Hot Metal Desulfurization with Na_2O-CaO and CaO-Al_2O_3 fluxes

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ABSTRACT

The rate of hot metal desulphurization with Na_2O-CaO and CaO-Al_2O_3 flux was studied. Optimum composition has been observed with both flux at Na_2O-50mass%CaO and CaO-38mass%Al_2O_3. In case of Na_2O-CaO system, large amount of unknown sulfur was observed and phosphorus in hot metal promoted desulphurization. These mechanism was qualitatively explained by considering change in Na_2O activity with flux composition and hot metal phosphorus content. In case of CaO-Al_2O_3 flux, presence of optimum composition was explained by both effect of equilibrium between solid CaO-Al_2O_3 slag and hot metal and change in microstructure of CaO with Al_2O_3 addition.

1.INTRODUCTION

In hot metal pretreatment process, not only dephosphrization but also desulphurization function is important. The equilibrium or the kinetics of dephosphorization has been studied in detail[1,2]. However, study on desulphurization kinetics of hot metal has been done comparatively few. To establish the efficient hot metal pretreatment process, to reveal desulphurization reaction mechanism is essential.

Usually, it is known that reactivity of CaO base flux is less than that of soda base flux. So, soda ash or soda ash and lime mixed flux are used as a desulfurizer[3,4] after dephosphorization in real operation. In this study, laboratrial experiment has been made and reaction between hot metal and Na_2O-CaO or CaO-Al_2O_3 flux was discussed.

2.EXPERIMENTS

The experiment has been done using the resistance heating furnace at 1350℃. Carbon saturated iron was dissolved in crucible of 0.04m in inside diameter and adjusted chemical composition. Next, desulfurizer was added from the upper side and the desulphurization treatment was begun. Treatment time was 40 min. Metal samples were taken in some interval and change in hot metal composition was analyzed. In case of Na_2O-CaO flux, magnesia crucible was used and for CaO-Al_2O_3 flux, graphite crucible was used. The flux used in each experiment is mechanically mixed powder reagents. Experimental conditions are shown in Table 1.

In case of desulphurization with Na_2O-CaO flux, most of experiments were performed under high hot metal phosphorus content of 0.1 mass% and a part of experiments was performed under lower initial phosphorus content of 0.015 mass%. Flux which consists of Na_2O and SiO_2 was also used for comparison under low phosphorus content.

In case of experiments with CaO-Al_2O_3 flux, phosphorus was not added to hot metal. A part of experiments was performed with Al added fluxes and Al addition to hot metal before flux addition.

Additionally, immersion experiment of lime into hot

Table1 Experimental conditions.

	Metal composition(mass%)			Flux composition(mass%)			
	[%S]	[%P]	[%Al]	Na_2O	CaO	Al_2O_3	Al
Na_2O -CaO	0.05	0.10 or 0.015	0	100 ~ 0	0 ~ 100	0	0
	0.05	0.015	0	$Na_2O·SiO_2$, $2Na_2O·SiO_2$			
CaO -Al_2O_3	0.05	0	0	0	100 ~ 40	0 ~ 60	0
	0.05	0	0	0	69.8 ~ 45.9	26.6 ~ 47.6	3.6 ~ 6.5
	0.05	0	0.05	0	100 ~ 40	0 ~ 60	0

metal was performed at 1350℃ to observe reacted layer of lime with hot metal. The experiment with a different initial silicon and aluminum content was done. Spherical lime specimen ground to about 20 mm diameter was dipped in hot metal and was made to react with hot metal for 1h and observed the structure in the vicinity of contact side with the molten iron, and analyzed a reacted layer with SEM.

3. RESULTS

3.1 Reaction mechanism of hot metal and Na_2O-CaO flux.

Fig.1 shows the behavior of sulfur content when hot metal of high phosphorus content was treated by the mixing flux of Na_2O and CaO. The desulfurization rate was remarkably small only for CaO and the change in the sulfur content was hardly seen at this experiment time 40 min. On the other hand, in the case of Na_2O containing flux, remarkable desulphurization was caused in initial 10 min and after that, tendency of resulfurization has been seen. Fig.2 shows the relationship between degree of desulphurization and Na_2O mixing ratio after 40 min. The maximum degree of desulphurization was achieved with flux of Na_2O-50mass%CaO when treated hot metal of high phosphorus content with Na_2O-CaO flux as shown in Fig.2. Lower desulphurization degree was indicated when treated hot metal of low phosphorus content compared with high phosphorus content at the same Na_2O mixing ratio. On the other hand, the highest desulphurization rate was shown with Na_2O-SiO_2 flux. Final total slag weight was estimated and residual rate of Na_2O after treatment was calculated from analyzed Na_2O content in slag. The Na_2O fraction of residue showed the tendency which decreased with an increase in Na_2O mixing ratio for the high phosphorus content hot metal. A high fraction of residue was shown in the Na_2O-SiO_2 flux compared with the Na_2O-CaO flux. When hot metal of low phosphorus content was desulfurized by the Na_2O-CaO flux, it was about 2 mass% and extremely low fraction of residues.

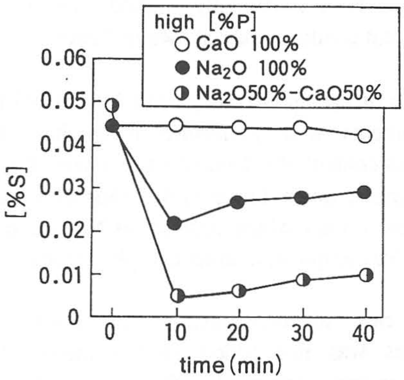

Fig.1 Change in sulfur content with time.(Na_2O-CaO)

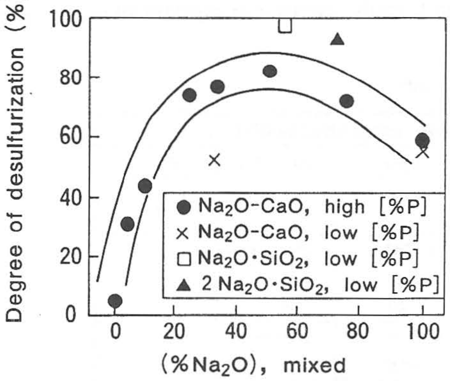

Fig.2 Relationship between Na_2O mixing ratio and degree of desulfurization.(Na_2O-CaO)

Material balance of sulfur before and after treatment was calculated. Amount of unknown sulfur is shown in Fig.3. The amount of unknown sulfur increased with increase in Na_2O mixing ratio and it was estimated that about 70% was unknown sulfur in the condition of Na_2O-50masss%CaO. In addition, the tendency with a little unknown sulfur was seen in the condition of low phosphorus content compared with the high phosphorus content condition.

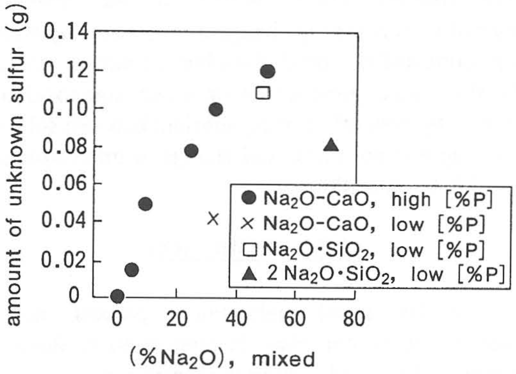

Fig.3 Relationship between amount of unknown sulfur and Na_2O mixing ratio.

Fig.4 shows the example of change in content of hot metal element with time when hot metal of high phosphorus content were treated with Na_2O-CaO flux. The result of model calculation was additionally shown in Fig.4. Decarburization reaction is caused in every phosphorus content of hot metal and dephosphorization reaction took place when initial phosphorus content was high. The example of composition of slag is shown in Table2. When hot metal of high phosphorus content was treated, P_2O_5 of 4.32 mass% was included in the slag. On the other hand, when hot metal of low phosphorus content was treated,

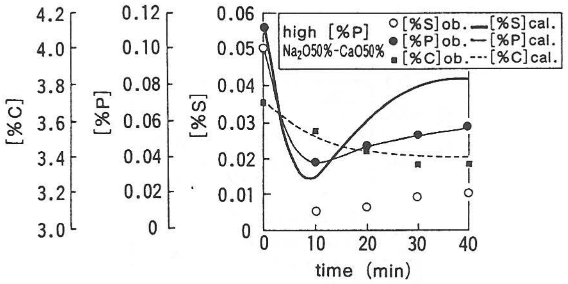

Fig. 4 Behavior of elements in hot metal during treatment.

Table 2 Example of slag composition after treatment.

Added flux (mass%)		Initial Aimed	Slag composition after treatment(mass%)			
Na_2O	CaO	[%P]	Na_2O	CaO	P_2O_5	Fe_tO
33.3	66.7	0.100	8.4	71.3	4.32	2.2
		0.015	0.3	75.5	0.11	16.9

P_2O_5 content was low and FeO content was high. P_2O_5 will decrease activity of Na_2O. As a result, rate of evaporation reaction of Na_2O afterwards decreases. On the other hand, much FeO has been generated with decomposition of Na_2O at initial stage when phosphorus content was low. P_2O_5 is acid oxide and may lower sulfide capacity of slag, but if there was no acid oxide in slag, Na_2O may easily decompose and result in increase of oxygen activity at slag metal interface and reduction of rate of desulfurization. The reason why higher desulfurization rate was achieved by $Na_2O\cdot SiO_2$ flux compared with $2Na_2O\cdot SiO_2$ flux, may be attributed to lower oxygen activity caused by more reduction of Na_2O activity by existence of more SiO_2.

Reaction mechanism of slag-metal interface is considered by reaction model analysis. Reactions (1) through (7) were considered. In this experiment, the evaporated chemical species was not identified.

$$\underline{S}+2\,\underline{O}=SO_2\,(g) \qquad (1)$$

$$(Na_2O)+\underline{S}+3\,\underline{O}=(Na_2SO_4) \qquad (2)$$

$$(Na_2O)=2\,Na(g)+\underline{O} \qquad (3)$$

$$\underline{C}+\underline{O}=CO(g) \qquad (4)$$

$$2\,\underline{P}+5\,\underline{O}=(P_2O_5) \qquad (5)$$

$$Fe+\underline{O}=(FeO) \qquad (6)$$

$$2\,Na(g)+\underline{S}=(Na_2S) \qquad (7)$$

Harashima et al.[5] reported SO_2 formation during simultaneous dephosphorization and desulfurization of hot metal treatment with CaO based flux. In this model analysis, reaction of equation (1) was considered and generation of SO_2 is assumed to progress only at the slag metal interface. A basic idea of the model is the same as coupled reaction model[6].

Fig.4 showed a change of hot metal composition by the experiment and the calculation when hot metal of high phosphorus content was desulfurized as an example by the flux of Na_2O50mass%-CaO50mass%. Measured sulfur content was much smaller than that of calculation. This discrepancy is due to difference in amount of evaporated sulfur.

Another possibility of sulfur evaporation is decomposition of Na_2S by reaction (8),(9) or (10) in slag bulk phase after Na_2S transferred from slag-metal interface to slag bulk phase. As shown in Fig.5, equilibrium partial pressure of SO_2 by reaction of equation (8) was with in the range of 1×10^4-1×10^6 Pa between 0-5 min and the possibility causing SO_2 is enough.

$$(Na_2S)+3(FeO)=(Na_2O)+SO_2(g)+3Fe \qquad (8)$$

$$(Na_2S)+2(FeO)=2\,Na(g)+SO_2(g)+2Fe \qquad (9)$$

$$(Na_2S)+CO(g)=COS(g)+2Na(g) \qquad (10)$$

The difference of sulfur vaporization amount by phosphorus content of hot metal in Fig.3 can be qualitatively explained. That is, when phosphorus content is high, oxygen activity at slag metal interface becomes lower through reaction (5), compared with a low phosphorus content case. As a result, the Na_2S generation rate through reaction (7) from hot metal to slag phase is large and as a result, amount of Na_2S which disappears by reaction (8) increases from slag bulk side to atmosphere. The reason why optimum Na_2O mixing ratio was observed can be explained by mechanism mentioned above. As increase Na_2O mixing ratio, generation rate of Na_2S increases at slag metal interface, and the gaseous desulfurization reaction rate also increases and overall desulfurization reaction rate increases. In case of excess Na_2O addition, oxygen activity at slag metal interface may be increased by increment of Na_2O decomposition reaction rate. As a result, rate of Na_2S formation at slag metal interface may be decreased and overall rate of desulfurization decreases.

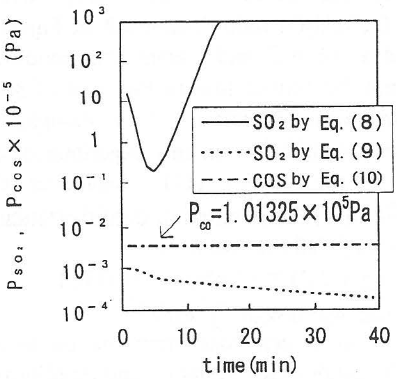

Fig.5 Equilibrium partial pressures.

3.2 Desulfurization mechanism with CaO-Al_2O_3 flux.

Change in sulfur content with time are shown in Fig.6 when treated with CaO-Al_2O_3 flux. In initial 10 min, the rate of desulfurization was very low, and sustained to desulfurize until 40 min or more. Fig.7 shows the relationship between final Al_2O_3 content of slag and sulfur and aluminum content of hot metal after 40 min. The lowest sulfur content was observed when Al_2O_3 content was 38%. Aluminum content of hot metal increased with increase in Al_2O_3 content in spite of no aluminum addition to flux or hot metal.

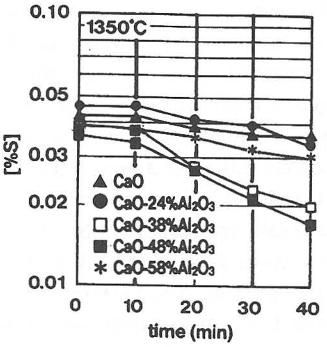

Fig.6 Change in sulfur content with time.(CaO-Al_2O_3)

In CaO-Al_2O_3 phase diagram, no molten slag cannot exist at 1350℃. So, the slag phase is consists of two of CaO, 3CaO・Al_2O_3, 12CaO・7Al_2O_3, CaO・Al_2O_3 etc.(abbreviated C_3A, $C_{12}A_7$, CA, etc.). Activity of CaO and Al_2O_3 at this time will take a constant value between these phase boundaries. Fujisawa et al.[6] investigated the solubility of CaS into CaO-Al_2O_3 molten slag at 1600℃. According to this, the value is about only 4at% and not depend on CaO/Al_2O_3 ratio. The result of Fujisawa et al. were gained at 1600℃ and molten slag conditions. CaS solubility may be further low in the case of solid CaO-Al_2O_3 compounds. Therefore, it is thought that the desulfurization equilibrium in this experimental condition is decided by the reaction (11) . Moreover, CaS may saturated after the little progress of desulfurization reaction is and activity of CaS may be unity.

$$3\,CaO(s) + 3\,\underline{S} + 2\,\underline{Al} = 3\,CaS(s) + Al2O3(s) \qquad (11)$$

$$[\%S]eq=(a_{CaS}^{3}\,a_{Al2O3}/a_{CaO}^{3}\,f_{\underline{S}}^{3}\,a_{\underline{Al}}^{2})^{1/3} \qquad (12)$$

a_{CaO} and a_{Al2O3} is estimated from the thermodynamics model of Yamada's oxide systems[7] and equilibrium sulfur content was in the order of 0.001mass% in case of CaO-C_3A region. However, observed sulfur content after treatment was much larger than the calculated equilibrium one as shown in Fig.7. It is thought not to reach the equilibrium at the experiment time of 40 minutes.

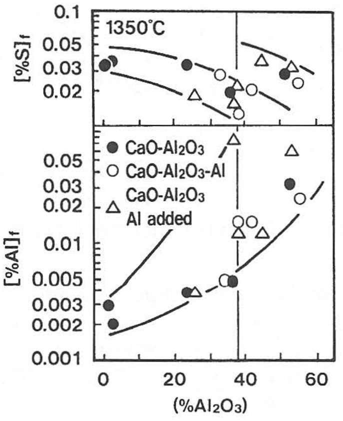

Fig.7 Relationship between (%Al_2O_3) and final [%S] or [%Al]

In order to discuss the desulfurization rate, simple bulk diffusion model calculation was performed. In this calculation, the diffusivity, D_S, on the slag side was treated as a fitting parameter and diffusivity of CaS, Al_2O_3 and CaO evaluated under the assumption that D_S is common among these speicies by thinking about CaS, Al_2O_3, and CaO here as a diffusion species. Results are shown in Fig.8

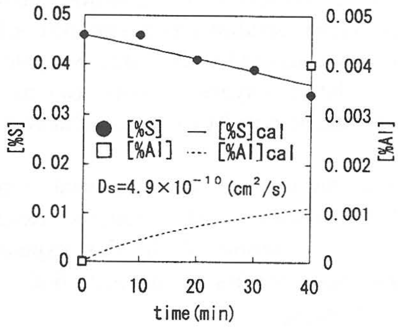

Fig.8 Change in sulfur and aluminum content with time. Flux composition is CaO-24mass%Al_2O_3.

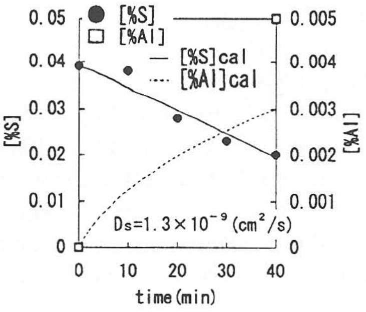

Fig.9 Change in sulfur and aluminum content with time. Flux composition is CaO-38mass%Al_2O_3.

and Fig.9. Evaluated diffusivity is largely different in each experimented case and in both cases, behavior of aluminum could not be also explained. From this result, the rate of desulfurization cannot be explained by simple bulk diffusion mechanism.

Actually, crack development was in a reacted region of CaO and Al_2O_3 was observed in CaO immersion experiment. There is a possibility of crack development in CaO and this enhances desulfurization with Al_2O_3 addition by increase in reaction specific area. In this case, spinel compound of $CaAl_2O_4$ may be formed when experimenting on desulfurization with the CaO-Al_2O_3 powder mixture. It is known that when a spinel phase is formed in solid state reaction between MgO and Al_2O_3, MgO-spinel interface is easily collapsed[8]. A similar phenomenon has been also reported in ZnO-Al_2O_3 system which generates $ZnAl_2O_4$ spinel phase[9]. Moreover, it has been reported that the pore distribution of lime influences the rate of desulfurization of hot metal with solid lime by Kawagishi et al.[10] and Ueda et al.[11]. It can be thought that this contributes to an increase in specific area for the infiltration of the molten iron into solid lime.

In CaO immersion experiment, reacted region which includes larger cracks compared with CaO bulk unreacted zone was observed in case of hot metal containing aluminum and in this region, high content of Al_2O_3 and CaS was observed. This result supports the mechanism mentioned above.

4. CONCLUSION

(1) When hot metal of high phosphorus content was desulfurized with Na_2O-CaO flux, the composition that the desulfurization rate becomes the maximum appeared.

(2) The rate of desulfurization of the low phosphorus content hot metal with Na_2O-CaO flux indicated a small value compared with the case of the high phosphorus concentration.

(3) The results of (1) and (2) can be qualitatively explained by decrease in Na_2O activity by acid oxide, result in reduction of decomposition rate of Na_2O and the oxygen activity at slag metal interface.

(4) Large amount of unknown sulfur was observed. It became more remarkable, higher the hot metal phosphorus content was. It was suggested that sulfur evaporation reaction occurred in slag bulk phase.

(5) In desulfurization with CaO-Al_2O_3 flux, the maximum rate of desulfurization was obtained at stoichiometric composition of $3CaO \cdot Al_2O_3$.

(6) The possibility of increase in rate of desulfurization by Al_2O_3 addition is the change in crack generated more frequently with high mixing of Al_2O_3. It is most likely that increase in specific reaction area by the crack development enhanced the desulfurization.

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