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MAGNESITE BASE DESULFURIZER OF METALLURGICAL PHYSICAL CHEMISTRY RESEARCH

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This topic put carbon thermal vacuum method in combination with magnesium based desulfurization technology with magnesite reduction of magnesium vapor directly on hot metal desulphurization. This is a new type of desulfurization technology, the retrieval related literature at home and abroad was not reported in the recent ten years, according to the relationship between heat of desulfurizer preparation MgO style content can reach 50 %.It was found that the desulfurizer sample with 50 % MgO content was in accordance with the requirements, without adding flux, but its viscosity did not meet the requirements; adding 1 % flux (CaF_2), the sample viscosity was significantly reduced, and about 1 400 °C sample viscosity suitable for hot metal pretreatment desulfurization.

Key words: metallurgy, desulfurization, magnesite, heat of metal, viscosity

INTRODUCTION

At present, the domestic and foreign metallurgical circles have explored new desulfurizers [1] to replace or partially replace magnesium desulfurization agent [2]. By searching the relevant literatures at home and abroad for the past ten years, it has been found that there are many literatures on magnesite as a small amount of desulfurization additives. The study of the use of magnesite to restore the metal magnesium directly to the desulfurization of the literature is rare. China is the world's largest magnesite resources in the country[3], the use of magnesite to restore the direct removal of magnesium metal can be achieved, will replace the existing magnesite → metal magnesium → passivation of magnesium particles → hot metal pretreatment desulfurization production process[4], to simplify the production process, reduce energy consumption and production costs for the metallurgical industry energy efficiency, improve product quality, to achieve low carbon emissions and green metallurgy to contribute [5].

EXPERIMENTAL EPUIPMENT, PRINCIPLE AND ITS SCHEME

In this paper, the viscosity of desulfurizer was measured by the RTW-10 type physical property measuring instrument produced by Northeastern University. The equipment was mainly composed of computer, high temperature furnace and rotary viscosity device. The heating element is molybdenum silicide and the furnace temperature range is 0 ~1 600 °C. During the experiment, 1,5 L / min of nitrogen is passed to protect the graphite crucible and the graphite sleeve from being oxidized at high temperatures.

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The melting point of the desulfurizer is measured by the melting point of the Liaoning University of Science and Technology. The melting point melting speed measuring instrument is mainly composed of three systems: point light source system, high temperature heating furnace system and slag image enlarging imaging system. The resulting melting temperature is measured by the hemisphere method. Since the measured conditions are not in the constant temperature state or in the equilibrium state, the temperature obtained by the measurement is not the melting point or the melting temperature defined in the usual thermodynamics, but a relatively comparative Simple and practical with semi-empirical properties of the temperature.

The magnesite-based desulfurizer is a spherical or other shaped particles composed of MgO, a carbonaceous reducing agent, a heat generating agent, a reaction accelerator, a pH adjuster and the like, where in the carbonaceous reducing agent is graphite and the heat generating agent is an aluminum heat , The reaction promoter is SiO_2; the pH adjuster is CaO; the heat agent aluminum heat agent should be mixed according to the chemical reaction theory requirement quantity, the proportion of each material is: MgO accounts for 45 ~ 72 % of the total mass of the mixed material; Reducing agent accounted for 14 ~ 18 % of the total mass of the material; heating agent accounted for the total mass of mixed materials 8 ~ 16 %; reaction accelerator accounted for 1 ~ 4%; pH regulator accounted for 1 ~ 10 % [7]. Table 1 is the specific ratio of the material when the experiment, the results are as follows:

Due to the high melting point and almost no melting of the carbonaceous reducing agent in the desulfurizer system, the physical and chemical properties of the desulfurizer system containing no carbonaceous reducing agent are studied in this experiment.

Table 1 The ratio of desulfurization agent / %

C	MgO	Al_2O_3	SiO_2	CaO
16	45	7,6	10	21,4
15	50	7,6	8,4	19
14	60	5,7	6	14,3
14	70	4,8	3	8,2
14	75	3,8	1,8	5,4

EXPERIMENTAL RESULTS AND DATA ANALYSIS

Analysis of melting point results

Table 2 **The sample melting temperature**

Sample height	MgO content / %				
	45	50	60	70	75
1/5	1 350 °C	1 353 °C	1 355 °C	1 360 °C	1 370 °C
1/2	1 400 °C	1 408 °C	1 410 °C	1 418 °C	1 420 °C
4/5	1 420 °C	1 422 °C	1 430 °C	1 445 °C	——

Table 2 is the melting temperature of different samples, experiments show that the melting point of the samples increases with the increase of MgO composition. The thermodynamic calculation shows that the reaction temperature of carbon-reduced magnesia is 1 854 °C. If the reaction is carried out under the condition of hot metal temperature (1 250 °C ~ 1 300 °C), the pressure of magnesium vapor must be less than 0.99 4kPa. If the reaction is in hot metal temperature (1 350 °C ~ 1 400 °C), the magnesium vapor pressure must be less than 1,004 kPa. So to make the desulfurization agent can play a better desulfurization effect, at least the melting point of less than 1 400 °C, so this group does not meet the requirements of the melting point.

Since then, in view of the relationship between the main reaction and the proportion of heat, we increase the amount of Al_2O_3, according to the heat ratio to match the desulfurization agent [8], Table 3 shows the specific ratio of desulfurization agent, the results are as follows:

Table 3 **Desulfurization agent ratio / %**

C	MgO	Al_2O_3	SiO_2	CaO
13.6	45	25,7	7	8,7
15	50	28,6	2,8	3,6

As can be seen from Table 3, the desulfurizer system consists essentially of MgO and Al_2O_3, and the MgO - Al_2O_3 phase diagram is as follows:

It can be seen from Figure 1, spinel phase area up to 1 900 °C, for the magnesium-rich spinel, spinel phase solid solution is small, and contains trace of magnesite.

Through the analysis of the melting temperature of different samples in Table 4, the melting temperature of the desulfurizer system meets the requirements and the melting effect is very good. In order to study the reason of its low melting point, it has carried out XDR diffraction experiment:

Figure 2 shows the XRD pattern of the desulfurizer system. According to the phase analysis and chemical analysis, the main component is CaO - MgO - Al_2O_3 - SiO_2 quaternary amorphous and contains a certain amount of spinel and a very small amount of perovskite.

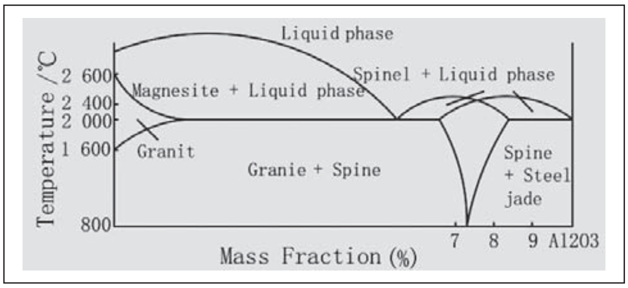

Figure 1 MgO - Al_2O_3 phase diagram

Table 4 **Sample melting temperature**

Sample height	MgO content /%		
	45	48	50
1/5	1 250 °C	1 251 °C	1 253 °C
1/2	1 343 °C	1 344 °C	1 345 °C
4/5	1 345 °C	1 347 °C	1 348 °C

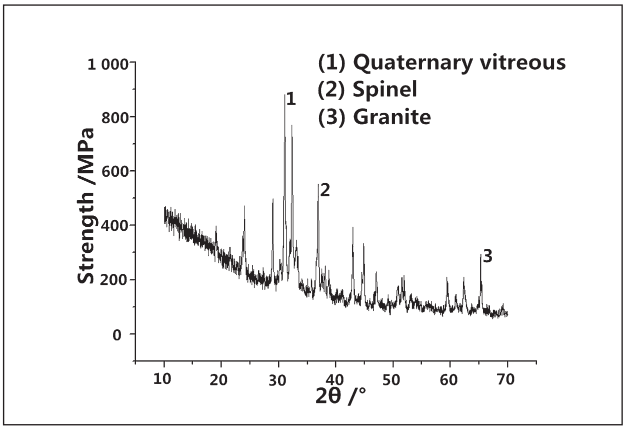

Figure 2 Desulfurization agent XRD diffraction pattern

The experimental results are consistent with the phase diagram analysis, that is, in the molten state, there is a large amount of free MgO.

Analysis of viscosity results

In this paper, the desulfurizer system with 50 % MgO content was selected as the original sample for viscosity measurement. The experimental results were as follows:

Figures 3, 4, 5 are the original desulfurization agent, adding 1 % CaF_2, adding 2 % CaF_2 viscosity and temperature curve, in which Figures 3, 4, the viscosity - temperature curve is very smooth, and Figure 5 viscosity - the temperature curve has a clear inflection point, showing a short slag characteristics.

In addition to the above three figures, we also measured the addition of 0,5 % CaF_2 desulfurization system viscosity, the experiment concluded that when the temperature below 1 470 °C, the rotor due to large resistance to stop, indicating that the sample viscosity exceeds the measurement range. Then we try to add flux CaF_2 to 0,5 %, 1 %, 2 % respectively; when adding 0,5 %, try to add the flux of the original desulfurizer. The viscosity of the sample is significantly increased, and the viscosity of the sample is about 20 %, and the viscosity of the sample is about 3 000 °C. The viscosity of the sample is suitable

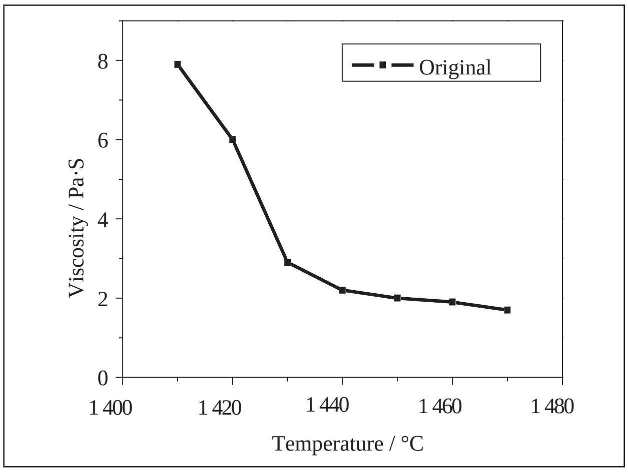

Figure 3 Original sample viscosity and temperature diagram

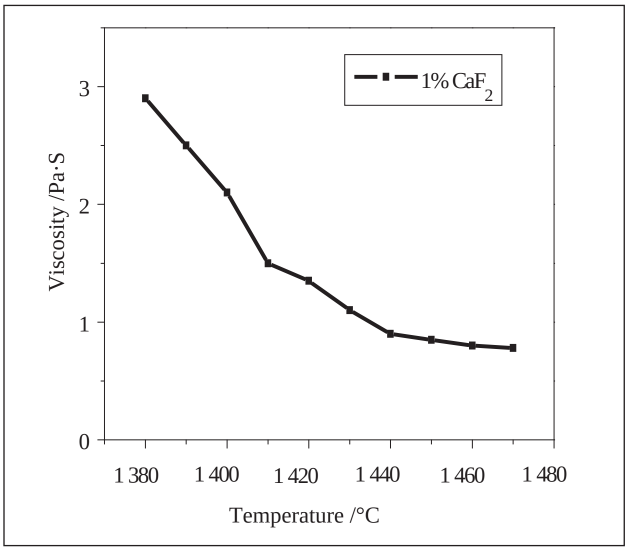

Figure 4 Addition of 1 % CaF_2 sample viscosity and temperature diagram

for hot metal pretreatment. 1 470 ~ 1 420 °C, the viscosity of the sample is lower than 1 %, when the temperature is lower than 1 420 °C, the viscosity increases sharply; In summary, with the appropriate viscosity of the desulfurization agent for adding 1 % CaF_2 containing MgO 50 % of the desulfurizer system.

CONCLUSION

(1) According to the relationship between the main reaction and the heating agent to prepare the desulfurization agent, the measured sample melting temperature meet the requirements, and the melting effect is very good.

(2) The viscosity of the desulfurizer determined by the melting point determination does not meet the viscosity requirements of the hot metal pretreatment desulfurization, and the flux is added.

(3) Adding 1 % flux (CaF_2), the sample viscosity is significantly reduced, and about 1 400 °C sample viscosity suitable for hot metal pretreatment desulfurization.

(4) XRD diffraction analysis results, the desulfurizer in the 1 400 °C melting state of its main component of CaO - MgO - Al_2O_3 - SiO_2 quaternary amorphous, and

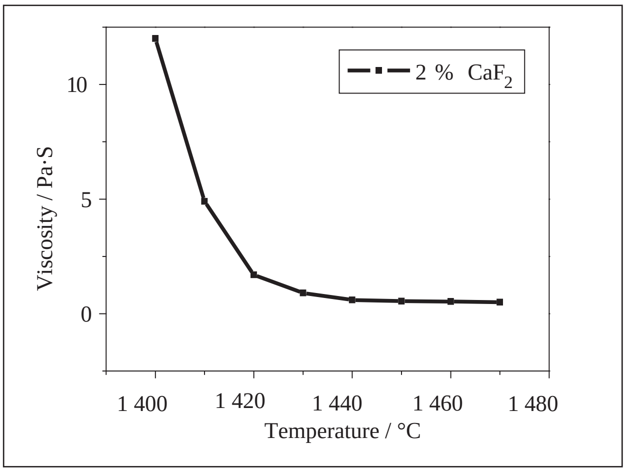

Figure 5 Addition of 2 % CaF_2 sample viscosity and temperature diagram

contains a certain amount of spinel and a very small amount of periclase.

In summary, the best desulfurization agent ratio is added 1 % flux, MgO content of 50 % of the desulfurizer system, and in the molten state of a large number of free MgO.

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Note: Wei Ye is responsible for English language, Anshan, China. Kun Liu is the corresponding author.