SILICOTHERMIC REDUCTION OF DOLOMITE ORE UNDER INERT ATMOSPHERE

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Abstract — Magnesium metal was produced from dolomite ore under inert atmosphere using ferrosilicon as a reducing agent. The kinetics of the silicothermic reduction process was studied at a temperature range from 1150-1300 °C. The charges studied are in the form of briquettes. The parameters studied are silicon stoichiometry, temperature and time of preheating, calcium fluoride additive, molar ratios of calcium oxide/magnesium oxide, flow rate of inert gas, briquetting pressure, temperature and time of reduction process. The maximum reduction extent of about 92% was achieved when using charges in the form of briquettes containing 2.5 wt.% CaF₂, CaO/MgO molar ratio of 1.6 and using silicon as reductant with its weight ratio/MgO equals 1.45 at 1300 °C for 5 hours. The discussion takes into considerations the type of intermediate compounds formed during the reduction and the mechanism of the silicothermic reduction process. It was found that the silicothermic reduction process of dolomite ore is a solid-state reaction controlled by diffusion of reacted species and the apparent activation energy obtained equals 306 KJ.mol⁻¹.

Résumé — On a produit du magnésium-métal à partir de minerai de dolomite en atmosphère inerte en utilisant du ferrosilicium comme agent de réduction. On a étudié la cinétique du procédé de réduction silico-thermique dans une gamme de température de 1150-1300 °C. Les charges étudiées avaient la forme de briquettes. Les paramètres étudiés incluent la stœchiométrie du silicium, la température et la durée de préchauffage, l’addition de fluorure de calcium, les rapports molaires oxyde de calcium/oxyde de magnésium, le taux d’écoulement du gaz inerte, la pression de mise en briquette, la température et la durée du procédé de réduction. La réduction maximum d’environ 92% a été obtenue lorsqu’on utilisait des charges en forme de briquettes contenant 2.5% en poids de CaF₂, avec un rapport molaire CaO/MgO de 1.6 et avec du silicium comme agent de réduction, avec un rapport de son poids/MgO égal à 1.45, à 1300 °C pendant 5 heures. La discussion prend en considération le type de composés intermédiaires formés lors de la réduction et le mécanisme du procédé de réduction silico-thermique. On a trouvé que le procédé de réduction silico-thermique du minerai de dolomite était une réaction à l’état solide contrôlée par la diffusion des espèces ayant réagi; on a obtenu une énergie d’activation apparente égale à 306 kJ.mol⁻¹.

INTRODUCTION

Today magnesium is produced industrially either from dolomite ores by thermal reduction of magnesium oxide [1-3] using reactive metals (such as aluminum, silicon or their alloys) as a reductant [4-14] or from magnesium chloride by an electrolytic process [15-18].

The recovery of the magnesium from dolomite ores by using silicon (silicothermic process) was investigated by many authors. It was reported that completion of this process occurs via the formation of intermediate compounds such as calcium silicide [19-23] or calcium magnesium silicate $Ca_3Mg(SiO_4)_2$ [19,21] where their formations are dependent on temperature.

The silicothermic process was reported as a solid-state reaction controlled by the rate of diffusion of the solid reactants. It was found that this reaction could be carried out under inert atmosphere instead of a vacuum [24-26]. The effect of a calcium fluoride addition has been studied by many authors [9,11,27-30].

The present work aims to study the different parameters affecting the kinetics of the silicothermic process of magnesium production from dolomite ore under inert atmos-
phere. The discussion will take into consideration the type of intermediate compounds formed during the reaction and the mechanism of the process.

**EXPERIMENTAL**

**Raw Materials**

A sample of dolomite ore (Um Bogma, Sinai) was provided by the Sinai Manganese Company (Egypt). The ore was crushed in a jaw crusher to 3 cm and ground in a roller mill to 1 mm and finally pulverized to 74 μm by using a vibrating mill. A representative sample was taken from the pulverized ore and used throughout this investigation. The complete chemical analysis of this sample and the dolime produced from its calcination at 1000 °C for one hour are given in Table I.

Table I – Chemical analysis of dolomite ore and calcined dolomite (dolime).

<table>
<thead>
<tr>
<th>Component</th>
<th>Dolomite Wt.%</th>
<th>Dolime Wt.%</th>
</tr>
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<tbody>
<tr>
<td>CaO</td>
<td>29.20</td>
<td>53.85</td>
</tr>
<tr>
<td>MgO</td>
<td>18.89</td>
<td>34.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.50</td>
<td>4.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.98</td>
<td>1.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.20</td>
<td>2.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
<td>0.34</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.89</td>
<td>-</td>
</tr>
<tr>
<td>L.O.I*</td>
<td>46.00</td>
<td>-</td>
</tr>
</tbody>
</table>

*loss of ignition

A sample of ferrosilicon was provided by the Egyptian Ferroalloys Company (EFACO) to be used as a reductant. It was ground to 1 mm size in a disk mill and pulverized to 74 μm in a vibrating mill. The complete chemical analysis of this sample showed that it contains in weight percentage: 74.8 Si, 23.36 Fe, 0.09 C, 0.31 Ca, 0.003 S, 0.031 P and 1.41 Al. Pure grade calcium oxide was used as a fluxing agent and calcium fluoride of reagent grade was used as the catalyst in this study.

**Reduction Technique**

The reduction process was carried out in the retort made from a heat resistant high Ni-Cr steel tube. The retort was externally heated by using a regulated resistance furnace having a maximum temperature of 1300 °C. The retort is closed at one end and open at the other. The open end of the retort is closed by using a rubber stopper with a tube for the input of argon gas and two terminals of U-shaped copper cooling tube. The outlet of the inert gas from the retort is carried out through a fixed tube near the open end of the retort. The cooling copper tube is used to condense the produced magnesium vapour near the reaction zone.

The reduction experiments were carried out by using dolime. The required weight ratios of dolime, calcium oxide, ferrosilicon and calcium fluoride were mixed thoroughly. The mixed charges were homogenized by rotating for 20 minutes in a porcelain ball mill. The briquetting of the charge was carried out under different pressures of up to 700 MPa using a bench scale hydraulic press. The briquettes have a diameter of 1.4 cm and a thickness of about 0.5 cm. The produced briquettes were used directly for the reduction experiments.

About 10 gm of charges (briquettes) were put in a boat made from heat resistant high Ni-Cr steel alloy. The charged boat was inserted in the retort at room temperature. The flow of inert gas argon was adjusted over the charge at different rates ranging from 0.08-0.25 L/min. The charges were subjected to a preheating cycle at temperature ranges from 600 - 1000 °C for different periods of up to 3 hrs. The charge was cooled to room temperature under argon gas atmosphere and the temperature of the furnace was raised to the required reduction temperature ranging from 1150-1300 °C. After approaching the required reduction temperature, the preheated charge was inserted again in the furnace to perform the reduction process for different periods up to 8 hours. At the end of the reduction experiments, the retort moved away and the reduced charge was lifted to cool to room temperature under argon atmosphere. After cooling, the condensed magnesium product was collected and weighed. The residue obtained was also weighed and analyzed for magnesium.

The extent of reduction process was calculated according to the following formula

\[
\text{Extent of reduction} \% = \left( \frac{(\text{Mgo} - \text{Mg}_r)}{\text{Mgo}} \right) \times 100
\]

where \( \text{Mgo} \) is the initial quantity of magnesium in the sample and \( \text{Mg}_r \) is the residual magnesium in the reduction residue. The raw materials and the reduction products were investigated physically and chemically.

**Method of Calcium and Magnesium Determinations**

Calcium and magnesium were determined in the fusion filtrate of samples (original or residues) by complexometric titration against a standard EDTA solution. Calcium was determined by adjusting the pH 13.3 in the presence of solo-chrom dark blue, where the colour changes from purple violet to blue. The total hardness (calcium and magnesium) was determined at pH 10 adjusted by a buffer solution (ammonia/ammonium chloride) and using Eriochrome Black T as an indicator, the magnesium content was calculated by the difference. The interference of iron and other metals were avoided by adjusting the pH of the solution in...
RESULTS AND DISCUSSION

Effect of Silicon Stoichiometry

The variation of the reduction extent of magnesium evolved as a function of silicon stoichiometry added to the charge is given in Figure 1 for reduction experiments carried out at 1250 °C for 3 hours under argon flow rate of 0.08 L/min. The stoichiometry of the silicon in the charge (X) was calculated according to the following equation:

\[ 2\text{MgO(S)} + 2\text{CaO(S)} + \text{Si(S)} \rightarrow 2\text{Mg(g)} + \text{Ca}_2\text{SiO}_4(S) \]  

The results show that the reduction extent increases from 15% to a value of about 30% as silicon stoichiometry increases from 1X to 2X, respectively. After this, the reduction extent decreases to a lower value of 16% at 8X.

X-ray analysis of the reduction residues for charges containing sample 2XSi and sample 8XSi revealed the presence of calcium magnesium silicate phase \( \text{Ca}_3\text{Mg(SiO}_4\text{)}_2 \) in excess in the charge containing 8XSi [31]. The presence of excess silicon may promote the dissolution of magnesium oxide in excess calcium silicate formed as a result of the reduction process in the form of calcium magnesium silicate [26]. The formation of this phase may prevent the direct contact of silicon with magnesium oxide and it may enhance the consumption of magnesium oxide and calcium oxide needed to complete the reduction process. As a result the reduction extent decreased.

Effect of the Preheating Temperature

The variation of the reduction extent of magnesium as a variable of the preheating temperature for reduction experiments of charge containing 2XSi preheated at different temperatures for 1 hour and reduced at 1250 °C for 3 hours under the rate of argon gas of 0.08 L/min is given in Figure 2. The preheating of charges enhanced the reduction extent from 30 to 41% as the preheating temperature increased from 700 to 800 °C respectively. At a higher preheated temperature of 1000 °C, the reduction extent decreased to 24%.

X-ray diffraction (XRD) analysis of the sample preheated at 1000 °C (Figure 3) revealed the formation of the phases \( \text{Ca}_3\text{SiO}_5 \), \( \text{Fe}_2\text{Si} \) and \( \text{CaSi}_2 \) as well as \( \text{CaO}, \text{MgO} \) and \( \text{Si} \) phases. The reaction taking place at 1000 °C may be

\[ 2\text{Si(S)} + 2\text{FeSi}_2(S) + 5\text{CaO(S)} \rightarrow \text{Fe}_2\text{Si}(S) \]  
\[ + 2\text{CaSi}_2(L) + \text{Ca}_3\text{SiO}_5(S) \]  

The occurrence of such a reaction during this preheating step can consume the free calcium oxide available for the reduction process and the formation of the calcium silicate (\( \text{Ca}_3\text{SiO}_5 \)) phase. This phase can prevent the direct contact of \( \text{CaSi}_2 \) and magnesium oxide leading to an incomplete reduction process. A similarity between the intensities of lines belonging to the \( \text{CaSi}_2 \) phase in both preheated samples at 1000 °C and its residue after reduction process was also noticed. This indicates that \( \text{CaSi}_2 \) probably did not take place in the reduction process. On the other hand, a weak intensity of silicon peaks in the reduced sample indicates its reaction with MgO during the reduction process to form silicates and magnesium metal.
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Effect of Preheating Time

Figure 4 shows the variation of magnesium reduction extent with the time of preheating for charges preheated at 800 °C. The increase of preheating time from 30 to 60 minutes enhanced the reduction extent from 30 to 44%, respectively. By increasing the time of preheating by one hour, the reduction extent lowered again to approach a minimum value of 20% after three hours.

The XRD results of the preheated samples at a constant temperature of 800 °C for 1 and 3 hours and their residues after reduction process are shown in Figures 5 and 6, respectively. It was noticed that the Fe₂Si phase was present with lower intensity in the preheated sample for 1 hour but with higher intensity in a sample preheated for 3 hours. It is also observed that Ca₃SiO₅ phase is present in the preheated sample for 3 hours. These results indicated that the decrease in the reduction extent is mainly due to the formation of the Ca₃SiO₅ phase. Also, increasing time of preheating enhances the dissociation of FeSi₂ as the following reaction [32]

\[ 2\text{FeSi}_2(S) \rightarrow \text{Fe}_2\text{Si}(S) + 3 \text{Si}(S) \]  

The increase of silicon formation is confirmed by its higher intensity lines for the samples preheated for 3 hours and the presence of Fe₂Si lines, (Figure 6). Excess of formed silicon in the preheated sample for 3 hours has probably reacted with CaO to form CaSi₂ [22] and Ca₃SiO₅ during the reduction process according to the following reaction

\[ 5\text{Si}(S) + 5 \text{CaO}(S) \rightarrow 2 \text{CaSi}_2(L) + \text{Ca}_3\text{SiO}_5(S) \]  

This reaction is confirmed by the lower intensity of lines belonging to the CaO phase in the reduction residue of
the 3 hour preheated sample than the 1 hour preheated sample. As well, an increased silicon content in the preheated sample before its reduction and the presence of Ca$_3$SiO$_5$ phase can prevent the direct contact of either CaSi$_2$ formed and silicon with magnesium oxide to complete its reduction process. As result, the reduction extent lowered as the preheating period increased by 1 hr.

**Effect of Calcium Fluoride**

Figure 7 shows the variation of the magnesium reduction extent with calcium fluoride percentage added to the charges containing 2XSi preheated at 800 °C for 1 hour and reduced at 1300 °C for 4 hours under argon atmosphere (0.08 L/min). The reduction extent increased from 44% to 64% as the calcium fluoride weight percentage increased up to 2.5%. A reverse effect was observed after this value where reduction extent decreased from 64 to 43% as the calcium fluoride increased from 2.5 to 3.5%, respectively.

The results obtained from X-ray analysis of the reduction residues of samples containing 2.5% and 3.5% calcium fluoride and without calcium fluoride addition are given in Figure 8. The main phases identified are calcium oxide, magnesium oxide and calcium silicate (Ca$_2$SiO$_4$). A calcium silicide (CaSi$_2$) phase was identified in the residue of...
the charge containing 2.5% calcium fluoride but existed as traces in the residue of the charge containing 3.5% calcium fluoride. However, the silicon phase disappeared in the residue of the charge without calcium fluoride, occurred as traces with 2.5% calcium fluoride and was well identified in the residue of the charge containing 3.5% calcium fluoride. Therefore, the role of calcium fluoride is apparently accompanied with the formation of the calcium silicide phase during the reduction process. It is noticed experimentally that the residues obtained at the end of the reduction process were more dense by increasing the calcium fluoride addition which indicated sintering of the reaction product.

The promotion of magnesium reduction extent up to 2.5% calcium fluoride may be due to the fact that an increase in the calcium fluoride concentration increases the activity of both calcium oxide and silica which in turn promotes the formation of calcium silicate during the calcium silicide formation according to the following reaction:

\[
\text{CaO} + \text{Si} \rightarrow \text{CaSi} + \text{O}_2
\]
4 CaO(S) + 5 Si(S) → 2 CaSi2(L) + Ca2SiO4(S)
\( \Delta G^o_{1500 K} = -53.02 \text{ kJ} \) \( (5) \)

At higher ratios of calcium fluoride, the excess formation of the calcium silicate phase prevents the direct contact between the reacted calcium oxide and silicon which decreases the calcium silicide formation. This state is proved by the presence of high intensity lines belonging to the silicide phase and very weak intensity for lines belonging to the silicon phase in charge containing 2.5% calcium fluoride. However, the intensity of the X-ray lines belonging to calcium silicide phase is weak and the silicon lines are strong for charge containing 3.5% calcium fluoride (Figure 8). The reaction belonging to the formation of calcium silicide can be written as follows:

\[ 2 \text{CaO(S)} + 5 \text{Si(S)} \rightarrow 2 \text{CaSi}_2(L) + \text{SiO}_2(S) \]
\( \Delta G^o_{1500 K} = +25.48 \text{ kJ} \) \( (6) \)

2 CaO(S) + SiO2(S) → Ca2SiO4(S)
\( \Delta G^o_{1500 K} = -78.2 \text{ kJ} \) \( (7) \)

From a thermodynamics viewpoint, Reaction 7 is more likely to occur. It may be that calcium fluoride can promote Reaction 6. It should be mentioned here that our results are in agreement with other investigators [9,19] who suggested that the promoting effect of calcium fluoride added up to 2.5% during the reduction process is due to its mineralizing effect by the formation of low melting point phases which increase the contact between the calcium silicide phase and the magnesia.

**Effect of Calcium Oxide Addition**

Different experiments were carried out on charges containing 2XSi, 2.5 wt.% calcium fluoride and different molar ratios of CaO/MgO ranging from 1.1 to 1.7. The charges were preheated at 800 °C for 1 hour followed by reduction.

![Fig. 8. XRD of reduced samples with calcium fluoride additive, 2.5 and 3.5%.](image-url)
at 1300 °C for 4 hours under argon atmosphere at a constant flow rate of 0.08 L/min.

The results in Figure 9 show that the reduction extent increases from 64 to 85% as the molar ratio CaO/MgO increased from 1.1 to 1.6. Increasing this ratio by more than 1.6 is accompanied by a decrease in the reduction extent reaching about 78% when using 1.7 molar ratio of CaO/MgO.

The results of X-ray diffraction for the reduction residues of selected samples are given in Figure 10. It is clear that the relative intensities of calcium silicide CaSi₂ and magnesium oxide lines of reduction residue of a sample containing CaO/MgO molar ratio 1.6 are lower than that obtained for the residue of a sample having CaO/MgO molar ratio 1.7. This proves that the reaction between calcium silicide and magnesium oxide is promoted by added calcium oxide up to 1.6 molar ratio. On the other hand, excess addition of calcium oxide retards the magnesium reduction extent due to the formation of calcium silicate phase (Ca₃SiO₅) as a result of maximum distribution of calcium oxide in the charges and so decreases the direct contact of calcium silicide with magnesium oxide. This result is confirmed by the presence of high relative intensity lines of calcium silicide phase in the X-ray diffraction for residue of CaO/MgO molar ratio 1.7.

**Effect of Flow Rate of Inert Gas**

A series of experiments was performed on samples containing 2%Si, 2.5% weight calcium fluoride and CaO/MgO molar ratio 1.6 preheated at 800 °C for 1 hour and reduced at 1300 °C for 1 hour. Figure 11 shows the variation of magnesium reduction extent with variation of flow rate of argon gas. It is clear that the magnesium extent increases from 36% to about 56% as the flow rate increases from 0.08 L to 0.250 L/min, respectively. The flow rates higher than 0.250 L/min have no effect on the reduction extent of magnesium. This indicates that flushing of the magnesium vapour from the reacted charge reaches its optimum value at a rate of flow ≥ 0.250 L/min. Also, it indicates that the diffusion of the magnesium vapour through the boundary layer around the reacted particles can play a role during the reduction process. Kinetically, the boundary layer formed during the reduction process should be removed in order to obtain a maximum reduction extent.

**Effect of Briquetting Pressures**

This series of experiments was carried out using the same experimental conditions as mentioned above at a gas flow rate of 250 mL/min. Figure 12 shows the relation obtained between the magnesium reduction extent as a variable of pressing pressure used to form the briquettes. It is obvious that the reduction extent increases from 36% to 60% by increasing the pressing pressure from 80 to 450 MPa, respectively after which it becomes constant by increasing pressing pressure above 450 MPa. This increase may be explained by the fact that the increase of the pressing pressure enlarges the contacting areas between the reacted particles inside the briquettes which in turn is reflected in higher magnesium reduction extent. It is possible that the components of the charge approach the maximum contact after a pressing pressure ≥ 450 MPa; hence a maximum magnesium reduction extent is constant.

It is known that when increasing the pressing pressure during the preparation of briquettes, the micropores between the reacted particles should be decreased. The decrease of the micropores can create an obstacle for the diffusion of magnesium vapour through it to outer surfaces of briquettes. In contrast, our results show that an increase in the pressing pressure increases the magnesium reduction extent. This indicates that the diffusion of magnesium vapour through the micropores has no effect on the reduction extent of magnesium. Indeed, the reaction is affected by the enlargement of reacted contact areas between the reactants indicating that the reduction is probably controlled by the diffusion of magnesium between the reactants in the solid state.

**KINETICS OF SILICOTHERMIC REDUCTION PROCESS**

**Reduction Isotherms.**

The kinetics of dolime reduction process was studied under all optimum conditions obtained, which are summarized in Table II. Figure 13 shows the reduction isotherms obtained...
**Table II – Optimum conditions for reduction of dolomite.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reductant stoichiometry*</td>
<td>2XSi</td>
</tr>
<tr>
<td>Reductant weight ratio with respect to MgO in charge</td>
<td>1.45</td>
</tr>
<tr>
<td>Calcium fluoride in weight **</td>
<td>2.5 %</td>
</tr>
<tr>
<td>CaO/MgO molar ratio</td>
<td>1.6</td>
</tr>
<tr>
<td>Rate of inert gas flow rate (Argon)</td>
<td>0.25 L/min</td>
</tr>
<tr>
<td>Pressing pressure of briquettes</td>
<td>450 MPa</td>
</tr>
<tr>
<td>Preheating temperature</td>
<td>800 °C</td>
</tr>
<tr>
<td>Preheating time</td>
<td>1 hour</td>
</tr>
</tbody>
</table>

* Using ferrosilicon (75 %).
** With respect to the total charge.
for the variation of magnesium reduction extent at different periods of up to 5 hours and at temperatures of 1150, 1200, 1250 and 1300 °C. The magnesium reduction extent increases as reduction temperatures increase and gradually with time approach nearly constant value. The maximum reduction extent of about 92% was obtained at 1300 °C for 5 hours.

Figure 14 shows photomicrographs for reduction residues obtained after different reduction periods at 1300 °C. It shows the metallic phase formed in a matrix of the reduction product calcium silicate. The metallic phase quantity decreases as the reduction period increases. Figure 15 shows a photomicrograph for residue obtained after 2 hours reduction time at 1200 °C. It shows the same structure as that obtained for the sample reduced at 1300 °C for 30 minutes.
The types of elements and their quantities in the metallic phase observed in mineralogical investigation of residues obtained at 1300 °C were ascertained by using a scanning electron microscope. Figure 16 shows the emission diffraction spectrum obtained for the distribution of different elements existing in the metallic phase with their percentages. The main elements after a 30 minute reduction period are Mg, Ca, Si and Fe in molar ratios of 1.61 : 1.11 : 0.57 : 0.01, respectively. On the other hand, the main elements after 2 and 3 hour reduction periods are Ca, Si and Fe in molar ratios of 1.73 : 0.80 : 0.14 and 1.68 : 1.00 : 0.09, respectively. The results of the investigation on matrix are given in Figure 17 which shows the distribution of the different existing elements and their percentages for the sample reduced at 1300 °C for 2 hours. The main elements are Ca, Mg, Si, O and Fe in molar ratios of 1.7 : 0.08 : 0.6 : 2.0 : 0.1, respectively. From these molar ratios the expected main phases in the matrix are probably calcium silicate (Ca$_2$SiO$_4$) and iron.

Applicability of Solid State Diffusion Models.

Some solid state diffusion models were investigated to find which kinetic equation can fit the reduction isotherms obtained in Figure 13. It is found that the model postulated by Ginstling and Brounstein $[1-(2/3)\alpha - (1-\alpha)^{2/3}] = Kt$, is the most applicable model for all reduction isotherms up to 85% reduction extent where $\alpha$ is the reaction extent, $t$ is the time in minutes and $K$ is the reaction rate constant. The mean value of the reaction rate constants at different reduction temperatures were calculated and their logarithmic values were plotted against the reciprocal of absolute reduction temperatures according to Arrhenius equation to give a straight line (Figure 18). The apparent activation energy is 306 kJ/mol as calculated from the slope of this line. This value of the activation energy is slightly higher than that obtained by other investigators [5]. Also, it may be confirmed that the reaction is controlled by the diffusion process existing in the solid state.
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Mechanism of the Silicothermic Reduction Process Under Atmospheric Pressure

The following facts can be deduced from the present investigations:

1. The reduction process is diffusion in solid state.
2. Presence of a metallic phase in the reduction residue indicates its liquification during the reduction process. This metallic phase is not purely calcium silicide (CaSi$_2$) only, as previously reported [9,19,33] but, according to the scanning electron microscopic investigation, it is a mixture of metallic phases of magnesium, iron, silicon and calcium formed during the reduction process.
3. The matrix consists of calcium silicate and remnants of magnesium oxide phase.
4. Iron that initial exists in ferrosilicon is distributed in metallic and matrix phases.

Depending on these facts the mechanism of the silicothermic reduction process of magnesium oxide present in dolime to magnesium metal may be visualized as follows:

1. At the beginning of the reduction process, the calcium oxide reacts at phase boundaries with silicon to form liquid calcium silicide and solid calcium silicate phase according to the following equation

$$4 \text{CaO} + 5 \text{Si} \rightarrow 2 \text{CaSi}_2 + \text{Ca}_2\text{SiO}_4$$

$$\Delta G^\circ_{1400 \text{K}} = -6.7 \text{ kJ}$$

2. The liquid calcium silicide subsequently reacts with magnesium oxide to give magnesium vapour according to the following equation

$$5 \text{MgO} + \text{CaSi}_2 \rightarrow 5 \text{Mg} + \text{CaO} + 2 \text{SiO}_2$$

$$\Delta G^\circ_{1400 \text{K}} = +539.7 \text{ kJ}$$

It should be mentioned that the magnesium metal produced during the reduction process must pass with liquid state before its evaporation. Indeed, the liquid magnesium dissolves in the reducant calcium silicide phase forming the intermetallic phase (Ca - Mg - Si - Fe) which was detected by the scanning electron microscope. Removal of magnesium from this metallic phase is essential to complete the reduction process.

3. The excess calcium oxide reacts with silica to obtain calcium silicate according to the following equation

$$4 \text{CaO} + 2 \text{SiO}_2 \rightarrow 2 \text{Ca}_2\text{SiO}_4$$

$$\Delta G^\circ_{1400 \text{K}} = -155.12 \text{ kJ}$$

4. The overall reaction of the reduction process can be written as follows

$$2 \text{CaO} + 2 \text{MgO} + \text{Si} \rightarrow 2 \text{Mg} + \text{Ca}_2\text{SiO}_4$$

$$\Delta G^\circ_{1400 \text{K}} = +152.5 \text{ kJ}$$

It is clear that steps 1 and 3 may occur spontaneously. Therefore, the reaction in step 2 may be considered as a rate controlling step.
CONCLUSIONS

1. Adjustment of molar ratio of calcium oxide/magnesium oxide in the silicothermic reduction process of dolime is essential (1.6).

2. The suitable ratio of silicon in the reductant ferrosilicon calculated with respect to magnesium oxide in the silicothermic charges is 1.45.

3. Preheating of charges used in the silicothermic reduction process (at 800 °C for 1 hour) promotes the process.

4. Using calcium fluoride in weight percentage of 2.5 in the charges for silicothermic process accelerates the reduction process.

5. Using charges in form of briquettes (pressed at 450 MPa) gives higher reduction rates.

6. The magnesium metal formed during the silicothermic process is partially dissolved in the calcium silicide phase before its evaporation.

7. The silicothermic reduction process is a solid-state reaction controlled by diffusion of reacted species in solid state. The apparent activation energy of the reduction process is about 306 kJ/mol.

REFERENCES


CANADIAN METALLURGICAL QUARTERLY