Magnesium Technology 2013
Edited by: Norbert Hort, Suveen N. Mathaudhu, Neale R. Neelameggham, and Martyn Alderman
TMS (The Minerals, Metals & Materials Society), 2013

Research on new type materials preparation for magnesium production by Silicothermic process

WEN Ming, ZHANG Ting-an, DOU Zhi-he, REN Xiao-dong, ZHANG Rui, ZHOU Lian

(School of Materials and Metallurgy of Northeastern University, Key Laboratory of Ecological Utilization of Multi-metal Inter grown Ores of Education Ministry, Shenyang, China 110819)

Key words: Dolomite; Bentonite; Composite binder; Silicothermic process

Abstract

During the magnesium preparation process of the silicothermic process, dolomite was made into pellets after calcination process, about 5% fine materials would be produced which can't be used and lead to high energy consumption and high-cost. Based on in-situ reduction of dolomite-based desulfurization theory, this paper proposed a new technology that dolomite was made into the pellets first and then was calcined to prepared the pellets with higher reactivity and stability. The results indicate that: In contrast with dolomite pellets prepared by single binder, dolomite pellets prepared by composite binder are dominant in functions without fine materials produced, the size of pellets is uniform, the falling strength can reach 2.5 times per 0.5 m, and the compressive strength gets 80N as well.

Introduction

Magnesium metal and its alloys have many properties such as high specific strength, high thermal and electric conductance, high impact resistance, good electromagnetic shielding，ease of machining and recovering. So that it has become the third widely applied metallic engineering material[1~6]. The production methods of metal magnesium can be divided into two processes: molten salt electrolysis and silicothermic process. In contrast, silicothermic process has become the main production method because the rich and high-grade ore of dolomite and magnesite. [6~12]

During the magnesium preparation process of the silicothermic process, about 5% fine materials would be produced – in the dolomite calcination step which can not be used and leads to high energy consumption and high-cost. This paper proposed a new technology of preparing magnesium metal that dolomite was made into the pellets along with the reducing agent first and then was calcined to prepared the pellets. Dolomite pellets was mainly composed of dolomite, reducing agent and binder. Reducing agent was 75Si-Fe, a certain amount of binder was added into the dolomite to improve the strength and the sintering performance of the pellets as well. The pellets have higher activity and stability to improve the resource utilization and to reduce the energy consumption of calcining. Pelletizing experiments with bentonite, organic binder and organic/inorganic composite binder were conducted. According to the mixing effects of the dolomite in the binder and the quality of the pellets, the reasonable choice of the binders was put forward.

Experiment

<u>Material</u>

The chemical composition and main phase of dolomite are shown in table Ⅰ and Figure1.

The chemical component of 75Si-Fe of dolomite are shown in table Ⅱ.

The experimental equipment needed can be divided into two main parts: the material preparation equipment and the pelletizing equipment.

The material preparation equipment: Crusher, Rod Mill, Vibration Rod, Abrasive Tool, Mortar, Sieve,

Electronic Balance, Platform Scale of 10 kg, Mixing Bowl, Mixing Machine,101# Electric Blast Drying Oven.

Table Ⅰ Chemical composition of dolomite

Compound	MgO	CaO	Al_2O_3	SiO_2	Na	K	Fe
Content / %	21.73	31.05	0.16	0.44	0.02	0.005	0.07

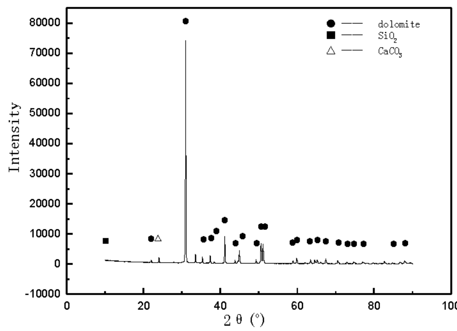

Figure 1 The main phases of dolomite

Table Ⅱ Chemical component of 75Si-Fe				
Element	Si	Al	S	C
Content / %	75.6	1.24	0.091	0.015

The pelletizing equipment: Disc Pelletizer, Atomization Sprinkler, Scraper.

The pelletizing equipment: Disc Pelletizer, Atomization Sprinkler, Scraper.

The main experiment process: the raw ore including dolomite, reducing agent and fluorite catalyst are crushed and ground, and the finely powder are mixed with binder according to a certain ratio first; then the mixture is made into pellets by disk balling machine and the pellets are calcined in sintering furnace; the influence of binder type on the quality of pellets are investigated.

Results and discussions

Pelletizing capabilities of dolomite

Not all materials are capable of pelletizing, the superior sphericity is needed[13]. In the dolomite pellets, the ingredient of dolomite is more than 80% both in mass fraction and volume fraction, so the sphericity of dolomite was mainly considered.

The sphericity of finely ground materials is the performance of water dripping into pellets and its mechanical action density in the natural state. It can be considered as the formation and growth rate in the pelletizing process. So that the sphericity is a composite indicator, it can be determined by an index (k).

$$k = \frac{W_a}{W_b - W_a} \tag{1}$$

In the equation:

W_a——The largest molecule wet capacity of the fine material，%；

W_b——Capillary wet capacity of the fine material，%。

The sphericity of fine material can be divided into the following series：

k<0.20 non-sphericity

k=0.20~0.35 low-sphericity

k=0.35~0.60 medium-sphericity

k>0.80 high-sphericity

The largest wet capacity of the fine material（%）can be calculated by the following equation：

$$W_a = \frac{(Q_1 - Q_2) \times 100}{Q_2} \tag{2}$$

In the equation：

Q_1——pressurized sample quality，g；

Q_2——dried sample quality，g。

Capillary wet capacity of the fine material：

$$W_a = \frac{Q_3 \times 100}{Q_4} \tag{3}$$

In the equation：

W_a——Capillary wet capacity，%；

Q_3——sample quality water absorption，g；

Q_4——sample quality dried，g。

The table Ⅲ indicates that dolomite is with the sphericity of k=0.90 itself which can be regarded as good quality in pelletizing. So that dolomite pelletizing is feasible.

Table Ⅲ Performance test results into a ball							
Q_1 g	Q_2 g	W_a %	Quality of ball after water absorption	Q_4 g	Q_3 g	W_b%	k
5.712	5.508	3.70	7.573	7.036	0.537	7.63	0.94
5.601	5.402	3.68	8.074	7.518	0.556	7.40	0.99
5.472	5.275	3.73	6.452	5.981	0.471	7.87	0.90

The particle size distribution of pellets made by different binders

The composite binder is mixed by organic and inorganic binders by certain proportion. In the pelletizing process, investigation on 0.5kg materials with the pelletizing 1h, sieved by a group of circular screens with the aperture 4, 8, 10, 15, 20, 25mm and the particle size analysis was done.

The figure 2 indicates that there is just a little difference in particle sizes between the pellets prepared by bentonite and prepared by pure water. And there is no uniform size in pellets prepared by bentonite. And the pellets prepared by organic binder had a larger particle size, which can not meet the requirement of sintering. The pellets prepared by composite binder had a uniform particle size which is mainly between 10-15mm with excellent effect.

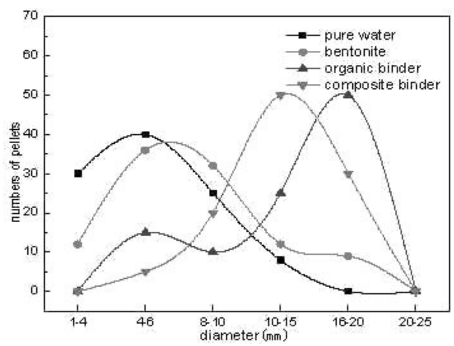

Figure 2 Particle sizes distribution of pellets prepared by different binder

Water content of pellets prepared by different kinds of binders

Dried fine materials cannot be rolled into pellets without a binder, so water must be added in the pelletizing process. Water is quite a significant factor in the pelletizing process. Figure 3 indicates that the addition of binder can improve the water content of the pellets. When the water content of pellets reaches the limitation of the bound water content, the capillaries in the pellets would be thinner, so that better plasticity and better quality of the pellets can be reached.

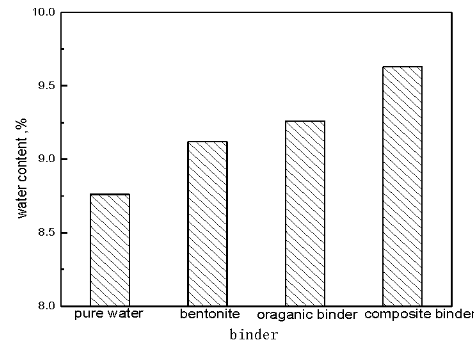

Figure 3 Water content of pellets prepared by different binder

Dropping strength of pellets prepared by different kinds of binders

The figure 4 indicates that there is just a little difference in dropping strength between wet-pellets and dried-pellets which are prepared using the same binder. But there is quite a big difference in dropping strength among pellets prepared by different binders Both the wet-pellets and dried-pellets prepared by composite binders have better dropping strength which can get 2.5times per 0.5m or above.

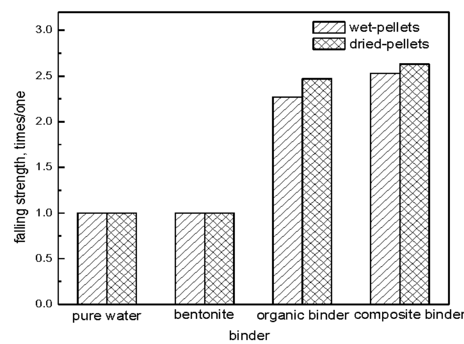

Figure 4 Falling strength of pellets prepared by different binder

Compressive strength of pellets prepared by different binder

Figure 5 indicates that the binders have a quite effect on compressive strength (whether wet-pellets or dried-pellets). The pellets prepared by pure water have the lowest compressive strength; the pellets prepared by composite binders have the highest compressive strength in all. The dried-pellets prepared by composite binders can reach the compressive strength of 80N per one or more, it's mainly because the water-soluble substance in the composite binder, during the drying-process, the water-soluble substance is forced to the surfaces of the green pellets via the effect of capillary force, relatively compact shells are formed quickly after drying which can improve the compressive strength obviously.

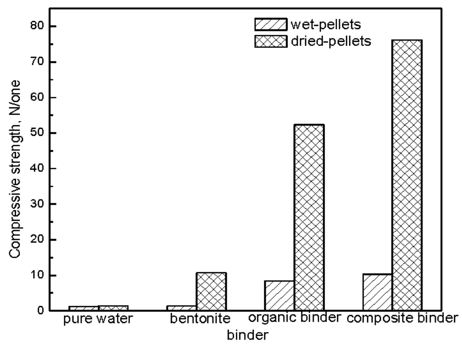

Figure 5 Compressive strength of pellets prepared by different binder

Magnesium loss in the pellets in different sintering temperatures

Sintered the pellets prepared by composite binder in sintering furnace, and investigated the magnesium loss ratio. Shown in figure 6 which indicates the ratio can reach 0.2%, and it is far less than the 5% caused by sintering pure dolomite. And due to the addition of binders in the pellets, no fine materials were formed in the sintering-process, the source utilization was improved and the environment was protected as well.

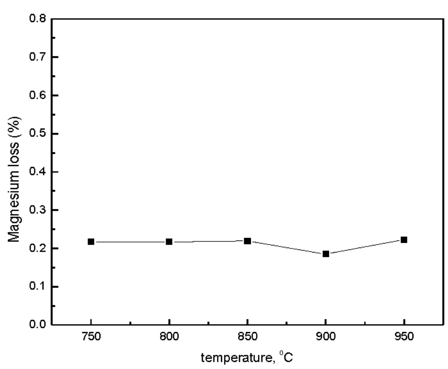

Figure 6 Magnesium loss in different sintering temperatures

The figure 7 indicates that there was no $CaCO_3$ or $MgCO_3$ in the sintered pellets; CaO and MgO were formed in the sintering-process via XRD detection (during the process of acid-dissolution, there was no bubble formed, also proved there was no $CaCO_3$ or $MgCO_3$ from other side). Moreover, the detection result indicates that silicon was not oxidized in the process which is to the benefit of subsequent magnesium reduction.

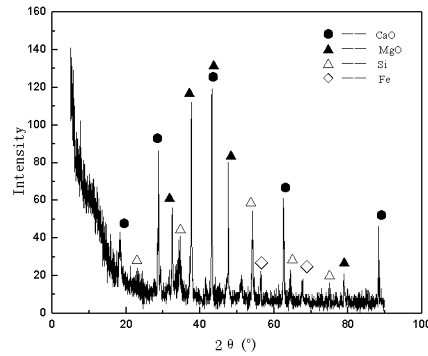

Figure 7 The phase of sintered dolomite pellets

Conclusion

1. Dolomite is with the sphericity of k=0.90 itself which can be regarded as good quality in pelletizing. So that dolomite pelletizing experiment is feasible.

2. The pellets prepared using a composite binder had uniform particle size; bentonite alone is not suitable for dolomite pelletizing; there is no fine material formed in the pellets prepared using a composite binder; the dropping strength of pellets prepared by composite binder can reach 2.5 times per 0.5m and the compressive strength can reach 80N per one.

3. The magnesium loss ratio can reach 0.2% during the sintering-process and no silicon is oxidized.

4. Composite binder which has little impurity, fine and uniform particle, high surface area, good expansibility, cohesiveness and plasticity can improve the quality of the dolomite pellets.

ACKNOWLEDGEMENT

This research was supported by National Natural Science Foundation(NSFC) (51274064,51074044, 51002025).

References

1. BAO Rong Hua, ZHOU Jin Sheng. World magnesium metal supply and demand situation and coping strategies [J]. China Mining Magazine, 2009, 18(12), 7-9.

2. Mustafa Kemal Kulekei. Magnesium and its alloy applications in automotive industry[J]. Int. J. Adv. Manuf. Technol., 2008, 39: 851-865.

3. F.H. Froes, D. Eliezer and E. Aghion. The science, Technology, and Applications of Magnesium[J]. Light Metals, 1998, (9): 30-34.

4. XU Ri Yao. Magnesium metal production technology [M]. Central South University Press, 2003, 1-11.

5. XU Ri Yao. Silicothermic process magnesium metal production technology [M]. Central South University Press, 2003, 4-15.

6. XU Ri Yao. The extraction metallurgy manual of non-ferrous metals (magnesium) [M]. Beijing: Metallurgical Industry Press. 1992, 4-6.

7. Mustafa Kemal Kulekei. Magnesium and its alloy applications in automotive industry[J]. Int. J. Adv. Manuf. Technol., 2008, 39: 851-865.

8. F.H. Froes, D. Eliezer and E. Aghion. The science, Technology, and Applications of Magnesium[J]. Light Metals, 1998, (9): 30-34.

9. B.Humes. Vacuum Engineering as Related to the Dolomite Ferro-Silicon Process, Reduction and Refining of Non-Ferrous Metals[J]. Trans A.I.M.E, 1944, 159: 353.

10. J.R. Wynnyckyj, L.M. Pidgeon. Equilibria in the Silicothermic Reduction of Calcined Dolomite[J]. Metallurgical Transactions, 1971, 2(4): 979-985.

11. J.M. Toguri, L.M. Pidgeon. High-temperature studies of metallurgical process-The thermal reduction of calcined dolomite with silicon[J]. Canadian J. Chem., 1962, 40: 1769-1776.

12. D. Minić, D.Manasijević, Jelena Đokić, et al. Silicothermic Reduction Process in Magnesium Production-Thermal analysis and characterization of the residue[J]. Journal of Thermal Analysis and Calorimetry, 2008, 93(2): 411-415.

13. ZHANG Yi Min. Theory and technology of pellets [M]. Beijing: Metallurgical Industry Press. 1997，76-130.