Effects of Additives and Temperature on the Dissolution Rate and Diffusivity of MgO in CaO–Al₂O₃ Slags under Forced Convection

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The dissolution rate of dense magnesia specimen in calcium aluminate based melts was measured in air over the temperature range of 1 450–1 600°C, using a rotating disk/cylinder technique. The measured dissolution rates were strongly dependent on the rotation speed with the results indicating mass transfer in the slag phase to be the rate-limiting step. At a given rotation speed, the dissolution rate was strongly dependent on the slag chemistry and temperature. The diffusivity of MgO in the slag was calculated from the dissolution rate and solubility data, using known mass transfer correlations. Addition of FeO_x and CaF₂ and increasing the temperature, resulted in substantial increase in the dissolution rate and deduced diffusivity of MgO in the slag.

KEY WORDS: magnesia; dissolution rate; diffusivity.

1. Introduction

Magnesia based refractories are widely used in many metallurgical furnaces and ladles as linings, especially in the steel industry, due to their high corrosion resistance and excellent high temperature strength. However, even these linings undergo degradation owing to mechanical abrasion and chemical reactions with the liquid slags at high temperatures. Wear of magnesia based refractories poses serious economic problems because of the high cost of the refractories as well as the disruption of the plant-operating schedule.¹⁾ Various factors affect the dissolution of solid oxides such as magnesia in the molten slag, these include; solubility of solid oxide in the melt, formation of a solid phase on the solid oxide/slag interface, viscosity and diffusivity. The effects of slag chemistry and temperature on most of these properties could be estimated by phase equilibria data and the available models.^{2–12)} Diffusivity of oxides in the melt is a fundamental quantity, which could control the dissolution rate of oxides in the melt. However, very limited work has been done in the past on determining the diffusivity of magnesia in the molten slag.

Zhang *et al.*¹³⁾ measured the diffusivity of MgO in the CaO–FeO–CaF₂–SiO₂ slags (CaO/SiO₂=1, FeO_x=45 wt% and CaF₂=2–20 wt%) over the temperature range 1 300–1 400°C under stagnant conditions. They used the concentration of magnesia in the slag and applied Fick's second law for calculation of diffusivity. The average diffusion coefficient in the liquid slag calculated by the authors was 4.49×10^{-6} cm²/s. A magnesiowustite layer was ob-

served on the magnesia/slag interface, growing with time. Ukyo *et al.*¹⁴⁾ measured the inter-diffusivity of MgO in the FeO–30wt%CaO–45%SiO₂ and CaO–40wt%SiO₂–20%Al₂O₃ slag in the temperature range 1 350–1 450°C using the diffusion couple method. The order of magnitude of their measured diffusivity was 10^{–5} cm²/s. Umakoshi *et al.*¹⁵⁾ measured the dissolution rate of sintered magnesia in CaO–FeO–SiO₂ slags of CaO/SiO₂=1 (FeO_x=20 to 65 wt%) in the temperature range 1 350 to 1 425°C using the rotating cylinder technique. The dissolution of MgO proceeded through the formation of a (Fe, Mg) O solid solution layer at the interface and its dissolution. They applied the dimensionless mass transfer correlations and estimated the diffusivity of MgO as 1×10^{-5} to 3×10^{-5} cm²/s at 1 400°C.

Published literature on diffusivity of magnesia in slags is fairly limited and the effect of additives on the diffusivity of magnesia has not been quantified. Therefore, it was decided to measure the dissolution rate and chemical diffusivity of MgO in the slag using a rotating disk/cylinder. The forced convection created by this technique under well-defined hydrodynamic conditions, minimizes the effect of natural convection that normally occurs in the conventional tracer-diffusivity measurements. The slag in this technique is agitated to a sufficient degree to render a comparable condition to those expected in stirred steelmaking reactors. Furthermore, the controlled forced convection imposed through this technique allows the determination of the effects of additives such as FeO_x and FeO_x+CaF₂ on the dissolution rate and diffusivity of magnesia in the slag.

2. Experimental

The compositions of the pre-melted master slags used in this study are listed in **Table 1**. A calcium aluminate master slag A was prepared from a mixture of reagent grade calcium carbonate and alumina with a target slag composition of $\text{CaO}-55\text{wt}\%\text{Al}_2\text{O}_3$. The mixture was melted in a graphite crucible (90-mm O.D. and 300-mm high) contained in a clay bonded graphite susceptor, which was heated by a 15 kW induction furnace to about $1\,550^\circ\text{C}$. The slag was cooled down in the crucible and then crushed in a jaw crusher to a particle size of $<2\text{ mm}$. Other master slags (B–D, Table 1) were prepared by mixing 5 and 10 wt% of reagent grade additives (Fe_2O_3 and CaF_2) with the master slag and melting the mixture in a platinum crucible in air, followed by quenching on a copper plate.

Dissolution experiments were performed using a rotating disk apparatus, shown schematically in **Fig. 1**. In each experiment, about 60 g of pre-melted slag contained in a Pt–13%Rh crucible (4 cm in diameter and 5 cm deep), was placed on an alumina platform in the hot zone of a vertical tube furnace. The furnace was heated with MoSi_2 heating elements and the temperature of the furnace was maintained to $\pm 1^\circ\text{C}$, by a programmable Eurotherm controller.

During the experiments, the temperature inside the furnace was measured using a Pt/Pt–13%Rh thermocouple located in an alumina thermocouple sheath positioned in the alumina platform, very close to the level where the platinum crucible rested. The magnesia samples were cylindrical crucibles (20 mm OD, 16 mm ID and 30 mm in height) with about 1% porosity supplied by Fuji Sho, Inc Japan.

Table 1. Chemical composition of slags investigated (wt%) in the present work.

Master slag	CaO	Al_2O_3	FeO_x	CaF_2
A	45	55	-	-
B = A + 5% FeO_x	42	50.7	5.4	-
C = A + 10% FeO_x	40.2	48.7	9.7	-
D = A + 10% FeO_x + 5% CaF_2	39	45.8	9.9	3.7

Fig. 1. Schematic arrangement of experimental apparatus.

For each experiment, a magnesia crucible was cemented to a 8 mm diameter alumina tube using an alumina-zirconia cement and then connected to steel shaft, which was driven by a variable speed motor. The rotation speed was varied with a speed controller and monitored with a digital tachometer, which was accurate to within 1 rpm.

The pre-melted slag contained in the platinum crucible was positioned about 10 mm below the magnesia rotating specimen during the heatup at the rate of $90^\circ\text{C}/\text{h}$. The melt was then equilibrated at the required temperature for 1 h. At the start of a run, the platinum crucible was raised to allow partial immersion of the specimen into slag to a depth of about 15 mm. After commencing the rotation of the sample, the melt was sampled through the top of the furnace at regular time intervals using a cold 2-mm-diameter Pt rod attached to a stainless steel rod. The Pt rod was dipped into the melt, and quickly removed from the furnace and quenched in water. This enabled slag samples (300 to 500 mg) to be collected with each dip. The samples were then dried and crushed in a tungsten-carbide ring mill for chemical XRF analysis.

The solubility of magnesia in the slag used was determined by reacting about 0.6 gram of magnesia (a piece from the magnesia specimen used in the rotating experiments) with about 0.5 gram of slag in a platinum capsule located in a muffle furnace under static conditions. After the required reaction time, the capsule with its contents was withdrawn rapidly from the furnace and air quenched. The capsule was cut in half along its length and both sections were mounted in a resin mixture and then polished. The compositions of the frozen slag specimens were analyzed by Scanning Electron Microscope (Philips LS30) after carbon coating.

3. Results

The effect of rotation speed on the concentration of dissolved magnesia in the master slag A at $1\,450^\circ\text{C}$ is shown in **Fig. 2**. The results show that the magnesia concentration increased with the period of rotation of magnesia samples in slag. Increasing the rotation speed resulted in the increase of magnesia concentration and dissolution rate for a given time. At a rotation speed of 60 rpm, the concentration of magnesia changed linearly with time and even after 50 min, the saturation of 5 wt% was not approached. At

Fig. 2. Concentration of MgO (wt%) in the slag for various rotation speeds at $1\,450^\circ\text{C}$.

Fig. 3. Variation of dissolution rate of magnesia in master slag A with the rotation speed at 1450°C.

higher rotation speeds, inspection of the magnesia sample after the end of the reaction time revealed that there was a substantial reduction in the immersed area of the magnesia specimen. This happened after 20 to 30 minutes of the reaction time, where the concentration of magnesia in the slag started to approach a plateau. The initial dissolution rate of magnesia was determined from the slope of a linear curve fitted to the magnesia concentration data for reaction times of up to 20 minutes, where the average contact area between the magnesia specimen and slag assumed to be constant. This approximation and the errors from curve fitting result in the estimated error bars of about 20% in the specific dissolution rate.

The results of the dissolution rate of magnesia in master slag A obtained at different rotation speeds are presented in Fig. 3. This plot shows that the initial dissolution rate increased with the rotation speed, thus suggesting that the measured dissolution rates are controlled by mass transfer in the slag phase. A rotation speed of 90 rpm was chosen for all subsequent experiments, where the effects of additives to the slag at various temperatures were investigated under conditions where mass transfer in the liquid phase controls the dissolution process.

Examination of the samples from the static experiments carried out at 1450°C (in platinum capsule) showed no evidence of the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ being present near the slag–MgO interface. Formation of a halite solid solution phase containing 98% MgO, 1.5% Al_2O_3 and 0.5% CaO at the slag–MgO interface was predicted through our thermodynamic modelling. However, formation of such a solid solution phase on the surface of the MgO sample is unlikely to hinder the dissolution rate of MgO into the slag.

The influence of Fe_2O_3 on the dissolution of MgO was studied by adding 5 wt% and 10 wt% Fe_2O_3 to the calcium aluminate slag. An attempt was made to study the influence of CaF_2 on the dissolution rate of MgO in the slag, but after addition of 5 wt% CaF_2 , the slag was not fully molten at the experimental temperature of 1450°C. Therefore, 5 wt% CaF_2 was added to slag with 10 wt% Fe_2O_3 . The initial rates determined from the dissolution curves as a function of the experimental temperature are presented in Fig. 4. The data show that addition of FeO_x 10%+ CaF_2 5% mixture to the master slag increased the dissolution rate by a factor of 4–6, while addition of FeO_x 10% and FeO_x 5% increased the rate by a factor of 2–3 and 1.5–2, respectively.

Fig. 4. Variation of dissolution rate of magnesia sample in slags (different additives) with temperature.

Fig. 5. SEM analysis of the bulk slag after reaction in various times at 1400°C and in air.

The solubility of magnesium in the base slag A and slags with additives was determined by reacting the magnesia samples with static slags at various temperatures, quenching and analysing the samples by SEM. The reaction time of 3 h was assumed to be sufficient for the slag to reach saturation with an MgO-rich phase. This was confirmed by reacting a piece of dense magnesia with base slags in a platinum capsule in air at 1400°C for reaction times of 0.5, 1, 2, 4, 8 hours and air quenching. The concentrations of MgO and other components in the liquid slag analysed with SEM are presented in Fig. 5. These results show that, after 30 min, the slag approached equilibrium, which agreed well with the phase diagram.²⁾ It was shown in Fig. 2 that during the rotating disc/cylinder experiments; the oxide melt is not equilibrated with MgO within 60 min of reaction at 1450°C, while during the static experiments equilibrium was achieved after 30 min. Apart from having a thinner slag layer in the static experiments, the calculated contact area between the magnesia sample and the molten slag is expected to be considerably higher in the static experiments. These differences must have resulted in faster approach to equilibrium between the slag and MgO.

The measured solubility of magnesia at 1450°C was found to be near 9 wt% and increased to about 12 wt% by increasing the temperature to 1600°C (Table 2). The solubility of magnesia in the slag did not show a dependence on the additives used. Thus, the effect of additives on the dissolution rate is unlikely to be related to the driving force for

Table 2. The solubility of magnesia in the slags with additives.

Slags	Magnesia Concentration (wt%)			
	1450 °C	1500 °C	1550 °C	1600 °C
A	8.3	8.6	10.2	11.2
B = A + 5% FeO _x	9.1	9.7	10.3	11.4
C = A + 10% FeO _x	9.1	9.6	10.9	11.8
D = A + 10% FeO _x + 5% CaF ₂	9.1	9.8	11.2	12.2

Fig. 6. Dependence of dissolution rate of magnesia in master slag A on $A\omega^{1/2} + B\omega^{3/4}$.

the transport of magnesia across the liquid boundary layer adjacent to the magnesia/slag interface.

4. Discussion

It is expected that when the dissolution is controlled by mass transfer in the liquid slag, the dissolution rate of a disk would increase linearly with square root of rotation speed¹⁶⁾ and in the case of a rotating cylinder the increase in rate would be proportional to the rotation speed raised to the power of 3/4.¹⁷⁾ Accordingly, for the rotating specimen used in the present work, the dependence of dissolution rate on rotation speed should lie between the expected dependence for a disk and cylinder, with the total mass transfer being a sum of the two components, *i.e.*:

$$\text{Rate}_{\text{total}} \propto A\omega^{1/2} + B\omega^{3/4} \quad \text{.....(1)}$$

Where; ω is the rotating speed in rad/s, and the coefficients A and B are dependent on the physical properties of the slag and contact area between the disc and cylinder with the slag.*1

Figure 6 shows the apparent linear dependence of the initial rate on the $(A\omega^{1/2} + B\omega^{3/4})$ which provides evidence that liquid phase mass transfer played a major role in controlling the dissolution of these samples over the rotation speed of 30 to 120 rpm.

It was shown in Fig. 4 that addition of Fe₂O₃ and Fe₂O₃+CaF₂ increased the dissolution rate of magnesia in slag. The experimental results on solubility of magnesia in these slags have shown the MgO solubility does not depend significantly on the presence of additives, the observed effect of Fe₂O₃ and Fe₂O₃+CaF₂ additives on the rate of MgO

dissolution is most likely through modifying the transport properties of the slag. This would be in accord with the findings of Hamano *et al.*¹⁸⁾ and Lee *et al.*,¹⁹⁾ where the addition of CaF₂ and transition metal oxides to the slag, enhanced the transport properties of slag and subsequently increased the rate of dissolution of lime and alumina in their slags.

A number of researchers^{15,19,20)} have deduced the diffusivity data in slags from dissolution rate data under forced-convection utilizing a rotating disk/cylinder technique. A well-known equation obtained by Levich¹⁶⁾ is commonly used, in which the dependence of mass transfer coefficient (k_{disk} , cm/s) on the angular velocity of the disk (ω , rad/s) and physical properties of the liquid phase (kinematic viscosity, ν and diffusivity, D) is expressed as:

$$k_{\text{disk}} = 0.621D^{2/3}\omega^{1/2}\nu^{-1/6} \quad \text{.....(2)}$$

For the cylinder side of the rotating sample, Eisenberg *et al.*¹⁷⁾ investigated the mass transfer from rotating cylinders of benzoic acid into water-glycerol solvents in which, the mass transfer coefficient (k), peripheral velocity (V , cm/s) and Schmidt number (Sc) were expressed as a function of Reynolds number (Re). The modified correlation by Kosaka *et al.*,²¹⁾ which was obtained from analysis of dissolution of rotating metal cylinders in various molten metallic systems at elevated temperatures, was selected by the present authors for the analysis of high temperature data. This correlation is shown below:

$$k_{\text{cylinder}} = 0.065Re^{-1/4}Sc^{-2/3}V \quad \text{.....(3)}$$

It is reasonable to assume that the total mass flux from the rotating magnesia sample (j_{total}) to the liquid slag could be expressed as the sum of the mass fluxes from the disk (j_{disc}) and cylinder (j_{cylinder}), *i.e.*:

$$j_{\text{total}} = j_{\text{disc}} + j_{\text{cylinder}} \quad \text{.....(4)}$$

Equation (4) can be written as:

$$k_{\text{total}} \cdot A_{\text{total}} \cdot \Delta C = k_{\text{disk}} \cdot A_{\text{disk}} \cdot \Delta C + k_{\text{cylinder}} \cdot A_{\text{cylinder}} \cdot \Delta C \quad \text{.....(5)}$$

Where k , A and ΔC represent mass transfer coefficient (cm/s), surface area in contact with the melt (cm²) and the concentration gradient for dissolution mol/cm³.

By substituting Eqs. (2) and (3) into Eq. (5) and rearranging the terms, it can be shown that:

$$k_{\text{total}} = \frac{r}{r+2h} \cdot 0.621D^{2/3}\omega^{1/2} \left(\frac{\rho}{\mu} \right)^{1/6} + \frac{2h}{r+2h} \cdot 0.055D^{2/3}r^{1/2}\omega^{3/4} \left(\frac{\rho}{\mu} \right)^{5/12} \quad \text{.....(6)}$$

$$k_{\text{total}} = D^{2/3}(A\omega^{1/2} + B\omega^{3/4}) \quad \text{.....(7)}$$

Where; D , r and h are chemical diffusivity, radius of rotating sample and the depth of immersion of the sample in the melt, respectively.

It should be noted, that by considering the relationship between the mass transfer coefficient and viscosity, the dependence of the mass transfer on the slag viscosity is rela-

*1 A and B are calculated from the kinematic viscosity of slag and the geometry of wetted area of the rotating sample in the melt using Eqs. (6)–(8).

tively small, thus change in viscosity is unlikely to be the predominate factor in the increase in the magnesia dissolution. The dependence of the mass transfer on diffusivity is stronger, thus the marked increase in dissolution rate and mass transfer are likely to be predominantly caused by the increase in the diffusivity of magnesia in the slag.

For the calculation of the total mass transfer coefficient (k_{total}) from the experimental data, the ratio of the dissolution rate over the concentration gradient of magnesia between the magnesia–slag interface (C_s) and the bulk slag (C_b) and density of slag was equated to the total mass transfer coefficient as:

$$k_{\text{total}} = \frac{\text{Rate}_{\text{total}}}{(C_s - C_b) \cdot \rho_{\text{slag}}} \dots\dots\dots (8)$$

The physical properties of the slag were estimated using the Urbain's viscosity model²²⁾ where according to the Slag Atlas,²⁾ the discrepancies between the experimental values and the predicted data by this model are about ± 25 –30%, which are similar to the uncertainties in the experimental data on slag viscosity. The slag density was estimated from the method proposed by Mills *et al.*,²³⁾ where the standard deviation of data predicted by the model compared to the experimental values was reported to be about ± 2 –3%. According to the Urbain's viscosity model,²²⁾ the viscosity of the slag A decreases from about 12.8 to 5.2 poise as the temperature is increased from 1450 to 1600°C. Additions of FeO_x and CaF_2 also tend to reduce the slag viscosity and when 10% FeO_x and 5% CaF_2 were added to slag A to form slag D, a 40% decrease in the viscosity could be expected at 1450°C. On applying the Eq. (6), it can be shown that the measured changes in the dissolution rate and hence the changes in the mass transfer coefficient can not be explained by the estimated changes in slag viscosity alone.

By equating Eqs. (6) and (8), and rearranging the terms, the diffusivity of magnesia in the slag was deduced from the rate data. **Figure 7** shows the values of diffusivity for the slag containing various additives. The uncertainty in calculation of the slope of initial dissolution rate, weight of molten slag bath, immersed area of lime sample in the slag and dissolution rate data would result in about $\pm 33\%$ uncertainty in the estimation of diffusivity data.

The diffusivity of magnesia in the base slag was found to be about $3.7 \times 10^{-6} \text{ cm}^2/\text{s}$ at 1450°C and increased to $1.4 \times 10^{-5} \text{ cm}^2/\text{s}$ as the temperature increased to 1600°C (Fig. 7). Addition of 5 wt% FeO_x to the master slag A increased the diffusivity by a factor of 5 at 1450°C while at 1600°C the diffusivity increased by a factor of 2. Additions of FeO_x 10% increased the diffusivity by a factor of 6 to 3 depending on the temperature. The diffusivity of magnesia in the slag with addition of (FeO_x 10% + CaF_2 5%) increased by 27 to 7 times in the temperature range of 1450 to 1600°C.

The magnesia diffusivity in the present work is compared with the available data in the literature (**Table 3**). The magnesia diffusivity in the slag without additives was an order of magnitude higher than the data obtained by Zhang *et al.*¹³⁾ on diffusivity of magnesia in the $\text{CaO-FeO-CaF}_2\text{-SiO}_2$ slag at 1300–1400°C. Apart from the difference in experimental techniques in both works, this could be ex-

Fig. 7. The diffusivity of magnesia in the slag with respect to temperature and additives.

Table 3. Magnesia diffusivity data from the literature review and the present work.

Researcher	Method	Slag chemistry	Temperature (°C)	Diffusivity (cm ² /s)
Zhang <i>et al.</i> (1994)	Static dissolution	CaO-FeO-CaF ₂ -SiO ₂ CaO/SiO ₂ = 1, FeO _x = 45 wt% CaF ₂ = 2-20 wt%	1300 – 1400	4.49 × 10 ⁻⁶
Ukyo <i>et al.</i> (1982)	Diffusion couple	FeO – 30 wt% CaO – 45 % SiO ₂ CaO- 40 wt% SiO ₂ – 20 % Al ₂ O ₃	1350 – 1450	2 × 10 ⁻⁵ - 3 × 10 ⁻⁵
Umakoshi <i>et al.</i> (1981)	Rotating cylinder	CaO – FeO _x – SiO ₂ CaO/SiO ₂ = 1 FeO _x = 20 to 65 wt%	1350 – 1425	1 × 10 ⁻⁵ - 3 × 10 ⁻⁵
Present work	Rotating cylinder/disk	CaO – Al ₂ O ₃ CaO/Al ₂ O ₃ = 0.81 Additives: FeO _x and FeO _x +CaF ₂	1450 – 1600	1 × 10 ⁻⁵ - 1.2 × 10 ⁻⁴

plained by formation of a protective layer of magnesio-wustite in their experiments, which slowed down the diffusion of MgO in liquid phase. The result of the present work is in a good accord with the data by Ukyo *et al.*¹⁴⁾ who found the MgO diffusivity in the FeO-CaO-SiO_2 slag to be about $10^{-5} \text{ cm}^2/\text{s}$. There is an excellent agreement between the results from this work and the results obtained by Umakoshi *et al.*¹⁵⁾, who deduced the MgO diffusivity in the $\text{CaO-FeO}_x\text{-SiO}_2$ slags of $\text{CaO/SiO}_2=1$ ($\text{FeO}_x=20$ to 65 wt%) at 1400°C with the same experimental technique. Although the FeO_x content of considered slags in both works was different, the diffusivity data have the same order of magnitude and addition of FeO_x increases the diffusivity of MgO in the slag.

The measured diffusivity of MgO in the present work is comparable with those measured by the present authors for diffusivity of CaO which varied between 1.32×10^{-5} and $1.03 \times 10^{-4} \text{ cm}^2/\text{s}$ depending on temperature and additives used.²⁴⁾

The relationship between the structure of melts and their transport properties is believed to be a key to fundamental understanding of the mechanism of diffusion in melts and effect of additives on the diffusivities. Saito *et al.*²⁵⁾ measured diffusivity of calcium in CaO-SiO_2 and $\text{CaO-Al}_2\text{O}_3$ slags and also compared their viscosity and specific electric conductivity based on the published data. They found no large differences in the mentioned quantities, however the

diffusivity and specific conductivity in aluminate melts were shown to have higher values than their respective values for silicate melts and the viscosity of aluminate melts were about the same as or slightly lower than those of silicate melts. They postulated that in the neighbourhood of the composition $\text{CaO}:\text{Al}_2\text{O}_3=1:1$, the greater part of Al_2O_3 exists as the tetrahedra structure of aluminate ion AlO_4^{5-} similar to that of SiO_4^{4-} in basic CaO-SiO_2 slags. However, the trend and degree of formation of network structure of aluminate ions were not as strong as those of silicate ions. Zhang *et al.*²⁶⁾ has arrived at similar conclusions from Molecular Dynamic Simulation studies. Thus it may be deduced that in calcium aluminate slags, the structure and physical properties of melts would be dependent on composition and hence additives such as FeO_x and CaF_2 could have marked effects.

The findings of the present work show that FeO_x and the mixture of FeO_x and CaF_2 had strong effects on the dissolution rate of magnesia in the slag. As these additives lower the viscosity of the slag and increase the diffusivity considerably, they will result in considerably higher dissolution rates of magnesia refractories. Therefore, a balance should be sought to adjust the level of FeO_x in a way to satisfy the refining characteristics of the melt and at the same time, taking into account the life of refractory linings.

5. Conclusion

The dissolution rate of MgO was measured in $\text{CaO-45wt\%Al}_2\text{O}_3$ based slag in the temperature range 1 450 to 1 600°C under the conditions where the liquid slag mass transfer played a significant role in controlling the dissolution. The average dissolution rate of magnesia in the base slag over a temperature range of 1 450–1 600°C, was of the order of magnitude of 10^{-5} ($\text{g}/\text{cm}^2\cdot\text{s}$). Additions of 5 and 10 wt% FeO_x increased the dissolution rate by about a factor of 2 and 3, respectively. Addition of 10 wt% Fe_2O_3+5 wt% CaF_2 had even a more significant effect and increased the rate of dissolution by a factor of 4 to 6, depending on the temperature.

The solubility of MgO in the slags was measured through a series of phase equilibria experiments. The results showed the solubility to increase with temperature by about 3 wt% as the temperature was increased from 1 450 to 1 600°C. The effect of additives on the solubility of MgO in the calcium aluminate based slag was small and insignificant at various temperatures.

The diffusivity of MgO in the calcium aluminate melt was deduced by using the data on dissolution rate and solu-

bility of magnesia in the slag. At 1 450°C the diffusivity in the calcium aluminate was about $10^{-5}\text{ cm}^2/\text{s}$ and increased to about $10^{-4}\text{ cm}^2/\text{s}$ with addition of Fe_2O_3 and CaF_2 at 1 600°C. The additives had considerable effects on enhancing the diffusivity of MgO in the slag.

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REFERENCES

- 1) J. Bygden, T. DebRoy and S. Seetharaman: *Ironmaking Steelmaking*, **21** (1994), 318.
- 2) V. D. Eisenhuttenleute: *Slag Atlas*, 2nd ed, Verlag Stahleisen GmbH, Dusseldorf, (1995), 616.
- 3) P. V. Riboud, Y. Roux, D. Lucas and H. Gaye: *Fachber. Huttenprax. Metallweiterverarb.*, **19** (1981), 859.
- 4) G. Urbain: *Steel Res.*, **58** (1987), 111.
- 5) H. Hu and R. G. Reddy: *High Temp. Sci.*, **28** (1988), 195.
- 6) S. Seetharaman and D. Sichen: *Metall. Mater. Trans. B*, **25B** (1994), 589.
- 7) L. Zhang and S. Jahanshahi: *Metall. Mater. Trans. B*, **29B** (1998), 187.
- 8) L. Zhang and S. Jahanshahi: *Metall. Mater. Trans. B*, **29B** (1998), 177.
- 9) K. C. Mills and S. Sridhar: *Ironmaking Steelmaking*, **26** (1999), 262.
- 10) T. Iida, H. Sakai, Y. Kita and K. Shigeno: *Trans. Iron Steel Inst. Jpn.*, **40** (2000), 110.
- 11) A. Kondratiev and E. Jak: *Metall. Mater. Trans. B*, **32B** (2001), 1015.
- 12) A. Kondratiev and E. Jak: *Metall. Mater. Trans. B*, **32B** (2001), 1027.
- 13) P. Zhang and S. Seetharaman: *J. Am. Ceram. Soc.*, **77** (1994), 970.
- 14) Y. Ukyo and S. Goto: *Tetsu-to-Hagané*, **68** (1982), 117.
- 15) M. Umakoshi, K. Mori and Y. Kawai: *Tetsu-to-Hagané*, **67** (1981), 1726.
- 16) V. G. Levich: *Physicochemical Hydrodynamics*, Prentice-Hall, (1962), 69.
- 17) C. W. Eisenberg and W. Tobias: *Chem. Eng. Prog. Sym. Ser.*, **51** (1955), 1.
- 18) T. Hamano, M. Horibe and K. Ito: *ISIJ Int.*, **44** (2004), 263.
- 19) M. Lee, S. Sun, S. Wright and S. Jahanshahi: *Metall. Mater. Trans. B*, **32B** (2001), 25.
- 20) X. Yu, R. J. Pomfret and K. S. Coley: *Metall. Mater. Trans. B*, **28B** (1997), 275.
- 21) M. Kosaka and S. Minowa: *Tetsu-to-Hagané*, **52** (1966), 22.
- 22) G. Urbain, F. Cambier, M. Deletter and M. R. Anseau: *Trans. Br. Ceram. Soc.*, **80** (1981), 139.
- 23) K. C. Mills and B. J. Keene: *Int. Mater. Rev.*, **32** (1987), 1.
- 24) S. H. Amini, M. P. Brungs, S. Jahanshahi and O. Ostrovski: *Metall. Mater. Trans. B*, **37B** (2006), 773.
- 25) T. Saito and K. Maruya: *Sci. Rep. Res. Inst.*, **A-10** (1958), 306.
- 26) L. Zhang, S. Sun and S. Jahanshahi: *J. Non-Cryst. Solids*, **282** (2001), 24.