

# WETTING AND SPREADING MECHANISM OF MgO SUBSTRATE BY IMPURITY PHASE

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The microstructure of the refractory material is closely related to its properties, and the wettability between the liquid phase and the crystal phase in the refractory material is an important factor determining the microstructure. In this study, the wetting behavior of different C/S silicate impurity phases on solid MgO substrates at 1 450 °C was explored by the sessile drop method, and the spreading mechanism of the system was discussed. The driving force of the wetting process is the dissolution of the MgO substrate. At 1 450 °C, the equilibrium contact angles of M1-M3 were measured to be 0, 4 ° and 11 ° respectively. The M4 sample did not wet and the contact angle hardly changed.

*Key words:* magnesia refractory; MgO; wetting; contact angle; microstructure

## INTRODUCTION

Magnesia-based refractories are widely used in cement rotary kilns, steel ladle, and converters, due to high melting point, chemical stability in a basic environment. In magnesia refractories, CaO and SiO<sub>2</sub> are the main impurity components present, and the different C/S ratios of magnesia refractories have different phase combinations, which determine the wettability of silicate phase and the microstructure of the refractory material. The continuous or isolated distribution of silicate phases at the grain boundaries of magnesium oxide, which has an important influence on the properties of magnesium oxide based refractory products.

Researchers have previously paid great attention to the wetting behavior of refractories with different types of slag, and some corrosion mechanisms have been proposed[1-4]. However, few studies have been carried out regarding the wettability between impurity phase and main crystal phase inside the refractory to elucidate spreading mechanisms, in order to fundamentally improve the properties of the material. In fact, the impurity phase is the weakest link of the refractory material. Under high-temperature conditions, the impurity phase melts and softens first. The composition and properties of the liquid phase and the distribution between the liquid phase and the crystal phase have a great influence on the high temperature performance of the material.

In this study, the wetting behavior between impurity phases and MgO crystalline phase is very important to understand the damage of the internal structure of the magnesia brick, which will have certain theoretical guiding significance for improving the high temperature properties of magnesia refractory.

## EXPERIMENT

### Experiment raw material

The chemical composition of impurity phase melts with C/S molar ratio of 0,6, 1, 1,5 and 1,8, were prepared by mixing certain amounts of CaO and SiO<sub>2</sub> analytically pure (AP) chemical reagents. Chemical composition of the melt samples is shown in Table 1.

Table 1 **Chemical composition of the samples and number of the sample**

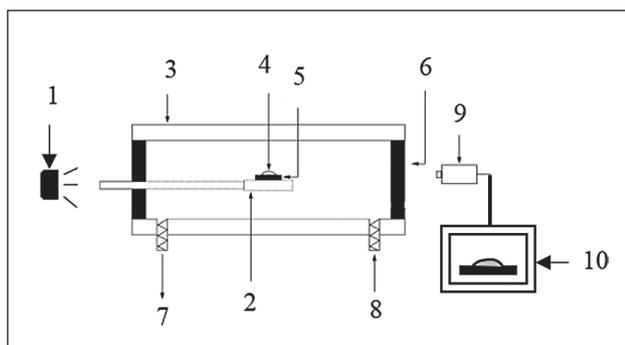
No.	Molar ratio	Composition / mass %	
		CaO	SiO <sub>2</sub>
M1	0,6	35,9	64,1
M2	1	48,3	51,7
M3	1,5	58,3	41,7
M4	1,8	62,7	37,3

After being well mixed, the sample was pressed into a cylinder with dimension of  $\phi$  3 mm  $\times$  3 mm and weight of approximately 20 mg, the MgO substrate was 10 mm  $\times$  10 mm  $\times$  3 mm in dimension, 3,88 % in porosity, and 99 % in purity.

### Experimental setup and procedure

In this study, the contact angle between the slag and the MgO substrate was measured by the sessile drop method. The experimental setup is shown in Figure 1. The melts sample and MgO substrate were placed in the experimental apparatus and the temperature was raised from room temperature to 1 450 °C at a rate of 10 °C / min. When the melt gradually melted and formed a distinct liquid at the bottom edge of the sample, it was regarded as initial contact angle[5], that is, “zero time”. High-speed camera is used to observe and capture a continuous image of the dynamic wetting between the

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1 lamp; 2 Stage; 3 Alumina tube; 4 melt sample; 5 MgO substrate; 6 quartz window; 7 gas outlet; 8 gas inlet; 9 high-speed camera; 10 recorder

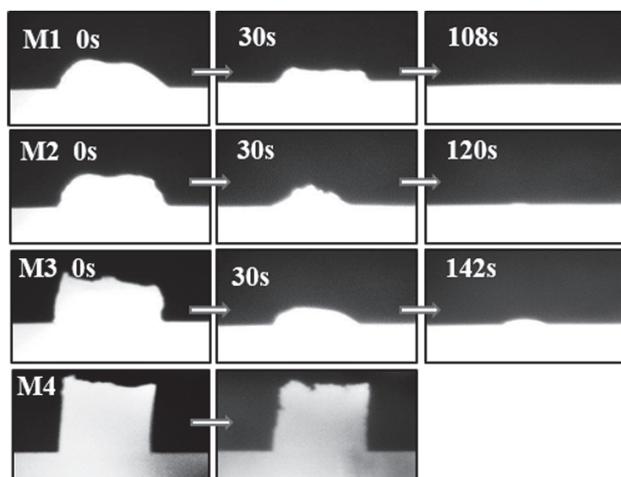
**Figure 1** Schematic experimental setup of wetting process

slag phase droplets and the substrate until the contact angle no longer changes. The contact angles were calculated by analyzing these photos with a self-made software. For the accuracy of the experiment data, the contact angle is the average of the left and right ones.

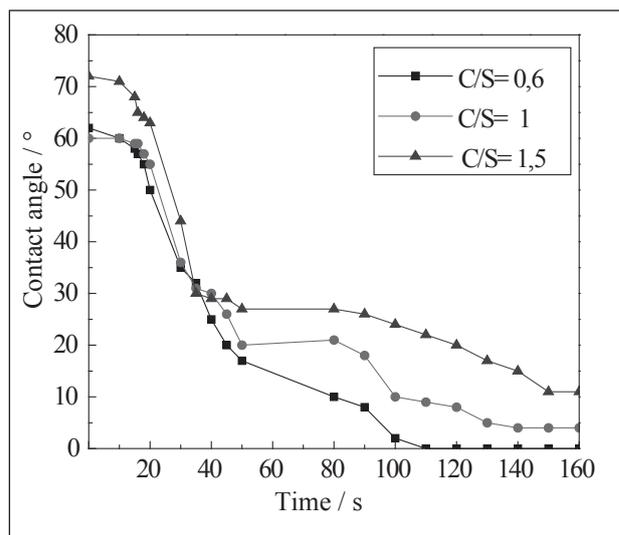
After the experiment, the furnace was cooled down to the room temperature. After cooling, the sample was cut longitudinally and made into a metallographic sample. Interface microstructure and element distribution was detected by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

## RESULTS AND DISCUSSION

The spreading and wetting behavior of impurity phase melts on MgO substrate is shown in Figure 2. It is seen that the liquid drop spreads out on the substrate with time. All tablets melted fast and spread uniformly on the substrate. The initial apparent contact angle ( $\theta$ ) of each system was less than  $90^\circ$ . As the holding time is extended, the melt gradually softens. At a certain time, the melt collapses instantaneously and then spreads slowly until the contact angle does not change. After spreading, the sample A was almost completely wetted on the MgO substrates.



**Figure 2** Wetting behavior of MgO substrate by sample M3 at  $1450^\circ\text{C}$

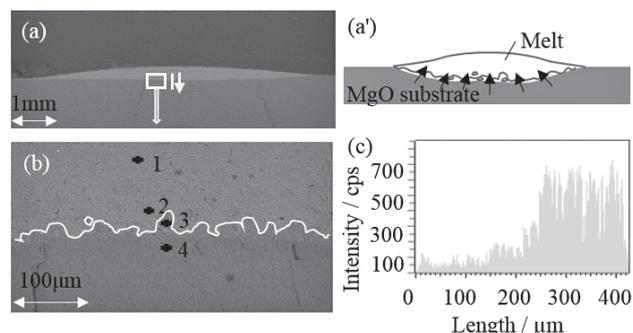


**Figure 3** Time change of apparent contact angle of impurity phase on MgO substrate holding at  $1450^\circ\text{C}$

As shown in Figure 3, It is obvious that the contact angle changes very rapidly in the early stages, then gradually approaches an equilibrium value. The equilibrium contact angle differs with the different C/S molar ratio.

The dissolution rate of MgO is affected by the composition of the impurity phase. Initially, the melt does not contain MgO, so the driving force for the dissolution of MgO in the melt is very high, so when the wetting begins, the contact angle drops rapidly under the driving force of high concentration difference, as shown in Figure 3, along with the magnesium oxide. The dissolution of the melt, the concentration difference on both sides of the interface gradually decreases, and the driving force for the dissolution of MgO in the melt is weakened until equilibrium is reached, and the wetting ends, the equilibrium contact angles of M1-M3 were measured to be  $0^\circ$ ,  $4^\circ$  and  $11^\circ$  respectively.

As shown in Figure 4 (a), Figure 4 (a') is a schematic figure of the wetting process shown in Figure 4(a). The substrate dissolves significantly into the melt during wetting and forms a depressed crater below the droplets. The dissolution traces of the MgO substrate are almost coincident with the three-phase lines of the droplet, which reflects the driving of the dissolution to the wetting process. In addition, the depth of dissolution



**Figure 4** SEM, EDS line, and spot scanning of impurity phase -MgO substrate (M3:C/S=1,5)

gradually deepens from the three-phase line to the center of the droplet.

Figure 4 (b) exhibits the cross-section microstructure of the sample M3. Line scanning marked with a yellow line is performed using EDS. Mg element results are shown in Figure 4 (c), and the scanning direction is indicated by a yellow arrow. Table 2 shows the results of spot measurements. The spot and line scanning results revealed that some MgO in melt with an obvious concentration gradient from the interface to the bulk melt. Because the original sample was nearly free of MgO, it is reasonable to assume that part of the MgO dissolved into the melt.

According to Fick's law, MgO dissolution flux ( $J$ ) is in direct proportion to the concentration difference of MgO of the bulk and interface ( $C-C_0$ ) [6]. As the wetting progressed, the dissolution rate of MgO decreased, which might explain why the contact angle reduced slowly at the later stages (Figure 3).

$$J = -\frac{D}{\delta}(C - C_0)$$

where:

$J$  is the MgO dissolution flux / mol / m<sup>2</sup>·s

$D$  is the inter-diffusion coefficient / m<sup>2</sup> / s

$\delta$  is the boundary layer thickness / m

$C$  is the MgO concentration of the bulk / mol / m<sup>3</sup>

$C_0$  is the MgO concentration reaction interface / mol / m<sup>3</sup>

Table 2 Element contents of selected points / wt. %

Element	Mg	Ca	Si	O
Spe,1	4,39	27,42	25,41	42,78
Spe,2	8,55	25,40	23,51	42,55
Spe,3	30,77	3,84	20,39	45,01
Spe,4	60,10	0,24	-	39,65

## CONCLUSIONS

The wetting behavior of different C/S ratio impurity phases on solid MgO substrates at 1 450 °C. Except for the sample with C/S = 1,8, there is almost no change.

The other samples can be melted on the substrate, and the contact angle decreases rapidly at the initial stage. As the holding time increases, then slowly spread on the substrate. The equilibrium contact angles of M1-M3 were measured to be 0, 4 ° and 11 ° respectively. After the wetting experiment, no significant reaction product layer formed at the solid-liquid interface. The driving force of the wetting process is the dissolution of the MgO substrate.

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**Note:** The responsible translator for English is Yan Wu, University of Science and Technology Liaoning, Anshan, China