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Structure of Slag(X)[†]

— Desulfurization —

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Abstract

In this review, an important behavior of slag to desulfurize molten metal is summarized. Classical parameters to define the desulfurizing power are arranged and the effect of various additive components is given.

KEY WORDS: (Slag) (Structure) (Desulfurization)

1. Introduction

In the case of steelmaking, the harmful effects of sulfide in steel on the mechanical properties such as ductility, corrosion behavior and so on have been discussed in everywhere.[1)-4)] According to recent study concerning intergranular corrosion of 304 stainless steel, sulfur content below 0.03 weight% did not show remarkable harmful effect.[5)] It is said that a solute segregation of phosphorus will easily induce an intergranular fracture in alloy steel. Likewise, solidification cracking is an important problem to obtain good quality of stainless steel welds, and it was discussed as for the relationship between (P+S) and Cr_{eq}/Ni_{eq}.[6)]

Recently, with the new development using out-of-furnace refining process to enhance desulfurization as well as dephosphorization, it became possible to obtain steel containing low phosphorus and sulfur.

However, there exists difficult conditions such as rapidly solidification of weld in comparison with that of steelmaking, so that it seems impossible to proceed desulfurization reaction during welding.

In this review, the fundamental concept of desulfurization in the field of steelmaking, and the possibility to attain lower content of sulfur in weld is discussed.

2.1 Fundamentals

2.1 Activity coefficent of sulfur in molten iron

In **Fig. 1**, the effect of coexisting element on the activity coefficient of sulfur is shown[7)]. From this diagram, it will be anticipated that the ironmaking in blast furnace is an effective process to increase an activity coefficent of sulfur because a large amount of carbon, silicon and phosphorus is contained in pig iron. For that reason, the transfer of sulfur from pig iron to molten slag becomes easier[8)].

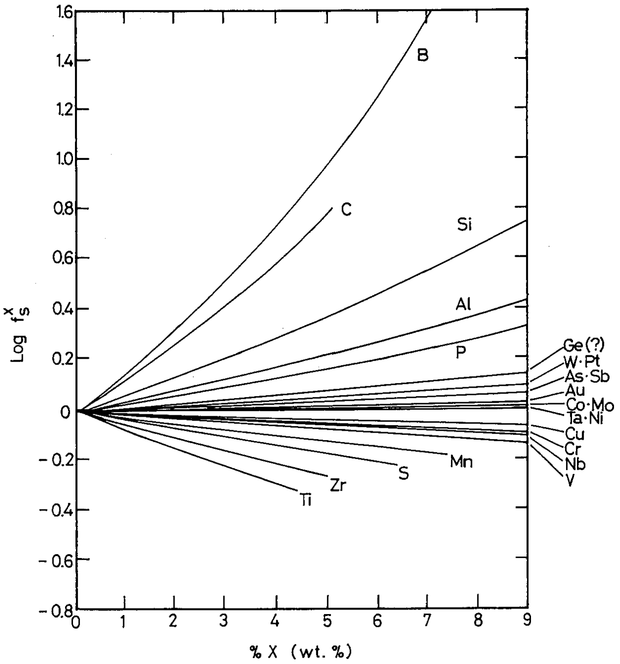

Fig. 1 The effect of various elements on the activity coefficient of sulfur in liquid iron[7)]

2.2 Formation energy of sulfide

It is an important matter to know what kind of additive in welding flux is effective and it is necessary to explain the factor of which people aims.

To remove sulfur from the molten metal, a detailed comparison of the formation energy of sulfide has been made. Based on this standpoint, additive such as calcium, magnesium, carbide or lime was thrown into molten pig iron to remove sulfur.[9)-12)]

Formation energy of typical sulfide is given as follows:[13)]

$$CaO_{(slag)}+S_{(in\ Fe)}=CaS_{(slag)}+O_{(in\ Fe)} \qquad (1)$$

$$G^{\circ}_{1873^{\circ}K}=+53,100J$$

[†] Received on September 30, 1982

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$$Fe_x0_{(slag)}+S_{(in\ Fe)}=FeS_{(slag)}+O_{(in\ Fe)} \quad (2)$$
$$G^{\circ}_{1873^{\circ}K}=+61{,}900J$$
$$MnO_{(slag)}+S_{(in\ Fe)}=MnS_{(slag)}+O_{(in\ Fe)} \quad (3)$$
$$G^{\circ}_{1873^{\circ}K}=+F3{,}100J$$
$$MgO_{(slag)}+S_{(in\ Fe)}=MgO_{(slag)}+O_{(in\ Fe)} \quad (4)$$
$$G^{\circ}_{1873^{\circ}K}=+140{,}000J$$

From these values, desulfurizing power increases according to the order of MgO,MnO,Fe_xO, and CaO and it can be anticipated that the addition of MgO in flux is ineffective to remove sulfur from the molten iron.

2.3 Parameter used to determine desulfurizing power

2.3.1 Excess Base (EB)

Based on the principle of molecular theory[14)-16)] that a compound having fixed composition according to the determined ratio, basic component/ acidic component, can be formed in slag, so that excess free uncombined basic component can be calculated with the following equation.

$$EB=nCaO+nMgO+nMnO-4nP_2O_5 -2nAl_2O_3-nFe_2O_3 \quad (5)$$

where n is the number of moles of oxide per 100 grams of slag.

This concept is identical to M_L[17)] indication of Mr. Mori that Al_2O_3 and TiO_2 are assumed to work as acidic componennt in slag.

In **Fig. 2**, the relationship between desulfurizing power of practical slag and the excess base is shown.[18)] It is analogized that the operating temperature is not a serious problem. However, it is assumed that Fe_xO and CaF_2 in slag was treated as ineffective neutral component to induce the excess base. Afterwords, it will be given that Fe_x0 content in slag has a remarkable effect on desulfurizing power.

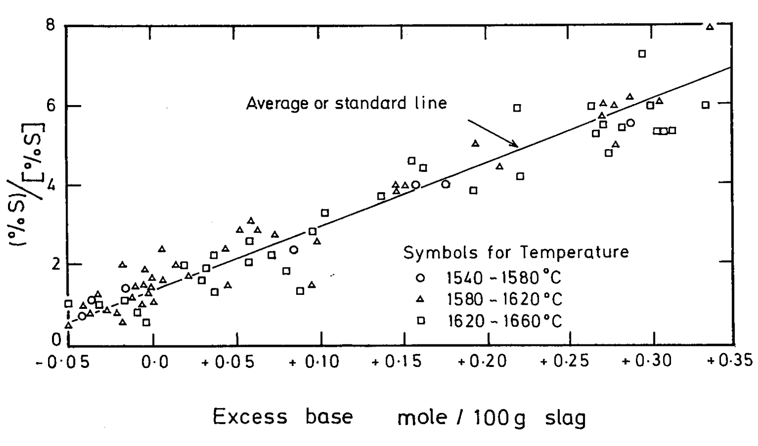

Fig. 2 Relation between sulfur partitioning and "excess base" for basic open-hearth furnace type slags at 1540°-1660°C[18)]

In **Fig. 3**, the relation between desulfurizing power and the content of Fe_xO in slag is given.[19)] From this result, it will be accepted that under a basicity the more Fe_xO content in slag is, the less desulfurizing power becomes.

Further, the following equation has been given to obtain excess base in the acid-rich region of the neutral composition of slag.[20)]

$$EB=nCaO+2/3\,nMgO-nSiO_2-nAl_2O_3 \quad (6)$$

The result using this equation is compared with the desulfurizing power in **Fig. 4** and it will be seen that below EB=0 it becomes a nonlinear.

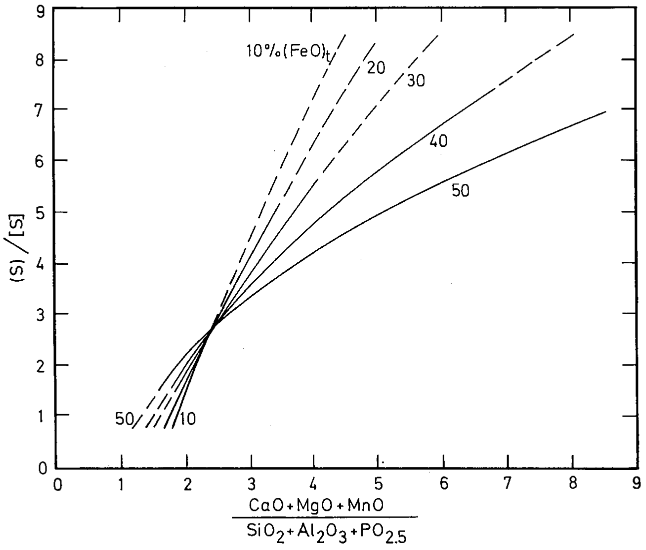

Fig. 3 Desulfurization ratio vs the molar ratio of bases to acids at various molar iron oxide concentration in the temperature range 1570° to 1630°C[19)]

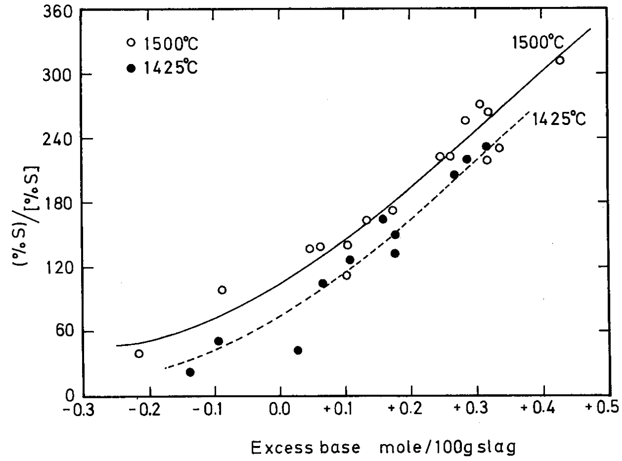

Fig. 4 Relation between sulfur partitioning and"excess base" for blast-furace type slags at 1425° and 1500°C[20)]

2.3.2 *S-O ratio*

In the basical slag, the following charge transfer between oxygen and sulfur occurs.[21)]

$O^{2-}_{(slag)}+S_{(in\ Fe)}\quad S^{2-}_{(slag)}+O_{(in\ Fe)}$ (7)

When the sulfur content of the order of 0.5% is containd in slag, we can postulate as $a_{O^{2-}},=N_{O^{2-}}$, and free oxygen ion in slag is considered to be used for the formation of acidic anion. Accordingly, the apparent equilibrium constant of eq.(7) can be induced as follows:

$K'_S=(N_{S^{2-}})\ [a_O]\ /(N_{O^{2-}})\ [\%S]$ (8)

However it must be remembered that sulfur transfer from molten metal to slag does not depend on the activity of oxygen ion of molten metal as bulk, but on that at the interface between slag and molten metal. If the following relation, $f_S=f_O=1$, is hold, the equilibrium constant of eq.(7) can be simplified as follows:

$K''_S\,(a_{O^{2-}})/(f_{S^{2-}})=(\%S)/\ [\%S]\ \cdot\ [\%O]$ (9)

Here, the right member is termed S-O ratio.[19)]

In **Fig. 5**, the relation between S-O ratio and SiO_2 content in slag is shown.[19)] From this result, it will be seen that with the increase of SiO_2 content in slag the sulfurizing power becomes the less. In this case, it becomes obvious that Fe_xO content in slag determines the desulfurizing power and CaO/SiO_2 ratio in slag is not main factor for the desulfurizing power.

The fact can be confirmed by rearranging the result obtained.

2.3.3 *Sulfide Capacity*

When slag equilibrated with the determined atmospheric condition of partial pressures of sulfur and oxygen, the following reaction occurs.

$O^{2-}+1/2S_2=S^{2-}+1/2\ O_2$ (10)

From this equation, it can be written as follows:

$C_S=(\%S)\ P_{O_2}/P_{S_2}$ (11)

and C_S is named sulfide capacity.[22)−27)]

In **Fig. 6**, C_S is compared with a basicity R below-described for a refining slag composed from $CaO-MgO-SiO_2-Al_2O_3$ system.[28)]

$R=N_{CaO}+(N_{MgO/2})/N_{SiO_2}+(N_{Al_2O_3/3})$ (12)

From this diagram, it will be anticipated that partial oxygen pressure in an atmosphere relates to desulfurizing power because it governs the distribution function of silicon, manganese and sulfur between molten metal and slag.

That is to say, the following reaction proceeds.

$Mn_{(in\ Fe)}+1/2\ O_2=MnO_{(\ell)}$ (13)

$Si_{(in\ Fe)}+1/2\ O_2=SiO_{2(\ell)}$ (14)

$2e^-+S_{(in\ Fe)}+1/2\ O_2=S^{2-}+O_{(in\ Fe)}$ (15)

Combined with these relations, the following relations could be induced.

$[\%S]\ /(\%S)=K\ [\%Mn]\ /(\%MnO)$ (16)

$[\%S]\ /(\%S)=K\ [\%Si]\ /(\%SiO_2)$ (17)

The equilibrium constant of eq.(10) may be rearranged as follows:[26)]

$K_1=P_{O_2}^{1/2}(a_{S^{2-}})/P_{S_2}^{1/2}(a_{O^{2-}})=C_S(f_{S^{2-}})/(a_{O^{2-}})$ (18)

where $f_{S^{2-}}$ represents an activity coefficient of sulfur ion in slag.

On the other hand, an equilibrium constant of transfer reaction of sulfur from molten metal to slag can be obtained as follows:

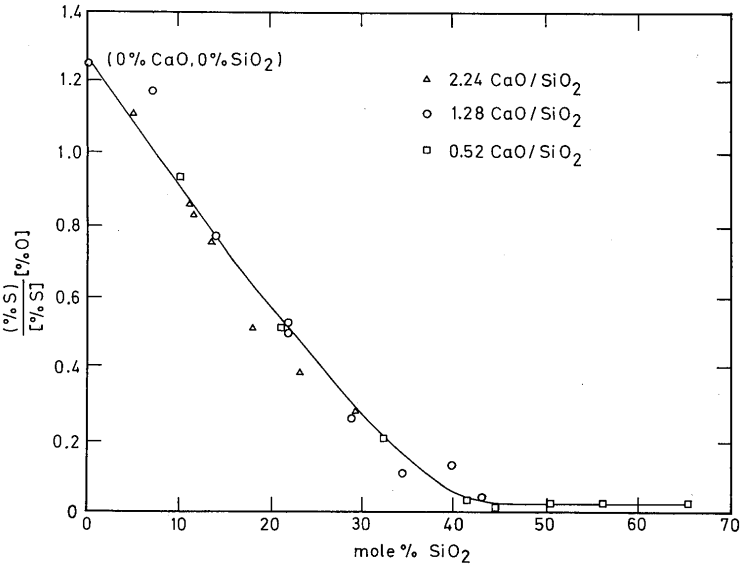

Fig. 5 The ratio (S)/ [S] · [O] calculated from gas-slag equilibria data at 1550°C vs the mol% silica in the slag system $CaO-SiO_2-(Fe_xO)$[19)]

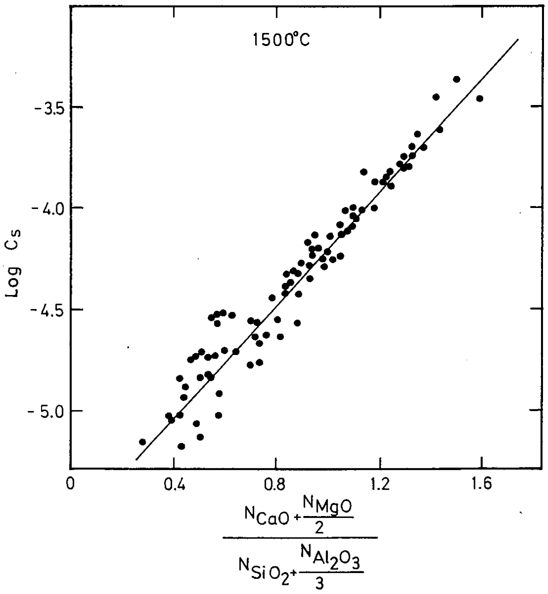

Fig. 6 Correlation of sulfide capacity measurements with the emprical ratio[28)]

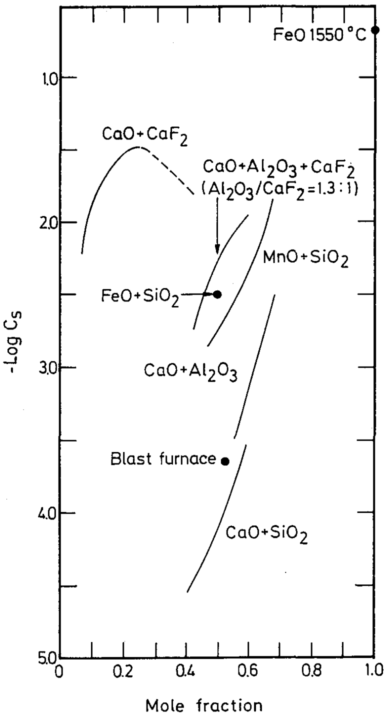

Fig. 7 The sulfide capacities of various aluminate, silicate and fluoride melts at 1500°C[23),25)]

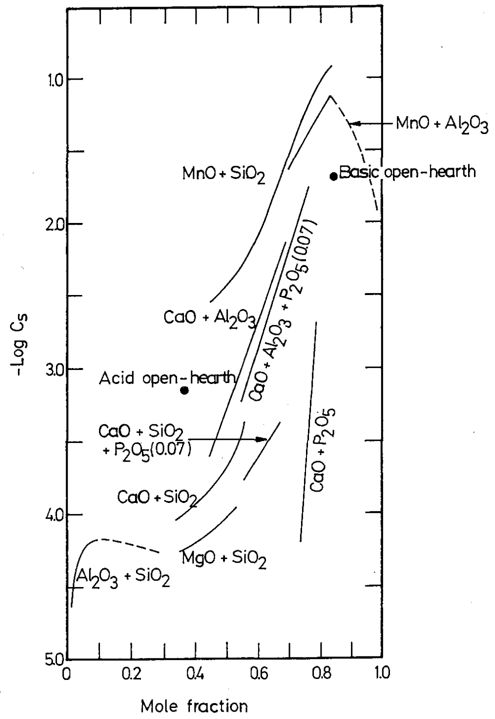

Fig. 8 The sulfide capacities of various aluminate and phosphate melts at 1650°C[23),24)]

$$S_{(in\ metal)}=S^{2-}_{(slag)} \qquad (19)$$

$$K_2=(a_{S^{2-}})/\ [a_S] \qquad (20)$$

By combining the equations (19)and(20),

$$K_3=K_1\times K_2=\ [a_S]\ \ (f_{S^{2-}})/(a_{S^{2-}})(a_{O^{2-}}) \qquad (21)$$

can be obtained.

From this relation, the following equation can be introduced.

$$(a_{S^{2-}})\ [a_S]\ =C_S(f_{S^{2-}})/K_3(a_{O^{2-}}) \qquad (22)$$

Accordingly, it is obvious that the more sulfide capacity is, the more desulfurizing power becomes if ($f_{S^{2-}}$) and ($a_{O^{2-}}$) are constant, respectively,.

In **Figs. 7** and **8**, relationship between mole fraction of base or CaO in slag and the sulfide capacity is shown.[23)~25)] Summarized result obtained is as follows:[26)]

1) That C_S decreases with the decrease of basicity of slag coincides with the result above-described.

2) Basic oxides, CaO, Fe$_x$O, MgO, and MnO, as well as acidic oxides do not have equivalent work against the value of ($a_{O^{2-}}$)/($f_{S^{2-}}$).

3) When compared the sulfide capacity of binary system's silicate, CaO shows same effect as MgO.

4) C_S value of manganese and ferrous silicates is greater.

5) According to the order of P_2O_5, SiO_2 and Al_2O_3, C_S increases at the case of binary system containing CaO.

6) In the binary system of MnO-Al_2O_3, there exists a maximum at 0.82N_{MnO} so that it will show solubility limit of MnO at 1650°C. The reason why C_s rapidly decreases above 0.82N_{MnO} is considered to be a little solubility of sulfur in solid MnO.

7) To show a maximum in C_s of the binary system on Al_2O_3-SiO_2 depends upon the composition of mullite ($3Al_2O_3\cdot 2SiO_2$).

8) The appearence of maximum in the terms, (6) and (7), is based upon the amphoteritic property of Al_2O_3, and the rise of C_s within acidic region dues to discharge of oxygen ion from Al_2O_3.

9) Similar behavior of Al_2O_3 can be recogneized in the system of MgO-SiO_2-Al_2O_3. The evidence that C_s decreases at the conditions, constant SiO_2 and $N_{Al_2O_3}<N_{MgO}$, when Al_2O_3 was substituted by MgO, and the increase of C_s at the condition, $N_{Al_2O_3}/N_{MgO} > 1.5$, can be proved by thinking that Al_2O_3 shows basical property.

10) C_s value of a binary system of CaF_2-CaO is very greater and it is considered that the CaO saturation is at 0.26 N_{CaO}. As for the partition of sulfur between gas and slag phases, the following relation can be thought.

$$1/2S_{2(gas)}+(2F^{-})_{(slag)}=2F_{(gas)}+(S^{2-})_{(slag)} \qquad (23)$$

However, the interpretation that desulfurizing power becomes greater because of lower equilibrium pressure of fluorine gas phase is not right, but the reason is caused by dehydration of CaF_2 and the formation of CaO. This thought can be understood from that C_s of CaO-CaF_2 system is lower than that of the systems, CaF_2-Al_2O_3 and CaF_2-Al_2O_3-SiO_2,.

11) In the case of steelmaking slag, C_s value at 1500°C can be expressed as follows:

$$\log C_s = -5.57 + 1.39R \qquad (24)$$

where $R = N_{CaO} + 1/2N_{MgO} / N_{SiO_2} + 1/3N_{Al_2O_3}$

12) It is not numerized for steelmaking slag containing Fe_xO.

13) It must be emphasized that sulfide capacity means degree of reaction about atmospheric sulfur contacting with molten slag.

14) Of course, sulfur participating between molten metal and slag increases when C_s takes great value. However, there exits many factors to determine sulfur partition. that is to say, it is not considered the effect of various components in slag on the activities of sulfur and oxygen.

15) C_s about manganese silicate is greater than that of calcium silicate, but by considering that oxygen ion activity for manganese silicate is greater than that of calcium silicate it can be solved that sulfur partition between molten metal and slag decreases by substituting CaO in slag by MnO.

3. Relation Between Basiccty of Slag and Desulfurizing Power[29)]

3.1 High basicity slag ($CaO+MgO/SiO_2+Al_2O_3>2.3$)

In this case, Fe_xO and CaF_2 in slag can be considered to be neutral component.

As desulfurizing reaction, it follows that

$$FeS + (CaO) = (CaS) + (Fe_xO) \qquad (25)$$

whereby basical and acidic component in slag is regarded to react each other with the ratio of 2:1.

In **Fig. 9**, Fe_xO content in slag and(%S)/a_S is compared. It will be seen that the desulfurizing power diminishes with the decrease of Fe_xO content in slag.

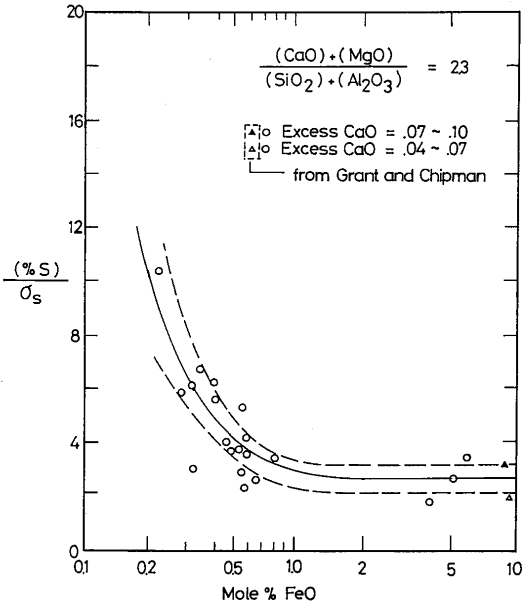

Fig. 9 Effect of iron oxide in the slag upon desulfurization ratio for slags of higher basicity of T=1600° to 1700°C. Neutralization of acids on 2:1 basis[29)]

3.2 Intermediate basicity slag ($CaO+MgO/SiO_2+Al_2O_3=1\sim2.3$)

For this region of slag composition, it is considered that basical and acidic components react with the ratio of 1;1 and that also Fe_xO and CaF_2 in slag is thought as neutral. Desulfurizing power depends upon the content of CaO and Fe_xO in slag, and the reaction of eq.(25) proceeds right hand by reducing Fe_xO in slag when the condition is under severer reducing atmosphere.

3.3 Acidic slag ($Fe_xO>10\%$)

In the slag of system MnO-SiO_2, desulfurizing reaction depends on the following partition.

$$[FeS] = (FeS) \qquad (26)$$

When a certain degree of CaO is contained in slag, CaS can be formed.

4. Influence of Various Components on The Desurizing Power

4.1 Effect of SiO_2

As shown in Fig.(5), desulfurizing power decreases by increasing SiO_2 content in slag.[19)]

4.2 Effect of carbon

As shown in **Fig. 10**, desulfurizing power increases with the decrease of cabon content at the case

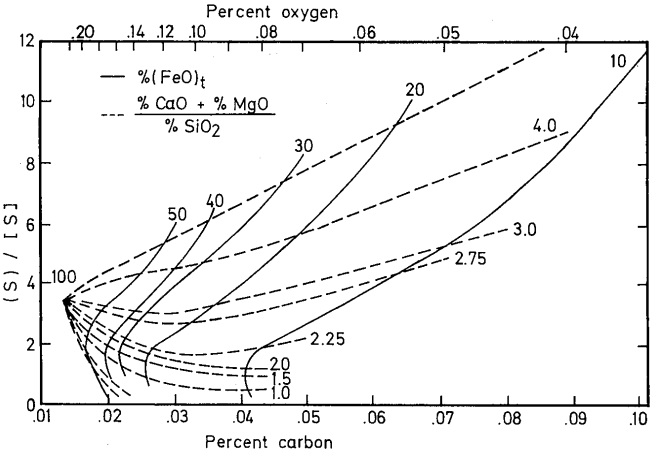

Fig. 10 Relationship among carbon and oxygen contents of the metal, the sulfur ratio, and the slag composition on a mol function basis at 1600°C[19)]

of flux composition having basicity of 1.5-2.0 under constant Fe_xO content (atmosphere, SO_2/CO mixed gases,$P_{O_2}=1\times10^{-5}$, $P_{S_2}=6\times10^{-4}$ under).[19] However, the increase of the basicity of flux increases the desulfurizing power by *increasing carbon content* under constant Fe_xO content in slag.

4.3 Effect of manganese[30]

When 8% MnO was added in the flux of system, CaO (40-50)-SiO_2(35-25)-Al_2O_3(15)-MgO(10),reversion of sulfur into metal occurs because it acts to give oxygen to metal as well as Fe_xO in slag. This behavior is contrary to the thought that MnO can be considered to be basical composition in flux.

MnO in basical flux is immediately reduced and reversion of sulfur can be found instantaneously. On the other hand, MnO in acidic flux works to reverse sulfur slowly. Instead, on either case, reaction towards reduction was recogneized more slowly than the case of Fe_xO containing flux. In **Fig. 11**, an example of additional effect of MnO in a flux on the reversion of sulfur in molten metal is shown.

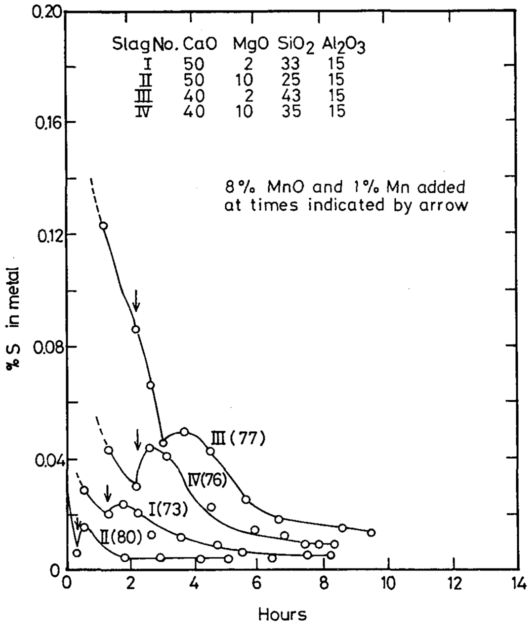

Fig. 11 Comparison of slags I to IV wherein Mn and MnO are added during the heat[30]

4.4 Effect of MgO[30]

Based on an assumption that basical and acidical components in flux combine each other to form stable compound with the ratio of 1:1, the desulferizing power and the excess base (in this case, free CaO+MgO) is compared in **Fig. 12**. From the result, it can be seen that MgO in flux diminishes the desulfurizing power.

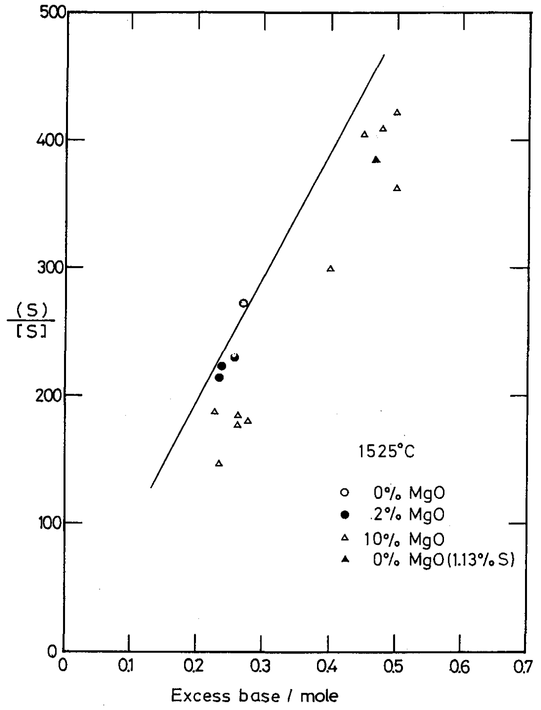

Fig. 12 Desulfurization ratio vs"excess base" at 1525°C comparing 2 and 10% MgO slags relative to the zero MgO line for slags at 1.65%S[30]

4.5 Effect of CaF_2

Recently with the desire to obtain good quality of steel containing lower content of sulfur and phosphorus, an importance of adjustment of slag composition to fulfil such a requirement can be recogneized. In **Fig. 13**, the product of the ratio of the concentration of sulfur in slag and metal, and the total iron oxide content in slag is compared with a function of the sum of acidic constituents in slag.[31] From this experiment, it was concluded that CaF_2 in slag did not show any remarkable role on the desulfurizing power. However, in the other experiment, it was indicated a question about the thermodynamical treatment.[32]

In **Fig. 14**, the additional effect of CaF_2 into a slag having the ratio, $CaO/SiO_2=1.28$, on the desulfurizing power is given as an example.

In general, acid complexes such as $Si_3O_9^{-6}$ and $Si_2O_7^{-6}$ can be considered to form in a slag of $CaO/SiO_2 \leq 1.28$ and therefrom it is satisfactory to think that the increase of the oxygen ion activity, that is to say, the increase of sulfide capacity in slag may occur. However it is wanted to do a detailed structural study about slag in future.

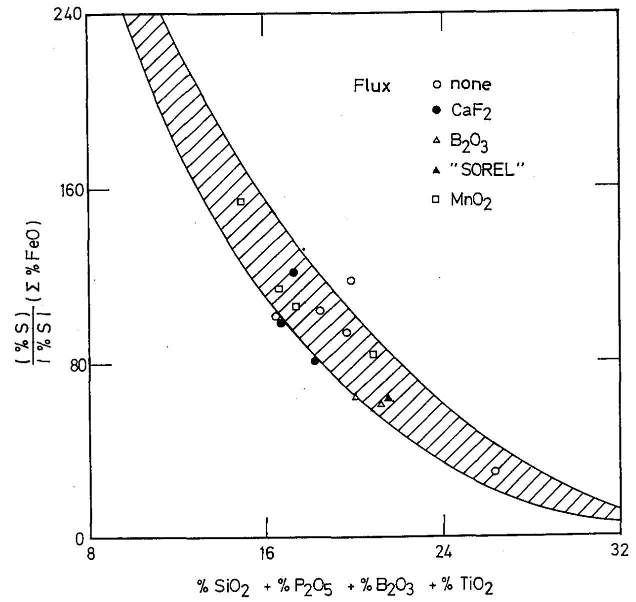

Fig. 13 Equilibrium relation for sulfur distribution between slag and metal; present data compared to a large number of plant data, represented by the hatched band[31)]

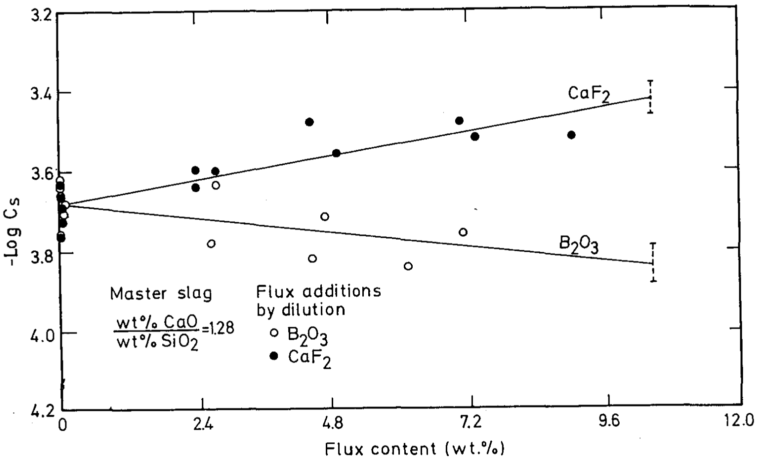

Fig. 14 The effects of CaF_2 and B_2O_3 additions on the sulfide capacities of melts with fixed CaO/SiO_2 ratio equal to 1.28 at 1503°C[32)]

4.6 Effect of the oxides of chromium and vanadium[33)]

It was presented that the oxides of chromium and vanadlum decrease the desulfurizing power of slag because the oxides act as network formers or acidic components in slag.

4.7 Effect of Na_2O and $Na_2B_4O_7$

From the olden time, it has been known that the addition of alkali metal oxide such as Na_2O, BaO, and SrO shows prominent desulfurizing power.

The desulfurizing power can be arranged with a following order:[34)]

$Na_2O > BaO > SrO > CaO > MgO$

Reduction of SiO_2 to metallic silicon in molten metal depends on the bonding strength of metasilicate and therefore the value decreases with the order above-described. With increasing the content of metallic silicon in molten metal, sulfur content in molten metal decreases. However, it must remember that the vaporization of sodium from the slag becomes greater with the increase of operating temperature, and the composition of slag changes to acidic with the time passage.

When it was added with the form of Na_2CO_3, the following reaction proceeds.

$$(FeS)+(Na_2CO_3)+[Si] =(Na_2S)+(SiO_2)+[Fe]+\{CO\} \quad (27)$$

If excess Na_2CO_3 above to be combined with sulfur is added, the following reaction occurs.

$$(Na_2CO_3)+[Si]=(Na_2O\cdot SiO_2)+[C] \quad (28)$$

In the case of 50% CaO-30% CaF_2-20% $Na_2B_4O_7$ system, it is considered that the addition of special component makes an activity of CaO to be higher and deminates the viscosity. For the desulfurizing power, CaF_2 as well as $Na_2B_4O_7$ is considered to effective.[35)]

5. State of Sulfur in Slag

At present, it is an important matter to determine the state of sulfur in slag from the viwpoint of architectural and civil engineerings. It is doing detailed investigation for the microscopical problems, because a large quantity of iron-and steel-makings slag can be produced in Japan.

Using chemical analysis, it was certified that sulfide equilibrium is of importance at oxygen pressures $10^{-5}-10^{-6}$ atm.and sulfate equilibrium is of importance at oxygen pressures $10^{-3}-10^{-4}$ atm..[36),37)]

We have applied the chemical shift study using emission X-ray spectrometry to identify the state of sulfur in slag of the system Na_2O-SiO_2 containing iron ion and sulfur.[38)] In **Fig. 15**, the result obtained is given. From this diagram, it has been concluded that slag produced in air shows the formation of sulfate and slag under $P_{O_2}=10^{-6.7}$ atm. shows the half chemical shift value between elementary sulfur and sulfate. Further it was certified that the ratio of Na_2O/SiO_2 did not give change on chemical shift value.

Also the detailed investigation using electron spin resonance (ESR) and optical absorption of visible ray was performed to know state of sulfur in slag.

Table 1 Summary of optical absorption, ESR and S K_α X-ray emission measurements[38)]

Method	Noticed peak	Detectable state	Partial oxygen pressure (atm.)		
			0.21	$10^{-5.1}$	$10^{-6.7}$
ESR	peak near g=6.0	$Fe^{3+}-S^{2-}$ interaction	unchanged	unchanged	increase
Optical absorption	peak near 24000 cm^{-1}	$Fe^{3+}-S^{2-}$ interaction or polysulphude ions	undetected	detected	detected
Emission S K_α X-ray	chemical shift	valency state	S^{6+}	——	S^0, S^{6+} and small S^{2-}

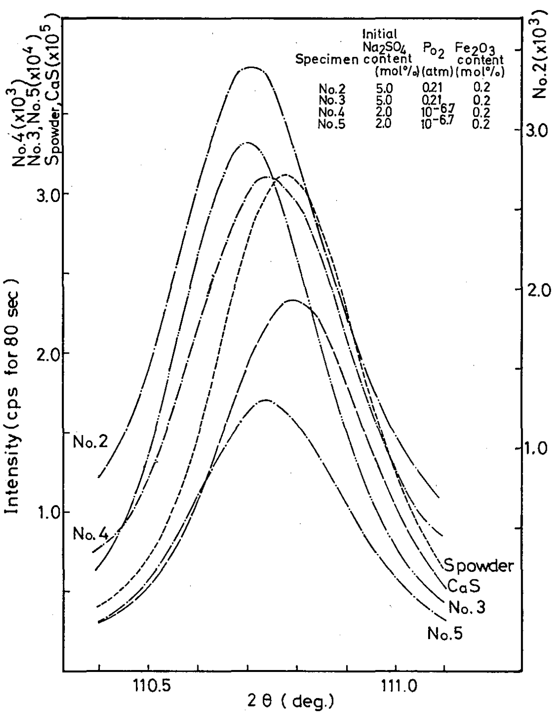

Fig. 15 K_α X-ray emission spectra of soda silicate with iron and sulfur[38)]

The summary of the results is given in **Table 1.** As conclusion, it seems appropriate to think that the state of sulfur in slag of the system Na_2O-SiO_2 changes from S^{6+} to S^{2-} via polysulfide ions such as intermediate stage with the decrease of oxygen partial pressure in atmosphere regardlss of the existence of iron ion in slag. Further $Fe^{3+}-S^{2-}$ interaction occurs when the formation of S^{2-} begins at $P_{O_2}=10^{-6}\sim10^{-7}$.

5. Summary

It is an important matter to produce a good quality of steel and weld metal. Especially, the harmful effect of sulfur in metal has been emphasized.

In this review, the author have summarized the parameters to deterine the desulfurizing power of slag. with the development of out-of-furnace refining process to remove sulfur and phosphorus in steelmaking, the importance of basic component such as Na_2O to be contained in slag has attracted attention.

The achievement using physical means such as ESR and X-ray emission chemical shift study to determine the state of sulfur in slag in our laboratory was refered. In future, it will be achieved the good choice of slag composition to remove sulfur during short time in welding with the fundamental clarification of the structure of slag.

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