J. Min. Metall. Sect. B-Metall. 58 (1) (2022) 19 - 28

Journal of Mining and Metallurgy,
Section B: Metallurgy

THE EFFECT OF CALCIUM FLUORIDE ON EXTRACTING MAGNESIUM FROM MAGNESITE AND CALCIUM CARBONATE BY SILICOTHERMAL REDUCTION IN FLOWING ARGON

J.-H. Guo [a, b], **D.-X. Fu** [a, b], **J.-B. Han** [a, b], **Z.-H. Ji** [a, b], **Y.-S. Wang** [a, b], **T.-A. Zhang** [a, b, *]

[a] School of Metallurgy, Northeastern University, Shenyang, China
[b] Key Laboratory for Ecological Utilization of Multimetallic Mineral (Ministry of Education), Northeastern University, Shenyang, China

(Received 18 March 2021; accepted 08 July 2021)

Abstract

At present, the production of magnesium is mainly carried out semi-continuously with ferrosilicon as reducing agent under high temperature and high vacuum. In order to continuously produce magnesium, a new method of extracting magnesium from low-grade magnesite and calcium carbonate by silicothermal method in flowing inert gas was proposed. The effects of calcium fluoride (CaF_2) on decomposition rate, decomposition kinetics, reduction rate of magnesia, and crystal type of dicalcium silicate in reduction slag were investigated in the paper. The experimental results showed that calcium fluoride could accelerate the decomposition of carbonate, and had no side effect on the calcined products. In addition, the analysis results of DTA curves showed that calcium fluoride could reduce the decomposition reaction activation energy and the reaction temperature of carbonate in the prefabricated pellets. The results of reduction experiments showed that proper calcium fluoride could promote the reduction rate of magnesia, and in the temperature range of 1250℃ ~ 1350℃, with the same timeframe, the corresponding calcium fluoride contents were 5%, 3%, and 1% respectively when the reduction rate reached the maximum. Excessive calcium fluoride reduced the reduction rate of magnesia, but it promoted the transformation of dicalcium silicate to γ phase in the reduction slag.

Keywords: *Magnesium; Calcium fluoride; Magnesite; Dicalcium silicate; Silicothermal process*

1. Introduction

Magnesite resources are rich in China, accounting for about one third of the world magnesite production [1]. It is mainly distributed in Liaoning Province with proven reserves of 3.4 billion tons [2]. Magnesite is an important raw material for magnesium industry and refractory industry, which is widely used in metallurgy, building materials, chemical industry, and other industries [3-5]. Magnesite is considered as one of the most important refractory materials because of its high fire resistance. However, there are impurities such as silica, calcium oxide, and iron oxide in magnesite, which react with magnesia and produce low melting point phases at high temperature, such as merwinite and monticellite, which have adverse effects on the thermomechanical properties of magnesia refractories [6]. Therefore, high-grade magnesite in China is widely exploited, while low-grade magnesite is discarded or stockpiled, resulting in a waste of resources. Therefore, more attention has been increasingly paid to how to efficiently and comprehensively utilize low-grade magnesite resources. As magnesite is rich in magnesium, it can be used as raw material for magnesium production in the work.

Magnesium and its alloys are widely used in transportation, aerospace, and other fields due to their unique properties, such as better reducibility, specific strength and light weight, and have become the third largest metal engineering materials after steel and aluminum [7, 8]. The main production method of magnesium is Pidgeon process. Since the Pidgeon process was put forward in 1941, it has developed rapidly in China due to its simple technology and flexible scale, but it has also increasingly highlighted the problems of high labor intensity, interrupted production and high energy consumption [9-11]. Therefore, some new processes such as the aluminothermal process [12], carbothermal process [13, 14], and MTMP process [15] have been studied, which also provide new ideas for industrial

---

[*] *Corresponding author: zta2000@163.net*

https://doi.org/10.2298/JMMB210318045G

magnesium production.

Pidgeon process is a method of extracting magnesium by thermal reduction in vacuum. The process implies that dolomite is first calcined at about 1150°C to obtain dolime. When the dolime is cooled at room temperature, the dolime, ferrosilicon (containing 75% Si) and calcium fluoride, are mixed and pressed into pellets, and finally the pellets are reduced in vacuum. From the above process, it can be seen that there is a problem that the high-temperature dolime needs to be cooled to room temperature, resulting in heat loss. In addition, due to the reduction of raw materials under high temperature and high vacuum conditions, the whole magnesium production process needs to be operated intermittently, which increases the magnesium production cycle. In order to solve the above problems and consider the comprehensive utilization of low-grade magnesite. Zhang et al. [16] proposed the process of magnesium production by silicothermal method with prefabricated pellets in flowing inert gas, and the process flow is shown in Fig. 1. In this process, the mixture of magnesite and calcium carbonate was used to replace dolomite. The specific process proposed that dolomite (magnesite and calcium carbonate), ferrosilicon, and calcium fluoride were mixed and pressed into pellets (called prefabricated pellets), and then the pellets were calcined and reduced in flowing inert gas. Finally, the generated magnesium vapor was carried to the crystallizer for condensation by flowing inert gas. Therefore, calcination and reduction were carried out in a reduction tank. The advantage of this method is that it can make full use of the low-grade magnesite, realize the integration of calcination and reduction in the smelting process, and avoid the loss and water absorption of highly activity calcined white in the process of transportation and storage. In addition, because the whole process is not carried out in vacuum, continuous production of magnesium can be realized. Due to the existence of flowing argon, the convection heat transfer can also be increased and the heat transfer efficiency can be improved, and the argon can be recycled.

In the traditional industrial production of magnesium by Pidgeon process, it was often necessary to add a certain amount of calcium fluoride to the material to improve the reduction rate of magnesium oxide in the reduction process. Previous studies [17-19] had shown that CaF_2 could increase the reaction energy on the surface of oxide, accelerate the interaction between materials, and reduce the reaction temperature. However, due to the excessive CaF_2 content, the reduced slag would bond to the reduction tank in a semi molten state, which made it difficult to slag out. For the novel magnesium production technology, the preparation process, properties, and calcination decomposition kinetics of pellets were investigated [20, 21], and the reduction kinetics and element diffusion mechanism were studied by thermogravimetric experiments and isothermal reduction experiments [22, 23]. However, the effect mechanism of CaF_2 on the calcination and reduction process of magnesium production process with prefabricated pellets was still unclear. In addition, previous studies on the role of CaF_2 in magnesium smelting were carried out in vacuum, and there were no relevant reports in flowing argon. Therefore, in this paper, the influence of CaF_2 on the calcination and reduction process in the process of magnesium production in flowing argon was studied by using prefabricated pellets, and the influence of CaF_2 on the reduction slag in the reduction process was also explored, which had a certain guiding significance for continuous production of magnesium by using prefabricated pellets.

2. Experiments

2.1. Raw materials

The raw materials used in this experiment were magnesite from Haicheng, Liaoning Province, China, and analytical grade calcium carbonate. Magnesite and calcium carbonate were mixed according to the molar ratio of calcium to magnesium 1: 1 instead of dolomite. The chemical composition of magnesite is shown in Table 1. In the experiment, the reducing agent and additive were ferrosilicon and calcium fluoride respectively. The content of silicon in ferrosilicon was 74.13%, which was from Anyang, Henan Province, China. Calcium fluoride was a

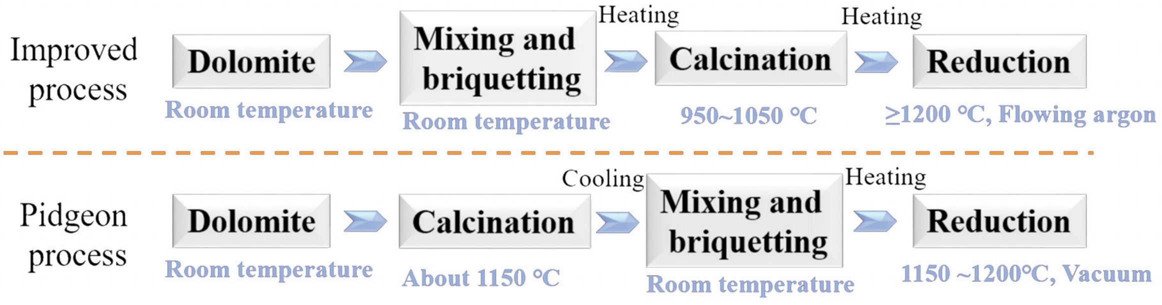

Figure 1. *Comparison of improved process and Pidgeon process*

chemical reagent purchased from Sinopharm Chemical Reagent Co., Ltd.

Table 1. *Chemical composition of magnesite*

Ore	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Magnesite/%	51.92	0.75	0.19	0.74	0.90	45.50

2.2. *Experimental apparatus*

The experiment was carried out in a vacuum resistance furnace, and the schematic diagram of the equipment is shown in Fig. 2. The temperature of the furnace could reach 1600 °C, and the temperature control system was programmed in different stages so that the calcination and reduction process could be carried out successively. The resistance furnace was equipped with a vacuum pump, the air in the furnace was exhausted before the experiment so as to realize the exchange of vacuum and argon, which could prevent the oxidation of ferrosilicon and reduce the experimental error.

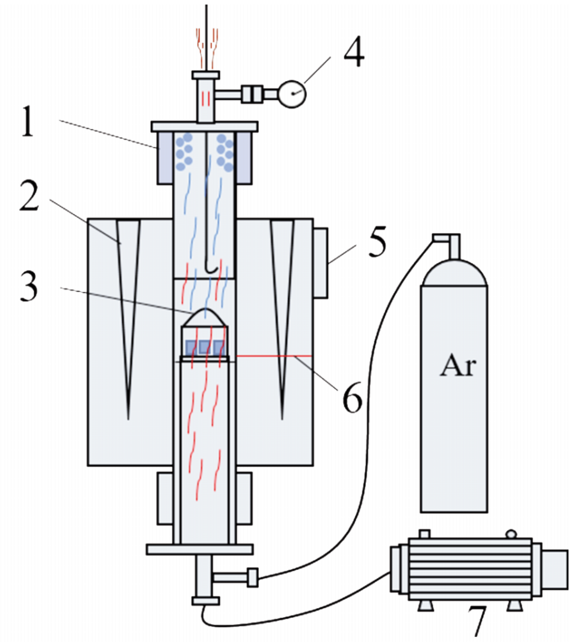

Figure 2. *Schematic diagram of the equipment: 1—Water jacket; 2—Silicon-Molybdenum bar; 3—Porous crucible; 4—Vacuum display instrument; 5—Control dial; 6—Thermocouple; 7—Vacuum pump*

2.3. *Experimental procedures*

The magnesite and ferrosilicon were crushed and finely ground to about 200 mesh, and then mixed according to the molar ratio of magnesite, calcium carbonate, and ferrosilicon of 2:2:1. The amount of calcium fluoride was added according to different experiments, and the addition range was 0~10% of the total mass of the above three raw materials. The mixed powder was pressed into cylindrical pellets with diameter of 15 mm by hydraulic equipment, and the briquetting pressure was 209.07 MPa. Due to the difference between the temperature displayed in the furnace and the temperature at the pellet reaction position, in order to ensure the accuracy of the experimental data, the temperature of the pellet reaction position and the temperature of different positions in the furnace were remeasured by thermocouple before the experiment. The temperature mentioned in this paper was the temperature remeasured by thermocouple. Then the prefabricated pellets were placed in the corundum crucible with holes, and calcined in the furnace at 1000 °C for 1 h. After that, the crucible was lifted 25 cm away from the reaction zone, and the furnace continued to heat up. It should be emphasized that the pellets would not carry out reduction reaction during the heating up process of the furnace. After reaching the reduction temperature, the crucible was put back to the original position for reduction experiment. The specific isothermal reduction operation method had been described in detail in the previous literature [23]. After the experiment, the phase analysis and magnesium content in the cooling slag were determined by X-ray diffraction (XRD, Bruker D8, Germany) and inductively coupled plasma emission spectrometer (ICP-OES, Optima 8300DV, Perkin-Elmer, USA), respectively. The reduction rate of magnesium was calculated by formula (1).

$$\eta_{\mathrm{Mg}} = \frac{M_1 \times \alpha - M_2 \times \beta}{M_1 \times \alpha} \qquad (1)$$

where η_{Mg} is the reduction rate of magnesium, M_1 is the initial mass of prefabricated pellets, α is the magnesium contents of the prefabricated pellets, M_2 is the mass of magnesium slag, β is the magnesium content of magnesium slag.

3. Results and discussion

3.1. *Effect of CaF_2 on the decomposition rate of prefabricated pellets*

In the experiment, prefabricated pellets were used as raw materials for magnesium production, and they had to be calcined before the reduction process. Therefore, the effect of CaF_2 on the calcination of prefabricated pellets was studied. In order to eliminate the effect of ferrosilicon on the calcination of pellets, the mixture of magnesite and calcium carbonate was only added with different content of calcium fluoride (0%, 3%, 5%, and 10%). Fig. 3 shows the effect of CaF_2 on the decomposition rate of the mixture of magnesite and calcium carbonate after calcination at 1000 °C for different time. The results showed that the decomposition rate of raw materials with CaF_2 was faster than that of 0% CaF_2, but the decomposition rate of pellets remained unchanged after 30 min and fluctuated around 48.86% (theoretical calcination decomposition rate). The XRD analysis of the calcined product is shown in Fig. 4. It was found that the product phases were MgO, CaO, and CaF_2, and no other phases were produced, which indicated that CaF_2 did not participate in the reaction during the calcination process, but only accelerated the calcination decomposition rate.

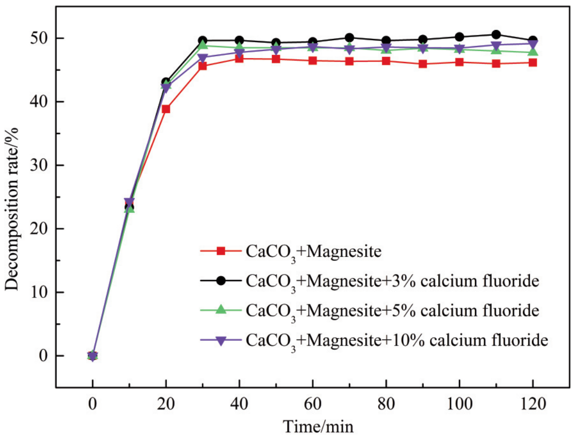

Figure 3. *Effect of CaF_2 on decomposition rate of the mixture of magnesite and calcium carbonate (1000°C)*

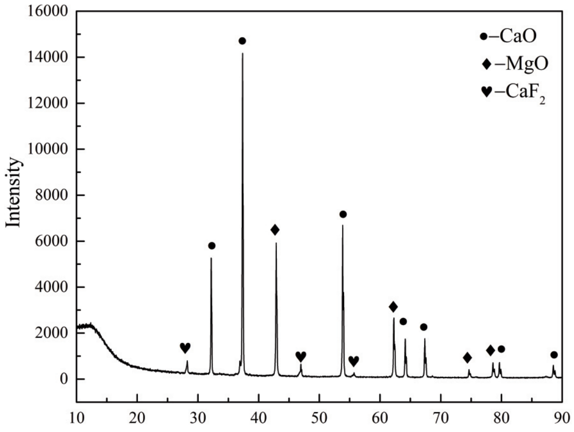

Figure 4. *XRD analysis of calcined products (3% CaF_2)*

3.2. Effect of CaF_2 on decomposition kinetics

The effect of CaF_2 on the calcination of prefabricated pellets was investigated by using a synchronous thermal analyzer (NETZSCH STA 449F3, Germany). The heating rate was 8 °C·min^{-1}, the temperature range was 25 °C ~ 1100 °C, the protective gas was argon, and the flow rate was 30 ml·min^{-1}. The DTA curves of carbonates and carbonates containing 3% CaF_2 were investigated, as shown in Fig. 5. The endothermic peaks of DTA curve were analyzed comprehensively, and the results are shown in Table 2. From the analysis results, the peak values of calcium carbonate and magnesite with CaF_2 were 855.3 °C and 676.6 °C respectively, which were lower than those of calcium carbonate and magnesite without calcium fluoride. In addition, the peak areas were smaller.

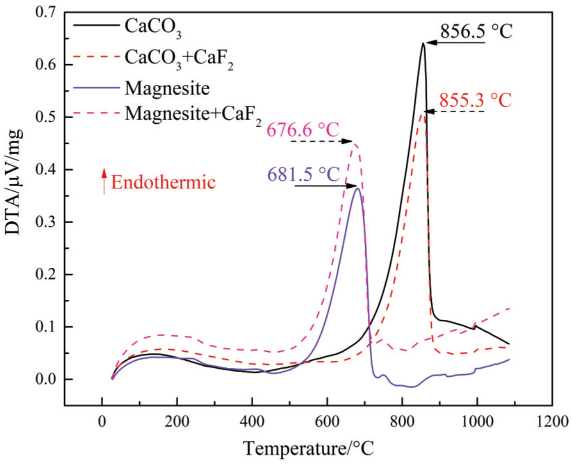

Figure 5. *DTA curves of carbonates and carbonates containing CaF_2*

Table 2. *Comprehensive analysis of endothermic peak*

Sample	Peak values/°C	Temperature range/°C	Peak area /μVs·mg^{-1}
$CaCO_3$	856.5	756.8~872.0	299.3
$CaCO_3$+CaF_2	855.3	758.4~875.1	268.0
Magnesite	681.5	581.7~716.8	247.4
Magnesite+CaF_2	676.6	586.7~711.1	247.0

In view of the above phenomena, the dynamic analysis and calculation were carried out. Dynamic thermal analysis method is generally used to calculate the kinetic parameters of thermal decomposition of solid materials. So far, there are many methods to calculate the kinetic parameters, such as ASTME693, ASTME2890, ASTME2070, Ozawa-Flynn-wall method, Freeman-Carroll method, Kinserger method, etc. [24-26], among which Kinserger method and Freeman Carroll method are more commonly used, but each has its own advantages and disadvantages. In this paper, the Freeman-Carroll method was used to calculate the kinetic parameters of decomposition of magnesite and calcium carbonate with calcium fluoride. According to the basic kinetic equation:

$$\frac{d\alpha}{dT}=\frac{A}{\Phi}e^{-E/RT}(1-\alpha)^{n} \tag{2}$$

where: α is the conversion; E is the activation energy and A is the pre-exponential factor; T is the temperature, K; R is the gas constant (J·mol^{-1}·K^{-1}); n is reaction order; and Φ is the heating rate, K·min^{-1}.

Formula (2) was derived and expressed by logarithm and subtraction:

$$\frac{\Delta\lg I}{\Delta\lg S''}=-\frac{E}{2.303R}\cdot\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\lg S''}+n \tag{3}$$

where: I is the value of DTA curve, V·g^{-1}, that is, the temperature difference between the sample and the reference material; T is the temperature, K; $S''$is the area of DTA curve from T to T_{∞}, (Vs·g^{-1}); T is the temperature of the reaction at a certain time; and T_{∞} is the temperature at which the reaction ends.

According to the formula (3), the curves of $\Delta lgI/\Delta lgS''$ and $\Delta(1/T)/\Delta lgS''$ were drawn. The slope was $-E/2.303R$, the intercept was the reaction order n, and R was 8.314 J·mol^{-1}·K^{-1}.

According to the DTA results in Fig. 5, the fitting curves of $\Delta lgI/\Delta lgS''$ and $\Delta(1/T)/\Delta lgS''$ of carbonate were obtained, as shown in Fig. 6. The results showed that the decomposition activation energy of magnesite was 162.33 kJ·mol^{-1} and the reaction order was 0.68; while the decomposition activation energy of magnesite with CaF_2 was 157.96 kJ·mol^{-1} and the reaction order was 0.54. For calcium carbonate, the calculation results showed that the decomposition activation energy of calcium carbonate was 135.65 kJ·mol^{-1}, and the reaction order was 0.12; while the decomposition activation energy of calcium carbonate with CaF_2 was 121.86 kJ·mol^{-1}, and the reaction order was 0.31. Through comparative analysis, the activation energy of carbonates ($CaCO_3$, $MgCO_3$) added with CaF_2 was lower than that of carbonates without CaF_2. Therefore, although CaF_2 did not participate in the reaction in the calcination stage, it reduced the decomposition activation energy of carbonate and accelerated the decomposition rate.

3.3. Effect of CaF_2 on reduction rate of MgO in prefabricated pellets

In the process of magnesium production by silicothermal method, the reduction temperature and time are the important factors affecting the reduction rate of MgO. The higher the reduction temperature is, the faster the reduction rate is, and the shorter the reduction time to reach equilibrium is. Previous studies [17, 27] had found that the addition of CaF_2 could increase the reduction rate and shorten the equilibrium time, i.e., the addition of CaF_2 could increase the reduction rate of MgO in the same reduction time. Most of the previous studies focused on the traditional Pidgeon process and aluminothermal process, which was characterized by the reduction process in vacuum, reduction temperature not more than 1250°C, and calcium fluoride addition not more than 6% [18, 19]. In this paper, magnesium was extracted by prefabricated pellets in flowing argon, so the effect of CaF_2 on the reduction rate of magnesium oxide was studied. The experimental conditions were as follows: reduction temperature was above 1250°C (1250°C, 1300°C, and 1350°C), CaF_2 content was 0 ~ 10% of the total mass of carbonate and ferrosilicon, argon flow rate was 0.2 m^3·h^{-1}, and reduction time was 2 h.

Fig. 7 shows the effect of CaF_2 content on the reduction rate of MgO at different temperatures. It could be seen from Fig. 7 that when the content of CaF_2 was 2%, the reduction rate of MgO could reach

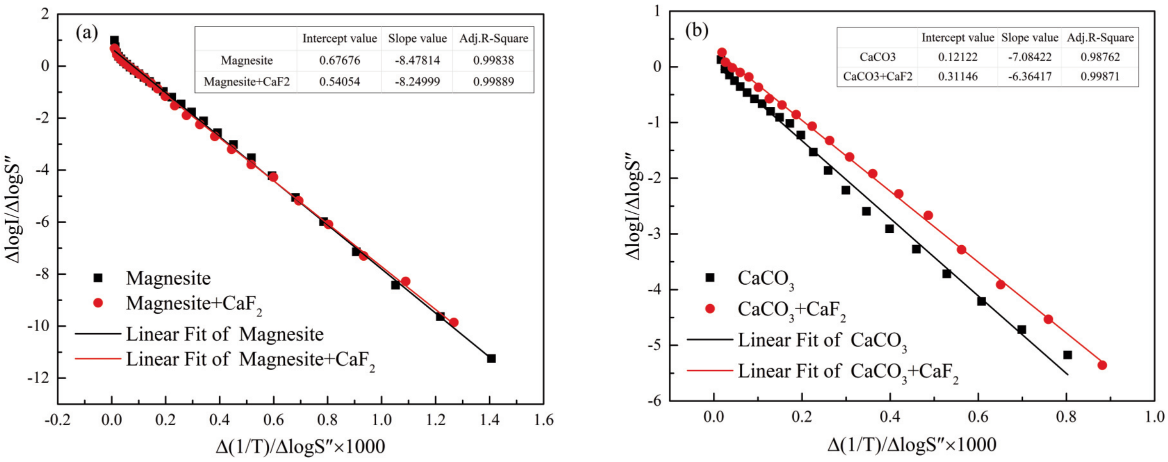

Figure 6. *The fitting line of DTA results of magnesite and calcium carbonate; a- magnesite; b- $CaCO_3$*

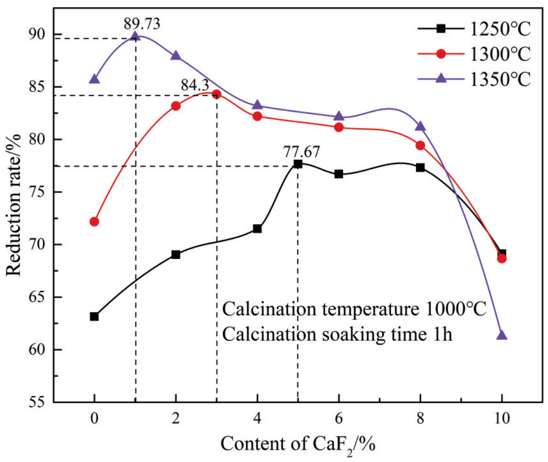

Figure 7. *Effect of CaF$_2$ content on reduction rate at different temperatures*

83.18% after reduction at 1300℃ for 2 h, which was 15.24% higher than that of 0% CaF$_2$ under the same conditions. Therefore, adding appropriate amount of CaF$_2$ could improve the reduction rate. This phenomenon could be explained as follows: due to the high activity of F- ion, it could increase the lattice defects of magnesium oxide; and the radius of F- ion and O- ion was close, it could destroy the surface lattice of magnesium oxide, distort the magnesium oxide crystal, increase the crystal activity, and promote the fracture of Mg-O bond [27]. Compared with the bond energy, the bond energy of MgO was 347 kJ·mol^{-1}, and that of SiO$_2$ was 460 kJ·mol^{-1}. The bond energy of Mg-O bond was less than that of Si-O bond, which indicated that Si-O bond was more stable. Once Mg-O bond broke, O combined with Si atoms to form more stable Si-O bond, and Mg left the reaction system as Mg atoms. Therefore, after the addition of CaF$_2$, the melting point of the whole reaction material decreased, forming a melting system with certain fluidity, which was conducive to the contact between MgO, Si, and F- ion, and improved the reduction rate of MgO [17]. An interesting phenomenon could also be found in Fig. 7 that the reduction rate of MgO decreased due to the excessive content of CaF$_2$, which was consistent with the results reported by other researchers [28]. With the increase of reduction temperature, this phenomenon was more obvious. That was, with the increase of temperature, the content of CaF$_2$ decreased when the reduction rate of MgO reached the maximum. For example, at 1250 ℃, when the reduction rate of MgO was the highest (77.67%), the content of CaF$_2$ was 5%. At 1300 ℃ and 1350 ℃, the reduction rate of MgO was the highest (84.30% and 89.73%), and the content of CaF$_2$ was 3% and 1%, respectively. This may be due to the higher temperature, the more active molecules and the faster reaction rate, so adding a small amount of CaF$_2$ in the raw material could obtain better reduction effect.

3.4. Effect of CaF$_2$ content on phases in reduction slag

In the process of metal smelting, CaF$_2$ is usually used as a flux agent to reduce the melting point of reactants. In the magnesium production process, CaF$_2$ interacts with the reduction products to reduce the melting point of the reduction slag. Therefore, under the experimental conditions, with the increase of CaF$_2$ content, the slag obtained after the reduction process was more compact and sintered, and the slag adhered to the bottom of the crucible at high temperature. The SEM analysis was carried out on the slag reduced by prefabricated pelletscontaining 4% CaF$_2$ at 1350 ℃, as shown in Fig. 8. The surface scan results showed

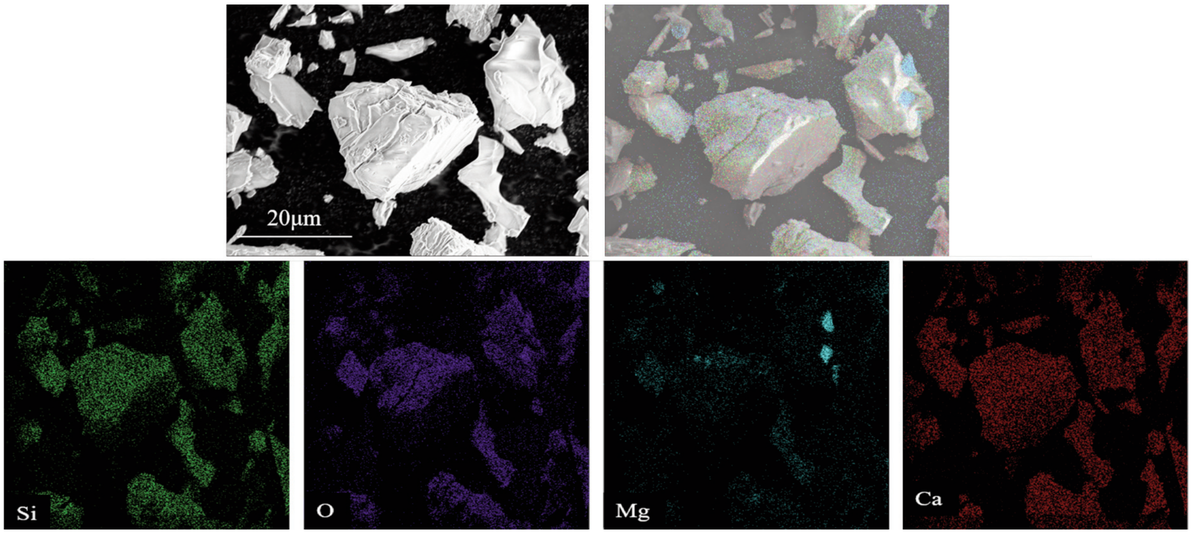

Figure 8. *SEM of reduction products of prefabricated pellets containing 4% CaF$_2$ at 1350℃*

that some unreacted MgO was wrapped by dicalcium silicate phase and could not participate in the reduction reaction. Therefore, the excessive formation and sintering of dicalcium silicate phase prevented the direct contact between MgO and Si, hindered the diffusion of reactants in the reduction process, and reduced the reduction rate of MgO in the same time.

The XRD analysis was carried out on the reduced slag, and the results were shown in Fig. 9. It could be seen from Fig. 9 (a) that after reduction at 1250 ℃, Ca_2SiO_4 phase and unreacted MgO phase were the main phases in the reduced slag. However, with the increase of CaF_2 content, the crystal type of a large amount of dicalcium silicate in the cooled slag changed from monoclinic β-Ca_2SiO_4 to orthorhombic γ-Ca_2SiO_4. This transformation could also be found in the slag reduced at 1300 ℃ in Fig. 9 (b) and 1350 ℃ in Fig. 9 (c). The difference was that with the increase of reduction temperature, the content of CaF_2 required for this transformation gradually decreased, corresponding to 3% and 1% respectively. These data were consistent with the CaF_2 content corresponding to the maximum reduction rate of magnesium oxide in Fig. 7.

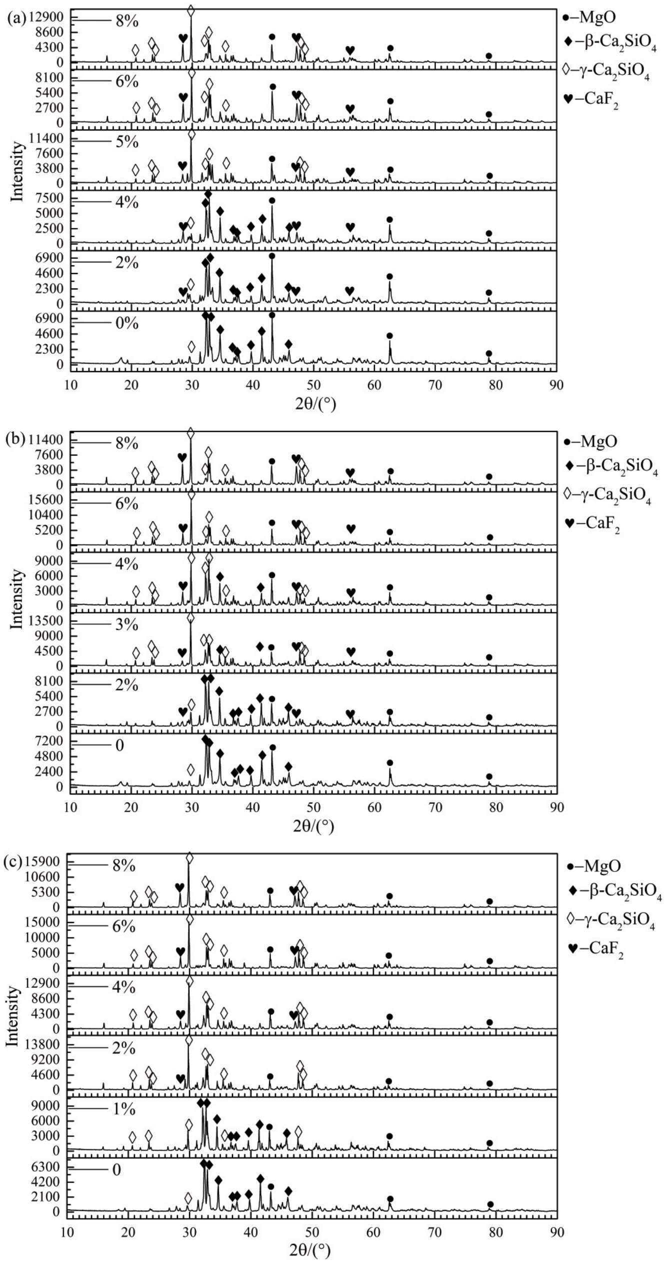

Figure 9. *XRD patterns of reduction slag with different content of CaF_2; (a)-1250℃; (b)-1300℃; (c)-1350℃*

3.5. Effect of CaF_2 and MgO on crystal type of dicalcium silicate

Generally, dicalcium silicate is γ-Ca_2SiO_4 at room temperature, which has a typical olivine structure. The [SiO_4] tetrahedron in the structure is connected by [CaO_6] octahedron to form a three-dimensional structure, and the coordination number of Ca^{2+} is 6. The [SiO_4] tetrahedron of high temperature dicalcium silicate is also connected by the calcium oxygen polyhedron, but the Ca^{2+} coordination number is not fixed. With the change of temperature, phase transformation can occur between different crystal types of dicalcium silicate, even accompanied by obvious volume change, in which the volume increase of about 13% is produced when β-Ca_2SiO_4 transforms into γ-Ca_2SiO_4, which is also the reason for the pulverization of high temperature magnesium slag when cooling down [29, 30]. Previous studies have shown that [31, 33], in addition to the different crystal types of dicalcium silicate caused by temperature, foreign ions could also cause dicalcium silicate to present different crystal types. The solid solution of foreign ions into dicalcium silicate crystal could prevent the transformation of high temperature crystal type to low temperature crystal type in the process of temperature drop, thus stabilizing β-Ca_2SiO_4 or even α-Ca_2SiO_4 to room temperature. The phenomenon that dicalcium silicate changed from β to γ with the change of CaF_2 content in Fig. 9 may be due to the joint action of MgO and CaF_2. Therefore, the effect of MgO on dicalcium silicate was studied experimentally. Firstly, MgO, CaO, and SiO_2 were mixed according to the molar ratio of (0.5-2.5): 2: 1, and then kept at 1300 °C for 2 h. The products were cooled to room temperature and analyzed by XRD, as shown in Fig. 10. It could be seen from the Fig. 10 that with the increase of MgO content, β-Ca_2SiO_4 was stably stored to room temperature, indicating that MgO could be used as a stabilizer of β-Ca_2SiO_4. Only when the molar ratio of MgO to CaO was greater than or equal to 2: 2, MgO could stabilize β-Ca_2SiO_4 to room temperature.

Based on the above research and analysis in Fig. 9 and Fig. 10, under the experimental conditions, the molar ratio of MgO, CaO, and Si in the prefabricated pellets was 2: 2: 1, so MgO could stabilize the β-Ca_2SiO_4 in the reduced slag, which could keep β-Ca_2SiO_4 at room temperature. This phenomenon could also be seen in Fig. 9. When there was no CaF_2 in the raw material, the main phase in the reduction slag was β-Ca_2SiO_4. However, when a certain amount of CaF_2 was added to the raw material, the stabilizing effect of MgO on β-Ca_2SiO_4 could be broken and dicalcium silicate could be changed from β-Ca_2SiO_4 to γ-Ca_2SiO_4. Therefore, CaF_2 can promote the transformation of dicalcium silicate to γ-Ca_2SiO_4 in the reduction slag of magnesium production by silicothermal process with prefabricated pellets.

4. Conclusions

In this work, the effect of CaF_2 on the process of magnesium production by silicothermal process with prefabricated pellets in flowing argon was investigated. The experimental results were the following:

(1) In the process of calcination, CaF_2 could accelerate the decomposition rate of the prefabricated pellets, and had no side effect on the calcined products; through the analysis and calculation of differential thermal experiment, CaF_2 could reduce the decomposition activation energy of calcium carbonate and magnesite in the prefabricated pellets, and reduce the reaction temperature.

(2) In the process of reduction, appropriate CaF_2 could promote the reduction rate of MgO. At 1250 °C ~ 1350 °C for the same time, when the reduction rate was the highest, the CaF_2 content in the prefabricated pellets was 5%, 3%, and 1%, respectively.

(3) MgO had a stabilizing effect on β-Ca_2SiO_4 in the reduced slag. When a certain amount of CaF_2 was added, the stabilizing effect of MgO on β-Ca_2SiO_4 could be broken and dicalcium silicate could be changed from β-Ca_2SiO_4 to γ-Ca_2SiO_4.

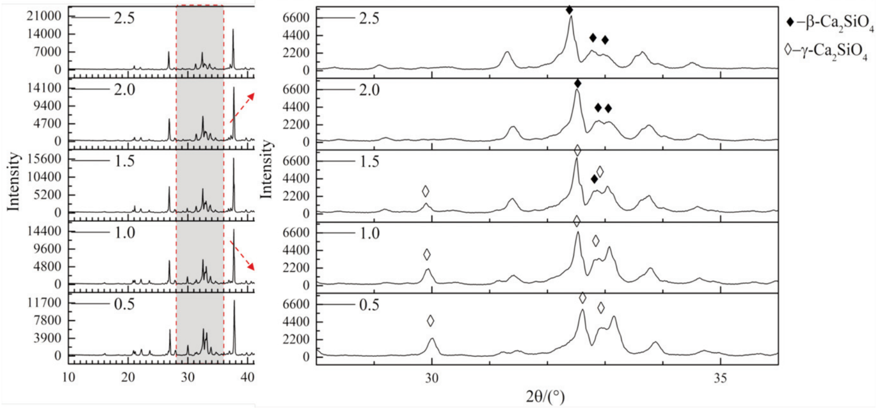

Figure 10. *(a) XRD patterns of MgO-CaO-SiO_2 reaction system; (b) Partial enlarged XRD pattern*

Acknowledgments

This work was supported by National Natural Science Foundation of China under Grants (U1508217; 51504058), the Fundamental Research Funds for the Central Universities of China (N162504003).

Author contributions

Conception and design of study: J.-H. Guo, D.-X. Fu, T.-A. Zhang. Acquisition of data: J.-H. Guo, Z.-H. Ji, Y.-S. Wang. Analysis and/or interpretation of data: J.-H. Guo, D.-X. Fu. Drafting the manuscript: J.-H. Guo. Critical revision: J.-H. Guo.

Statement of the manuscript

This manuscript is our original unpublished work, it has not been submitted to any other journal for reviews and present submission to Journal of Mining and Metallurgy, Section B: Metallurgy is not a duplicate sent to another publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Y. He, M. Jiang, Present situation of mining and utilization andexisting problems of magnesite resource of our country, Refractories &Lime, 37 (3) (2012) 25-28. https://doi.org/10.16425/j.cnki.1673-7792.2012.03.007.

[2] L. Tian, A. Tahmasebi, J. L. Y, An experimental study on thermal decomposition behaviorof magnesite, Journal of Thermal Analysis and Calorimetry, 118 (2014) 1577-1584. https://doi.org/10.1007/s10973-014-4068-9.

[3] Y. N. Zhao, G. C. Zhu, A technology of preparing honeycomb-like structure MgO from low grade magnesite, International Journal of Mineral Processing, 126 (10) (2014) 35-40. https://doi.org/10.1016/j.minpro.2013.11.006.

[4] Q. J. Gao, G. Wei, X. Jiang, H. Y. Zheng, F. M. Shen, Characteristics of calcined magnesite and it's application in oxidized pellet production, Journal of Iron and Steel Research International, 21 (4) (2014) 408-412. https://doi.org/10.13228/j.boyuan.issn1006-706x.2014.04.009.

[5] Q. D. Hou, X. D. Luo, M. T. Li, D. An, Z. P. Xie, Non-isothermal kinetic study of high-grade magnesite thermal decomposition and morphological evolution of MgO, International Journal of Applied Ceramic Technology, 00 (2021) 1-8. https://doi.org/10.1111/ijac.13708.

[6] C. Ghosh, A. Ghosh, H. S. Tripathi, J. Ghosh, M. K. Haldar, Studies on densification, mechanical, microstructural andstructure–properties relationship of refractory aggregates prepared from Indian magnesite by changing lime-silica ratio, Ceramics International, 40 (10B) (2014) 16791–16798. https://doi.org/10.1016/j.ceramint.2014.08.018.

[7] A. Kumar, S. Kumar, N. K. Mukhopadhyay, Introduction to magnesium alloy processing technology and development of low-cost stir casting process for magnesium alloy and its composites, Journal of Magnesium and Alloys, 6 (3) (2018) 245-254. https://doi.org/10.1016/j.jma.2018.05.006.

[8] R. E. Brown, Magnesium in the 21st century, Advanced Materials & Processes, 167 (1) (2009) 31-33.

[9] B. L. Mordike, T. Ebert. Properties-applications-potential, Materials Science and Engineering: A, 302 (1) (2001) 37-45. https://doi.org/10.1016/s0921-5093(00)0135 1-4.

[10] J. D. Du, W. J. Han, Y. H. Peng, Life cycle greenhouse gases, energy and cost assessment of automobiles using magnesium from Chinese Pidgeon process, Journal of Cleaner Production, 18 (2) (2010) 112-119. https://doi.org/10.1016/j.jclepro.2009.08.013.

[11] F. Cherubini, M. Raugei, and S. Ulgiati, LCA of magnesium production: Technological overview and worldwide estimation of environmental burdens, Resources, Conservation and Recycling, 52 (8-9) (2008) 1093-1100. https://doi.org/10.1016/j.resconrec.2008.05.001.

[12] D. X. Fu, N. X. Feng, Y. W. Wang, J. P. Peng, Y. Z. Di, Kinetics of extracting magnesium from mixture of calcined magnesite and calcined dolomite by vacuum aluminothermic reduction, Transactions of Nonferrous Metals Society of China, 24 (3) (2014) 839–847. https://doi.org/10.1016/S1003-6326(14)63133-2.

[13] Y. Tian, B. Q. Xu, B. Yang, C. B. Yang, T. Qu, D. C. Liu, Y. N. Dai, Magnesium production by carbothermic reduction in vacuum, Journal of Magnesium and Alloys, 3 (2015) 149-154. https://doi.org/10.1016/j.jma.2015.04.001.

[14] C. B. Yang, Y. Tian, T. Qu, B. Yang, B. Q. Xu, Y. N. Dai, Magnesium vapor nucleation in phase transitions and condensation under vacuum conditions, Transactions of Nonferrous Metals Society of China, 24 (2) (2014) 561-569. https://doi.org/10.1016/S1003-6326(14)63096-X.

[15] M. Abdellatif. Review of the development work on the Mintek thermal magnesium process (MTMP), Journal South African Institute Mining Metallurgy, 111 (2011) 393-399.

[16] T. A. Zhang, Z. H. Dou, Z. M. Zhang, Y. Liu, G. Z. Lv, J. C. He, A rapid and continuous process for magnesium production. CN104120282-B, 2015. [Patent].

[17] Y. W. Wang, J. You, N. X. Feng, W. X. Hu, Influence of CaF2 addition on vacuum aluminothermic reduction, Chinese Journal of Vacuum Science and Technology, 32 (10) (2012) 889-895. https://doi.org/10.3969/j.issn.1672-7126.2012.10.07

[18] C. Wang, C. Zhang, S. J. Zhang, L. J. Guo, The effect of CaF2 on the magnesium production with silicothermal process, International Journal of Mineral Processing, 142 (2015) 147-153. https://doi.org/10.1016/j.minpro.2015.04.017.

[19] T Zhang. Investigation on the reaction between MgO-CaO-CaF2 and Al-C powders to extract magnesium under atmospheric pressure, Journal of Magnesium and

Alloys, 7 (2) (2019) 328-334. https://doi.org/10.1016/j.jma.2019.0300 1.

[20] J. H. Guo, T. A. Zhang, D. X. Fu, J. B. Han, Z. H. Ji, Z. H. Dou, Research on properties of prefabricated pellets of silicothermic process after calcination in flowing argon atmosphere, Magnesium Technology, (2020) 303-307. https://doi.org/10.1007/978-3-030-36647-6_45.

[21] M Wen, T. A. Zhang , Z. H. Dou, Y. Guan, R. Zhang, Two-stage calcination of dolomite pellets for mg-extraction by silicothermic reduction in vacuum, Chinese Journal of Vacuum Science and Technology, 34 (11) (2014) 1242-1245. https://doi.org/10.13922/j.cnki.cjovst.2014.11.19.

[22] D. X. Fu, T. A. Zhang, L. K. Guan, Z. H. Dou, M. Wen,., Magnesium production by silicothermic reduction of dolime in pre-prepared dolomite pellets, JOM, 68 (12) (2016) 3208-3213. https://doi.org/10.1007/s11837-016-2034-7.

[23] J. H. Guo, D. X. Fu, J. B. Han, Z. H. Ji, Z. H. Dou, T. A. Zhang, Kinetics of extracting magnesium from prefabricated pellets by silicothermic process under flowing argon atmosphere, Journal of Mining and Metallurgy Section B-Metallurgy, 56 (3) (2020) 379-386. https://doi.org/10.2298/JMMB200712031G.

[24] Y. S. Che, Z. H. Hao, J. P. Zhu, Z. H. Fu, J. He, J. X. Song, Kinetic mechanism of magnesium production by silicothermy in Argon Flowing, Thermochimica Acta, 681 (2019) 178397. https://doi.org/10.1016/j.tca.2019.178397.

[25] S. Vyazovkin, Computational aspects of kinetic analysis. Part C. The ICTAC Kinetics Project - The light at the end of the tunnel?, Thermochimica Acta, 355 (2000) 155-163. https://doi.org/10.1016/S0040-6031(00)00445-7.

[26] A. K. Burnham, Computational aspects of kinetic analysis. Part D: The ICTAC Kinetics Project-Multi-thermal-history model-fitting methods and their relation to isoconversional methods, Thermochimica Acta, 355 (2000) 165-170. https://doi.org/10.1016/S0040-6031(00)00446-9.

[27] Y. Tian, H. X. Liu, B. Yang, T. Qu, Y. N. Dai, P. Peng, Magnesium extraction from magnesia by carbothermic reduction in vacuum, Chinese Journal of Vacuum Science and Technology, 32 (9) (2012) 814-819. https://doi.org/10.3969/j.issn.1672-7126.2012.04.08

[28] I. M. Morsi, K. A. E. Barawy, M. B. Morsi, S. R. Adbel-Gawad, Silicothermic reduction of dolomite Ore under inert atmosphere, Canadian Metallurgical Quarterly, 41 (1) (2002) 15-28. https://doi.org/10.1179/cmq.2002.41.1.15.

[29] I. M. Pritts, K. E. Daugherty, The effect of stabilizing agents on the hydration rate of β-C2S, Cement and Concrete Research, 6 (6) (1976) 783-795. https://doi.org/10.1016/0008-8846(76)90008-9.

[30] M. Regourd, Crystal chemistry of Portland cement phases, Applied Science Publishers, New York, 1983.

[31] X. J. Feng, S. Z. Long, Effect of minor ions on the stability of β-C2S and its mechanism, Journal of the Chinese Ceramic Society, 13 (4) (1985) 424-431.

[32] Z. Y. Wang, M. Wang, Z. J. Wen, W. Zhang, Progress on study of dicalcium silicate and low calcium cement with dicalcium silicate as a main mineral composition, Materials Review, 30 (1) (2016) 73-78. https://doi.org/10.11896/j.issn.1005-023X.2016.01.012

[33] K. Fukuda, I. Maki, S. Ito, T. Miyake, Structural change in phosphorus-bearing dicalcium silicate, Journal of the Ceramic Society of Japan, 105 (2) (1997) 117-121. https://doi.org/10.2109/jcersj.105.117.

UTICAJ KALCIJUM FLOURIDA NA EKSTRAKCIJU MAGNEZIJUMA IZ MAGNEZITA I KALCIJUM KARBONATA SILIKOTERMIČKOM REDUKCIJOM U PROTOČNOM ARGONU

J.-H. Guo [a, b], D.-X. Fu [a, b], J.-B. Han [a, b], Z.-H. Ji [a, b], Y.-S. Wang [a, b], T.-A. Zhang [a, b, *]

[a] Metalurški fakultet, Severoistočni univerzitet, Šenjang, Kina
[b] Glavna laboratorija za ekološku upotrebu višemetalnih minerala (Ministarstvo prosvete), Severoistočni univerzitet, Šenjang, Kina

Apstrakt

Proizvodnja magnezijuma se trenutno uglavnom vrši polukontinuirano uz prisustvo ferosilicijuma kao redukcionog sredstva pod visokim temperaturama i u vakuumu. Da bi se postigla kontinuirana proizvodnja magnezijuma predložena je nova metoda ekstrakcije magnezijuma iz magnezita niskog kvaliteta i kalcijum karbonata putem silikotermičke metode u protočnom inertnom gasu. U radu je ispitavan uticaj kalcijum flourida (CaF_2) na brzinu razlaganja, kinetiku razlaganja i vrstu kristala dikalcijum silikata u redukcionoj šljaci. Rezultati eksperimenta su pokazali da kalcijum fluorid može ubrzati razlaganje karbonata i da nema neželjenih efekata na kalcinirane proizvode. Pored toga, rezultati analize DTA krivih je pokazala da kalcijum fluorid može smanjiti energiju aktivacije reakcije razlaganja, kao i temperaturu reakcije karbonata u prefabrikovanom peletu. Rezultati redukcionih eksperimenata su pokazali da bi odgovarajući kalcijum fluorid ubrzao postupak redukcije magnezijuma u temperaturnom opsegu od 1250 ℃ ~ 1350 ℃ i u istom vremenskom okviru kada je odgovarajući sadržaj kalcijum flourida 5%, 3% i 1%, odnosno kada je brzina redukcije dostigla maksimalnu vrednost. Višak kalcijum fluorida je smanjio brzinu redukcije magnezijuma, ali ubrzao je transformaciju dikalcijum silikata u γ fazu u redukcionoj šljaci.

Ključne reči: *Magnezijum; Kalcijum fluorid; Magnezit; Dikalcijum silikat; Silikotermički proces*