Mechanism of Dissolution of Burnt Lime into Molten Slags Containing Iron Oxide.

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ABSTRACT

The rate of dissolution of burnt lime into FeO-SiO_2 slag was greater than that into CaO-SiO_2-FeO slag. There were two dissolution steps of burnt lime into FeO-SiO_2 slag. The First one was the decomposition of burnt lime into the grains which were larger than 10 μm, after penetration of the slag into the pores of the lime. The second one was the decomposition of the grains into the smaller particles which were about 1 μm in size and dissolved into the slag.

On the other hand, solidus calcium silicates precipitated at a distance 30~150 μm from the surface of the burnt lime in CaO-FeO-SiO_2 slag. The results indicate that the rate of dissolution of burnt lime into CaO-FeO-SiO_2 slag was controlled by mass transfer through the boundary layer between burnt lime and slag.

1.INTRODUCTION

In high quality and high purity steel making process, a rapid dissolution of lime is important to promote desulphurization and dephosphorization of the metal. According to the previous investigations, the rate of dissolution of lime into molten slag depended on the lime property[1-4] and on the slag composition[5,6]. The soft burned lime dissolved into the slag more rapidly than the hard burned one did. Furthermore, because of less formation calcium silicate layer near the interface between lime and slag contained large amount of FeO[5,6], it is obvious that FeO should play the important role for rapid slagging reaction of lime. In this study, the rate of dissolution of burnt limes calcined under various conditions were measured by a rotating immersion method to clarify the mechanism of slagging reaction of burnt lime in FeO-SiO_2 or in CaO-FeO-SiO_2 slag.

2.EXPERIMENTS

Lime stones with large grain and with fine grain were cut into cylinders of which form were 4mm inner diameter × 14mm outer diameter × 24mm height. The cylindrical lime stones were kept at 600℃ for 1hour in a electric furnace, and then they were heated at 7℃ per minute for the rate of raising temperature up to each temperature at 900,1000,1100 or 1200℃. The continuous heating for 1 hour or 12hour at each temperature mentioned above was performed. Fig.1 shows the grain growth of a burnt lime, NA, obtained from the calcination of a lime stone of large grain[7].

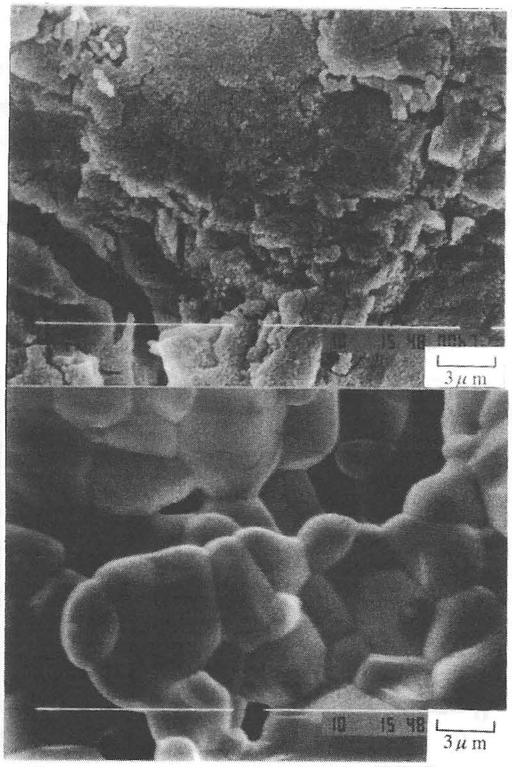

Fig. 1. **SEM microstructure of the burnt lime showing grain growth.**
(a) 1100℃, 1hr. (b) 1200℃, 12hr.

The slag of which compositions were FeO(63.3 mass%)-SiO_2(37.5 mass%) and CaO(32.0 mass%)-SiO_2(38.0 mass%)-FeO(30.0 mass%) were melted down in the iron crucible under Ar-CO atmosphere at required temperature at 1300℃, 1350℃ and 1400℃. After preheating the burnt lime just above slag surface, the specimen was immersed into slag, and then it was run at speed 20, 50 and 100 rpm.

On the measurement of the dissolution rate of burnt lime in the FeO-SiO_2 slag, a small amount of molten slag were sampled with copper rod. Sampling for slag was performed at one minute intervals until six minutes passed and at two minutes intervals after six minutes passed. Concentration of CaO in the quenched slags was measured by atomic absorption analytical method. In the case of in the CaO-SiO_2-FeO slag, a decrease of outer diameter of the specimen was measured by a slide calipers at ten points. The burnt limes were also examined by mercury penetration method, SEM observation, and EPMA analysis.

3.RESULTS

3.1 Dissolution into FeO-SiO_2 slag

Time dependence of CaO concentration in FeO-SiO_2 slag was shown in Fig.2.The concentration of CaO in the slag is 2.1~2.2 mass% when the whole of the specimen dissolves. As shown in Fig.2, the concentration of CaO shows the greater maximum value, 4.2 mass%, for soft burnt lime, NA, obtained from the lime stone of large grain.

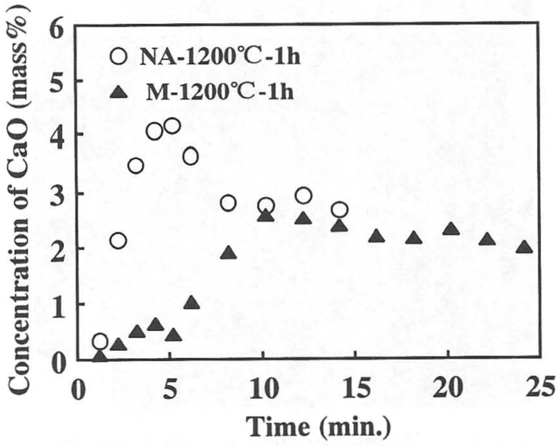

Fig. 2. Time dependence of CaO concentration in molten slag.

On the other hand, the concentration of CaO shows the smaller maximum value, 2.6 mass% for hard burnt lime, M, obtained from the lime stone of fine grain. The time required to reach the maximum value of concentration of CaO is shorter for soft burnt lime, NA, than that is for hard burnt one, M. It is indicated that the decomposition of lime has occurred in the slag.

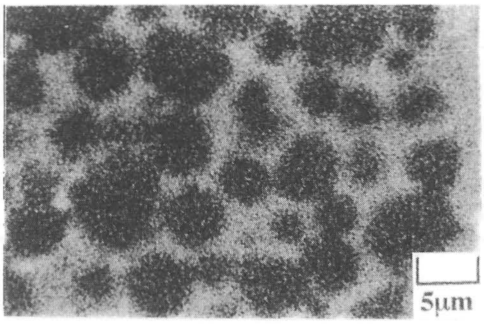

Fig. 3. X-ray image of Si in reaction layer of lime after immersion into molten slag. (NA-1200℃-1hr.)

Fig.3 shows the charastaristic X-ray image of Si in reaction layer of the soft burnt lime, NA, with slag. Image of Si was observed in the pores larger than 1μm, and that of Fe was observed in the pores of all sizes. Because the precipitation of calcium-silicate, $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ was observed in the pores where FeO-SiO_2 slag penetrated, it is speculated that the component SiO_2 was consumed in the pores for the formation of calcium -silicate[3,6], and then, FeO melt saturated with CaO penetrated into the smaller pores. As the lime dissolved into FeO-CaO melt easily[2], the burnt lime decomposed into the grains which are 10 μm order in size, and the decomposition of these grains into smaller particles which are 1 μm order in size occured.

3.2 Dissolution into CaO-FeO-SiO_2 slag

Fig.4 shows the effect of the calcination conditions on the ratio of dissolution of lime.The immersion into slag for these limes was performed at 1300℃ for 30 minutes.The figure indicates that the lime, NA, changes to a soft burnt lime easily, and that the lime, M, has a tendency to be a hard burnt lime. The ratio of dissolution for burnt limes, NA, calcined at 900℃~1100℃ for 1hour, showed great value because of their porous property.

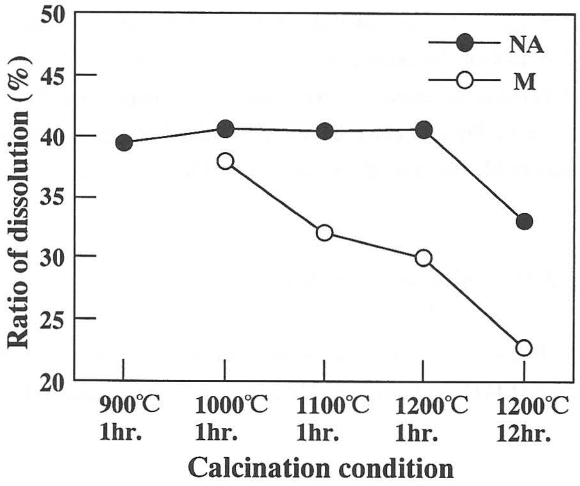

Fig. 4. Relation between ratio of dissolution of the burnt limes into CaO-FeO-SiO_2 slag and calcination conditions.

Fig.5 shows the relation between the ratio of dissolution and the pore volume. The ratio of dissolution was in proportion to the pore volume[3].

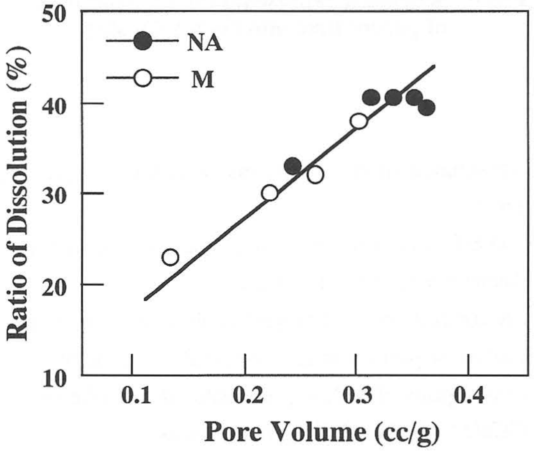

Fig. 5. Relation between the ratio of dissolution into CaO-FeO-SiO_2 slag and pore volume.

Fig.6 shows concentration profile of Ca, Si and Fe near the lime-slag interface of burnt lime after immersion into the slag. Dicalcium silicate, 2CaO· SiO_2, precipitated a part from the surface of the lime. The FeO-CaO melt, which penetrated through the pores, was produced between the dicalcium silicate and the surface of the lime. The distances where calcium silicate precipitated were 30 μ m ~ 150 μ m.

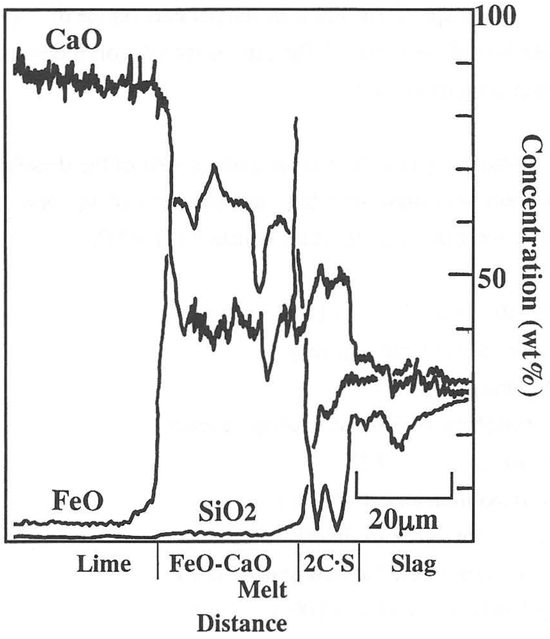

Fig. 6. Concentration profile of Ca, Si and Fe on the boundary between lime and slag.

Fig.7 shows the effect of the revolution speed on the decrease of the radius of the lime cylinder as a function of immersion time. The revolution speed were 20, 50, and 100rpm. The linear relation between the decrease of the radius and immersion time were observed at every revolution speed. The dissolution rate was defined by the slop of these straight line. The dissolution rate increased as increasing the

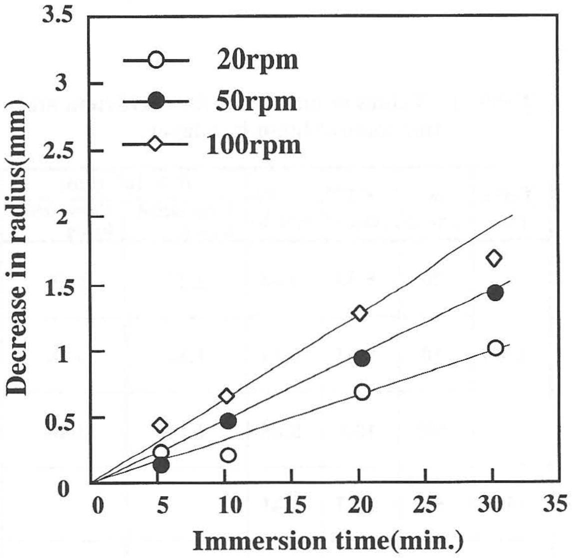

Fig. 7. Effect of the revolution speed on the rate of dissolution of lime into CaO-FeO-SiO_2 slag.

revolution speed.The effect of temperature on the dissolution rate was also examined.The rate of dissolution increased as increasing temperature.

Assuming that the rate controlling step of the dissolution process was mass transfer, the thickness of the boundary layer were obtained from the equation (1) ~(3)[6].

$V= -dr / dt = AU^S \quad \cdots(1)$

V: dissolution rate (cm/sec)

A: constant

u: periphery velocity of rotating cylinder

$V=K(n_s - n_b) \quad \cdots(2)$

K: mass transfer coefficient (cm/sec)

n_s: content of CaO at interface (g/cm^3)

n_b: content of CaO at bulk slag (g/cm^3)

$-dr/dt=K \rho_b \Delta(\%CaO)/100 \rho \quad \cdots(3)$

ρ_b: density of slag

$\Delta(\%CaO)$: difference between content of CaO at interface and its in bulk slag

ρ : density of CaO (g/cm^3)

The boundary layer thickness, δ_m (δ =D/K), was estimated from the mass transfer coefficient and the diffusivity of lime of 10^{-5}cm/sec in CaO-FeO-SiO_2 slag[6]. On the other hand, the boundary layer thickness, δ_c, was estimated from the equation obtained by the method of dimensional analysis[6]. The results are shown in Table I . The values of the mass transfer coefficient increased as the rotational speed increased. The value of boundary layer thickness, δ_m, decreased as the rotational speed increased. The value of it indicated $2.2\times10^{-2}\sim1.1\times10cm^{-2}$ smaller than that of the boundary thickness, δ_c, obtained from the dimensionless equation. Neverthless, it is concluded that the value of the boundary thickness obtained by this study are reasonable because of the results of EPMA analysis.

Table I Values of mass transfer coefficient and thickness of boundary layer.

Temp (℃)	*m* (rpm)	$V\times10^5$ (cm/s)	$k\times10^4$ (cm/s)	$\delta\times10^2$ (cm)	
				Caluculated from *k*	Caluculated by Eq
1300	20	5.53	4.48	2.23	6.65
	50	8.03	6.51	1.54	3.76
	100	10.9	8.85	1.13	2.46
1350	50	10.7	7.41		
1400	50	15.2	9.25		

3.3 Mechanism of dissolution

Fig.8 and Fig.9 show the mechanism of dissolution in the case of FeO-SiO_2 slag and CaO-FeO-SiO_2 slag respectivly.

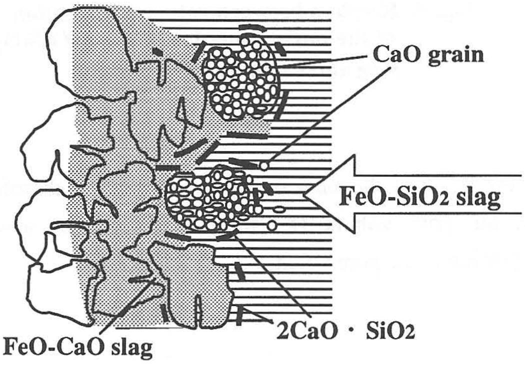

Fig. 8. Schematic representation of dissolution of porous lime into FeO- SiO_2 slag

Dissolution of burnt lime into FeO-SiO_2 slag occurs as follows;

1. FeO-SiO_2 slag penetrate through the pores of which diameter are greater than 1 μ m.
2. The composition of the liquidus phase adjacent with the wall in the pores change to FeO-CaO,because of consumption of SiO_2 to precipitate calcium silicate ($2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$) in the pores[8].
3. Burnt lime decompose into grains larger than 10 μ m, because CaO dissolves into FeO-CaO melt easily.
4. Subsequently, the grains also decompose into particles smaller than 10 μ m which dissolve into slag.

Dissolution of burnt lime into CaO-FeO-SiO_2 slag occurs as follows.

1. CaO dissolves into slag at surface of lime diffuses toward bulk.
2. Calcium silicate ($2CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$) precipitate in the boundary layer, surrounding the surface of burnt lime[3,4,6,9].

3. Because of consumption of SiO_2 for calcium silicate precipitation in the boundary layer, composition of melt between the surface of the lime and calcium silicate layer changes to FeO-CaO[4,6], and then this melt can penetrate through the pores.
4. CaO dissolved or decomposed into particle smaller than 1 μm into FeO-CaO melt at the surface of lime diffuse toward bulk slag. On the other hand, component of the bulk slag permeates through the calcium silicate layer towards the lime-slag interface.

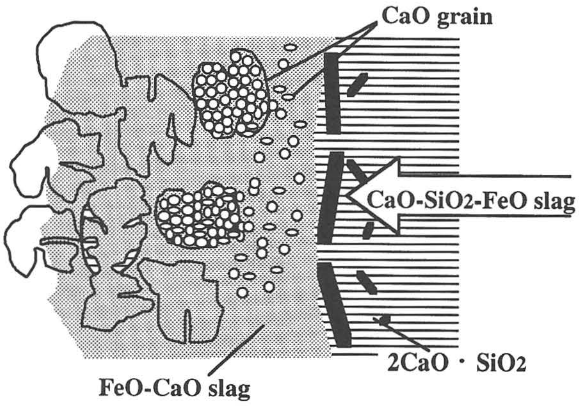

Fig. 9. Schematic representation of dissolution of porous lime into CaO-FeO- SiO_2 slag

CONCLUSION

In dissolution process for burnt lime into FeO-SiO_2 slag, there are two steps. The first one is decomposition of lime into grains larger than 10 μm. The second one is dissolution of particles smaller than 10 μm from decomposition of the grains. The rate controlling step on the dissolution of burnt lime into CaO-FeO-SiO_2 slag is mass transfer in the boundary layer between lime and slag.

REFERENCES

1. K.H.Obst, J.Stradtmann and G.Tromel, "Reducing the Blowing Time in the LD Process by the Use of Special Lime Products," Journal of the Iron and Steel Institute, May 1970, pp.450-455.

2. R.Scheel and F.Oeters, "Investigations into the Process of Lime Dissolution," Arehiv fur das Eisenhuttenwesen, vol.42, No.11, November 1971, pp.769-777.

3. F.Oeters and R.Scheel, "Studies of the Dissolution of Lime in CaO-FeO-SiO_2 Slags," Archiv fur das Eisenhuttenwesen, Vol.45, No.9, September 1974, pp.575-580.

4. C.A.Natalie and J.W.Evans, "Influence of Lime Properties on Rate of Dissolution in CaO-SiO_2-FeO-Slags," Ironmaking and Steelmaking, No.3, February 1979, pp.101-109.

5. W.J.Schitt and G.W.Healy, "Kinetics of Lime Dissolution in CaO-FeO-SiO_2 Slags," Ceramic Bulletin, Vol.50, No.12, July 1971, pp.954-957.

6. M.Matsushima, S.Yadoomaru, K.Mori and Y.Kawai, "A Fundamental Study on the Dissolution Rate of Solid Lime into Liquid Slag," Transactions ISIJ, Vol.17 1977, pp.442-449.

7. M.Kawahara , T.Mitsuo , Y.Sassa and K.Katoh , "Effects of Calcination Condition on the Reactivity of Burnt Lime with Water and on the Desulphurization Reaction of Hot Metal ," Tetsu to Hagane , Vol.75 , No.3 , 1989 , pp. 462-469.

8. L.Hachtel, W.Fix and G.Tromel, "Investigations into the Dissolving of Lime Single-Crystals in FeO_n-SiO_2 Heats," Archiv fur das Eisenhuttenwesen, Vol.45, No.9, September 1974, pp.575-580.

9. K.F.Behrens, J.Koenitzer and T.Kootz, "The Effects of Lime Properties on Basic Oxygen Steelmaking," Journal of Metals, July 1965, pp.776-781.