The formation of an inner slag layer during the dissolution of MgO particles in ladle slag

Deyong Wang, Maofa Jiang, Xiaobing Li, Tongsheng Zhang and Chengjun Liu
Dept. Ferrous Metallurgy, School of Materials and Metallurgy, Northeastern University, 110004, P. R. China

Abstract: The presence of nonmetallic inclusions is a significant problem during clean steel production. One of the major tasks in steelmaking is to control the amount, size, and distribution of inclusions, as well as to removing them from molten steel as much as possible. In this present work, four types of slag with different basicity, MgO and Al_2O_3 content were used to simulate the ladle refining slag. The effects of slag composition and temperature on the dissolution rate of MgO particles were investigated using the direct dissolution method. The experimental results show that the dissolution rate of MgO particles strongly depends on the slag compositions and temperature. During dissolution process, once spinel product forms around the MgO core, the dissolution rate decreases remarkably. The formation and function of the inner slag layer between the MgO core and the spinel product were investigated in detail. The inner slag was possible to act as a transfer passage for Mg element from the MgO core to the spinel product. The rate-limiting step of MgO dissolution was determined by the diffusion of spinel product toward the bulk slag.

Keywords: MgO particle, ladle slag, dissolution mechanism, spinel product

1. Introduction

Refractory materials made of magnesia, which is widely used as the material of choice for ladle liners or sliding nozzles, have the high melting point, low thermal expansion coefficient, and good slag-corrosion resistance. When magnesia refractory in the ladle contacts molten steel for a long duration, a dissolution reaction between refractory and molten steel occurs, which can induce the movement of inclusions into liquid steel; particularly, in the case of vacuum refining, acceleration of the degradation of MgO–C bricks is achieved easily [1]. Also, the dissolution of magnesia inclusions in molten slag is an important part of the overall removal of inclusions, and many investigations have been carried out to study the dissolution behavior and kinetics of the same [2–4]. However, the dissolution mechanism of magnesia inclusions in molten slag is still not clear. Recently, the novel technique of high temperature confocal scanning laser microscopy (CSLM) has offered an easy approach to observe the in-situ dissolution process of inclusions in molten slags [5–10]. Nevertheless, inclusion particles are not easy to be tracked during the micro-region analysis after specimen cooling, and the results obtained by the CSLM technique are insufficient to describe the dissolution process and mechanism.

In this present work, experiments on dissolution of MgO particles in various synthetic ladle slags have been carried out, and the process has been studied in terms of the kinetics and mechanism. MgO particles are added directly into molten slag, the dissolution boundary is investigated by scanning electron microscopy (SEM), Shimdazu SSX-550 Japan, with energy dispersive spectrometer (EDS) analysis. The effects of slag composition and temperature on the dissolution behaviors were investigated. The dissolution mechanism has also been discussed in the context of the results obtained.

2. Experimental

The experimental materials include the ladle slag and the prepared MgO particles. The experiments were conducted at 1843K or 1893K. The ladle slags in this study were prepared by mixing high-purity chemical reagents, and slag compositions are shown in Table 1. Here, the variation of slag composition contains basicity (CaO/SiO2), Al2O3 and MgO content. The Special explanation for No.2 slag, to make the same experimental condition, 3.0 wt % CaF2 was added to decreasing the slag melting point.

A crucible made of high-purity MgO (>99 %) was crushed to yield small MgO particles, which were then separated though the sieve with 40-50 mesh. The particles are found to be spherical under an optical microscope, and the average diameter is measured in the range of 300–350 μm.

Table 1 Experimental conditions applied in this present study

No.	Mass fraction, wt.%					w(CaO)/w(SiO_2)	T/K
	CaO	Al_2O_3	SiO_2	MgO	CaF_2		
1	36.0	20.0	36.0	8.0	0	1.0	1843
2	54.0	20.0	18.0	8.0	3.0	3.0	1843
3	36.0	20.0	36.0	8.0	0	1.0	1893
4	40.0	20.0	40.0	0	0	1.0	1843
5	39.0	40.0	13.0	8.0	0	3.0	1843

Each experiment was carried out in a platinum crucible (30-mm diameter, and 50-mm height). Approximately 60 g of slag powder were placed into the crucible and heated in an electric resistance furnace under high-purity argon atmosphere, with a flow rate of 1.0 L/min. When the furnace reached to the desired temperature, molten slag was held for 30 minutes to achieve sufficient homogenization of the composition. The MgO particles were baked for 24 hours at 973 K in an electric muffle furnace before the experiments. Approximately 1.5 g of MgO particles, enclosed by an aluminum foil, were added into liquid slag using a quartz bar. Subsequently, the slag was quickly stirred for 10 seconds with an alumina bar to disperse the inclusion particles. After the particles were added into the slag, slag samples were drawn out at 15, 30, 60, 120, and 360 seconds from the molten slag by an alumina dipper and quenched to room temperature. The cooled samples were mounted and polished carefully to observe the variations in particle size and boundary composition using an optical microscope and scanning electric microscope (SEM) respectively.

3. Results and Discussion

3.1 Effects of slag composition and temperature on the dissolution rate

The dissolution rates of a MgO particle in various molten slags are shown in Fig. 1. The dissolution rate is seen to improve with increase in the basicity of the slag (Fig. 1 a). Based on the molecular theory of molten slag, increasing the CaO/SiO2 value can decrease the slag viscosity, in addition to improving the dissolution kinetics; therefore, the dissolution process is accelerated. In addition, the SEM results prove that no reaction products, such as spinel (MgAl2O4), are formed around the MgO core in the case of slag basicity being 3.0, which will be discussed below. It is easy to understand that MgO particles directly dissolve in the bulk slag with less resistance being without the formation of reaction products. The dissolution rate of MgO particles in the slag containing 20% Al2O3 is about 1.6 times higher than that of particles in the slag containing 40% Al2O3 (Fig. 1 b). High Al2O3 concentration in slag improves the driving force, making it stronger, and forms a thicker spinel product around the MgO core. The products, similar in structure to a wall, restrain the diffusion of elemental Mg into the slag bulk and decrease the dissolution rate. Furthermore, the dissolution rate of the particles in MgO-free slag is a little faster than that of the particles in MgO-containing slag (Fig. 1 c). On rising the slag temperature, the dissolution rate of MgO particle increases, which is shown in Fig. 1 d. Applying the Arrhenius Equation, it is concluded that slag viscosity decreases and diffusion rate of reaction products improves with an increase of temperature.

In each experiment, the size of the MgO particles are found to decrease almost linearly with time in the initial stages of dissolution. After reacting for 100 seconds, the dissolution rate becomes much slower. This observation leads to the conclusion that chemical reactions could be dominant at the initial stages of particle dissolution. With the formation of the spinel product on the surface of the MgO core, the diffusion of Mg element through the spinel layer becomes possible and this is the rate-limiting step.

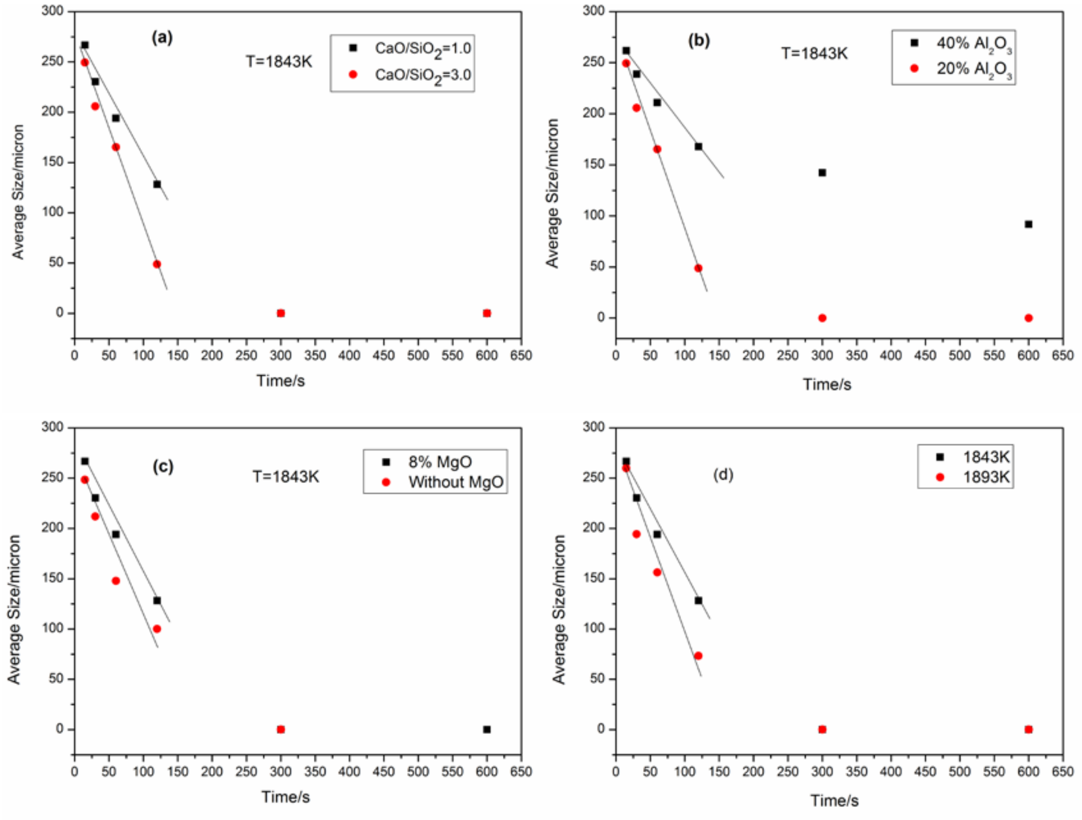


Fig.1 Effect of slag composition and temperature on the dissolution rate of MgO particles

3.2 Dissolution mechanism with formation of a product layer

The SEM images and a line-scanning analysis of MgO-particle dissolution in No.1 experiment at 15 seconds are shown in Fig. 2. An obvious ring-like layer of the spinel product is observed around the MgO particle in Fig. 2 (a), this process was designated as an indirect dissolution by Sandhage and Park [5,11,12]. A line-scanning study by EDS was carried out near the dissolution boundary region, it is shown in Fig. 2 (b) . From these data, the sequence of layers in the dissolution region can be described as being the undissolved MgO particle, the dissolution boundary, the inner slag, and the spinel product, respectively. In the cooled specimens, the character of the spinel product strongly depends on the slag composition, but other products such as CaSiO4 are not found in all experiments. The same results are observed in both experiment 4 and 5. However, the spinel layer formed in experiment 5 is thicker than that in experiment 1 and 4 at the same reaction time, it also induces the dissolution rate of MgO in experiment 5 is the slowest. This phenomenon reveals the differences in the dissolution rate of MgO particles in various molten slags.

A liquid slag region, whose composition is similar to the bulk slag, exists between the spinel layer and the MgO particle. In this present study, it was defined as the “inner slag layer”. The existence of the inner slag layer proves that both slag penetration toward the particle side and MgO dissolution toward the slag side occur simultaneously. The typical compositions of the inner slag for the dissolution of MgO in experiment 1 and 4, as analyzed by EDS, are given in Table 2. The CaO/SiO2 ratio in the inner slag is 0.73–0.92, which is slightly lower than that in the original bulk slag (CaO/SiO2 = 1.0). Therefore, the rate of diffusion of SiO2 toward the particle is concluded to be quicker than that of CaO. Similar results were reported by Oishi [13] and Park [5] for the dissolution reaction of Al2O3 and MgO in CaO-Al2O3-SiO2 slags.

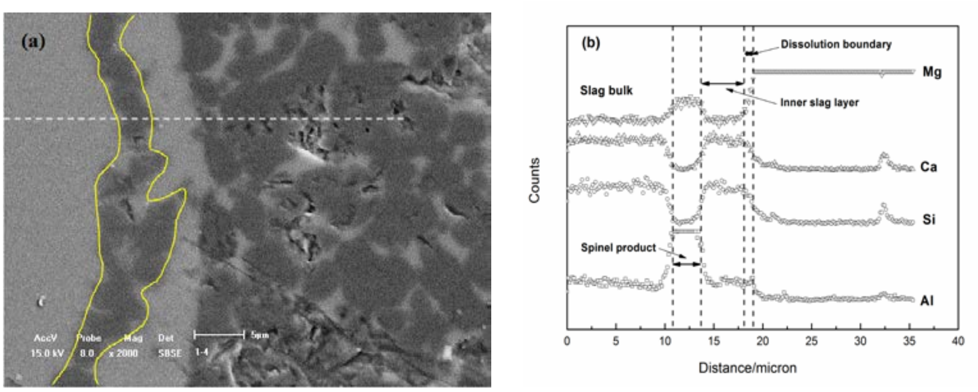


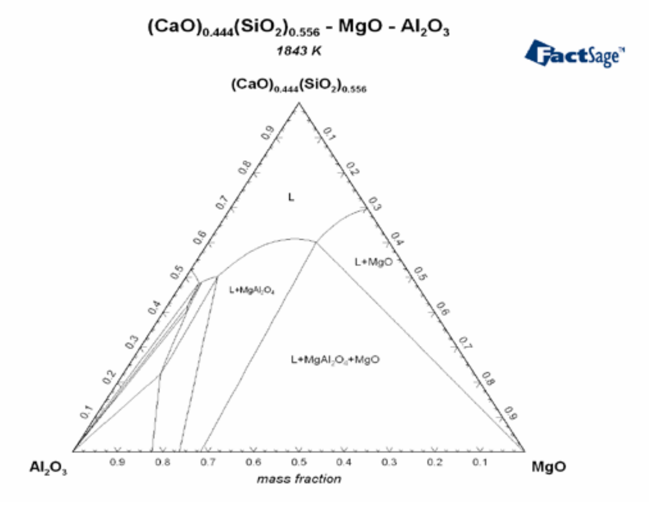
Fig. 2 SEM images and line-scanning results of MgO dissolution in experiment 1 (15 s)

In the SEM images, the dissolution boundary is observed as a very thin layer against the particle surface, with a distance of 1–2 μm. In the boundary, the Mg concentration decreases abruptly, whereas the concentrations of Ca, Si, and Al increase rapidly. It is possible that the MgO particle primarily reacts with the liquid slag in the boundary and forms the spinel on the surface of MgO particle. Once the spinel forms, the liquid flow and the large difference in lattice parameters between MgO and MgAl2O4 lead to a significant strain at the interface [14], which results in the spinel layer detaching from the MgO core and moving toward the bulk slag to form a ring-like wall. Consequently, a gap forms between the spinel wall and the MgO core, and the liquid slag fills it quickly and forms the inner slag. Therefore, the inner slag layer should be the penetrated liquid slag, not a liquid phase product.

From the data in Table 2, MgO concentration in the inner slag is seen to show a significant increase compared with that in the slag bulk. The CaO-SiO_2-Al_2O_3-MgO phase diagrams with certain CaO/SiO_2 ratio were calculated, as shown in Fig. 3, by the FactSage© software. If the compositions of the inner slag are marked in the phase diagrams, all the data are located at the single liquid–phase region but approach both L+MgO and L+spinel. But, it is still difficult to confirm whether these inner slags are co-saturated with MgO and $MgAl_2O_4$ or not. However, the inner slag found in this study should act as a mass-transfer passage between the MgO core and the spinel product. It can be predicted that the spinel product dissolves into the bulk slag, as the new spinel product forms continually due to the component supply from the inner slag layer. This dynamic process decides the thickness of the spinel product at different reaction times.

Table 2 Line-scanning results of the inner slag layer in experiment 1 and 4

Experiment No.	Point No.	MgO	Al_2O_3	SiO_2	CaO	CaO/SiO_2
		wt.%	wt.%	wt.%	wt.%	
1	1	15.02	15.30	38.14	31.54	0.82
	2	14.70	16.74	39.65	28.91	0.73
	3	10.87	19.03	38.30	31.80	0.83
	4	20.68	12.15	36.11	31.06	0.86
	5	18.57	46.41	19.06	15.96	0.84
	6	22.07	11.21	37.06	29.66	0.80
	7	19.78	39.89	21.88	18.45	0.84
	8	18.04	15.07	38.91	27.98	0.72
	9	20.97	9.29	39.38	30.36	0.77
	10	16.62	14.63	37.26	31.49	0.85
4	1	15.59	15.96	35.80	33.81	0.94
	2	14.81	17.80	35.01	32.38	0.92
	3	16.02	14.67	36.89	32.42	0.88
	4	19.14	26.71	28.78	25.37	0.88
	5	17.77	21.84	31.63	28.76	0.91
	6	18.89	21.43	45.85	13.83	0.30
	7	16.07	16.50	35.14	32.29	0.92
	8	21.40	11.70	37.90	29.00	0.76
	9	16.23	19.61	35.09	29.07	0.83
	10	17.05	14.77	37.45	30.73	0.82



$CaO/SiO_2=0.8$

Fig. 3 $CaO-SiO_2-Al_2O_3-MgO$ phase diagram by FactSage

3.3 Dissolution mechanism without product layer

The backscattered SEM images and the line-scanning analysis of MgO dissolution in experiment 2 at 15 seconds are shown in Fig. 4. The dissolution of MgO particles is observed to be different from that in experiment 1, and 4; the surface of the MgO particle appears very smooth, and no reaction product is observed. In Fig. 4(b), the Mg concentration decreases quickly, and Ca, Si, and Al increase simultaneously within the dissolution boundary. There are two different interpretations for these results. First, if the reaction product is formed on the particle surface during dissolution in experiment 2, and if the diffusion rate is more than that of the formation rate of reaction product, the reaction product cannot be found. Second, the MgO particles directly dissolve in the molten slag without forming the reaction product. Undoubtedly, the direct dissolution process is much faster than that of indirect dissolution with the formation of an intermediate reaction product, it can be confirmed by experimental result in Fig. 1 (a).

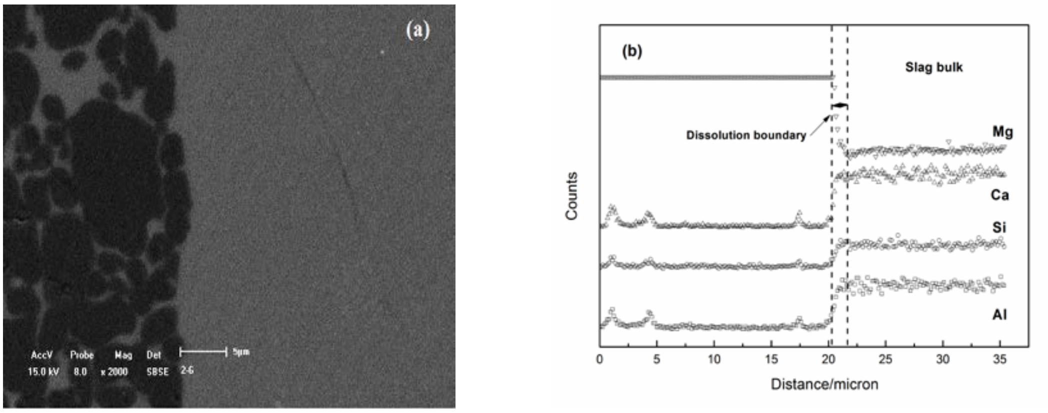


Fig. 4 SEM images and line-scanning results of MgO dissolution in experiment 2 (15 s)

The dissolution experiments in this present study are carried out under the static condition. However, in the practical production, both inclusion dissolution and refractory corrosion during ladle refining nearly occurs dynamically due to the stronger stirring of inert gas or the forced convection of liquid steel. To improve the dissolution rate of MgO inclusions, no (or lesser amounts of) ring-like spinel product is desired to form, which can be achieved by modifying the slag composition. The most efficient technique to achieve this is to increase the liquid flow to improve the diffusion rate of the spinel product. Conversely, to restrain the corrosion of the refractory material, the spinel product formed around the refractory should be thicker as much as possible, to ensure a better protection of the refractory material. Therefore, these results provide a better guideline for increasing the refractory life.

4. Conclusions

To removal the inclusion from molten steel or increase the refractory life, the dissolution process of MgO particles in CaO-SiO_2-Al_2O_3-MgO slags was investigated using a direct dissolution method in this study. The dissolution rate and the mechanism of MgO-particle dissolution strongly depend on the composition and temperature of the slag. Once the spinel product forms around the MgO core, the dissolution rate decreases remarkably. The inner slag layer should be the penetrated liquid bulk slag, not a liquid phase product, and it should act as a Mg-transfer passage between the MgO core and the spinel product. The limiting step of MgO-particle dissolution is the process of diffusion of the spinel product toward the bulk slag. To improve the dissolution rate of MgO inclusions, no ring-like spinel wall should be formed.

Instead, to restrain the corrosion of the refractory material, the spinel product formed around the refractory should be thicker as much as possible.

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