

Effect of Solid-solved FeO and MnO on Hydration of Free MgO in Steelmaking Slag

R Inoue¹, N Kado², T Iwama³ and S Ueda⁴

1.Researcher, Tohoku University, Sendai Miyagi 980-8577. ryo.inoue.e2@tohoku.ac.jp:

2.Researcher, JFE Mineral Company, Chiba Chiba 260-0835. n-kado@jfe-mineral.co.jp:

3.Asistant Professor, Tohoku University, Sendai Miyagi 980-8577.

takayuki.iwama.a6@tohoku.ac.jp:

4.Professor, Tohoku University, Sendai Miyagi 980-8577. tie@tohoku.ac.jp:

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ABSTRACT

Steelmaking slags are usually used as roadbed and civil engineering materials. However, the expansion phenomenon, which is caused by the volume expansion during hydration of free CaO and free MgO contained in steelmaking slag, is indispensable. Since the hydration of free MgO in steelmaking slag is much slower than that of free CaO, it is qualitatively considered that free MgO contributes to the hydration expansion of steelmaking slag over a long period of time. Similar to free CaO, free MgO consists of undissolved MgO and crystallized MgO in steelmaking slag. The latter precipitates during slag cooling. When divalent metal oxides (FeO, MnO, CaO) are dissolved in the crystallized MgO to form a MgO-based solid solution, it is expected to inhibit the hydration reaction similar to precipitated CaO. From the previous hydration test of Magnesioferrite, which was calcined after mixing MgO and Fe₂O₃ reagents, it was found that the higher the Fe₂O₃ concentration, the slower the hydration reaction progressed. In this study, by clarifying the influence of calcination conditions of MgO-FeO and MgO-FeO-MnO solid solutions, which were prepared by the calcination of mixture of MgO, FeO and MnO reagents, on their hydration reactivity, the effect of composition and thermal treatment on the formation of free MgO that is not hydrated (or easily hydrated) were discussed. To investigate the influence of MgO grain size, coarse MgO particles, which were obtained by crushing MgO crucible, were also used for heat treatment. With increasing the amount of FeO and MnO in the MgO-FeO-MnO solid solution, the hydration reaction became more suppressed. The expansion suppression effect was higher with solid-solved FeO than with solid-solved MnO. When the calcination temperature of the MgO-FeO solid solution was increased, the Fe³⁺/Fe²⁺ concentration ratio increased, resulting in a higher hydration rate.

INTRODUCTION

To achieve a better global environment, a recycling-oriented society has to be built. From the perspective of effective resource utilization, it is necessary to establish actively a reuse system for byproducts and waste from industries.

With regard to the reuse of iron and steel slags, various technologies have been conducted. Slow-cooled blast furnace slag is mainly used as road construction material, and granulated blast furnace slag is used as a cement admixture by taking advantage of its latent hydraulic property. Therefore, the utilization rate of blast furnace slag has reached almost 100% in a report of Nippon Slag Association (2023). On the other hand, steelmaking slag, whose annual amount is approximately 14 million tons in Japan in another report of Nippon Slag Association (2023), can be re-used as road construction materials, civil engineering materials, cement, concrete aggregate, etc. due to its hard and dense properties, as described in the reports of Ichihara (2010) and Nippon Slag Association (2023). When steelmaking slag is used as roadbed and landfill materials, lime phase (free CaO) and magnesia phase (free MgO) isolated in the slag react with water to form calcium hydroxide and magnesium hydroxide. From a report of Hori et al. (2012), because the volume after the hydration expands to approximately double, it causes road upheavals and ground cracks. Michikawa et al. (2016) investigated the hydration reactivity of steelmaking slag by estimating the expansion ratio of slag after hydration from the free CaO content in the slag.

Hori et al.(2012) said that aging treatments, which are performed to advance the slag expansion caused by free CaO before burial, include atmospheric aging and accelerated aging. In the former the slag is left in a slag yard for more than six months to promote hydration through rainfall, and in the latter the hydration reaction progresses by using steam or hot water. Sasaki and Hamasaki (2014) found that the higher the ambient temperature, the faster the slag expansion becomes stable, and in the case of steam aging, expansion stability is achieved in 48 hours. Namely, accelerated aging can be expected to provide stable hydration treatment in a short time. Inoue and Suito (1995) found that free CaO in steelmaking slag includes undissolved CaO and crystallized (precipitated during cooling) CaO, and in the latter divalent metal oxides (FeO, MnO, MgO) are solid-solved. The larger the amount of the solid-solved components, the more the hydration reaction of CaO was suppressed, and when the slag was slowly cooled below 1200°C, calcium ferrite precipitates in spots in the crystallized CaO, which significantly reduces the FeO concentration in the CaO matrix phase, showed that crystallised CaO becomes more easily hydrated.

On the other hand, regarding the hydration reaction of MgO, Ohira and Obata (2009) clarified the effect of particle size on the hydration of lightly calcined magnesia. Inoue et al. (2021) noted that

since the hydration reaction of pure MgO reagents proceeds slowly at room temperature and pressure, it is desirable to accelerate the hydration by thermal treatment under high temperature and pressure using an autoclave. Because of slow hydration rate of free MgO in steelmaking slag compared with that of free CaO, it has been qualitatively thought that MgO hydration contributes to the volume expansion of steelmaking slag over a long period of time.³⁾ Similar to free CaO in steelmaking slag, free MgO includes undissolved MgO and crystallized (precipitated during cooling) MgO, and divalent metal oxides (FeO, MnO, CaO) are solid-solved in the crystallized MgO and affect the hydration reaction, as reported by Inoue et al. (2021). They found that the higher the iron concentration, the slower the hydration reaction progressed, when Magnesio-wüstite synthesized by the calcination of the mixture of MgO and Fe₂O₃ reagents was hydrated. On the other hand, Amita et al. (1989) said that the size and morphology of crystals in MgO particle are influenced by heating.

In this study, the effect of calcination conditions on the hydration reactivity of MgO-FeO solid solution, which was prepared by calcination the mixture of MgO and FeO reagents, was clarified. Furthermore, by hydrating the MgO-FeO-MnO solid solution, the difference in hydration reactivity between MnO and FeO in solid solution was investigated. In addition, by comparing those results with the hydration properties of MgO reagent and heat-treated product of a commercially available dense MgO crucibles, the condition for producing free MgO that is not hydrated (or easily hydrated) was discussed.

EXPERIMENTAL

Sample preparation

Three types of MgO-FeO solid solutions with MgO/FeO mass ratio = 9/1, 8/2, and 7/3 were prepared. Their compositions are plotted with solid circle marks in the MgO-FeO phase diagram, which was presented by Wu et al. (1993), in Figure 1. It can be seen that all of them are solid solutions at 1400 to 1600°C.

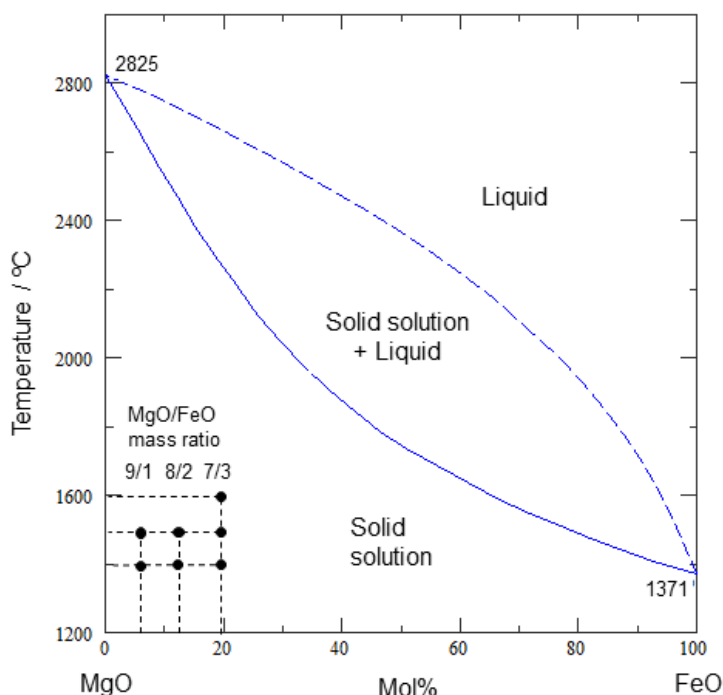


FIGURE 1 – Synthesized MgO-FeO solid solutions plotted in MgO-FeO phase diagram drawn by Wu et al. (1989).

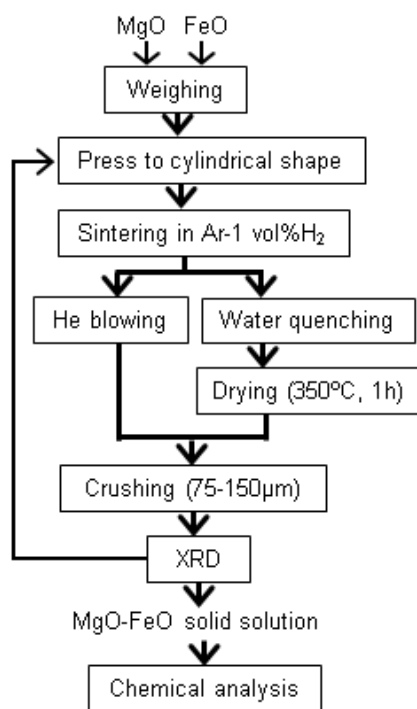


FIGURE 2 – Flow chart of preparation of MgO-FeO solid solution.

Figure 2 shows the synthesis of MgO-FeO solid solution. Appropriate amounts of special grade MgO reagent (manufactured by Wako Pure Chemical Industries, Ltd.) and FeO reagent (manufactured by Japan Pure Chemical Co., Ltd.) were weighed, mixed, and pressed to a cylindrical shape at 8 ton/cm². To prevent direct reaction between the MgO calcination crucible and the solid solutions,

pre-sintered MgO-FeO powder was placed on the inner bottom of the MgO crucible. The cylindrical sample was placed on the powder layer and slowly lowered to the soaking zone inside the vertical resistance furnace for calcination in an Ar flow (200 cm³/min), which was deoxidized by Ti sponge at 1073 K. Heating temperature and holding time are summarized in Table 1. In this table, a pure Al₂O₃ crucible with thin wall (SSA-S, type-T3, manufactured by Nikkato) was used instead of pure MgO crucible with thick wall to promote temperature drop by reducing the heat accumulation on the crucible wall during rapid cooling. After a given time, the crucible was taken out of the furnace and quenched by He gas blowing (hereinafter abbreviated as 'He quenching') or dipping into water (hereinafter abbreviated as 'water-quenching'). In addition, a MgO-FeO-MnO solid solution in which a part of FeO was replaced with MnO was also prepared using the same method. The obtained solid solution sample was ground to 75-150 μm for hydration treatment.

TABLE 1 – Calcination conditions for preparation of solid solution samples.

MgO/FeO/MnO mass ratio	Temp. (°C)	Time (h)	Crucible
7 / 3 / 0	1400	12	Dense MgO with thick wall
		24	
	1500	12	Dense MgO with thick wall Dense Al ₂ O ₃ with thin wall
	1600	12	
7 / 2 / 1	1400	12	Dense MgO with thick wall
8 / 2 / 0	1400		
	1500		
9 / 1 / 0	1400		
	1500		

Two types of pure MgO were employed for hydration treatment: special grade MgO reagent (manufactured by Wako Pure Chemical Industries, Ltd.) and a dense MgO crucible (MG-12, manufactured by Nikkato) pulverized to 75 to 150 μm.

Hydration treatment

An autoclave was used as the hydration reactor because hydration process is accelerated at high temperature and high pressure, as written in Dictionary of research (2023).

At first, a Teflon test tube was weighed (w_1). After an appropriate amount of the solid solution powder was charged into the test tube, its weight was measured (w_2). The difference between w_1 and w_2 corresponds to the initial sample weight before the hydration reaction. Several drops of distilled water were added into the test tube to moisten the solid solution powder. The test tube was then placed in a pressure vessel of an autoclave and subjected to hydration treatment at 120°C for 12 hours. After the test tube removed from autoclave was heated at approximately 110°C for 2 hours in a drying oven to remove excess moisture, the weight of the test tube was measured to determine the sample weight after hydration. This autoclave treatment was repeated two more times in the same manner. For comparison, similar experiments were also conducted using a MgO reagent and a powder obtained by pulverizing a dense MgO crucible.

Analysis

The mineral phases in solid solution samples were identified by powder X-ray diffraction (XRD).

Since it was found in preliminary experiments that the FeO amount in MgO-FeO solid solution cannot be evaluated from the relationship between MgO-FeO peak angle in XRD pattern and FeO concentration of MgO-FeO solid solution published by JCPDS-International Centre (2000), it was determined by chemical analysis. The total iron and Fe²⁺ concentrations in the MgO-FeO and MgO-FeO-MnO solid solution powders were determined according to the potassium dichromate titration method of Japanese Industrial Standards JIS-M-8202 and JIS-M-8213, respectively. The MgO and

MnO concentrations in the powder were determined by ICP emission spectrophotometry after dissolving 0.1 g of each powder with 10 mL of (1+1)HCl solution.

RESULTS AND DISCUSSION

Synthesis conditions of MgO–FeO solid solution

Number of calcinations

To investigate the change in the amount of solid-solved FeO with the number of calcination times of MgO–FeO solid solution, the following experiment was conducted. A mixture with MgO/FeO mass ratio = 7/3 was pressed to cylindrical shape and calcined in deoxidized Ar flow at 1400°C for 12 hours, then immediately quenched by He quenching. After pulverizing this to less than 150 μm, it was pressed again and sintered using the same procedure as the first heating. Figure 3 shows the XRD results for those two samples. In this figure, only the (Mg, Fe)O peaks are observed in both samples despite the different number of calcination, indicating that one calcination is sufficient for the synthesis of MgO–FeO solid solution.

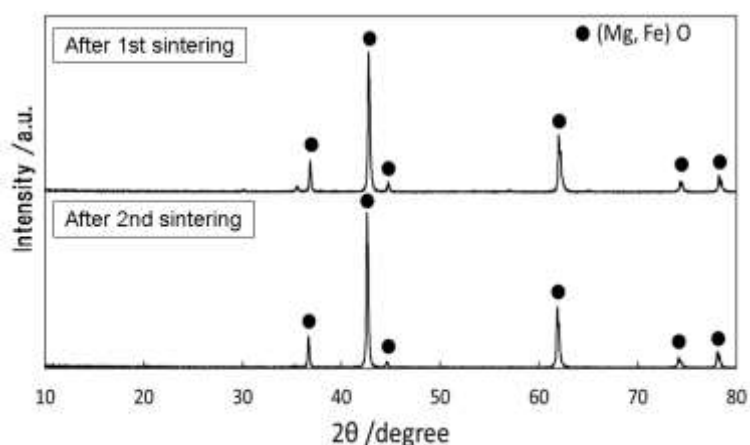


FIGURE 3 – Results of XRD analysis of MgO–FeO solid solution (MgO/FeO mass ratio = 7/3) calcined once and twice.

Table 2 shows the total iron and FeO concentrations determined by chemical analysis. In this table, the Fe³⁺ concentration is the difference between the total iron concentration and the Fe²⁺ concentration, and Fe₂O is the FeO concentration calculated assuming that all iron is present as FeO. It can be seen from the values listed in this table that the Fe³⁺ concentration is almost zero after second calcination, and that each solid solution contains approximately 30 mass% FeO. Therefore, one calcination is considered sufficient to synthesize MgO–FeO solid solution. In the subsequent solid solution synthesis, the calcination operation was performed only once. It should be noted that Fe³⁺ (Fe₂O₃) can dissolve in MgO according to MgO–Fe₂O₃ phase diagram¹⁵. The amount of solid-solved FeO and Fe₂O₃ will be explained later.

TABLE 2 – Variations of chemical composition of MgO–FeO solid solutions (MgO/FeO mass ratio = 7/3) depending on calcination number and quenching method.

Quenching	Calcination number	T.Fe	Fe ²⁺	Fe ³⁺	Fe ³⁺ /Fe ²⁺	FeO	MgO	Fe ₂ O
		(mass%)			ratio	(mass%)		
He blowing	1	23.75	23.49	0.26	0.011	30.22	69.4	30.55
	2	22.64	22.63	0.01	0.0004	29.11	70.8	29.13
Water	1	24.13	21.24	2.89	0.136	27.33	68.5	31.05

Quenching method

In the previous section, the heated sample with MgO/FeO mass ratio = 7/3 was rapidly cooled by He quenching. To investigate the influence of the quenching method on the synthesis of MgO–FeO solid solution, the MgO crucible containing cylindrical sample subjected to the same calcination operation was quenched in water. The total iron and FeO concentrations in this MgO–FeO solid solution are

listed in Table 2. According to XRD analysis, the sample obtained by water-quenching was also pure (Mg, Fe)O.

To clarify the influence of the quenching method on hydration behaviour, a sample with MgO/FeO mass ratio = 7/3, which was calcined once at 1400°C, rapidly cooled by He quenching or water-quenching, and crushed to a particle size of 75 to 150µm, was subjected to the hydration treatment using an autoclave three times. Table 3 gives the sample weight changes after each hydration treatment.

TABLE 3 – Mass change after hydration of MgO-FeO solid solutions (MgO/FeO mass ratio = 7/3) prepared by different quenching methods.

Hydration treatment	He quenching (69.4 mass%MgO)			Water-quenching (68.5 mass%MgO)		
	Weight (g)		Hydration rate (%)	Weight (g)		Hydration rate (%)
	Before hydration	After hydration		Before hydration	After hydration	
1st	0.5899	0.6021	6.67	0.7644	0.7924	12.0
2nd	0.6021	0.6095	10.7	0.7929	0.8135	21.0
3rd	0.6095	0.6018	12.0	0.8136	0.8328	29.2

The hydration rate of MgO can be determined by dividing the mass change after hydration by the mass when all MgO becomes Mg(OH)₂. For example, a sample of 0.5899 g (W_i) became 0.6021 g after the first autoclave treatment, so the mass change ΔW is expressed by equation 1.

$$\Delta W = 0.6021 - 0.5899 = 0.0122 \text{ [g]} \quad (1)$$

When assuming that this ΔW is entirely due to the MgO hydration reaction, MgO+H₂O = Mg(OH)₂,

$$\begin{aligned} \text{Reacted H}_2\text{O moles} &= \Delta W / (\text{H}_2\text{O molecular weight}) \\ &= 0.0122 / 18.00 = 6.78 \times 10^{-4} \\ &= \text{Reacted MgO moles} \end{aligned}$$

$$\begin{aligned} \text{Mass of hydrated MgO} &= (\text{Reacted MgO moles}) \times (\text{MgO molecular weight}) \\ &= 6.78 \times 10^{-4} \times 40.31 = 0.0273 \text{ [g]} \end{aligned}$$

$$\begin{aligned} \text{Mass of MgO in solid solution} &= W_i \times (\text{mass\% MgO}) / 100 \\ &= 0.5899 \times 69.4 / 100 = 0.4094 \text{ [g]} \end{aligned}$$

$$\begin{aligned} \text{Hydration rate} &= (\text{Mass of hydrated MgO}) / (\text{Mass of MgO in solid solution}) \times 100 \\ &= (\Delta W / 18.00 \times 40.31) / \{W_i \times (\text{mass\% MgO}) / 100\} \times 100 \\ &= 223.9 \Delta W / \{W_i \times (\text{mass\% MgO}) / 100\} \\ &= 22390 \times 0.0122 / (0.5899 \times 69.4) = 6.67 \text{ [%]} \end{aligned} \quad (2)$$

Table 3 shows the hydration rate of two types of MgO-FeO solid solutions with MgO/FeO mass ratio = 7/3, which were obtained by He quenching and water-quenching after the calcination at 1400°C, calculated by equation 2 after each autoclave treatment. In those two MgO-FeO solid solutions, the hydration rate increases with the number of hydration treatment.

From the relationship between the hydration rate after third hydration treatment in Table 3 and the FeO concentration of solid solution (Table 2), the hydration rate is high in the water-quenched sample with low FeO concentration and high Fe³⁺/Fe²⁺ concentration ratio. This is the same trend as the previous reports that the hydration of CaO (by Inou and Suito (1995)) and MgO (by Inoue et al.(2021)) was suppressed by the solid solution of divalent metal oxides.

To clarify the reason for the difference in hydration rate depending on the quenching method, the presence of microcracks in the samples after hydration was examined by SEM observation. However, no microcracks were observed on the surface of any sample. Furthermore, when the specific surface area of the sample after third hydration was determined by the gas adsorption method (BET method), it was 0.7282 and 0.7352 [m²/g] for the sample obtained by He quenching and water-quenching, respectively. Although the latter is slightly larger, it is difficult to conclude that the difference in specific surface area due to the quenching method would affect the hydration

reactivity. Table 2 shows that the sample after He quenching is not oxidized and contains a higher amount of FeO compared with that after water-quenching. Therefore, He quenching is used as the cooling method in the following experiments.

Effect of calcination conditions on hydration reactivity of MgO-FeO solid solution

MgO-FeO solid solutions were calcined by varying the mixing ratio of MgO and FeO reagents, heating temperature and duration, and the thickness of the crucible for calcination. The effects of those factors on the hydration reactivity of the solid solution were studied.

When XRD analysis was performed on the MgO-FeO solid solutions obtained under each calcination condition given in Table 1, only the (Mg, Fe)O peak was identified in all samples before hydration.

The mineral phases in the solid solution after third autoclave treatment were also identified using XRD. Figure 4 shows the results for the sample with MgO/FeO mass ratio = 7/3, which was calcined at 1400, 1500 or 1600°C for 12 hours and hydrated. Figures 5 and 6 show those with MgO/FeO mass ratio = 8/2 and 9/1, respectively, which were calcined at 1400 or 1500°C for 12 hours and hydrated.

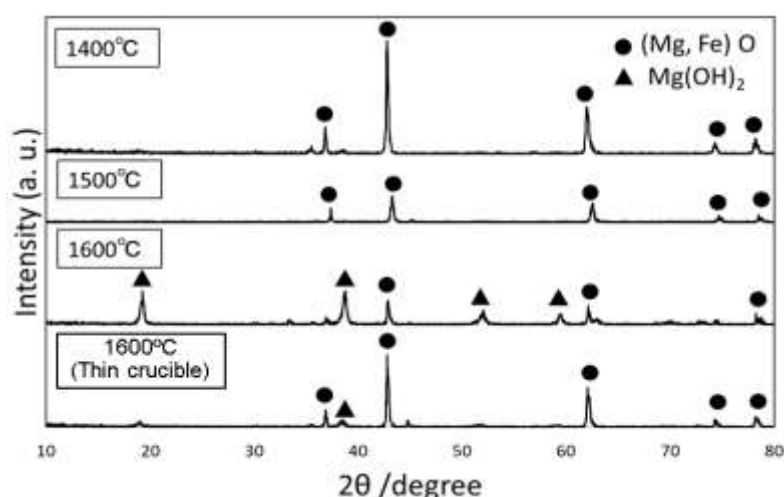


FIGURE 4 – XRD results after hydration of MgO-FeO solid solution (MgO/FeO mass ratio = 7/3) as a function of calcination temperature.

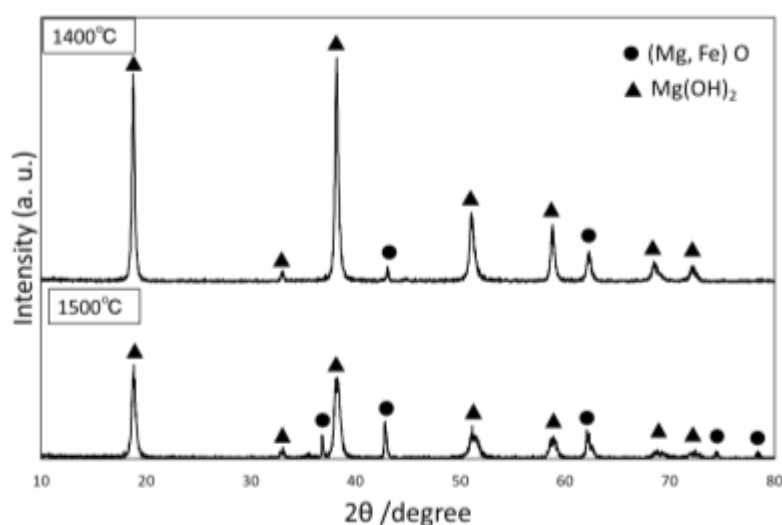


FIGURE 5 – XRD results after hydration of MgO-FeO solid solution (MgO/FeO mass ratio = 8/2) as a function of calcination temperature.

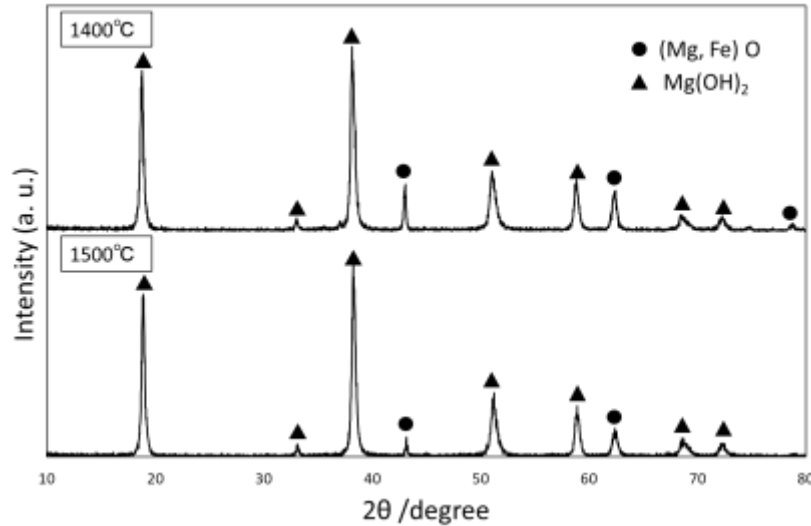


FIGURE 6 – XRD results after hydration of MgO–FeO solid solution (MgO/FeO mass ratio = 9/1) as a function of calcination temperature.

In all samples, only XRD peaks of (Mg, Fe)O and Mg(OH)₂ are observed. If only MgO in (Mg, Fe)O solid solution changes to Mg(OH)₂ during hydration, excess FeO should be generated as oxides or hydrates in terms of mass balance, but the XRD peaks of FeO, Fe₂O₃, Fe(OH)₂, FeO(OH), Fe(OH)₃, etc. were not observed in Figures 4 to 6. Therefore, it is considered that amorphous Fe-based hydrates were generated. From the comparison of these figures, the Mg(OH)₂ peak becomes higher with increasing the MgO/FeO mass ratio, but clear correlation between the calcination temperature and the XRD peak height of Mg(OH)₂ was not found.

Table 4 shows the chemical compositions of solid solutions determined by chemical analysis. Figure 7 shows the relationship between the FeO concentration and calcination temperature, and Figure 8 shows that between the Fe³⁺/Fe²⁺ concentration ratio and calcination temperature. In Figure 7, the effect of calcination temperature on the solid-solved FeO amount is small, while it can be seen from Figure 8 that the higher the calcination temperature and the lower the FeO concentration, the larger the Fe³⁺/Fe²⁺ concentration ratio becomes. This might be thought to be because only a small portion of the sample surface is oxidized by the atmospheric oxygen caught in the He gas blow during He quenching.

TABLE 4 – Chemical compositions of solid solutions prepared under various conditions.

MgO/FeO/MnO mass ratio	Temp. (°C)	Time (h)	T.Fe	Fe ²⁺	Fe ³⁺	Fe ³⁺ /Fe ²⁺	FeO	MgO	MnO	Fe ₂ O ₃
			(mass%)			ratio	(mass%)			
7 / 3 / 0	1400	12	23.75	23.49	0.26	0.011	30.22	69.4	—	30.55
	1500		23.29	22.64	0.65	0.029	29.12	69.9	—	29.96
	1600		23.44	22.43	1.01	0.045	28.86	69.7	—	30.16
	1600*		23.62	22.14	1.48	0.067	28.48	69.4	—	30.39
	1400	24	23.97	23.26	0.71	0.031	29.92	69.0	—	30.84
7 / 2 / 1	1400	12	15.22	14.74	0.48	0.033	18.97	69.8	9.94	20.10
8 / 2 / 0	1400	12	15.55	14.50	1.05	0.072	18.65	79.8	—	20.00
	1500		15.80	13.89	1.91	0.14	17.86	79.3	—	20.33
9 / 1 / 0	1400	12	8.00	7.09	0.91	0.13	9.12	89.5	—	10.29
	1500		7.89	6.72	1.17	0.17	8.64	89.7	—	10.15

* Dense Al₂O₃ crucible with thin wall.

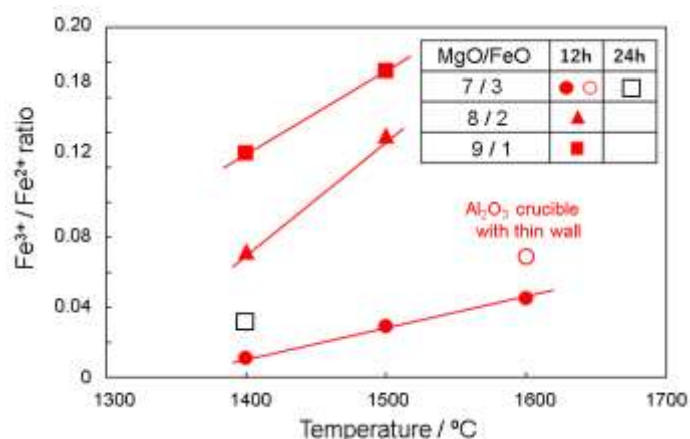
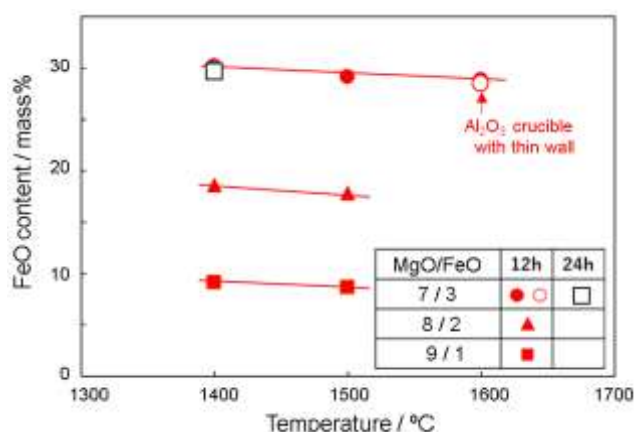


FIGURE 7 – Relationship between FeO content in MgO-FeO solid solution and calcination temperature.

FIGURE 8 – Relationship between Fe³⁺/Fe²⁺ ratio in MgO-FeO solid solution and calcination temperature.

Each sample was subjected to autoclave hydration three times. The results are listed in Table 5. The specific surface areas of MgO-FeO solid solutions (MgO/FeO mass ratio = 7/3, 8/2, 9/1) heated at 1400°C for 12 hours were determined by the BET method. The measured results are also shown in the same table. It can be seen from this table that the specific surface area increases with decreasing the amount of solid-solved FeO, and the hydration rate increases accordingly.

TABLE 5 – Mass change after hydration of MgO-FeO(-MnO) solid solutions prepared under various calcination conditions.

MgO/FeO/MnO mass ratio	Temp. (°C)	Time (h)	Weight (g)		Hydration rate (%)	Specific surface area (m ² /g)
			Before hydration	After 3 rd hydration		
7 / 3	1400	12	0.5899	0.6118	12.0	0.73
	1500		0.9009	0.9369	12.8	
	1600		1.0002	1.2408	77.3	
	1600*		1.0738	1.1565	24.8	
	1400	24	1.0642	1.1149	15.5	
7 / 2 / 1	1400	12	1.0542	1.1455	27.8	
8 / 2	1400	12	1.0080	1.2505	67.5	9.17
	1500		1.0631	1.3675	86.1	
9 / 1	1400	12	1.0958	1.4730	77.0	10.01
	1500		1.0043	1.4044	99.4	

* Dense Al₂O₃ crucible with thin wall.

Based on the values given in Table 5, the hydration rates plotted against FeO concentration and Fe³⁺/Fe²⁺ ratio of sample are shown in Figures 9 and 10, respectively, where the hydration rate is the value after third autoclave treatment. From Figure 9, the hydration rate increases with decreasing FeO concentration. At almost the same FeO concentration, the hydration rate increases with the calcination temperature. In Figure 10, the larger the Fe³⁺/Fe²⁺ concentration ratio, the higher the hydration rate becomes. This is thought to be because, as mentioned above, the higher the calcination temperature, the easier the sample is oxidized during He quenching, and the Fe³⁺/Fe²⁺ ratio becomes larger, resulting in easier hydration. The effect of solid-solved MnO on hydration reactivity of MgO-FeO will be described later.

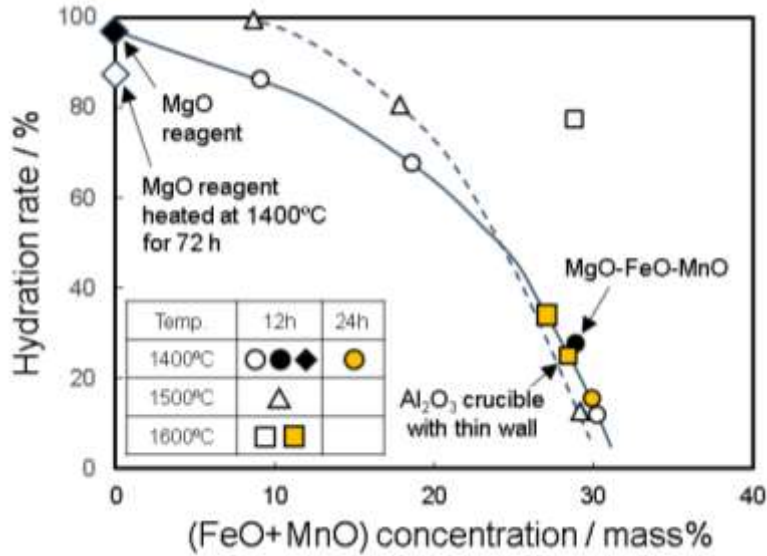


FIGURE 9 – Relationship between hydration rate and FeO (or FeO+MnO) content of MgO–FeO (MgO–FeO–MnO) solid solution as functions **calcination** temperature and time.

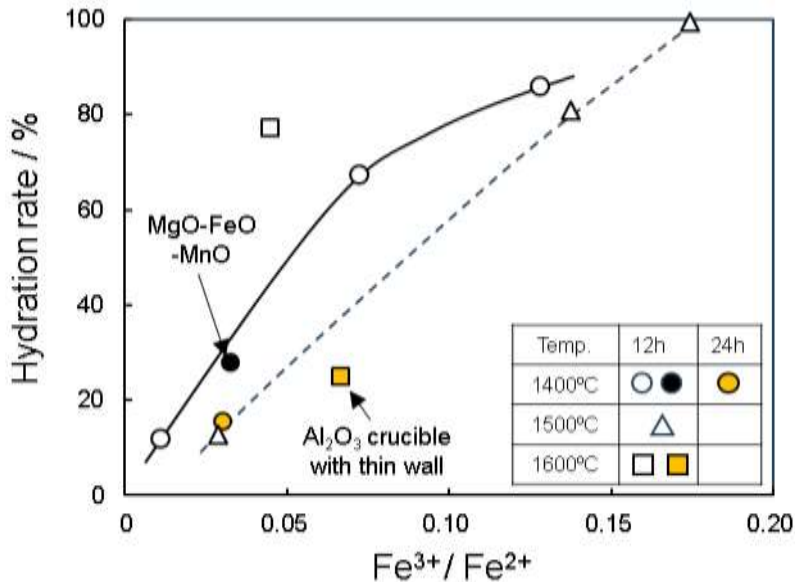


FIGURE 10 – Relationship between hydration rate and Fe^{3+}/Fe^{2+} ratio of MgO–FeO and MgO–FeO–MnO solid solutions as functions **calcination** temperature and time.

It is understood in the MgO-Fe₂O₃ system phase diagram, which was published by Phillips, Somiya and Muan (1961), shown in Figure 11 that the MgO-FeO sample with MgO/FeO = 7/3 calcined at 1400°C remains in the Magnesiowüstite region at rapid cooling, even if all FeO in this solid solution changes to Fe₂O₃ through oxidation. In contrast, at slow cooling, it will be in the coexistence region of Magnesiowüstite and Magnesioferrite at temperatures lower than point a (1374°C). In this region, when the iron concentration in Magnesiowüstite phase decreases toward point b with lowering temperature, the hydration reactivity of Magnesiowüstite increases with decreasing its iron oxide concentration, and the Magnesioferrite/Magnesiowüstite mass ratio **of** decreases. Therefore, the hydration rate increases by increasing Fe^{3+}/Fe^{2+} ratio due to the effect of hydration of the MgO-Fe₂O₃ system. It is concluded that by not only increasing the amount of solid-solved iron oxide but also rapidly cooling, the hydration of MgO–Fe oxide solid solution can be suppressed. In the samples obtained by **calcination** of MgO–FeO solid solution with MgO/FeO mass ratio = 7/3 at 1600°C for 12 hours using two types of crucibles with different wall thicknesses, it is found in Figure 9 that the hydration rate is lower when a thin-walled Al₂O₃ crucible is used, even though the Fe^{3+}/Fe^{2+} ratio is higher. The reason for this is not clear from this study, but it is presumed that the amount of heat

stored in the crucible was so small that the cooling was fast during He quenching. it is also possible that a small amount of Al_2O_3 was dissolved in the MgO-FeO solid solution and suppressed hydration.

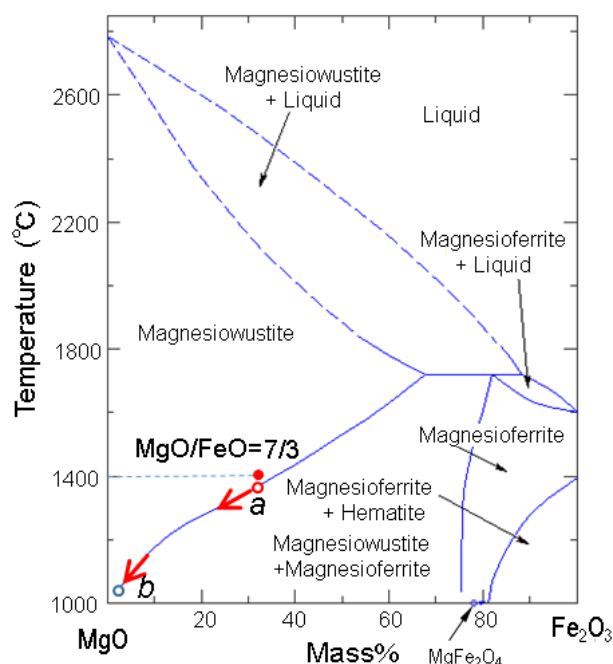


FIGURE 11 – Composition change of Magnesiowüstite during slow cooling in $\text{MgO-Fe}_2\text{O}_3$ phase diagram drawn by Phillips, Somiya and Muan (1961).

Effect of solid-solved MnO on hydration reactivity of MgO-FeO

The chemical composition and hydration rate of MgO-FeO-MnO solid solution are listed in Table 4 and 5, respectively. Relationship between hydration rate and FeO+MnO content of MgO-FeO-MnO solid solution is shown in Figure 9, in which the hydration rate is not significantly different when solid-solving MnO instead of FeO. The relationship between hydration rate and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for MgO-FeO-MnO solid solution shown in Figure 10 is near the line of that for the MgO-FeO solid solution. The relationship between $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and (FeO+MnO) content in the MgO-FeO-MnO solid solution was almost similar to that between $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and FeO content in the MgO-FeO solid solution, indicating that MnO did not affect the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. It is said from Figures 9 and 10 that the ability of solid-solved MnO to the hydration of MgO-FeO solid solution is slightly inferior to that of FeO.

Effect of thermal history on hydration reactivity of MgO

Since Amida et al. (1989) reported that the crystal size and morphology of MgO particles change with heating, it is expected that the hydration reactivity of pure MgO changes depending on the thermal history. In this study, two types of MgO powder, special grade MgO reagent powder and MgO crucible (MG-12 manufactured by Nikkato) pulverized to 75 to 150 μm , were heated at 1400°C for 12 or 72 hours in an Ar-1vol\%H_2 flow, and then rapidly quenched with He blowing. The effect of thermal history on MgO hydration rate was investigated by performing hydration treatment three times in an autoclave. The obtained results are listed in Table 6.

TABLE 6 – Changes in weight and hydration rate after hydration of MgO heated for various times.

Sample	Heating duration (h)	Before hydration		After 3rd hydration	
		Weight (g)	Specific surface area (m^2/g)	Weight (g)	Hydration rate (%)
MgO reagent	0	1.0881		1.5631	97.8
	12	1.0374		1.4842	96.5
	72	1.0589		1.4758	88.2
	0	1.5541	4.34	2.0882	77.0

Crushed MgO crucible	12	0.9963	1.1177	27.3
	72	1.0571	0.68	1.0863

Figure 12 shows the relationship between heating time at 1400°C and hydration rate for MgO reagent and MgO crucible-pulverized powder. In Table 6 and Figure 12, even when the MgO reagent is heated at 1400°C for 72 hours, the hydration rate decreases by only about 10% compared to the untreated one. However, when the MgO crucible powder is heated at 1400°C for 12 and 72 hours, the hydration rate is approximately 50% and more than 70% lower than that of the untreated one, respectively. The SEM observation revealed that calcination of the MgO reagent did not progress even after long-term heating, whereas calcination of the MgO crucible-pulverized particles powder easily progressed. This is thought to be because the MgO crucible contains a small amount of SiO₂ and Al₂O₃ as binders, which promotes fusion between the powders, making hydration difficult.

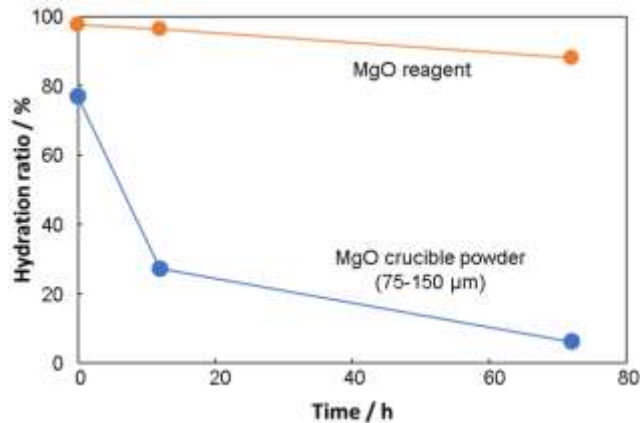


FIGURE 12 – Relationship between heating time at 1400°C and hydration rate for MgO reagent and MgO crucible powder.

To clarify the reason for the decrease in hydration reactivity due to calcination, the specific surface area of the MgO crucible powder (before hydration treatment) was measured using the BET method. The results are shown in Table 6. The specific surface area of the MgO crucible powder heated for a long time is significantly smaller than that of the unheated one. Since the specific surface area becomes smaller by calcination, hydration is suppressed. For the comparison of the hydration reactivity between MgO powders (Table 6) and MgO–FeO solid solutions prepared under various calcination conditions (Table 5), the hydration rates of MgO reagent powders heated for 12 and 72 hours are shown in Figure 9. The experimental point for MgO reagent heated for 12 hours is on the extrapolated curve of the relationship between FeO concentration and hydration rate of MgO–FeO solid solution heated for 12 hours. The relationship between hydration rate and the specific surface area is shown in Figure 13. In this figure, when comparing at the same specific surface area, the hydration rate of the MgO–FeO solid solution is lower than that of the unheated MgO crucible powder. This is also considered to be the effect of FeO solid solution.

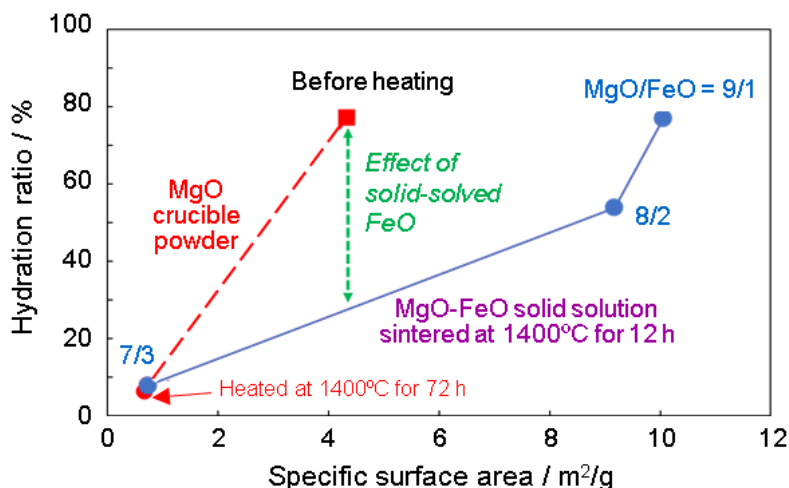


FIGURE 13 – Relationship between hydration rate and specific surface area for MgO-FeO solid solutions and MgO crucible powders.

CONCLUSIONS

To investigate the effect of solid-solved FeO on the hydration reactivity of free MgO in steelmaking slag, the preparation method of MgO-FeO solid solution was investigated, and conducted hydration experiments were performed on the synthesized MgO-FeO and MgO-FeO-MnO solid solutions using an autoclave. As a result, the following conclusions were obtained.

When the solid solution was rapidly cooled after calcination, a pure solid solution was obtained in one calcination process.

When MgO-FeO solid solution was hydrated under high temperature and pressure using an autoclave, the higher the amount of FeO dissolved in the MgO-FeO solid solution, the more the hydration reaction was suppressed.

When the calcination temperature of the MgO-FeO solid solution was increased, the Fe^{3+}/Fe^{2+} concentration ratio increased, resulting in a higher hydration rate.

Dense MgO crucible-pulverized powder had a lower hydration rate than commercially available MgO reagent.

The effect of heat treatment on the hydration rate of the MgO reagent was small. However, the longer the MgO crucible-pulverized powder was heated, the more the particles calcined and the specific surface area value decreased, resulting in a lower hydration rate.

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