} = \frac{D S}{\delta V} C_{MgO}. \quad (12)$$

During the smelting reduction, Mg vapor produced in reaction stirred the slag and changed the effective boundary layer thickness  $\delta$ . The relationship of  $\delta$  and the rate of mass transfer in slag could be depicted as followed (Wang and Chou, 1963):

$$\delta = k \left( \frac{dC_{MgO}}{dt} \right)^{-\frac{1}{2}} \quad (13)$$

where  $k$  was constant. Association Eq. (12) and Eq. (13), the rate of mass transfer in slag could be depicted as:

$$\frac{dC_{MgO}}{dt} = \left( \frac{D S}{k V} \right)^2 (C_{MgO})^2 = K^* (C_{MgO})^2 \quad (14)$$

The Eq. (7) and Eq. (14) were same, which indicated that the total process was controlled by mass transfer in slag.

#### 4. CONCLUSIONS

Magnesium oxide was smelting reduced by liquid ferrosilicon in slag at vacuum. The following results were obtained:

- The reduction extent of MgO increased by increasing the initial mass ratio of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, the addition of CaF<sub>2</sub>, the initial molar ratio of Si/2MgO, or reaction temperature. The final reduction ratio of MgO was achieved up to 97% when using the optional parameters of reaction temperature of 1600 °C, w(Al<sub>2</sub>O<sub>3</sub>):w(SiO<sub>2</sub>) ratio of 7 to 2, n(Si)/n(2MgO) ratio of 1.2 and reduction time of 2 hours.
- Based on the experimental data obtained, the smelting reduction kinetics was investigated between 1550 °C and 1600 °C. The results indicated that smelting reduction was the second order reaction, the apparent activation energy was 586 kJ mol<sup>-1</sup> and the overall process was controlled by mass transfer in slag.

#### ACKNOWLEDGMENTS

The authors would like to acknowledge financial support by Key Scientific Research Fund of Xihua University (Grant N° Z1320109) and the General Project of Sichuan Province Department of Education Fund for Nature (Grant N° 14201436).

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