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Dissolution of MgO Based Refractories in CaO-Al₂O₃-MgO-SiO₂ Slag

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Abstract

Dissolution of different types of MgO based refractories into molten CaO-Al₂O₃-MgO-SiO₂ slag was studied at 1873 K. The prepared refractory cubes were dissolved in both stagnant slag and slag stirred with different speeds. Even in a stagnant slag, the decarbonized commercial MgO-carbon refractory dissolved very fast. Formation of micro spinel particles by addition of either colloidal alumina or micro alumina powder in the MgO matrix efficiently reduced the dissolution. The dissolution of MgO refractories into slag was found to be controlled by the slag penetration into the MgO matrix. In the case of stagnant slag, the slag penetration would lead to the final dissociation of the decarbonized commercial MgO-carbon cube in less than 6 minutes. A slag penetrated layer was formed in the cubes with spinel particles formed in situ. The major dissolution took place between the MgO grains and the liquid in this penetrated layer. The increase of the thickness would slow down the dissolution process. In the case of forced convection, the slag penetrated layer was removed at high stirring speeds and partially removed at lower stirring speeds. The removal of the penetrated layer would enhance the dissolution process.

1. Introduction

Lifetime of carbon bonding MgO lining in the ladle furnace primarily depends on the decarburization process [1]. Due to the reduction of MgO by carbon in the MgO-C lining, mechanical abrasion and chemical reactions between the porous decarburized layer and the liquid slag during ladle treatment at the slag line and casting throughout the height of the melt would easily degrade the lining lifespan. The porous structure of the decarbonized refractory results in not only a high cost [2-3], but also the generation of non-metallic inclusion by the ladle glaze during ladle treatment [4-11].

Great attention has been paid to investigate the erosion/dissolution mechanism of MgO refractories in the liquid slag. Many studies have investigated the dissolution of MgO in the slag in general and CaO-Al₂O₃-SiO₂ based slag in particular by rotating cylinder technique. It has been reported that the dissolution process is controlled by mass transfer in the slag, and the rate of dissolution decreases while the slag is reaching MgO saturation [12-16]. Recently, Huang *et al.* studied the dissolution rate of MgO based refractory in CaO-Al₂O₃-SiO₂ slag stirred by gas at 1773 K [17]. They reported that the dissolution of sintered MgO was faster than that of the MgO-C refractory at the same stirring condition. These authors also found that the penetration of the slag into the refractory enhanced the dissolution [17]. As a matter of fact, both peeling off of the penetrated layer (erosion) and chemical dissolution contribute in the process of MgO entering into the slag.

In previous studies, the MgO based refractory using colloidal alumina as a new binder was studied [18-19]. An excellent resistance against slag penetration on the refractory was obtained. It evidently shows that the formation of in situ spinel in the matrix of MgO plays a significant role in limiting the slag penetration [18-19]. It would be valuable to investigate whether the resistance to dissolution of the new MgO refractory in the ladle slag can also be improved under the condition of forced convection.

As a continuation of a long term project to develop carbon-free magnesia based refractory, the main objective of the present work is to study the “dissolution” mechanism of the potential carbon-free MgO refractory in the ladle slag with forced convection. Microscopic examination is expected to reveal the main mechanism of the dissolution. By measuring the size change of MgO refractory cubes after reaction with liquid slag, the impacts of stirring speed and time on the MgO dissolution are studied.

2. Experimental

2.1. Materials and slag preparation

Four types of refractory samples in the form of cubes were studied. These refractories are listed in Table I.

Type MgO-A was prepared in the laboratory using dead burnt magnesite (DBM) and colloidal alumina suspension. The DBM supplied by INSERTEC, Spain, was a mixture of powder from two different particle size groups, ranging 0-0.25 mm and 0-1 mm, respectively. The mixture consisted 50% of powder in the 0-0.25 mm range and 50% powder in the 0-1 mm range. This mixture was found to result in best resistance to slag penetration [18]. 20 mass% colloidal alumina suspension (50% in H₂O, 45 nm APS) obtained from Alfa Aesar was added into DBM powder. After mixing, the dried mixture was pressed into pellets under the uniaxial pressure of 15 MPa. The pressed pellets were sintered in a muffle furnace at 1773 K for 8 hours.

Based on the results of previous studies [18-19], a testing MgO-spinel brick was manufactured by INSERTEC, Spain. Instead colloidal alumina, alumina powder (particle size about 5

micrometers) was used in the preparation of the bricks. This kind of refractory is named as MgO-B.

To compare the dissolution of the new refractories with the traditional MgO based refractory, a high density commercial MgO-carbon brick supplied by Vesuvius, UK, was investigated as well. The commercial cube after pre-firing contained 97.2 mass% MgO, 1.6 mass% CaO, and traces of other oxides according to the supplier. This refractory is named as MgO-C.

In view that the refractory at and above the slag line is always decarbonized after the first usage and the real dissolution reaction taking place is between decarbonized brick and the slag, samples of decarbonized MgO were also prepared. To burn out the carbon, the refractory was kept in air at 1373 K for 10 hours. The decarbonized refractory is named as MgO-D.

All the samples were cut out from the bricks or sintered pellets as cubes. The cubes measured about 8 x 8 x 8 mm in size. The densities and apparent porosities of the four types of MgO cubes are presented in Table I.

Table I Bulk density and apparent porosity of MgO cubes

Cube sample	Cube type	Bulk density (g/cm ³)	Apparent porosity (%)
MgO-A	Laboratorial MgO-spinel	3.1	12
MgO-B	Testing MgO-spinel	2.7	23
MgO-C	Commercial MgO-carbon	3.1	5
MgO-D	Decarburized MgO	2.6	28

The oxides along with their supplier and purity levels used for the slag preparation are presented in Table II. To remove the moisture and absolved gas, all the oxides were dried at 1173 K for 10 h. The powders of CaO (55 mass %), Al₂O₃ (30 mass %), MgO (8 mass %) and SiO₂ (7 mass %) were mixed in an agate mortar for 30 minutes. To prepare the pre-melted slag, the mixed oxides were pressed into the pellets, and the pellets were put into a graphite crucible. The outer surface of graphite crucible was painted by ZYP ZrO₂ coatings in order to reduce the oxidation. The painted graphite crucible with the slag pellets was heated up to 1973 K by an induction furnace in air. After completely melting, the slag was quenched in air. The pre-melted slag was crushed into small pieces and stored in a desiccator before use. The pre-melted slag was analyzed by X-ray Fluorescence (XRF); it had the composition of 53-54 mass% CaO, 31-33 mass% Al₂O₃, 8-9 mass% MgO and 6-7 mass% SiO₂.

Table II Supplier and purity of powders used for slag preparation

Oxide	Supplier	Purity
CaO	Sigma	99.90%
Al ₂ O ₃	Sigma	99.70%
MgO	Sigma	>99 %
SiO ₂	Alfa	99.50%

2.2. Experimental Setup and Procedure

Experiments were carried out in a high temperature vertical furnace. The experimental setup is schematically shown in Figure 1. The main components of the setup were a resistance furnace

with super Kanthal heating elements, an alumina reaction tube, a water-cooled quenching chamber and a lifting system. A water-cooled quenching chamber made by brass was placed on the upper end of alumina tube. High purity argon gas was introduced from the bottom of the alumina chamber, and led out from the top of the quenching chamber. Two gas inlets were placed at the sidewall of the cooling chamber to inject argon gas with high flow rate for quenching the sample. The temperature was controlled using a B type thermocouple (Pt-6% Rh/Pt-30% Rh). The measurement thermocouple (B type) was protected by an alumina sheath. The tip of the measurement thermocouple was placed just below the sample crucible. The whole system was sealed by O-rings.

In order to introduce forced convection, a specially designed stirring system was employed [20]. As shown in Figure 1, a Mo container was used to hold the working crucible made of Mo. A Mo cap was used to lock the working Mo crucible in a fixed position by Mo pins. The cap had a centrally placed guiding tube to keep the upper part of Mo stirrer rotating firmly, and therefore a constant stirring condition throughout the experiment. A Eurostar stirring motor was used to stir the slag along with the refractory sample eccentrically using a Mo stirrer (3mm in diameter). The upper part of the Mo stirrer was connected to the stirring motor using a long shaft made of stainless steel. The Eurostar stirring motor was mounted on a hydraulic lifting system. The lift enabled the sample holder to move both upward and downward, and also ensure the rapid quenching.

Fig.1 Experimental setup.

For each run, a MgO cube embedded by 35 g of pre-melted slag was placed in the working crucible. After placing the sample to the quenching position, the reaction chamber was then sealed, evacuated and flushed with argon gas. Thereafter, an argon flow of 0.03 L/minutes was maintained throughout the whole experiment. The furnace was then heated up to 1873 K. When the furnace reached the target temperature, the sample holder was lowered down step by step into the temperature zone of 1673 K. According to the phase diagram of the CaO-Al₂O₃-MgO-SiO₂ system, [21] the slag employed is solid at 1673 K. In order to reduce the effect of slag-melting on the MgO dissolution, as well as to avoid the thermal shock of the alumina tube, the sample holder was rested at the temperature zone of 1673 K for 20 minutes. Thereafter, the sample holder was lowered down all the way into the even temperature zone of the furnace. Preliminary experiment revealed that the pre-melted slag would need 40 seconds to become completely molten. The stirring was started after the melting of slag; and the zero-time (t=0) was noted. Different stirring speeds and experimental times were employed in the experiments. At the end of the experiment, the sample holder was rapidly lifted to the quenching chamber, and at the same time a high flow of argon gas was impinged on the sample holder to freeze the slag. The liquid slag was solidified in a few seconds. After cooling, the sample along with the crucible was taken out from the chamber. It should be mentioned that the MgO cube was found

staying at the bottom of the crucible. The Mo crucible with the slag was cut cross-sectioned going through the MgO cube by a diamond saw. The cutting position was about 4 mm from the bottom of the Mo crucible. The size of the remaining size of the cube was carefully measured under the light optical microscope.

The surface of the cross section was also analyzed by a scanning electron microscope (SEM, Hitachi TM3000, Japan) with energy dispersive spectroscopy (EDS).

3. Results

Table III lists the experimental conditions and the shapes (dimensions) of the remaining MgO cubes after experiments. The four types of MgO cubes described in Table I were studied. Experiments were conducted at 0, 50, 100 and 150 rpm stirring speeds at 1873 K. Experimental times ranged from 1 to 60 minutes.

Table III. Experimental conditions and the shape of remaining refractories after reaction

Test No.	Cube type	Stirring speed (rpm)	Stirring time (min)	Cubic shape remaining
T-1	MgO-A	0	6	Yes
T-2	MgO-A	0	10	Yes
T-3	MgO-A	0	60	No
T-4	MgO-A	50	6	Yes
T-5	MgO-A	50	10	Yes
T-6	MgO-A	50	15	No
T-7	MgO-A	100	6	Yes
T-8	MgO-A	100	10	No
T-9	MgO-A	100	15	No
T-10	MgO-A	150	6	Yes
T-11	MgO-A	150	10	No
T-12	MgO-B	0	60	No (Dissolved)
T-13	MgO-B	50	6	Yes
T-14	MgO-B	50	10	Yes
T-15	MgO-C	50	10	Yes
T-16	MgO-D	0	3	Yes
T-17	MgO-D	0	6	No (Dissolved)
T-18	MgO-D	50	1	No (Dissolved)

As examples, the photographs of the cross-sections of the four types of the MgO cubes after the reaction with liquid slag with stirring speed of 50 rpm are presented in Figure 2. For the refractory types of MgO-A, MgO-B and MgO-C, the remaining MgO part still keeps approximately its original cubic shape after 10 minutes of reaction with liquid slag as indicated by the markers in Figure 2(a) through (c). It should be mentioned that no MgO-D cube can be seen even after very short time of stirring (at 50 rpm). Figure 2(d) presents the cross-section of the sample after 1 minute. It is evidently seen that only small MgO particles remain. These small particles are expected to be the joined result of dissolution and corruption of the original MgO-D cube. Note that MgO-C cube shows the lowest dissolution rate in comparison with the others. This aspect will be discussed in the discussion part.

Fig. 2 Photographs of four types of MgO cubes in the slag stirred at the speed of 50 rpm (a) MgO-A cube after 10 minutes (b) MgO-B cube after 10 minutes (c) MgO-C cube after 10 minutes and (d) MgO-D cube after 1 minute.

Fig. 3 Photographs of MgO-D cube in the slag.

(a) after 3 minutes and (b) after 6 minutes of reaction with slag without stirring.

Figures 3(a) and 3(b) show the photographs of MgO-D cube after reaction with stagnant liquid slag for 3 minutes and 6 minutes, respectively. While MgO-D cube still remains after 3 minutes reaction, it has dissociated into small pieces after 6 minutes even without any stirring.

Fig. 4 Normalized lengths of remaining MgO cube as a function of stirring speed and time.

The fraction of dissolution of MgO cube in the liquid slag is described using the normalized length of the remaining MgO cube L_R , defined in the following equation,

$$L_R = \frac{L_{R1} + L_{R2}}{L_1 + L_2} \quad (1)$$

where L_1 and L_2 are the initial lengths of the MgO cube before the experiment in two perpendicular directions of the cross section. L_{R1} and L_{R2} (as marked in Figure 2(a)) are the lengths of the remaining MgO cube after the reaction with liquid slag.

Figure 4 is a plot of the normalized length L_R of MgO cubes as a function of stirring time and speed. For the MgO-A sample, the result does not show any substantial difference in the normalized length of L_R after 6 minutes stirring at lower stirring speeds. A big increase in the dissolution is seen when a stirring speed of 150 rpm is employed. On the other hand, the stirring speed has greater impact on the dissolution after 10 minutes stirring. After 10 minutes of stirring, the fraction of dissolution of MgO-A increases with the stirring speed up to 100 rpm. Further increase of the stirring speed has no effect on the fraction of dissolution for the same type of samples.

In fact, in the ladle treatment the velocity of the slag phase is not high. A stirring speed of 50 rpm is expected to represent the range of relative velocities of the top slag movement against the ladle lining. Therefore, the focus of dissolution experiments is given to the stirring of 50 rpm. In view that the dissolution of MgO-C is very slow and the dissolution MgO-D is extremely fast, the results are not plotted in Figure 4. A detailed discussion will be given later. Figure 4 shows that although MgO-B dissolved more into the slag than MgO-A after 10 minutes stirring, the difference in dissolution is small.

Fig. 5 SEM images of interface region between cube and stagnant slag in samples
 (a) MgO-A cube after 6 minutes and (b) MgO-D cube after 3 minutes.

Fig. 6 SEM images of interface region between MgO-A cube and slag at stirring speed of
 (a) 50 rpm for 6 minutes (b) 50 rpm for 10 minutes (c) 100 rpm for 10 minutes.

In order to understand the mechanism of dissolution of different MgO refractories, some quenched samples were examined by SEM and EDS analyses. Figure 5 shows the cube samples reacted with the stagnant slag, while Figure 6 shows the cube samples kept in the slag stirred at different speeds and times. All figures show layers outside the remaining core of the MgO cube. The outer layer is the slag bulk, the layer between the slag bulk and the MgO core is named as slag-penetrated layer. Dashed lines are marked on the figures in order to distinguish layers as seen in figures. The line marked between slag bulk and slag-penetrated layer is a boundary, on the right side of which MgO matrix is obviously seen. The other line is marked at the boundary between slag-penetrated layer and cube core. In the slag-penetrated layer, the spinel phase has vanished while in the MgO core, spinel particles are still observed in the MgO matrix.

In the bulk of slag, solid MgO particles are found. These particles can be classified into two different types as seen in Figure 5 and Figure 6. The first type of MgO grains appears as islands. These MgO islands are formed by detachment of MgO particles from the original MgO cube as seen in Figure 6(b) and Figure 6(c). Detailed discussion about the detachment will be given later in the discussion part. The second type of MgO particles is dendrites. The dendritic nature indicates that these particles have been precipitated from the liquid slag during cooling because of insufficient quenching. Precipitation of some other phases, *e.g.* $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, is also detected due to the insufficient quenching. Nevertheless, the precipitation of a small amount of solid phases would not affect the discussion of the dissolution of MgO refractory into the slag.

Figure 5(a) is taken from the sample MgO-A after reaction for 6 minutes with stagnant liquid slag, and Figure 5(b) is MgO-D with stagnant slag for 3 minutes. As seen in Figures 5(a)-5(b), the penetrated zone consists of mainly two phases, namely MgO islands and liquid phase. In Figure 5(a), concentration gradient is detected (by EDS analysis) in the liquid phase in the slag-penetrated layer due to the dissolution of spinel and MgO. The thickness of this layer is about 0.5 mm. On the other hand, MgO-D that has been decarbonized from MgO-C refractory shows the fastest dissolution in the slag. In Figure 5(b), it can be seen that the slag-penetrated layer is much thicker than that in Figure 5(a), it is around 3 mm. Note that no appreciable concentration gradient is found in this layer, and the composition of the penetrated liquid is very similar to the initial slag composition. It should be mentioned that even in the remaining core, big amount of liquid phase has penetrated into the MgO matrix. The liquid slag becomes the major phase in the structure. It looks like MgO-D cube is about to be dissociated in the next moment. The findings between Figure 5(a) and 5(b) suggest that slag penetration in MgO-A is far more limited than MgO-D.

Figure 6(a) through 6(c) present the SEM microphotographs of the interface region between MgO-A cube and slag at different stirring speeds. A comparison of Figure 6(a) and Figure 6(b) reveals that the fraction of liquid phase in the slag-penetrated layer increases with reaction time. The two figures also evidently show that the thickness of the slag-penetrated layer increases with time. The average thickness of slag-penetrated layer in Figure 6(b) is about 1.1 mm. The concentration gradient in the liquid layer of this sample is more profound. At position A (Figure 6(b)), the liquid phase has an average composition of 54 mass% CaO, 31 mass% Al_2O_3 , 8 mass% MgO and 7 mass% SiO_2 , which is very close to the composition of slag bulk (initial slag composition). On the other hand, the composition of Point B is about 43 mass% CaO, 42 mass% Al_2O_3 , 9 mass% MgO and 6 mass% SiO_2 . Despite the uncertainties involved in EDS analysis, the increases of both Al_2O_3 and MgO in the liquid are evident.

In accordance with the previous publication [18], in the region of “unreacted” core, 3 phases are identified in MgO-A namely (1) periclase phase, which is the main matrix of the refractory, (2) spinel phase, which is formed due to the addition of alumina particles, (3) traces of liquid, which is formed due to the presence of impurities in the DBM powder. It is worthwhile to mention that spinel phase is not detected in the penetrated layer. The increasing contents of Al_2O_3 and MgO in the liquid phase is because of the dissolution of spinel (and partially MgO) into the liquid.

To examine the effect of stirring speed on the dissolution, Figure 6(c) presents the microphotograph taken at the interface region in the MgO-A cube after stirring at 100 rpm for 10 minutes. In contrast to Figures 6(a) and 6(b), the slag-penetrated layer has almost vanished. It is evidently seen that a lot of MgO islands and particles have detached from the sample into the slag bulk. Some MgO islands have even been transported far away from the cube.

Fig. 7 SEM image of interface region between MgO-B cube and slag
at the stirring speed of 50 rpm for 10 minutes.

Figure 7 presents the SEM microphotograph taken at the interface region in MgO-B cube after stirring at 50 rpm for 10 minutes. Because of the difficulty to show all the layers in one microphotograph with the same magnification, the core of MgO-B is not included in the figure, but will be given later. It can be seen that similar to the case of MgO-A cube after 50 rpm stirring for 10 minutes (Figure 6(b)), a slag-penetrated layer is also formed. However, this layer is thicker than that in MgO-A, it is about 2 mm in thickness. Due to the dissolution of spinel, the concentration gradient is also found in this layer; but the gradient is smaller than that in the MgO-A sample having the same reaction time.

Figure 8 presents the SEM images of different types of MgO samples in the region of cube core after reaction with slag stirred at 50 rpm for 10 minutes. It should be mentioned that all the images are taken at the positions close to the boundary of the slag-penetrated layer.

In Figures 8(a) and 8(b), three phases are identified, *viz.* periclase matrix, spinel, and liquid. In the core of MgO-A, the grain boundary of MgO grains is mainly occupied by spinel phase. In contrast to MgO-A, it is evident in Figure 8(b) that the liquid phase is the major phase at the grain boundaries, while many unreacted spinel particles distributed in the liquid phase are also observed. Additionally, in comparison with MgO-A, the particle size of spinel in MgO-B is bigger. As already mentioned in the experimental section, micro-alumina powder was used in MgO-B refractory, while nano-colloidal alumina was used in MgO-A refractory. As expected, the main phases in MgO-C cube (Figure 8(c)) are periclase and carbon.

Fig. 8 SEM images in the region of unreacted core in samples

(a) MgO-A (b) MgO-B and (c) MgO-C with slag stirred at 50 rpm for 10 minutes.

4. Discussion

To begin the discussion, it should be pointed out that the amount of slag used in the experiments along with its composition was carefully chosen. The slag would not be saturated even after the entire MgO cube had been dissolved into the slag. This situation is very similar as the ladle treatment.

The solubility of MgO in the present slag, according to the phase diagram of the CaO-Al₂O₃-MgO-SiO₂ quaternary system is near 12 mass% at 1873 K [21]. In fact, it is well demonstrated by the result of MgO-B cube after in contact with slag for 60 min, where the cube mostly

dissolved into the slag as presented in Table III. The MgO content of the final slag composition is about 12.6 mass% by the analysis of XRF.

As shown by Figure 2(c) and Figure 8(c), MgO-C cube, which was cut out from traditional commercial carbon bonding MgO brick, has the best resistance against slag dissolution. The existence of carbon efficiently stops the penetration of slag into the refractory, and therefore hinders the dissolution. However, in a real ladle, the outer layer of MgO-carbon refractory gets decarbonized by either the reaction between MgO and carbon or/and oxidation. It is generally recognized that a decarburized layer is always formed on the original MgO-carbon lining after first heat.^[4-11] The lining usually consists of 3 layers after the first usage, viz. (1) the original MgO-carbon layer, (2) the decarbonized layer, and (3) the slag-infiltrated layer [7]. The thickness of the decarbonized layer is pretty big. This is especially true at and above the slag line. As a matter of fact, the dissolution of MgO refractory into the slag takes place mostly between the decarbonized MgO layer and slag. On consideration of this situation, the decarburized MgO refractory is investigated. This cube (named as MgO-D) was cut out from the commercial MgO-carbon refractory brick and decarbonized in order to simulate the decarburized layer. Since the main dissolution of MgO refractory is not due to the original MgO-carbon brick, but the decarbonized layer, the following discussion will focus on the mechanisms of the MgO dissolution in the case of MgO-A, MgO-B and MgO-D samples.

4.1 Mechanism without forced convection

In the cases of MgO cubes reacting with stagnant slag, 3 main steps are involved in the dissolution process, namely:

- (1) External mass transfer in the bulk of the slag.
- (2) Internal mass transfer in the pores of the refractory, by both slag penetration and diffusion.
- (3) MgO dissolution.

In the absence of stirring, the external mass transfer is due to natural convection and diffusion. The compositions of the liquid near the surface of the cube after different reaction times in the stagnant slag are found to be very close to the initial slag composition for all types of refractories. The negligible change in slag composition at the sample surface is in fact expected, since the slag is not saturated by MgO even when the whole sample has been dissolved. This negligible change of the MgO content in the liquid at the surface of the cube in comparison with the bulk of the slag is an evidence that external mass transfer is not the rate controlling step in the dissolution process. This reasoning is further confirmed by the comparison of the results shown in Figure 2 and Figure 3. As seen in Figure 3(b), the MgO-D cube has vanished after 6 minutes in a stagnant slag. On the other hand, the other types of cubes still keep approximately their cubic nature after 10 minutes of stirring. The substantially fast dissolution of MgO-D in the stagnant slag reveals evidently that the process is not controlled by the external mass transfer, viz. step 1. Hence, the dissolution process is expected to be controlled by step 2 and/or step 3.

A careful examination of Figures 2, 3, 5-8 reveals evidently that the dissolution behaviors of different types of MgO cubes are very different. As shown in Table I, MgO-D has the most porous structure. It has been found that the decarburized refractory has the poorest resistance to slag penetration and the liquid slag is sucked into the whole thickness of the refractory very quickly [19]. It is seen in Figure 5(b) that MgO-D has a profound amount of liquid phase throughout the whole MgO matrix. The dissolution is in fact a self-acceleration process. The dissolution of MgO makes the matrix more and more porous, which in turn enhances the liquid penetration and therefore accelerates the dissolution process. When the sample has been penetrated to a certain extent, the local convection of the liquid would eventually dissociate the

cube as evidently seen in Figure 3(b). The local flow in the liquid phase inside the “cube” could be introduced by natural convection or/and Marangoni flow. Note that the internal mass transfer in the liquid of the slag-penetrated layer is due to three fluxes, namely (1) flow due to penetration, (2) local flow due to natural convection or/and Marangoni flow, (3) diffusion. It is expected that the diffusion contributes much less than the other two factors.

On the other hand, MgO-A after in contact with slag for 6 minutes still remains. Figure 5(a) shows that a slag-penetrated layer is formed between the slag bulk and the MgO core. As mentioned in the result part, concentration gradient is found in the liquid phase through the slag-penetrated layer. The presence of concentration gradient is an evidence that step 2 is one of the controlling steps of the dissolution process. Note that step 3, the dissolution of MgO at the surface of the MgO particles in the slag-penetrated layer could be the other controlling step in the process. Since the chemical dissolution of MgO into slag is similar in MgO-A, MgO-B and MgO-D samples, the difference in the dissolution rate in these three types of sample can be contributed to the difference in penetration and the total surface area of the MgO particles in the slag-penetrated layers of these samples. Figure 5 also suggests that the chemical dissolution of the refractory takes place mostly on the surface of the MgO particles inside the slag penetrated layer, although the dissolution at the cube surface occurs as well. Because the total surface area of the particles in the slag penetrated layer is very much bigger than the surface of the cube, the contribution of the dissolution by the latter is negligible.

As reported in the previous publications [18-19], the addition of tiny alumina particles leads to the formation of micro spinel particle along the boundaries of the MgO grains. These micro spinel particles dissolve into the penetrated liquid very fast due to their tiny size and huge surface area. The presence of the micro spinel particles will efficiently reduce the porosity of the refractory and increase the resistance to slag penetration. Moreover, the dissolution of spinel particles results in the increase of both Al_2O_3 content and MgO content in the liquid oxide. The increases of these two oxides will eventually lead to the formation of solid calcium aluminate phase and therefore increase the resistance to slag penetration.

A careful examination of the microphotographs of the MgO-A and MgO-B samples indicates that the size of the spinel particles in the MgO-A refractory is smaller than that in the MgO-B refractory. This is because that nano alumina particles (alumina colloid) are used to prepare the MgO-A refractory while micro powder of alumina is used to prepare the MgO-B refractory. This difference can even be seen in the cube cores shown in Figures 8(a) and 8(b). Bigger spinel particles would lead to bigger porosity (see Table I). In addition, the bigger size of the spinel phase would also lead to the slower dissolution of this phase into the liquid oxide. Both bigger porosity and slower spinel dissolution would result in faster slag penetration. This would explain the bigger dissolution rate of MgO-B sample in comparison with MgO-A, though the difference is not substantial. The difference in the size of spinel phase can also well explain the difference in the microstructures between MgO-A and MgO-B samples shown in Figure 8(a) and 8(b). In the core of MgO-A after 10 minutes of reaction, only a little amount of liquid phase is seen. On the other hand, in the core of MgO-B after 10 minutes of reaction, the fraction of liquid phase is considerably higher.

It can be concluded that the presence of micro spinel particles efficiently increases the resistance to slag penetration. A good resistance to slag penetration contributes to reduce the dissolution of MgO in stagnant liquid.

4.2 MgO dissolution under forced convection

In the cases of MgO cubes reacting with stirred slag, the 3 steps discussed in the last section still take place in the dissolution process. As illustrated in Figure 4 and Figure 6(c), a lot of

MgO islands are found in the slag bulk. The number of MgO islands increases with the stirring time and stirring speed. The MgO islands are detached from the refractory sample due to the relative movement of the liquid around the cube. Hence, the peeling-off of the MgO particles from the cube surface is an important step parallel to the chemical dissolution.

The cube of MgO-D is dissociated completely after 1 minute stirring at 50 rpm. The time for the complete dissociation of the cube with stirring is much shorter than that without stirring (6 minutes, see Figure 3(b)). When 50 rpm stirring is applied, mechanical peeling off is very profound in the case of MgO-D refractory. As seen in Figure 3, the penetration of slag into the MgO-D sample is very fast even when no stirring is applied. The loose structure of MgO-D has very low resistance to the shear stress generated by the movement of liquid slag. MgO particles at the surface of cube would start being peeled off very soon after the penetration has taken place, and then the whole cube would dissociate. As already mentioned in the introduction section, the decarburized layer on the lining would be easily degraded by the mechanical abrasion and chemical reactions with the liquid slag during ladle treatment. This phenomenon is clearly demonstrated by the present experimental result of the MgO-D cube. As mentioned above, in an industrial ladle, the real slag-refractory takes place between the decarbonized MgO lining and slag without MgO saturation. The poor performance of MgO-D samples emphasizes the strong need of the development of new type of MgO based refractory.

The experimental results (see Figure 2 and Table III) indicate that under the condition of forced convection, both MgO-A and MgO-B refractory dissolve much slower than MgO-D into the liquid slag. As seen in Figure 6(a) and Figure 6(b), the fraction of liquid phase in the slag-penetrated layer and the thickness of the layer increase with reaction time. The concentration gradient increases also with the reaction time. These results reveal that the stirring at 50 rpm is not strong enough to remove the whole slag-penetrated layer. Hence, the peeling-off step along with steps 2 and 3 jointly control the rate of dissolution. Nevertheless, the stirring would peel off a part of the slag-penetrated layer, therefor the resistance of the layer to further liquid penetration is reduced. This would explain the increasing dissolution rate of the MgO-A refractory with the increase of stirring speed up to 100 rpm.

Figure 6(c) evidently shows that the slag-penetrated layer is almost completely removed at a stirring speed of 100 rpm. When the stirring speed increases to 100 rpm, forced convection plays an important role in the dissolution process in the case of MgO-A. As soon as the slag-penetrated layer has formed due to liquid penetration, the forced convection at this stirring speed (100 rpm) would remove the layer. For this reason, the dissolution process would be mostly controlled by penetration (the slowest step). Further increase would not affect the dissolution substantially. This is confirmed by the result of dissolution at 150 rpm. As shown in Figure 4, the increase of the stirring speed above 100 rpm increases the dissolution rate very little. It is worthwhile to mention the difference between the stagnant slag and slag stirred at speed above 100 rpm. In both cases, the dissolution is controlled by the liquid penetration. However, in the case of stagnant slag, the thickness of the penetrated layer increases with time leading to the increase of penetration resistance. In the case of slag stirred with speeds at and above 100 rpm, the removal of the slag-penetrated layer takes place as soon as the layer is formed. In the system with stirring speeds higher than 100 rpm, the resistance to penetration does not increase because of the constant removal of the slag-penetrated layer (Figure 6(c)). In the case of slag bath stirred at mediate speed (<100 rpm), the process would be jointly controlled by the liquid penetration and the peeling-off of the slag-penetrated layer.

The present results also reveal that the chemical dissolution at the surface of the cube is absolutely negligible in comparison with the removal of the slag-penetrated layer formed by liquid penetration. This finding would suggest strongly the importance of the study on the

mechanism of slag penetration. This finding is in good agreement with the observation of Huang *et al* [17]. They also found that the dissolution of different MgO refractories was affected greatly by the penetration of the liquid, and the refractory with better resistance to slag attack resulted in a slower dissolution rate [17].

Based on rotating cylinder technique, some researchers have reported that the rate of dissolution increases with the rotation speed [12-16]. This experimental finding is in accordance with the present results. However, the researchers suggest based on their experimental results that the mass transfer in the slag bulk is the controlling step. Although the present experiments are somewhat different from these publications [12-16], the peeling-off mechanism is well brought out by the reacted MgO cube along with the slag quenched from the experimental temperature.

As seen in Figure 4, the dissolution rate of MgO-B is slightly bigger than MgO-A. Following the above reasoning, the faster penetration in the MgO-B refractory in comparison with MgO-A refractory would be the explanation of the slightly worse performance of the MgO-B sample. As reported in the previous publications [18-19], the addition of colloidal alumina into MgO increases greatly the resistance of the refractory to slag penetration. The particle size of the colloidal alumina is at nano level, which results in spinel particles at micro level. The tiny spinel particles would not only increase the density of the refractory, but also dissolve into the liquid oxide rapidly which would hinder the dissolution of MgO into the penetrated liquid. On the other hand, alumina powder with micro sizes is used in MgO-B refractory. The bigger size of spinel particles (Figure 8(b)) would function less to increase the density of the MgO refractory (see Table I) and have lower dissolution rate to increase the resistance of the refractory against slag penetration. This would explain the slightly higher dissolution rate of MgO-B in comparison with MgO-A. However, the difference between MgO-B and MgO-A with respect to dissolution is not profound. Note that using micro alumina powder to replace colloidal alumina would reduce the production cost greatly. In view of the actable cost of the raw materials for the refractory industrial, MgO-B would be a very good potential candidate for the development of new refractory. It should be mentioned that in addition to the property of the resistance to slag penetration, the mechanical properties must be studied, in the future development.

5. Summary

Dissolution of MgO based refractories in CaO-Al₂O₃-MgO-SiO₂ ladle slag was investigated at 1873 K. Two new types of carbon-free MgO based refractories with the formation of micro spinel particles in the MgO matrix as binder were prepared. The dissolution experiments were conducted using these two new refractories along with the commercial MgO-carbon refractory; and the results were compared. In view that the dissolution of MgO refractory into the slag in a ladle took place mostly between the decarbonized layer and the slag, comparison was made mainly between the new types of refractories and the decarbonized commercial bricks.

It was found that the process consisted of 3 main steps, namely (1) External mass transfer in the bulk of the slag, (2) internal mass transfer in the pores of the refractory, by both slag penetration and diffusion, and (3) MgO dissolution. The experimental results showed evidently that the internal mass transfer in the slag-penetrated layer is the controlling step of the MgO dissolution. In the case of stagnant slag and slag stirred at low speed, an increase in the thickness of the slag-penetrated layer was noticed. The increase of the thickness of the slag-penetrated layer would slow down the slag penetration. In the case of slag stirred at higher speed, e.g. ≥ 100 rpm, the slag-penetrated layer was almost completely removed constantly, and therefore resulting in fast dissolution. The present results also showed evidently that the two types of new refractories had substantially better resistance to slag penetration in comparison with the

decarbonized commercial MgO-carbon refractory. In view of the reasonable cost for the production of the MgO-B refractory, this type of carbon-free MgO refractory could be a promising potential candidate to replace the present commercial magnesia ladle lining.

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