Magnesium Technology 2014
Edited by: Martyn Alderman, Michele V. Manuel, Norbert Hort, and Neale R. Neelameggham
TMS (The Minerals, Metals & Materials Society), 2014

EFFECT OF PHYSICAL PROPERTIES OF DOLOMITE ON CARBOTHERMIC REDUCTION

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Keywords: Carbothermic Reduction, Dolomite, Graphite, Magnesium

Abstract

Magnesium is widely utilized in machine building industry. Compared to other industry routes, carbothermic reduction method has many advantages in producing magnesium, particular saving energy and reducing cost. The mixture of calcined dolomite and graphite was agglomerated to cylinder, which was carried out under the condition with 1773K, 60min and 5000Pa. The effect of particle size, the mole ratio of C:MgO and pressure of agglomeration are studied and discussed. Furthermore, the decomposition of dolomite contains two stages. The optimal conditions (reduction ratio of MgO reaches to 69.64%) were: mole ratio of C:MgO is 3:1, pressure of agglomeration is 8MPa, particle size of calcined dolomite is 120-160 mesh.

Introduction

Magnesium is the lightest metal of all the commonly utilized metal and applied in car industry, medical industry and other industries [1-3]. The global production of magnesium is based on Pidgeon process [4] and electrolytic process. However the both process cause high cost and environment problem, such as emission HCl and Cl_2. The carbothermic reduction [5, 6] provides the potential process, which can produce magnesium with a lower-energy and higher-productivity than existing industrial routes [7].

The conditions of sample are the important factors in the process. Several investigations have been carried out to exam the magnesium recovery from the magnesia. Mohammad NUSGEH et al. [8] presented the results of an investigation on the effect of mechanical milling sample in carbothermic reduction route on magnesia. They carried out the experiments by milling the magnesia and graphite with keeping different times. And the characters of the mixture were analysis by SEM, SSA and XRD and had changed significantly. The reaction of milled mixture occurred at lower temperature than that of unmilled sample. Tian Yang et al. [9] investigated the other factors of carbothermic reduction on magnesia and coking coal. It clearly showed that the conditions of pellets and content of CaF_2 affected the losing ratio obviously. In our work, the effect of mole ratio of C:MgO, pressure of agglomeration and the particle size of calcined dolomite on the reduction ratio were researched.

Experiments

The chemical composition of the dolomite was investigated by XRF and given in Table Ⅰ. The main compounds of the dolomite were CaO and MgO.

Table Ⅰ. Chemical composition of dolomite, wt-%

CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3
53.04	2.67	0.48	42.31	0.65

The calcined dolomite was obtained after calcined at 1223K for 15min and separated to several size conditions by sieving process. The reduction experiments were carried out in the electronic furnace and the schematic of experimental system shown as Figure 1. The temperature was controlled with B type thermocouple, which could detective temperature precision 1K. The mixture (calcined dolomite and graphite) was forming to the shape with height-18mm and diameter-19mm. And the samples and mold are shown as

Figure 2. The mixture was put into the Al_2O_3 Crucible in the furnace. The argon was charged into the furnace at a rate of 66cm^3/min. The furnace was filled with argon air for 5min, and then the gas was drained out by vacuum pump. Then the protect air would been charged into the furnace again. These processes were recycling for five times. The samples was heated from room temperature to 573K at rate of 3K/min and held for 15min aim to remove the absorbed gas and water. Then the temperature was heated to 1773K at rate of 5K/min. The experiments were carried out under the condition with 1773K, 60min and 5000Pa. X-ray fluorescence (XRF), X-ray diffraction (XRD) and chemical analysis method were utilized in the experiments.

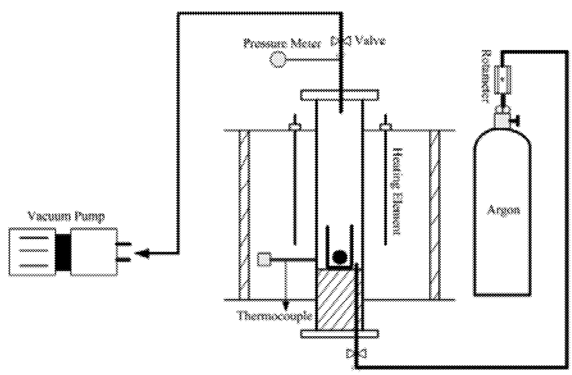

Figure 1.The schematic of experimental system

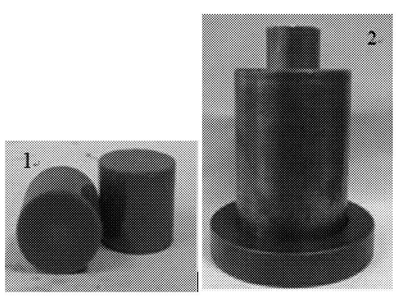

Figure 2.The photographs of samples (1) and mold (2)

Results and Discussions

Materials Prepared

The XRD patterns in Figure 3 indicated that $Mg(Ca)(CO_3)_2$ is the only Mg containing phase in dolomite. And the phases of calcined dolomite which only contained CaO and MgO were studied by XRD patterns. Figure 4 showed the DSC and TG curves of dolomite. It could be seen from Figure 4 that the mass of mixture decreased with increasing temperature from 373K to 1500K. The main mass losing of dolomite was absorbed water and gas at the temperature range of 373K to 573K. The decomposition of dolomite occurred as above 880K, which was proved by the TG curves. However, the TG curve changed to smooth when the temperature was above 1110K. It could be seen that the dolomite had decomposed completely. The decomposition of dolomite can be described as equation (1) and equation (2).

$$Mg(Ca)(CO_3)_2 = MgO + CaCO_3 + CO_2 \tag{1}$$

$$CaCO_3 = CaO + CO_2 \tag{2}$$

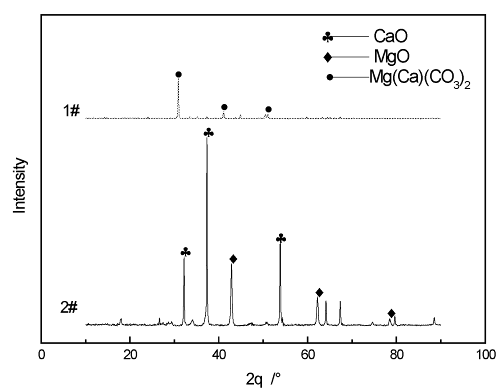

Figure 3.The XRD patterns of dolomite (1#) and calcined dolomite (2#)

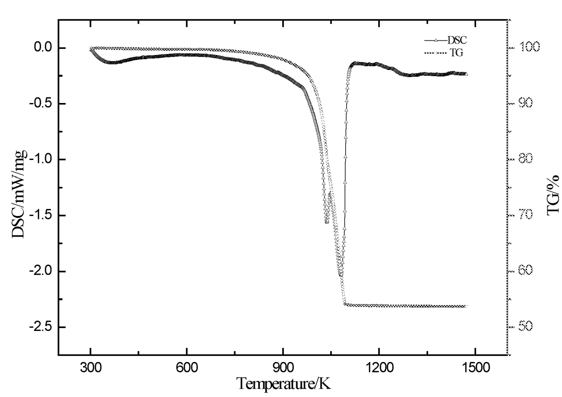

Figure 4.The DSC and TG curves of dolomite

Reduction Reaction

The main reaction was described as equation (4). And the thermodynamic feasibility of the reduction reaction had been considered and the Gibbs free energy ΔG_T was calculated with the results of ΔG_T<0. Furthermore, the XRD patterns of mixture were shown in Figure 5 which indicated that only Mg existed in sample 2# and proved that the reduction reaction between graphite and calcined dolomite occurred in the experiments. Then the reduction ratio used for evaluated the degree of reduction reaction could be calculated according to formula (5).

$$MgO(s)+C(s)=Mg(g)+CO(g) \quad \Delta G^0=618300-291.76T \tag{4}$$

$$R=\frac{m_1\times\beta-m_2\times\alpha}{m_1\times\beta}\times100\% \tag{5}$$

R: reduction ratio of calcined dolomite, %
m_1,β: the weight and mass percent of initial sample, g, %
m_2,α: the weight mass percent of final sample after reaction, g, %

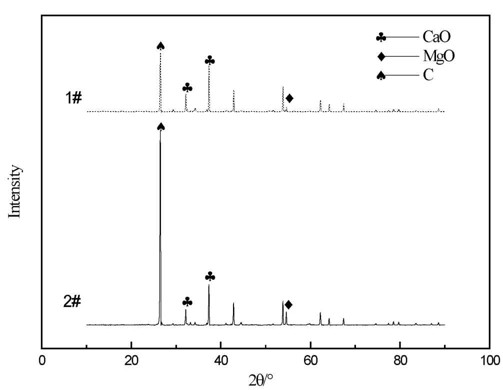

Figure 5.The XRD patterns of mixture
(1#: the final sample of C and calcined dolomite after reaction, 2#: the initial sample of C and calcined dolomite)

The effect of mole ratio of C:MgO on reduction ratio was shown in Figure 6. The samples were prepared with the conditions: the agglomeration pressure was 5MPa and the particle size of calcined dolomite was 160-200 mesh. The reduction ratio was 12.52% with the mole ratio 1:1 of C:MgO. And the reduction ratio increased quickly in the earlier stage with the mole ratio from 1:1 to 2:1 and reached to 55.48% with mole ratio of 2:1. It increased slower in the second stage with the mole ratio from 2.5:1 to 3:1 than first stage and reached to 62.31% with mole ratio 3:1. The reduction reaction between C and MgO could be described as a solid-solid reaction as equation (6), which was greatly affected by the contacting area of mixture powder. And the contacting area was increased significantly with the increasing of mole ratio, which was benefit for the reduction ratio. However when the mole ratio of C:MgO was higher than 2.5:1, the effect of mole ratio was not as greatly as the earlier stage. It could be explained by that the contacting area did not always keep increasing with the increasing of mole ratio.

$$A(s)+B(s)=C(g)+D(g) \tag{6}$$

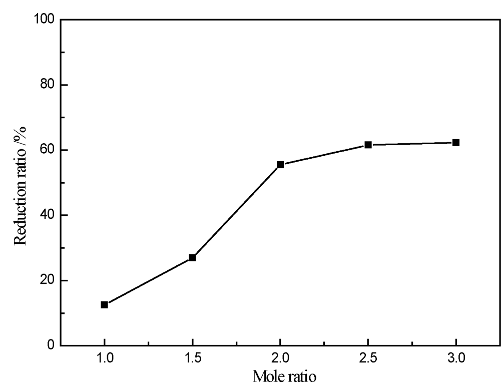

Figure 6.Effect of mole ratio of C:MgO on reduction ratio

Figure 7 shows the effect of agglomeration pressure on reduction ratio. The samples were prepared with the conditions: the mole ratio was 2:1 of C:MgO and the particle size was 160-200 mesh. The reduction ratio was 36.45% with agglomeration pressure of 2MPa and kept increasing until the agglomeration pressure reached 8MPa with reduction ratio of 68.51%. However it began to decrease when the agglomeration pressure was beyond 8MPa. It was probably because the path of compact mixture was blocked by increasing agglomeration pressure. The products of Mg (g) and CO (g) could not be released as soon as possible. The degree of reaction was limited with the increasing agglomeration pressure.

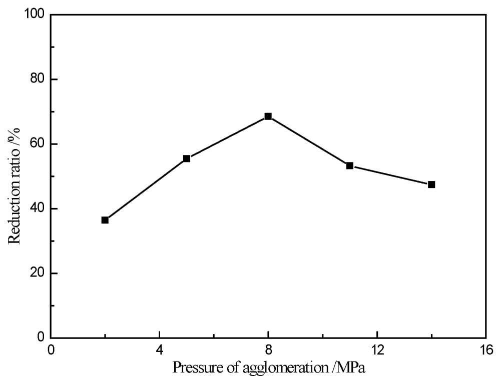

Figure 7.Effect of agglomeration pressure on reduction ratio

Figure 8 shows the effect of powder size on reduction ratio. The samples were prepared with the conditions: the mole ratio was 2:1 (C:MgO) and the agglomeration pressure was 5MPa. The reduction ratio reached to 62.56% with the size of 120-160 mesh. The phenomenon could be explained by relationship between contacting area of powder and the gas releasing path. When samples were prepared with 80-120 mesh, the contacting area of graphite and dolomite increased and the path has not been blocked completely. Therefore the reduction ratio increased. However when the size of samples decreased to 160-200 mesh, blocked path do much more effect than the increasing contact area to the reduction reaction. That was the reason the reduction ratio began to decrease.

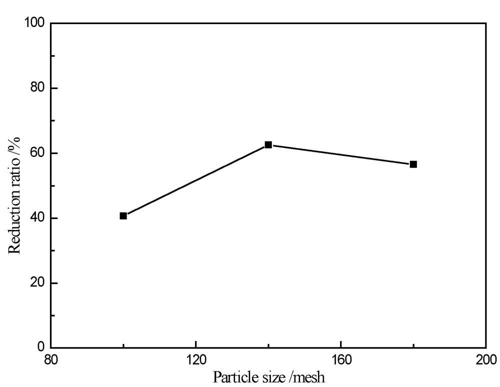

Figure 8.Effect of size of calcined dolomite on reduction ratio

According to our previous researches, other experiments were carried out under 1773K, 60min and 5000Pa with the physical properties: mole ratio of C:MgO was 3:1, pressure of agglomeration was 8Mpa, size of calcined particle was 120-160 mesh. And the reduction ratio reached to 69.64%.

Conclusions

The present work did not carry out the separation of reaction [4] products Mg and CO. we just focused on requirements for the forward reaction. We will carry out the separation of products Mg and CO to prevent back reaction in another study. According to present investigation, the following conclusions can be obtained:

(1) The decomposition of dolomite occurs as two steps. The dolomite decomposes to MgO and $CaCO_3$ at 880K firstly, and then $CaCO_3$ begins to decompose to CaO at 1050K.

(2) The reduction reaction between calcined dolomite and graphite occurs under the conditions with 1773K, 60min and 5000Pa.

(3) The reduction ratio of calcined dolomite is greatly affected by physical properties of the materials.

(4) The optimum conditions are: the mole ratio of C:MgO is 3:1, the pressure of agglomeration is 8MPa and the particle size of calcined dolomite is 120-160 mesh.

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