Dissolution of MgO-Al₂O₃ spinel and MgO in CaO-Al₂O₃-MgO-SiO₂ slag under forced convection

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Abstract

In this work, the dissolution mechanism of dense MgO-Al₂O₃ spinel and MgO rod into molten CaO-Al₂O₃-MgO-SiO₂ slag was investigated at 1873 K with forced convection. The dissolution experiments were carried out by employing a newly developed rotating cylinder method. The effect of rotation speed and reaction time on the dissolution rate was studied. The measured dissolution rates of both spinel and MgO were dependent on the rotation speed, indicating that mass transfer in the slag phase to one of the rate-limiting steps. It was also found that the dissolution rate of spinel in slag was enhanced more rapidly than that of MgO with the increasing reaction time and rotation speed. It was also found that the composition of the slag at the interface was far from equilibrium value between the slag and solid. The results implied that the chemical reaction at the solid-slag interface should be the other important step that jointly controlling the dissolution process.
1. Introduction

Understanding the mechanism of oxides dissolution, *e.g.* MgO and MgO-Al₂O₃ spinel, into the slag helps to solve two major issues in steelmaking. The dissolution of oxides affects the inclusions removal efficiency, which is one of the issues. A fast dissolution was suggested to enhance the entrapment of inclusion by the slag.¹ The other issue is to enhance the service lifetime of refractory lining. Refractory materials produced by MgO and MgO-Al₂O₃ spinel have been widely used for ladle lining. When the refractory contacts with the molten slag, a slow dissolution prolongs the refractory lifetime.²

Amini *et al.*³ measured the dissolution rate of MgO rod in CaO-45wt% Al₂O₃ based slag in the temperature range 1723 K to 1873 K. They found that mass transfer in liquid was the controlling step in the dissolution. Comparison between the theoretical curve and actual measured curve by Wang and Liu revealed that MgO particle dissolution is primarily controlled by a boundary layer diffusion mechanism in high silica calcia-alumina-silica-based slags, while once the formation of spinel layer covered the MgO particle, the limiting-step of MgO-particle dissolution is the process of diffusion of the spinel product toward the bulk slag.², ⁴ Regarding the kinetics of MgO-Al₂O₃ spinel dissolution, Fox *et al.*⁵ suggested that both MgO and MgO-Al₂O₃ spinel dissolution are governed by chemical reaction at the interface between the solid oxide and slag. While Monaghan *et al.*⁶-⁷ found that the mechanism of spinel dissolution was at least partially controlled by mass transfer in CaO-SiO₂-Al₂O₃ slag at 1777 K. Despite many studies have investigated MgO and MgO-Al₂O₃ spinel dissolution, the mechanism of dissolution still remains unclear. This is because the dissolution behavior of oxides could be affected by many factors, such as experimental setup, slag composition, and physical properties of the dissolved oxide.

In a previous work carried out in present laboratory, a new carbon-free MgO based refractory with in situ spinel formation was developed by adding colloidal alumina. Reactions between the refractory and ladle slag at 1873 K were studied.⁸-¹⁰ It was found that the dissolution behavior of spinel particles in the liquid at the grain boundaries played a crucial role in limiting slag penetration. To obtain an in-depth understanding of the role of spinel phase in MgO matrix in the refractory, it would be of great interest to investigate the mechanism of MgO-Al₂O₃ spinel and MgO dissolution in ladle slag at steelmaking temperature.

To study the dissolution of solid oxides by forced convection, a new rotating cylinder method was developed. In this method, a rotating cylinder was placed concentrically in a container fabricated by boring four holes into a blank material to create an internal volume with a quatrefoil profile.¹¹ The experimental results proved that this method was suitable for the dissolution study in contrast with the traditional rotating method. The presence of quatrefoil profile could efficiently enhance the mass transfer in the liquid. This method also allowed rapidly quenching the entire reaction system. By applying the new method, reliable results regarding the dissolution mechanism could be obtained.

To focus on the dissolution of oxide and avoid peeling-off of the material by shear stress, MgO-Al₂O₃ spinel rod and MgO rod with dense structure were chosen as starting materials in this study. The effect of rotation speed and time on the dissolution was studied by measuring the size change of the rod after reaction with slag.
2. Experimental

2.1 Materials preparation

Two different ceramic rods were studied, viz. MgO-Al₂O₃ spinel and MgO rod. For brevity, MgO-Al₂O₃ spinel is named spinel in the latter discussion. The spinel rod was prepared in the laboratory by using high purity of Al₂O₃ and MgO powders in the mole ratio of Al₂O₃: MgO=1:1. The α-phase Al₂O₃ powder (Purity 99.9%, <1 micrometer) was mixed with MgO powder (Purity > 99%, 325 mesh) in ethanol. The details of the raw materials used in present work is listed in Table I. A magnetic stirrer was used to get a better mixing. After 2 hours of stirring, the fully mixed powders was dried in the oven and thereafter, the mixture was pressed into rods under 10 MPa pressure in a laboratory-scale hydraulic press. The rods were then sintered in a muffle furnace at 1873 K by the heating rate of 3 K/minute, the dwell was 10 hours. The sintered spinel rod by the measurement of EDS had the weight ratio 28:72 of MgO:Al₂O₃.

Table I. Details of the used raw materials.

<table>
<thead>
<tr>
<th>Oxide name</th>
<th>Particle size</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>325 mesh</td>
<td>&gt;99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;1 micrometer</td>
<td>99.90%</td>
<td>Alfa Aesar</td>
</tr>
</tbody>
</table>

MgO rod was obtained from the high purity commercial magnesia. According to the supplier, this commercial MgO was treated in the high temperature (above 1873 K) for several hours in order to obtain the high density. Both of the oxide rods had 8 mm (± 0.5 mm) in diameter. The density and porosity of both types of rods are given in Table II.

Table II. Densities and porosities of ceramic rods.

<table>
<thead>
<tr>
<th>Rod type</th>
<th>Bulk density (g·cm⁻³)</th>
<th>Apparent porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO-Al₂O₃ spinel</td>
<td>3.2</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.4</td>
<td>&lt; 5%</td>
</tr>
</tbody>
</table>

2.2 Experimental setup and procedures

As already mentioned earlier, a new rotating method was developed and built up to study the dissolution in the liquid in another work. Figure 1 shows a schematic diagram of the experimental apparatus, details of the crucibles and support elements are shown in the inset. The apparatus has been described previously.
The dissolution experiments were conducted according to the following procedures. In the preparation for each run, 100 grams of the pre-melted slag were placed into the bottom of a working crucible. The pre-melted slag was prepared prior to the dissolution experiments. The initial composition of the slag was 53-54 mass% of CaO, 31-33 mass% of Al₂O₃, 8-9 mass% of MgO and 6-7 mass% of SiO₂. Note that the slag used in present work was not saturated with spinel and MgO. The working crucible was fabricated by boring four 18 mm diameters holes into a blank graphite in order to create an internal volume with a quatrefoil profiles. The working crucible were placed in a larger holder made of graphite. A ceramic rod was mounted on the connecter and inserted through the graphite disk as seen in Figure 1. Note that new slag and a new ceramic rod were used in each experiment. The reaction tube was sealed, evacuated and filled with argon gas. The sample assembly was rested at the water-cooled chamber before the experiment. The furnace was then ramped up to 1873 K at the heating rate of 1.5-2 K/minute. A constant argon flow of 0.05 L/minute was maintained during the heating and throughout the entire experiment. When the furnace reached the target temperature, the sample was slowly pushed down into the hot zone of the furnace by a lifting device where the lifting speed could be precisely controlled. Before lowering the sample to the final position, the sample holder was first rested at the temperature zone of 1623 K for 10 minutes in order to avoid thermal shock of the reaction tube and the same time limit the reaction between molten slag and graphite. The ceramic rod was placed to a position within the working crucible but above the slag, held there for a few minutes until the slag attained melt, and then immersed to a depth of about 20 mm. Experiments were conducted at 0, 50, 100 and 150 rpm rotation speed at 1873 K. At the end of each experiment, the ceramic rod was removed from the molten slag and the crucible assembly was rapidly pulled out from the hot zone into the quenching chamber. A high flow of argon gas was meanwhile purged into the chamber to help freeze the sample. For the investigation of dissolution mechanism, some rods were quenched inside the slag. After cooling, the crucible assembly was taken out from the quenching chamber and then dismissed the parts to obtain the sample. The dimensional changes of the rod were measured.

Some slag samples after experiment were collected and analyzed by the measurement of X-ray fluorescence (XRF). Samples were also subjected to the analysis of scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS).
3. Results

As examples, the photographs of ceramic rods after reaction with liquid slag are shown in Figure 2. Figure 2(a) is the spinel rod after rotation in the liquid slag at the speed of 50 rpm for 10 minutes, and Figure 2(b) is the MgO rod after rotation in the liquid at same rotation speed but for 30 minutes. It is evidently seen that there is a big difference in the dissolution between MgO and spinel. For the case of spinel rod, the position near the upper surface of the liquid is much thinner than the other places of rod where immersed into the liquid. It could be explained by the presence of turbulence at the interface between liquid and gas. This phenomenon became more significant when a higher rotation speed was employed. Because of that, the experimental time and rotation speed should be carefully chosen in this study.

![Figure 2](image.jpg)

Figure 2. Photograph of (a) Spinel rod after rotation in liquid for 10 minutes and (b) MgO rod for 30 minutes.

SEM and EDS were conducted to examine the morphology of the sample for the investigation of dissolution mechanism. Figure 3 shows the SEM images of the rod-slag interface. Both MgO and spinel rod have been rotated in the liquid slag at the speed of 100 rpm for 10 minutes. It is seen in both figures that the boundary between the rod and slag bulk is clear and sharp. The MgO dendrite as presented in Figure 3(a) and (b) is precipitation, due to cooling. The amount of slag penetrated into the rod is very little, therefore it is expected that the effect of slag penetration on the dissolution process is unimportant. EDS results show that there is no apparent composition change near the surface of rod. It should be mentioned that the EDS analysis has some uncertainties, but it is still helpful to compare the change of the liquid composition.
Figure 3. SEM images of (a) MgO rod and (b) spinel rod with slag rotated at the speed of 100 rpm

Figure 4 presents the normalized diameter of stationary ceramic rod as a function of time after reaction with slag. The normalized diameter $D_N$ is defined as

$$D_N = \frac{D}{D_0}$$

(1)

where $D$ is the diameter of ceramic rod after the experiment and $D_0$ is its initial diameter before the experiment. A linear relationship between $D_N$ and time is seen in the figure which indicates that the dissolution rate is independent of $\text{Al}_2\text{O}_3$ and MgO concentration in the slag. This figure also shows that the dissolution rate of spinel is higher than MgO in the slag without forced convection.
Figure 4. Normalized diameter of stationary ceramic rod, $D_N$, as a function of time in liquid slag.

Figure 5. Normalized diameter of ceramic rod, $D_N$, as a function of rotation speed for 10 minutes.

Figure 5 shows the effect of rotation speed on the dissolution of ceramic rod in the liquid slag. It can be seen that dissolution rates of both types of ceramic rods increase with the increase of rotation rate. It is apparent from the figure that the rotation speed has a bigger impact on the dissolution of spinel rod, the change of $D_N$ is from 0.87 to 0.62. While the effect of rotation speed on MgO dissolution is rather small as $D_N$ diminished from 0.99 to 0.96 when the rotation speed varies from 0 to 150 rpm.

Figure 6 presents the normalized diameter of spinel rod as a function of time with the increase in the rotation speed. Again, mechanical rotating is found to increase the rate of spinel dissolution in the liquid slag. The normalized diameter of MgO rod with increasing reaction time is plotted as a function of rotation speed in Figure 7. Despite the limited number of experiments in the study of MgO dissolution, a clear decreasing trend of $D_N$ with time can be observed. The rotating speed has somehow effect on the dissolution, but the effect is much less profound compared with spinel in Figure 6.
4. Discussion

The dissolution process of spinel and MgO rod in the slag involves two steps, namely (i) chemical reaction at the solid-slag interface and (ii) mass transfer in the bulk of slag caused by diffusion and convection. As forced convection is introduced into the reaction system, the contribution of diffusion on the mass transfer is expected to be negligible.

The results in Figure 6 and Figure 7 show evidently that the dissolution rates of spinel and MgO are both enhanced by rotation. By increasing the rotation speed, the mass transfer is enhanced due to the increased convection. This indicates that the dissolution process is controlled or partially controlled by mass transfer. As seen in Figure 5-7, the effect of rotation rate on the dissolution rate between spinel and MgO is such different. With increasing the rotation speed, the dissolution rate of spinel is increased more rapidly than MgO. If assuming that the dissolution process was solely controlled by the mass transfer in the bulk of slag, it would be expected that the dissolution rate of spinel and MgO should be comparable to each other, since
the mass of slag phase along with its initial composition is identical in both cases. As discussed earlier, the liquid composition in the vicinity of the rod is close to the composition in the slag bulk. This liquid composition is far from the composition of equilibrium between the solid and slag. Based on the above observations, it is reasonable to conclude that chemical reaction at the solid-slag interface is also an important step in the dissolution process. It can be concluded that dissolution process in both cases of MgO and spinel is controlled by the combination of both mass transfer in the slag bulk and chemical reaction.

As reported in the most literatures, the dissolution mechanism of spinel and MgO in the slag was mainly controlled by the mass transfer. The dissolution rate showed a great dependency on the slag composition and the velocity of convection. On the other hand, Fox et al reported that surface reaction appears to be the controlling the rate of MgO and spinel dissolution. Although the present experimental method for the dissolution study differs from others, the results shown in this work are partly in accordance with the findings in previous studies.

Since it is difficult to quantify the dissolution rates in a precise mathematical manner in this work, a qualitative discussion will be given to understand the large difference in dissolution rate between spinel and MgO. By assuming the chemical reaction is first order, the dissolution rate could be described as,

\[
\frac{dr}{dt} = A \frac{C_{eq} - C_{bulk}}{R_1 + R_2}
\]

In Equation (2), \(dr/dt\) is the total dissolution rate, \(A\) is the interface area between the rod and slag. \(R_1\) is the resistance due to the mass transfer in the slag bulk, and \(R_2\) is the resistance of chemical reaction. \(C_{bulk}\) is the concentration of the oxide in the bulk of slag and \(C_{eq}\) is the concentration of the dissolving oxide in a saturated slag in equilibrium with the pure oxide. The difference between \(C_{eq} - C_{bulk}\), the concentration difference \(\Delta C\), is the driving force for the whole dissolution process.

From the equation, it can be seen that the total dissolution rate is related to \(\Delta C\). In this work, the term of \(C_{bulk}\) could be measured by XRF analysis. As already discussed, the increase in MgO and Al\(_2\)O\(_3\) content in the slag phase is very little, since the amount of slag phase in both cases is large. \(C_{bulk}\) in the case of spinel is supposed to be the same as in the case of MgO. \(C_{eq}\) could be evaluated from the phase diagram. As seen the phase diagram of 30%Al\(_2\)O\(_3\)-CaO-MgO-SiO\(_2\) system in Figure 8, the solubility of MgO in current slag is near 12 mass% at 1873 K; whereas it is somewhat difficult to determine the solubility of spinel by the phase diagram. As the spinel phase contains Al\(_2\)O\(_3\) largely in mass percent (around 72 mass%), a semi-quantitative consideration could be discussed with respect to how an increase in the amount of Al\(_2\)O\(_3\) would affect the solubility of MgO in the slag. A careful comparison between phase diagram of Al\(_2\)O\(_3\)-CaO-MgO-SiO\(_2\) system containing 30 mass% Al\(_2\)O\(_3\) with the system containing 35 mass% Al\(_2\)O\(_3\) (Slag Atlas) reveals that the liquidus line for the liquid-MgO equilibrium shifts to the MgO-rich side. This indicates that a higher solubility of MgO could be acquired when the liquid contains higher content of Al\(_2\)O\(_3\). It could be suggests that \(\Delta C\) in spinel dissolution is larger than MgO dissolution. Moreover, taking into account the large amount of slag and the fact that the local chemical equilibrium at the slag-refractory interface is not reached, the driving force would be considered nearly constant in the dissolution process. Thus, the larger driving force for spinel dissolution could be the main reason for its rapid dissolution rate.
It should be mentioned that the effect of reaction between graphite and slag on the dissolution was also studied. A test run with 100 grams of slag was carried out by using the same experimental conditions and graphite crucible. The experiment duration was 30 minutes which was the longest experimental duration in this work. The results of chemical analysis in Table III indicate that the change of slag composition after experiments is extremely small. It is expected that the graphite-slag reaction would not have any appreciable influence on the dissolution.

Table III. Slag composition before and after test run

<table>
<thead>
<tr>
<th>Slag sample</th>
<th>Slag composition (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>Before test run</td>
<td>53.9</td>
</tr>
<tr>
<td>After test run</td>
<td>54.2</td>
</tr>
</tbody>
</table>

As discussed in the introduction section, the formation of spinel particles in MgO based refractory could effectively resist slag penetration. Previous results revealed that the dissolution
of spinel particles into the penetrated liquid made a profound contribution to limit the penetration.\textsuperscript{8,9} It was because that further penetration of slag in MgO refractory was slowed down, as the liquid phase at the grain boundaries of MgO grains was saturated by the dissolved spinel. To illustrate this aspect clearly, the SEM image of MgO based spinel refractory after in contact with slag is presented in Figure 9. This refractory was prepared by dead burnt MgO with an addition of 20 mass\% colloidal alumina and it was exposed to liquid slag at 1873 K for 30 min. The SEM image was taken at the area of the penetrated refractory close to the slag bulk. The absence of spinel particles at the grain boundaries in the left side of the image is shown evidently in Figure 9. As reported previously,\textsuperscript{8,9} the presence of concentration gradient in liquid phase was also an evidence to demonstrate the faster dissolution of spinel particles. For the dissolution behavior of spinel and MgO particles during the penetration process, step (i) and (ii) were also taking place at the grain boundaries, while mass transfer in the liquid was mainly caused by slag penetration. The initial slag composition in the penetration experiment was the same as in this work. The present findings explains evidently why the spinel particles dissolves in slag much profoundly than the MgO grains.

**Summary**

Dissolution of MgO-Al\textsubscript{2}O\textsubscript{3} spinel and MgO in CaO-Al\textsubscript{2}O\textsubscript{3}-MgO-SiO\textsubscript{2} slag was investigated at 1873 K. The experiments were conducted using spinel and MgO rods with dense structure. The results of dissolution rate evidently indicated that the dissolution was at least partially controlled by mass transfer, since both spinel and MgO dissolution showed the dependency on the rotation speed. The results also showed that the dissolution rate between spinel and MgO was not comparable, indicating that chemical reaction was also an important step. It could be concluded that the dissolution process of oxide rod was controlled by the combination of chemical reaction and mass transfer in the slag phase. Comparison of spinel and MgO dissolution showed that the dissolution rate of spinel was bigger than MgO. The fast dissolution of spinel was mainly attributed by its larger driving force.

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**Reference**

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