STUDIES OF THE DESULPHURIZATION OF MOLTEN PIG IRON BY MANGANESE

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CONTENTS

Synopsis

From the thermodynamical viewpoint of molten pig iron, the desulphurization by manganese is studied. The effective desulphurization is expected to be attained at lower temperature under the carbon saturation. The equilibrium between manganese and sulphur in carbon saturated liquid iron is shown by approximately $K'' = [\%\mathrm{Mn}][\%\mathrm{S}]$ which is valid in the ordinary blast furnace pig iron and it follows:

$$\log K'' = -9{,}763/T + 5.197$$

The presence of silicon tends to improve the desulphurization by manganese at carbon saturation but the effect is negligible up to 2% Si. On the other hand, the presence of phosphorus is somewhat reversely effected.

The desulphurization product is found at 1,500° C to be a solution where FeS dissolvs into MnS and the activity of MnS also is discussed.

Nomenclature

a_i	activity of component i
$e_i^{(j)}$	interaction parameter $\partial \log f_i / \partial w_j$
F°	free energy in standard state
f_i	activity coefficient of component i (Henry's Law)
$f_i^{(j)}$	interaction coefficient
K	equilibrium constant
N_i	mole fraction of component i
p_i	partial pressure of component i
T	absolute temperature
$X(\mathrm{g})$	gas X
$X(\mathrm{l})$	liquid X
$X(\mathrm{s})$	solid X
$\underline{X}$	component X in liquid iron
$[\% X]$	weight percentage of component X in liquid iron
γ_i	activity coefficient of component i (Raoult's Law)
Δ	change of a thermodynamic function
$\varepsilon_i^{(j)}$	interaction parameter $\partial \ln \gamma_i / \partial N_j$

Introduction

In the iron- and steel-making processes the desulphurization is one of the most important working conditions, since sulphur has a harmful effect on iron and steel quality such as so called red shortness. One of the important functions of to-day's iron blast furnace is the desulphurization of pig iron which is established by the basic slags in the furnace. However, this operation is based on those charges of relatively good qualities, as rich ores and good coke. If once especially the iron ore becomes poor how the blast furnace operation encounters difficulties may be clearly observed in the Japanese blast furnaces during and immeadiately after the World War II.[1] It was beyond the desulphurizing ability of blast furnace. In such cases, it may be desirable that the desulphurization is carried out after tapping of pig iron rather than by a large amount of slag inside the furnace.

Recently, several desulphurizing methods outside the blast furnace have developed. For example, the fluidized injection method[2] by which lime or calcium carbide powder is blowed into molten pig iron with nitrogen gas and the Kalling process[3] deviced by Kalling in Sweden are known as excellent methods. However, since these methods require some of skill and some installations, it may be somewhat difficult to apply to a large amount of pig iron.

It is well known that those pig irons produced for steel-making are generally reserved in the mixer and consequently decrease their sulphur content by precipitating manganese sulphide. It may be favorable if the manganese in the melts is more effective for lowering sulphur under any conditions. Those conditions may perhaps depend upon the reactivity for desulphurization of pig iron.

Then it becomes more important to know the most favorable condition for the desulphurization by manganese contained in the ordinary pig iron, in order to establish the more reasonable desulphurization throughout the whole iron- and steel-making processes. Moreover, in predicting the future of raw materials for iron blast furnace it will become more serious to obtain the effective desulphurization.

The present research has been pursued on the desulphurization by manganese under various conditions, especially on the standpoint of thermodynamical character of molten pig iron, and established the correct desulphurizing power of manganese.

Chapter I. Review of Literature on the Desulphurization by Manganese

1. Introduction

The desulphurization in the iron- and steel-making processes has been studied by many investigators, and also there is a considerable amount of informations in the literature concerning the desulphurization by manganese.

They are classified into three groups. First, the studies on the practical data of various works, second, those on the researches in laboratories and third, those based on the thermodynamical calculations. From this classification examining and summarizing the main researches in the literature, the authors try to solve some problems to obtain the exact knowledge of the desulphurization by manganese.

2. Studies in the practical works on the desulphurization by manganese

The contribution of manganese in liquid iron to desulphurization was already known early in the present century as an empirical fact; for example, it was seen in the paper of Heike.[4] He showed that the molten pig iron containing 0.15 per cent sulphur lowers its sulphur contents during transfering in the ladle with

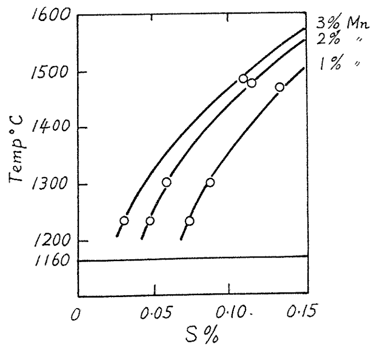

FIG. 1. Decrease of sulphur content in molten pig iron as temperature lowers (Heike).

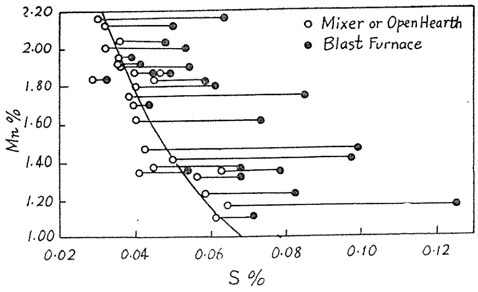

FIG. 2. Desulphurization of molten pig iron during transfering from blast furnace to mixer or open hearth furnace (Herty, Gaines).

decreasing temperature as shown in Fig. 1. Namely, it is expected to obtain considerably low sulphur pig iron at about 1,200° C if it contains manganese above 2 per cent. Herty and Gaines⁵⁾ first suggested a theoretical consideration about the desulphurization phenomena after tapping from blast furnace as a desulphurizing reaction. They examined precisely the behavior of manganese and sulphur of molten pig iron in the ladles from blast furnace to open hearth furnace or mixer and found the desulphurizing ability of manganese as Fig. 2. The curve in the Figure is recognized as the equilibrium of manganese and sulphur at the temperature of the open hearth furnace or the mixer. Moreover, they expressed the desulphurization reaction as follows,

$$\mathrm{FeS} + \mathrm{Mn} = \mathrm{MnS} + \mathrm{Fe} \tag{1.1}$$

and regarded its equilibrium constant as $K_s'' = [\mathrm{Mn}][\mathrm{S}]$ and found K_s'' is constant at definite temperature. The equilibrium condition of molten pig iron travelling in the ladle to the mixer was found as $[\mathrm{Mn}\,\%][\mathrm{S}\,\%] = 0.070$ at 1,315° C. Since then the idea that the desulphurization equilibrium is shown by K_s'' has been widely adapted and then remarkably developed in the laboratory works. Herty⁶⁾ showed further values as K_s'';

	1,300° C	1,366° C	1,580° C
K_s''	0.07	0.10	0.86

Daeves⁷⁾ gave the value of $[\mathrm{Mn}\,\%][\mathrm{S}\,\%]$ as 0.088 for thomas pig iron after tapping from blast furnace, but did not indicate its temperature. Geiger⁸⁾ showed the desulphurization in mixer at Bethlethem Steel Co. as follows.

No. of test	S% (B.F.)	S% (mixer)	Mn%
21	0.0867	0.040	1 ~1.5
89	0.070	0.035	1.5~2.5
26	0.073	0.031	2.0~3.0

In Japan also the behavior of sulphur in molten pig iron after tapping from blast furnace was studied. For example, at Kawasaki Iron and Steel works of

Nippon Kokan Co.,[9] it was reported that $K''_S = 0.88$ at tapping from blast furnace decreases to 0.04 at mixer, and also at Yawata and Hirohata works those data as shown in Fig. 3 were obtained.[10]

After all, it is clear that the main desulphurization effect of manganese in molten pig iron is limited after tapping from blast furnace and the lowering of temperature promotes the desulphurization.

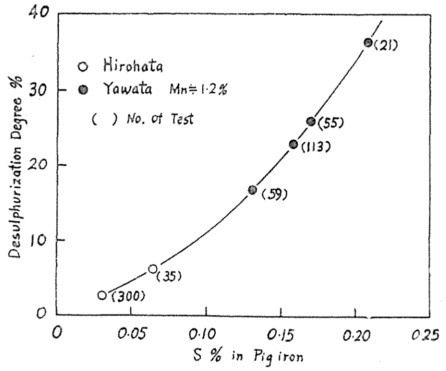

FIG. 3. Desulphurization degree of pig iron found in Japanese blast furnaces.

3. Studies in the laboratory on the desulphurization by manganese

It is by Schütz's work (1907)[11] that the desulphurization reaction of manganese has been first studied in laboratory. He examined the equilibrium between metal and slag which were formed by melting the mixture of Fe + MnS or Mn + FeS in a graphite crucible. It is doubtful whether the metal and slag phases were separated completely from each other as indicated by McCance.[12] The authors also tried the similar experiment as a preliminary work in the experiment as described later (Chapter VI), but the separation of both phases was difficult. Further, Herty and True (1925)[13] examined the reversibility of the desulphurization reaction of manganese by a similar experiment. Schenck and Söhnchen (1932)[14] determined the equilibrium between manganese and sulphur at 1,400° C in those iron melts which contained 2.9～5.4% C, 0～3.4% Mn and showed the desulphurization equilibrium curve. Meyer and Schulte (1934)[15] have studied the reaction FeS + Mn = MnS + Fe by a more detailed experiment. They melted those mixture of Fe, Mn, MeS in sinter corundum crucibles by the Tammann furnace and examined the solidified metals and slags. The results gave the following equilibrium data at 1,600° C about the pure Fe-Mn-S melts.

$$K_1 = (\mathrm{Fe})[\mathrm{Mn}]/(\mathrm{Mn})[\mathrm{Fe}] = 0.000425 \pm 0.000125$$
$$K_2 = [\mathrm{S}][\mathrm{Mn}]/(\mathrm{S})[\mathrm{Fe}] = 0.000725 \pm 0.000175.$$

They also discussed the value of $K''_S = [\mathrm{Mn}][\mathrm{S}]$ at 1,600° C which was 2.6 in carbon free iron melts, but 1.2 in carbon containing melts.* Furthermore the latter lowered to 0.75 with lowering of the temperature to 1,250～1,350° C. The addition of silicon of 3 to 5 per cent was effective for lowering sulphur content. Although they examined the many detailed experiments, it remains some doubt about the separation of metal and slag phases as above mentioned. Wentrup (1936)[16] investigated the effect of silicon, carbon and phosphorus on the desulphurization of molten pig iron by manganese. The large discrepancy of his data on the melts of Fe-C-Mn-S system at the temperature between 1,400° C and 1,600° C may be ascribed to their carbon contents which were scattered between 2.14 and 6.1 per cent. The data shows that the low carbon melts has generally high sulphur content and high carbon content is effective for desulphurization. Next, it is found

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* C 1.2～3.9%, Mn 2.35～6.66%.

that the addition of 2.1 per cent silicon is effective for lowering sulphur in the melts which have 3~4 per cent carbon, 1~2 per cent silicon, 0~2.0 per cent manganese. For example, at 1,300° C, sulphur content lowers from 0.09 to 0.07 by the addition of 2.1 per cent silicon in the range of 1~2 per cent manganese. These melts, however, were equilibrated in alumina crucibles and then were not saturated with carbon. The addition of 2 per cent phosphorus was also effective for lowering sulphur at 1,350° C. Their data are found about various constitutions of molten pig iron at several temperatures, but are not sufficient to determine the desulphurization equilibria at definite conditions. Moreover, the accuracy of their experimental method seems to be somewhat inferior. Oelsen (1938),[17] in his study on the desulphurization of soda, explained the sulphide slag as the desulphurization product by manganese on the molten pig iron at 1,600~1,620° C. However, the experimental procedure was not described. Matoba and Uno[18] measured the equilibrium of the molten iron containing manganese with the gas mixture of hydrogen and hydrogen sulphide at about 1,600° C. They gave the equilibrium constant K'' as follows, on the asumption that the desulphurization product is saturated with manganese sulphide.

$$\log K'' = -969/T - 0.106. \tag{1.2}$$

However, they did not determine about the carbon containing iron melts such as pig iron and it is doubtful whether the above equation is able to apply to the pig iron range.

Recently, Oelsen (1946)[19] determined the equilibrium between manganese and sulphur of the carbon saturated iron melts and compared with those of the carbon free melts at 1,570° C. Though his original paper can't be obtained, the equilibrium is shown as Fig. 4 which is quoted in "Basic Open Hearth Steel-making".[20] His data on the equilibrium between manganese and sulphur seem most detailed and reliable, though the effect of silicon or phosphorus has not been described.

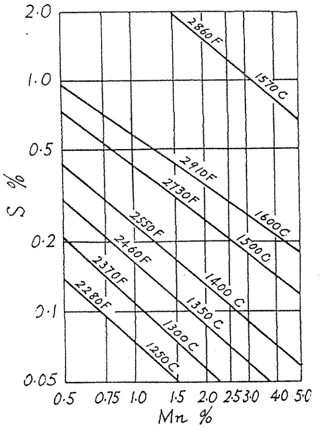

FIG. 4. Equilibrium between manganese and sulphur in carbon saturated iron (Oelsen). The line at 1,570° C represents the equilibrium in pure iron,

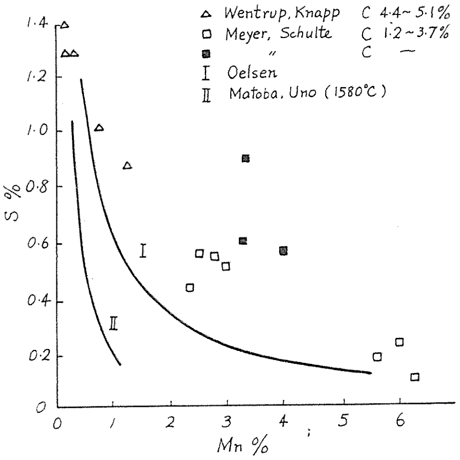

FIG. 5. Equilibrium between manganese and sulphur in liquid iron at 1,600° C.

Generally speaking, many works in the literature as above mentioned were fragmentary and the data were scattering even at the same temperature. For example, compared the data at 1,600° C with each other, it is surprizingly scattered as shown in Fig. 5. It seems that the particular attention was not given to the change of carbon content as for liquid steel or pig iron. Furthermore, the measured values at about 1,200° C are scarcely known except those of Oelsen, notwithstand the possibility of effective desulphurization at lower temperature.

4. Thermodynamical studies on the desulphurization reaction of manganese

Considering from chemical thermodynamics, the desulphurizing power of manganese is represented as the magnitude of the affinity for sulphur. From this standpoint of view, Shibata (1927)[21] first gave the theoretical consideration on the desulphurization reaction of manganese. He described the reaction as

$$\mathrm{FeS} + \mathrm{Mn} \rightleftharpoons \mathrm{MnS} + \mathrm{Fe}$$

and found the dissociation pressures of FeS and MnS by application of Nernst's equation as follows.

$$\log p_{S_2(\mathrm{MnS})} = -\frac{121{,}200}{4.575\,T} + 1.75 \log T + 2.43 \tag{1.3}$$

$$\log p_{S_2(\mathrm{FeS})} = -\frac{76{,}860}{4.575\,T} + 1.75 \log T + 2.43. \tag{1.4}$$

Then, equilibrium constant K was given by Eq. (1.5)

$$\log K = \log \frac{C_{\mathrm{MnS}}}{C_{\mathrm{Mn}} \cdot C_{\mathrm{FeS}}} = \frac{1}{2}[\log p_{S_2(\mathrm{FeS})} - \log p_{S_2(\mathrm{MnS})}]. \tag{1.5}$$

The values of K were calculated as follows.

Temp. °C	1,400	1,500	1,600	1,700
K	7.925	5.445	3.882	2.89

The desulphurization degree of manganese was taken as $C_{\mathrm{MnS}}/C_{\mathrm{FeS}} = C_{\mathrm{Mn}} \cdot K$ and was shown as Fig. 6.

It is observed that the desulphurization degree becomes better, the more manganese increases and the lower temperature descends, but there is a considerable doubt to apply that to the molten metal since the heat of fusion of iron or manganese and the heat of solution of sulphur in liquid iron were not taken into account in his calculation.

McCance (1938)[22] also calculated the equilibrium constant from the data of the dissociation pressure given by Britzke and Kapustinsky[23] and showed that $\log K = 5{,}820/T - 1.675$. The value of K at 1,600° C becomes 0.27 which is not agreed with Shibata's value. Sano (1936)[24]

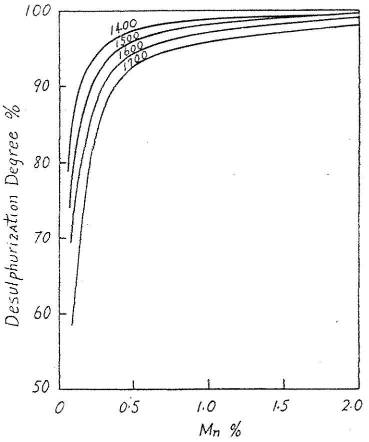

FIG. 6. Desulphurization degree of manganese calculated thermodynamically by Shibata.

examined the desulphurizing ability of manganese calculating by the chemical thermodynamical values. He calculated the dissociation pressure and the free energy change of formation of FeS from the reduction equilibrium data of FeS by hydrogen given by Britzke and Kapustinsky and then those of MnS by using the similar thermodynamical data obtained by Britzke, Kapustinsky and Wesselowsky[25] and then found the free energy change of the desulphurization reaction of manganese as follows:

$$\mathrm{FeS(l)} + \mathrm{Mn(l)} \rightleftharpoons \mathrm{MnS(l)} + \mathrm{Fe(l)} \tag{1.6}$$

$$\varDelta F^\circ = -20{,}591 + 3.518\,T\ln T - 0.001315\,T - 18.35\,T. \tag{1.7}$$

Then, the values of K is calculated from $\varDelta F^\circ = -RT\ln K$,

Temp. °C	1,600	1,650	1,700
$K = \dfrac{[\mathrm{MnS}][\mathrm{Fe}]}{[\mathrm{FeS}][\mathrm{Mn}]}$	14.42	12.32	10.60

There are not agreed with Shibata's data and Fig. 7 represents the relation between manganese per cent and [MnS]/[FeS] from the above data.

It can hardly avoid a conclusion that sulphur in iron is not practically possible to combine with manganese as manganese sulphide.

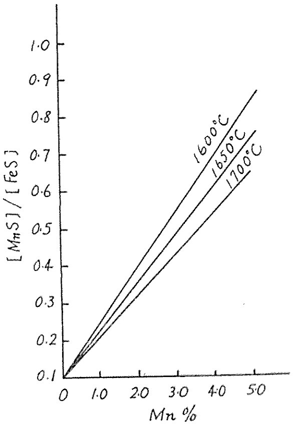

FIG. 7. Relation between manganese per cent and the ratio [MnS]/[FeS] calculated by Sano.

After all, from the conclusion of the thermodynamical calculation the desulphurizing power of manganese is extremely weak and then manganese is not expected to be useful for practical desulphurization. This conclusion, however, does not agree with many experimental data in practical works. In the theoretical calculations there are somewhat defectives, such as thermodynamical characteristics of sulphur dissolved in liquid iron. Although the activity coefficient of sulphur in liquid iron was accepted nearly unity, it has been recently considered as described in the following chapter, that it might be increased largely by the existence of carbon, silicon and so on, especially as in the pig iron. With due regard to the fact, Sano calculated again the desulphurization reaction thermodynamically and found the following equation.[26]

$$\varDelta F^\circ = -24{,}110 + 16.91\,T \tag{1.8}$$

$$\log K = \log\,[\mathrm{Mn}][\mathrm{FeS}] = \frac{5{,}369.945}{T} + 3.696. \tag{1.9}$$

The results suggest the possibility of lowering sulphur considerablly at about 1,200° C in any manganese content. Therefore since the desulphurization efficiency of manganese depends largely on the amount of activity coefficient of sulphur, the necessary thermodynamical characteristics will be discussed in the next chapter.

5. Conclusion

The discrepancies among the results obtained by the many investigators on the desulphurization reaction of manganese are found to be ascribed to the differences of the activity coefficient of sulphur in liquid iron rather than the experimental errors. Therefore, the correct knowledge of the desulphurizing ability of manganese will be obtained by the experiment or the calculation under definite activity coefficient of sulphur.

Chapter II. Thermodynamical Characteristics of Fe-C-S Solution and Thermodynamical Consideration of Desulphurization Reaction

1. Introduction

In recent years, the influences of various alloying elements on the activity coefficient of sulphur in liquid iron have been confirmed,[27)] although formerly the behavior of sulphur in liquid iron was not sufficiently understood. The results shows the necessity of discussing the desulphurization reaction of manganese on the standpoint of the activity of sulphur in liquid iron.

In the present chapter, considering the thermodynamical characteristics of the system of Fe-C-S solution which have been given in the literature, the authors try to give the thermodynamical consideration of the desulphurization reaction of manganese using the recent thermodynamical data.

2. Thermodynamical characteristics of Fe-C-S solution

As the basis for the molten Fe-C-S system, the equilibrium diagram of Fe-C-S system should be necessary. This system was studied formerly by Vogel[28)] and then by Sato.[29)] Fig. 8 was given by Sato and shows the range of the two immiscible phases in the liquid. This interesting fact is considered as based upon the difference of the liquid structures of molten Fe-C alloy and Fe-S alloy. The figure shows that the solubility of sulphur in liquid iron decreases remarkably by carbon addition.

It is generally accepted that the activity coefficient of component X increases with component Y, if the solubility of X is decreased by addition of Y. Thus, from the above diagram it will be recognized that the activity coefficient of sulphur in liquid iron may increase with carbon addition.

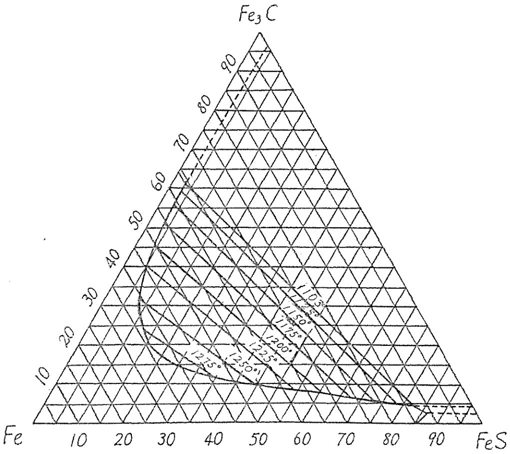

FIG. 8. Ternary diagram of the system Fe-Fe_3C-FeS (Sato).

On the two immiscible phases of Fe-C-S system several investigations have been given by such as Vogel,[28)] Sato,[29)] Schenck,[30)] Darken and Larsen,[31)] Naro and Lundquist[32)] and recently Turkdogan and Hancock.[33)] The main data on the sulphur solubility in the carbon saturated molten iron are summarized in Table 1. Although good agreement is not found between them, the solubility of sulphur in the carbon saturated molten iron seems to be nearly independent of the temperature, referring the recent research of Turkdogan *et al.*

TABLE 1. Compositions of Two Immiscible Phases of Fe-C-S System

Temp. (°C)	C-rich (C%)	Phase (S%)	S-rich (C%)	Phase (S%)	Experimental condition	Author
1,500	4.0	1.5	—	—	N_2 atmosphere	Darken and Larsen
1,500	4.23	1.77	0.90	26.5	A 〃	Turkdogan and Hancock
1,350	3.78	1.94	0.72	26.9	A 〃	〃
1,200	3.60	1.82	0.35	28.4	A 〃	〃
1,245	2.12	2.5	0.65	15.2	—	Vogel and Ritzau
1,205	2.8	1.2	0.45	20.5	—	〃
1,160	3.4	1.0	0.3	25.9	—	〃

Thus, the solubility of sulphur in molten iron is found to be only about 1.8 per cent and this is equilibrated with the melt contained 0.9% carbon and 26.5% sulphur at 1,500° C. Now, since the chemical potential of sulphur in both phases should be equal, the activity coefficient of sulphur in carbon rich melt must be large. However, only from those data the important information on the activity coefficient of sulphur can't be obtained.

On the other hand, the chemical behavior of sulphur in molten Fe-S binary alloy was found by Sherman, Elvander and Chipman[34] as shown in Fig. 9. It is observed that the activity coefficient of sulphur in this binary alloy deviates negatively from Henry's Law in above 1% sulphur, and the relation between $\log f_s$ and

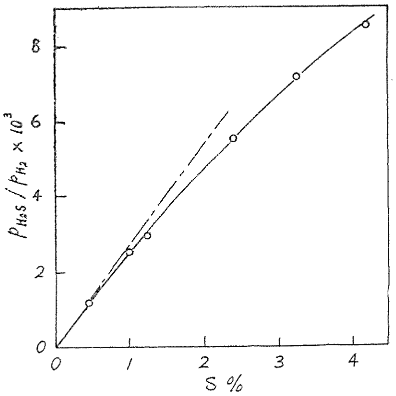

FIG. 9

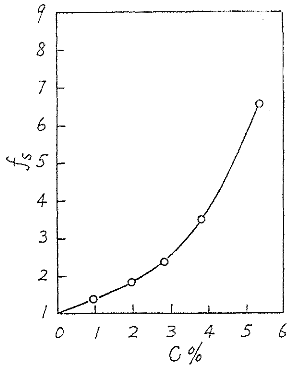

FIG. 11

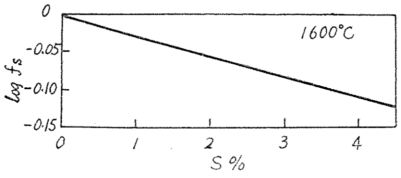

FIG. 10

FIG. 9. Equilibrium between sulphur in liquid iron and gas mixture, at 1,600°C (Sherman, Elvander, Chipman).

The broen line represents Henry's law.

FIG. 10. Logarism of the activity coefficient of sulphur as a linear function of concentration.

FIG. 11. Effect of carbon content on activity coefficient of sulphur in iron at 1,600° C (Morris, Buehl).

sulphur per cent is also shown as a linear function as Fig. 10. Assuming that the extraporation of the relation to 26.5% S is valid approximately, logf_s becomes 0.2. Then, neglecting the effect of 0.9% carbon, the activity becomes $26.5 \times 0.2 = 5.3$ and the activity coefficient of sulphur in the carbon rich phase which has 4.23% carbon and 1.8% sulphur becomes $5.3/1.8 \fallingdotseq 3$. Namely, the activity coefficient of the high carbon iron melt may be nearly 3 and then pig iron may be advantageous for desulphurization rather than steel, especially in the discussion of desulphurization by manganese.

Nearly recently, the effect of carbon on the activity coefficient of sulphur in liquid iron was determined by Morris and Buehl[35] and the results shows that the above estimation does not largely make error. The relation between f_s and carbon per cent at 1,600° C is shown as Fig. 11 which seems to be most reliable to this day, and hence the following discussion will be based on their data.

3. Thermodynamical values of sulphur in liquid iron alloys

In early studies on the preliminary thermodynamical calculation of desulphurization the thermodynamical values of sulphur in liquid iron were not yet known sufficiently. Formely, the behavior of sulphur was simply considered as FeS(l), of which thermodynamical values were taken for the calculation. However, now it is not regarded as appropriate to assume the molecular FeS(l) in liquid iron, but it is recognized that the atomic sulphur is distributed at random in the quasi-crystalline lattice of molten iron, and accordingly that the existence of the third element causes an interaction to the sulphur atom. This effect may be found as the characteristic behavior of molten Fe-X-S alloy as described previously.

Now, the investigation by Sherman and Chipman[27] on the ternary iron melt of Fe-X-S system (X represents a third element) is very important to consider the desulphurization reaction. The effects of the third elements on the activity coefficient of sulphur in the ternary system were shown as the interaction parameter by Chipman[56] as shown in Table 2 and represented in Fig. 12.

TABLE 2. Interaction Parameter

$$\varepsilon_s^{(j)} = \frac{\partial \ln f_s}{\partial N_j}$$

j	$\varepsilon_s^{(j)}$
C	+6.0
Al	+6.5
Si	+7.5
P	+5.7
Mn	−5.7
Cr	−3.2
Ni	0

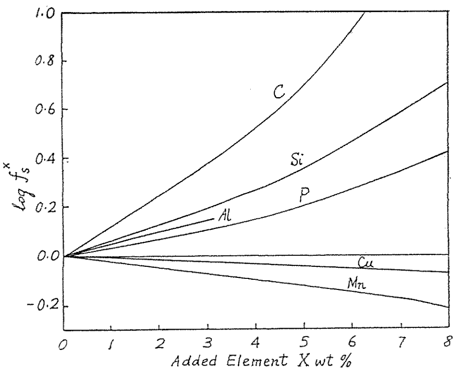

FIG. 12. Effects of several elements on the activity coefficient of sulphur (Sherman, Chipman).

In the multicomponent systems the activity coefficient of sulphur can be calculated by the simple relation derived by Wagner[37] in their lower concentrations as shown by the following equation.

$$f_S = f'_S \cdot f_S^{(3)} \cdot f_S^{(4)} \cdot \cdot \cdot \cdot f_S^{(i)}. \qquad (2.1)$$

While this relation is thermodynamically valid for extremely dilute solutions dissolved components 2, 3, 4, · · · i in component 1, its application to these solutions of higher concentration must be estimated only from experiment. For example, as shown in Fig. 12, the effects of Si and C are considerably large and so the application of the above relation is somewhat doubtful in their higher concentrations.

4. Thermodynamical values of manganese in liquid iron

It is well known that the behavior of manganese in liquid iron is ideal in the whole range of Fe-Mn binary system. Recently, Ohtani[38] examined the activities of manganese and carbon in the molten Fe-C-Mn alloy. He found that manganese shows negative deviation from Raoults Law at higher concentrations of carbon and manganese and obtained the following equation, showing the effect of carbon on the activity coefficient of manganese as $\gamma_{\mathrm{Mn}}^{(\mathrm{O})}$.

$$\log \gamma_{\mathrm{Mn}}^{(\mathrm{O})} = -3\, N_{\mathrm{Mn}} \cdot N_{\mathrm{C}}/(1 - N_{\mathrm{O}})^2 \qquad (2.2)$$

where N_{Mn}, N_{C} represented mole fraction of manganese and carbon and the standard state of the activity coefficient of manganese was taken as pure manganese. Applying the equation in the present consideration, the values of $\gamma_{\mathrm{Mn}}^{(\mathrm{O})}$ are found to be nearly unity in the carbon saturated iron melts under lower manganese concentrations. Namely, the behavior of manganese is also found to be ideal at the presence of carbon in the present work.

5. Thermodynamical calculation of desulphurization reaction of manganese

As above mentioned, since the enough knowledge of the thermodynamical behaviors of sulphur and manganese in liquid iron has been recently obtained, the authors try a thermodynamical calculation of the desulphurization reaction of manganese, using the nearest data of the concerning thermodynamical values. The reaction is shown as Eq. (2.3)

$$\underline{\mathrm{S}} + \underline{\mathrm{Mn}} = (\mathrm{MnS}) : K = \frac{a_{\mathrm{MnS}}}{a_{\mathrm{S}} \cdot a_{\mathrm{Mn}}}. \qquad (2.3)$$

If the desulphurization product is regarded as pure MnS, a_{MnS} becomes unity and Eq. (2.4) is written,

$$K' = a_{\mathrm{S}} \cdot a_{\mathrm{Mn}} = a_{\mathrm{S}}[\mathrm{Mn}\,\%]. \qquad (2.4)$$

If the free energy change of the reaction (2.3) is known, the equilibrium values of the desulphurization by manganese can be obtained. First, it is necessary to know the thermodynamical values of MnS for the calculation. The data on free energy of formation of MnS have been obtained as follows at considerably higher temperatures

$$2\,\mathrm{Mn} + \mathrm{S}_2 = 2\,\mathrm{MnS} \quad \Delta F^\circ = -138.020 + 37.72\,T \quad (1{,}517 \sim 1{,}803^\circ\,\mathrm{K}) \qquad (2.5)$$

Richardson and Jeffes.[39]

$$\Delta F^\circ = -137.400 + 38.2\,T$$

B.O.H.S.

Both agree well with each other, then now the data of Richardson *et al.* are taken.

On the sulphur in liquid iron, the recent equilibrium data of Sherman, Elvander, Chipman[84] are used:

$$\underline{S} + H_2 = H_2S(g) \qquad \Delta F^\circ = 9{,}840 + 6.54\,T. \tag{2.6}$$

The free energy of formation of H_2S shows Eq. (2.7) from B.O.H.S.[41]

$$2\,H_2(g) + S_2 = H_2S(g) \qquad \Delta F^\circ = -43{,}160 + 23.61\,T. \tag{2.7}$$

Substracting this from the Eq. (2.5),

$$Mn + H_2S = MnS + H_2 \qquad \Delta F^\circ = -47{,}430 + 7.055\,T. \tag{2.8}$$

For the fusion of manganese and the solution in liquid iron as 1% solution,[41]

$$Mn(s) = Mn(l) \qquad \Delta F^\circ = 3{,}560 - 2.38\,T \tag{2.9}$$

$$Mn(l) = \underline{Mn}\ (\%\ \text{in l Fe}) \qquad \Delta F^\circ = -9.11\,T. \tag{2.10}$$

Then, substracting the Eq. (2.9) and Eq. (2.10) from Eq. (2.8), it follows that,

$$\underline{Mn} + H_2S = MnS + H_2 \qquad \Delta F^\circ = -50{,}990 + 18.545\,T. \tag{2.11}$$

Combining Eq. (2.11) with Eq. (2.6), the following Eq. (2.12) will be obtained as the desulphurization reaction of manganese

$$\underline{S} + \underline{Mn} = (MnS) + Fe \qquad \Delta F^\circ = -41{,}150 + 25.058\,T \tag{2.12}$$

or

$$\log K = \frac{8{,}994.53}{T} - 5.483. \tag{2.13}$$

Hence, calculating K and K' from these equations, Table 3 and Fig. 13 are obtained.

TABLE 3. Equilibrium Constant K and K' of the Reaction (2.12)

	1,200° C	1,300° C	1,400° C	1,500° C	1,600° C
$\log K$	0.6233	0.2351	−0.1073	−0.4099	−0.6808
K	4.201	1.718	0.7802	0.3891	0.2085
K'	0.238	0.582	1.28	2.57	4.80

Now, taking the activity coefficient of sulphur into consideration in Eq. (2.1), the equilibrium curves between manganese and sulphur in pure iron and carbon saturated iron are compared approximately by calculating from Eq. (2.13). The calculation is based on the assumption that pure iron is liquid below 1,500° C and the effect of co-existence of manganese and sulphur on the carbon solubility can be neglected. The results are summarized in Fig. 14 at the temperatures between 1,500° and 1,200° C. It will be noted that the considerable desulphurization is expected in the existence of manganese above 1 per cent only at carbon saturation and at about 1,200° C, although it can't be attained in pure iron even at considerably higher manganese concentrations.

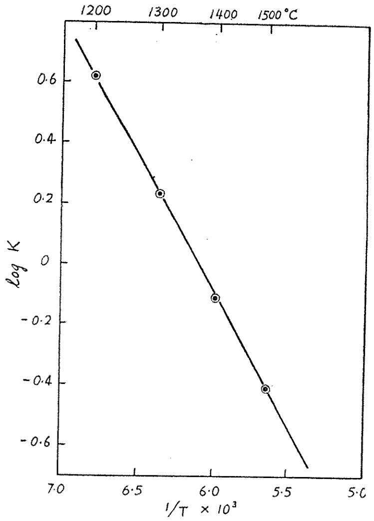

FIG. 13. Effect of temperature on the equilibrium constant of the desulphurization reaction (calculated).

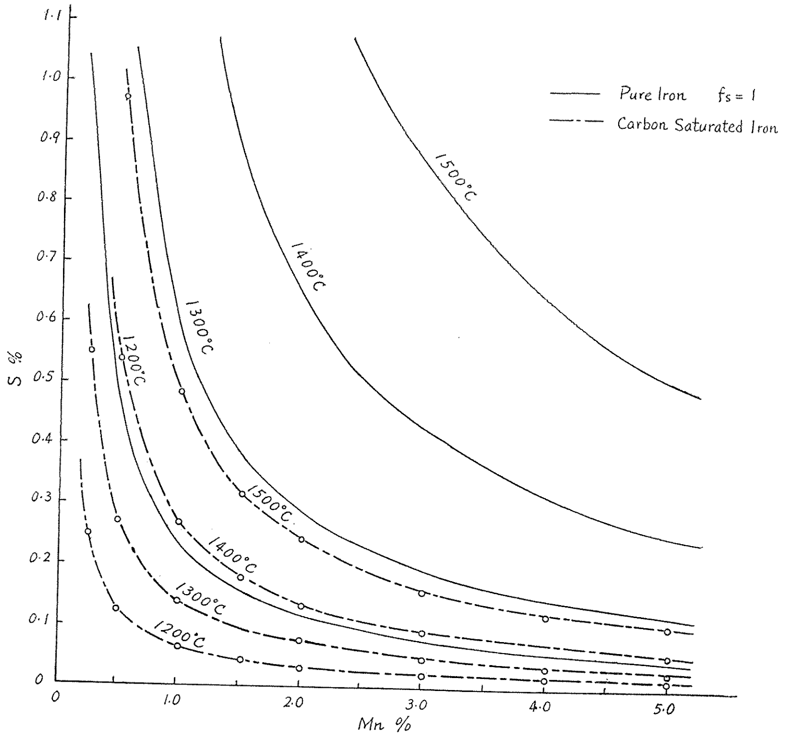

FIG. 14. Equilibrium between manganese and sulphur in liquid iron and carbon saturated iron calculated from thermodynamical values.

Chapter III. The Equilibrium between Manganese and Sulphur in Carbon Saturated Iron Melts

1. Introduction

Many investigations have been reported to this day on the desulphurization by manganese not only in the laboratory works but also in the practical operations. Especially the so-called natural desulphurization phenomena of molten pig iron has been well recognized,[5) 9) 10)] which occurs after tapping from Blast Frunaces. The mechanism of this desulphurization by manganese has been almost thoroughly investigated and it is believed that manganese sulphide or high manganese sulphide slag precipitates in molten pig iron and then separates out rising in the bath. However, comparing the desulphrization limits by manganese obtained by many investigators, it can't be said that these results are in good agreement. Furthermore, many investigations are incomplete and then there is no work except Oelsen's work[19)] that was carried out systematically in wide ranges.

It is necessary to obtain the intimate knowledge of the desulphurizing power of manganese, which always exists in molten iron during the iron- and steel-making processes, in order to establish the most reasonable method of desulphurization throughout the all processes. Then, briefly speaking, the desulphurizing power of manganese can be defined as the difference of the affinity of manganese to sulphur and of iron to sulphur. The authors have formerly determined the desulphurizing power of manganese by thermodynamical calculations on some assumptions and concluded that the desulphurizing power itself is not so strong as expected but rather weak (Ref. Chapter II). This fact means that manganese are nearely useless for desulphurization in pure iron or low alloy steel melts in which the activity coefficient of sulphur may be nearly unity. The pig iron, however, contains generally some amounts of carbon, silicon and manganese etc. and it has been recently recognized that the existence of these alloying elements has remarkable influence on the activity coefficient of sulphur in molten iron.[27)] Therefore, it may be easily desulphurized. Then, it follows that manganese is useful for desulphurization only in high sulphur potential as in the pig iron, inspite of its weak desulphurizing power. From this viewpoint, the reactivity for desulphurization of pig iron depends on its composition and then the desulphurizing effect by manganese may be also affected by the composition. The discrepancies in those results obtained by many investigators, as already mentioned, may be due to the fact that little attention was given to such behaviour of sulphur in liquid iron. In the present study, the authors try to show what are the conditions of molten pig iron for the most effective desulphurization by manganese and ascertain the desulphurizing power of manganese on the standpoint of sulphur potential. In this chapter, the equilibrium between manganese and sulphur in carbon saturated iron melts will be investigated.

2. Fundamental consideration on experimental procedure

The determination of the activity of sulphur in liquid iron is usually undertaken by the measurement of equilibrium between liquid iron and gas mixtures of hydrogen and hydrogen sulphide. Although this procedure may be applied to the present purpose, it takes a long time to reach the equilibrium and also some difficulties in the experiment are not avoided. Accordingly, in this study the equilibrium was attained directly by adding manganese to high sulphur iron melts at a definite temperature. For this purpose, the high frequency induction furnace is the most suitable for melting the sample as the induction stirring gives the uniformity of the melt. Thus, in the present work the high frequency induction furnace was used.

In the measurement of the equilibrium, the atmosphere must be strongly reducible to prevent the oxidation of the desulphurization products. Now, taking the crucible as graphite, extremely lower oxygen potential is obtained under carbon monoxide atmosphere. Namely, the measurement is made under the Boudouard equilibrium. However, it is to be considered whether the desulphurization product may really oxidize or not under the above condition. Now, assuming that the desulphurization product consists of FeS and MnS, some suggestions are found by a quotation from Uno's study[40] on their oxidation equilibria by carbon dioxide. He gave the following Eq. (3.1) and Eq. (3.2)

$$3\,FeS + 10\,CO_2 \rightleftharpoons Fe_3O_4 + 3\,SO_2 + 10\,CO$$

$$\log K_{FeS} = \log \frac{p_{CO}^{10} \cdot p_{SO_2}^{3}}{p_{CO_2}^{10}} = -\frac{52{,}669.7}{T} + 22.43 \qquad (690\sim890^\circ\,C) \tag{3.1}$$

$$MnS + 3\,CO_2 \rightleftharpoons MnO + SO_2 + 3\,CO$$

$$\log K_{MnS} = \log \frac{p_{CO}^{3} \cdot p_{SO_2}}{p_{CO_2}^{3}} = -\frac{18{,}290.6}{T} + 8.28. \qquad (600\sim1{,}000^\circ\,C) \tag{3.2}$$

Moreover, the Boudouard equilibrium is given,

$$2\,CO(g) \rightleftharpoons CO_2(g) + C(graph.)$$

$$\log K = \frac{8{,}407}{T} - 8.820. \tag{3.3}$$

Now, calculating p_{CO_2} from Eq. (3.3) under 1 atm of CO and then combining Eq. (3.1) and Eq. (3.2), p_{SO_2} is found as Table 5. Although Eq. (3.1) and Eq. (3.2) are valid below 1,000° C, they were assumed to be extrapolated to higher temperatures. The results shows that the values of p_{SO_2} are negligibly small under these conditions and then the equilibrium is not disturbed by oxidation of sulphide slags. The vapor pressure of sulphur in liquid iron and the decomposition pressures of FeS and MnS are also calculated from Eq. (3.4), Eq. (3.5) and Eq. (3.6),[41]

$$1/2\,S_2 = S\,(4.35\%\ C) \qquad \Delta F^\circ = -23{,}880 + 3.96\,T \tag{3.4}$$

$$Fe(l) + 1/2\,S_2(g) = FeS(l) \qquad \Delta F^\circ = -34{,}000 + 10.4\,T \tag{3.5}$$

$$Mn(l) + 1/2\,S_2(g) = MnS(s) \qquad \Delta F^\circ = -68{,}700 + 19.1\,T. \tag{3.6}$$

As shown in Table 6, the values of p_{S_2} are also negligible in the present experimental temperatures. The formation of COS is also calculated by Eq. (3.7)[40]

$$CO + 1/2\,S_2(g) = COS(g) \qquad \log K = \log \frac{p_{COS}}{p_{CO} \cdot p_{S_2}^{1/2}} = \frac{5{,}268.44}{T} - 5.207. \tag{3.7}$$

Inserting the above values of p_{S_2} in Eq. (3.7), p_{COS} becomes the order of 10^{-5}, which is small but gives some possibility of formation of COS under such conditions. However, the effect on the equilibrium of Mn and S in liquid iron may be neglected.

TABLE 5

T °K	$\log p_{CO_2(atm)}^{Eq(2.3)}$	$\log K_{FeS}$	$p_{SO_2(atm)}^{(FeS)}$	$\log K_{MnS}$	$p_{SO_2(atm)}^{(MnS)}$
1,773	-4.079	-7.27	9.6×10^{-17}	-2.036	5.3×10^{-15}
1,673	-3.795	-9.05	2.2×10^{-16}	-2.652	9.2×10^{-15}
1,573	-3.476	-11.05	5.4×10^{-16}	-3.347	1.7×10^{-14}
1,473	-3.113	-13.32	1.5×10^{-15}	-4.137	3.4×10^{-14}

TABLE 6

	p_{S_2} (atm)			
	1,773° K	1,673° K	1,573° K	1,473° K
$1/2\,S_2=S$ (4.35% C)	9.6×10^{-6}	4.2×10^{-6}	1.7×10^{-6}	7.4×10^{-7}
$Fe(l)+1/2\,S_2(g)=FeS(l)$	1.5×10^{-4}	4.7×10^{-5}	1.3×10^{-5}	3.6×10^{-6}
$Mn(l)+1/2\,S_2(g)=MnS(s)$	2.6×10^{-9}	2.5×10^{-10}	1.8×10^{-12}	9.1×10^{-13}

3. Materials and experimental apparatus

(1) *Materials*

The melts were prepared from weighed amounts of high purity Fe-C alloy, Fe-C-S alloy and Fe-C-Mn alloy, previously prepared in the laboratory. The Fe-C alloy was prepared from electrolytic iron and graphite powder in the graphite crucible which was made on a lathe from solid rods of good quality graphite. The Fe-C-S alloy was made by adding pure ferrous sulphide to the Fe-C melt. Ferrous sulphide was synthesized as follows: electrolytic iron was dissolved in nitric acid and thus produced $Fe(NO_3)$ was heated to ferric oxide, which was then reduced by hydrogen at 1,000° C for 2 hours and next sulphurized by hydrogen sulphide for 3 hours at 600~700° C.

Those alloy were analysed as follows.

	C	Si	Mn	P	S	Ni	Cr	Cu
Fe-C alloy	4.45	0.015	tr	0.005	—	0.003	0.006	0.003
Fe-C-S alloy	3.92	0.020	0.01	0.006	1.59	0.003	0.012	0.023

The Fe-C-Mn alloy was produced by adding electrolytic manganese to Fe-C melt in Argon atmosphere.

(2) *Apparatus*

The apparatus for the experiment is shown in Fig. 15 (a), (b). Fig. 15 (a) is a schematic diagram of the apparatus: Carbon monoxide was prepared by dropping formic acid into concentrated sulphuric acid in an evacuated flask and passed through four washing bottles containing sulphuric acid, 30% KOH solution, alkali pyrogallol solution, hot copper at 450° C in a combustion tube and two U tubes filled with phosphorus pentoxide. Purified and dried gas was introduced in the reaction tube set in the furnace.

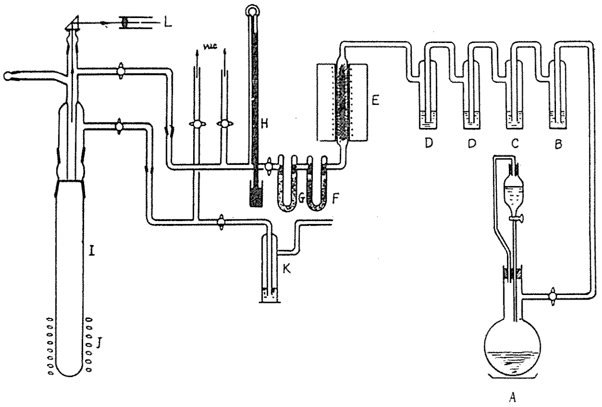

FIG. 15 (a). Experimental apparatus.

A, CO gas generator; *B*, H_2SO_4; *C*, KOH; *D*, Alkali pyrogallol; *E*, Cu-net furnace 450° C; *F*, Sodalime+$CaCl_2$, *G*, P_2O_5; *H*, Hg Manometer; *I*, Reaction tube; *J*, High frequency induction furnace; *K*, H_2SO_4; *L*, Optical pyrometer.

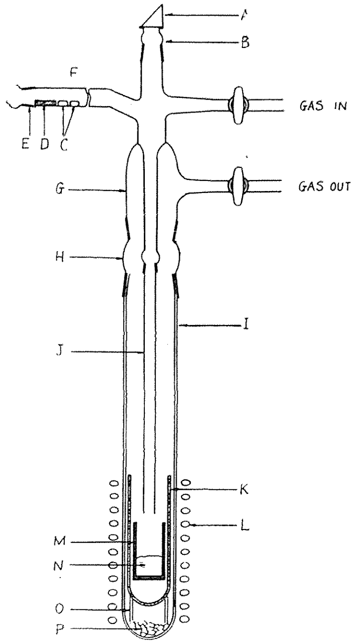

FIG. 15 (b). Furnace assembly.

A	Glass prism
B	Sampling window
C	Fe-Mn pieces
D	Magnet
E	Glass cap
F	Side branch
G	Glass cap
H	Glass cap
I	Quartz tube (40 mm I.D. × 500 mm)
J	Quartz tube for gas inlet
K	Heat insulation (Alumina crucible)
L	High frequency induction coil
M	Graphite crucible
N	Liquid metal
O	Alumina pipe
P	Quartz pieces

The furnace and it's accessories are shown in Fig. 15 (b). A silica tube glazed outside as well as inside, 500 mm long, 48 mm O.D., and 40 mm I.D., was used as a furnace tube. The bottom end of it was closed. The furnace tube was tightly equipped with an all-pyrex glass head and connected to vacuum system or CO gas path when necessary. The top of the head was designed to be opened for sampling. Every charge was melted in a graphite crucible (22 mm I.D., 50 mm depth) protected by a alumina crucible in the furnace tube.

Temperature measurements were made with a disappearing filament type optical pyrometer through the glass prism on the sighting window.

The power for inductive heating was obtained from an oscillating spark-gap type high frequency converter of 20 KVA. Efficient and continuous temperature control was obtained by varying the inductance in the high frequency circuit.

4. Experimental procedure and results

(1) *Experimental procedure*

The total weight of the charge was 25~30 grams. The Fe-C alloy and Fe-C-S alloy, previously mentioned, were weighed so as to obtain higher sulphur contents than expected equilibrium values and set in a graphite crucible in the furnace tube as shown in Fig. 15 (b). The Fe-Mn alloy for the use of addition was placed in the side branch D of the glass head in Fig. 15 (b). The graphite crucibles were previously degassed by heating in vacuum (10^{-4} mmHg) at somewhat higher temperature than in the experiment, lest the volatile matter should arise from the crucible during the experiment and disturb the optical reading. After the apparatus was ready, the atmosphere in the furnace tube was evacuated to vacuum and the metal was slowly melted for degassing. The metal was then solidified in vacuum and the purified and dried CO gas was slowly introduced and brought to the atmospheric pressure. The rate of flow was approximately 30~40 cc per min. After the steady flow was obtained, the induction unit was turned on and the metal was brought to the desired temperature. The Fe-Mn alloy in the side tube was then added to the melt immediately. The time required for the attainment of equilibrium between manganese and sulphur in the melt was determined referring to the time for which the residual sulphur showed constant value and also the metal was saturated with carbon. Preliminary experiments showed that the equilibrium between manganese and sulphur was attained in considerably short time after Fe-Mn addition and the residual sulphur attained constant within 15 min. at 1,300° C. The rate of solution of carbon in liquid iron was about 1% per hour near the saturation at 1,300° C for the melt containing sulphur. Generally, 1 hour was enough to attain saturation as shown in Fig. 16. For each measurement the holding time for the equilibrium was taken to be 60~90 min., depending on the mixing rate of the initial charge. After holding the desired temperature, the melt was sampled by dipping a thin walled quartz tube, 3~4 mm I.D., through the opening in the upper sampling window and drawing up a sample of approximately 10 g which was rapidly quenched into water. In order to get a quenching effect to the drawing sample a copper wire was previously set in the upper part of the quartz tube. These sampled pieces were entirely white cast iron, which was desira-

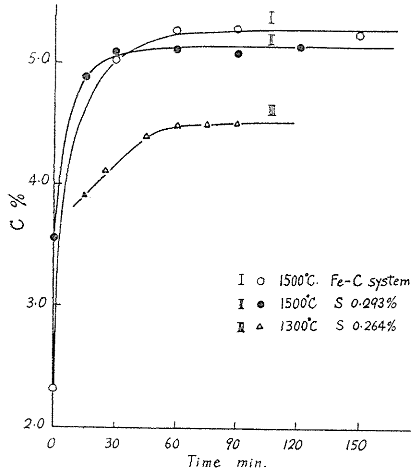

FIG. 16. Rate of solution of carbon in liquid iron in graphite crucible.

ble for minimizing the experimental error of carbon analysis. The whole piece was crushed and analysed for carbon using 25~65 mesh particles and for sulphur and manganese using −65 mesh powder. Carbon analysis was performed by the normal combustion method, sulphur was determined as the standard gravimetric method and manganese by the sodium bismuthate process.

To secure the attainment of true equilibrium, some heats were tried to attain equilibrium reversely from sulphide slag as the desulphurization product. This procedure was as follows: The Fe-Mn alloy was added to the melt at lower temperature than the desired temperature; for example, for the measurement of the equilibrium at 1,500° C the melt was desulphurized at 1,400° C and then attained to equilibrium at 1,500° C. This procedure was successfully carried out at the measurement of the equilibrium at 1,500° C and 1,400° C.

Optical readings were calibrated against the true temperature measured with Pt-PtRh thermocouples by dipping into the melt. The optical calibration scale was found to be unaffected by the addition of manganese and sulphur in the present experimental range.

(2) *Experimental results*

A large number of experimental runs were carried out at 1,200~1,500° C, and the equilibrium curves between manganese and sulphur were determined. The results were summarized in Table 7 and shown in Fig. 17. The mark ★ in Table 7 and ◉, △ in Fig. 17 represent the results from the reverse reaction above mentioned, namely these were desulphurized by Fe-Mn addition at 1,300° C and 1,400° C respectively and then attained to equilibrium at 1,400° C and 1,500° C. These are approximately on the same curves that of the former data and therefore it can

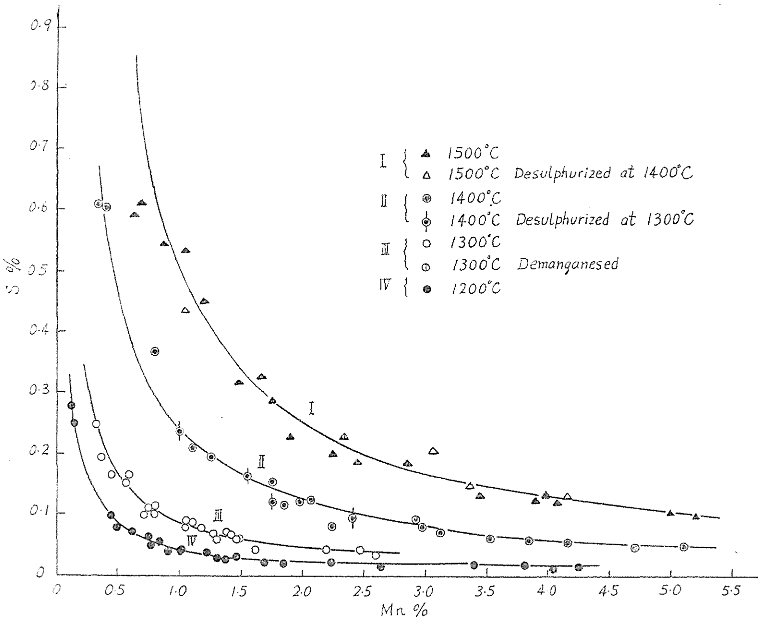

FIG. 17. Equilibrium between manganese and sulphur in carbon saturated iron at 1,200~1,500° C.

TABLE 7. Equilibrium Data

Melt No.	Temp. (°C)	Time (min.)	Initial (S%)	Metal pct. at equilibrium C			Mole fraction N_C			$K''=[S\%][Mn\%]$	$\log K'$	f_S	Remarks
				C	Mn	S	N_C	N_S	$-\Delta N_O^S$				
62	1,500	120	0.58	5.05	2.25	0.198	0.1982	0.0029	0.0038	0.446	−0.351	4.5	
65	〃	〃	0.65	5.07	2.46	0.188	0.1986	0.0028	0.0035	0.462	−0.335	4.5	
67	〃	〃	0.55	5.11	3.78	0.129	0.2002	0.0019	0.0026	0.503	−0.298	4.3	
★70	1,400→1,500	15→ 60	0.58	—	3.36	0.146	—			0.492	−0.308		Desulphurized by Fe-Mn addition at 1,400° C and attained to equilibrium at 1,500° C.
★71	〃	20→120	0.55	5.11	3.06	0.205	0.2002	0.0030	0.0022	0.628	−0.202	4.4	
★72	〃	20→ 60	0.30	5.18	4.15	0.135	0.2027	0.0021	0.0003	0.560	−0.301	4.4	
74	1,500	60	0.47	5.00	1.47	0.317	0.1965	0.0047	0.0050	0.467	−0.331	4.5	
77	〃	〃	0.32	4.98	1.75	0.290	0.1948	0.0042	0.0069	0.507	−0.295	4.4	
95	〃	〃	1.04	5.00	1.05	0.537	0.1958	0.0079	0.0055	0.563	−0.249	4.5	
96	〃	〃	1.03	4.98	0.71	0.613	0.1948	0.0090	0.0063	0.436	−0.361	4.5	
97	〃	〃	0.77	5.06	1.67	0.328	0.1985	0.0048	0.0031	0.548	−0.261	4.6	
99	〃	〃	0.67	5.06	2.33	0.232	0.1985	0.0034	0.0035	0.541	−0.267	4.5	
100	〃	〃	0.71	5.20	3.44	0.131	0.2029	0.0019	(−0.0003)	0.452	−0.345	4.6	
101	〃	〃	0.40	5.21	4.07	0.122	0.2030	0.0018	0	0.496	−0.305	4.4	
102	〃	〃	0.41	5.13	3.97	0.137	0.2007	0.0020	0.0022	0.543	−0.265	4.3	
103	〃	〃	0.30	5.17	5.19	0.094	0.2021	0.0014	0.0015	0.490	−0.310	4.1	
105	〃	〃	1.55	4.93	0.63	0.592	0.1950	0.0088	0.0061	0.372	−0.429	4.5	
106	〃	〃	1.14	4.98	0.87	0.546	0.1974	0.0081	0.0038	0.475	−0.323	4.5	
108	〃	〃	0.31	5.22	4.97	0.096	0.2031	0.0014	0.0004	0.474	−0.324	4.2	
109	〃	〃	1.57	4.92	0.44	1.139	0.1932	0.0167	0.0078	0.502	−0.299	4.3	
110	〃	〃	1.00	4.90	0.69	0.815	0.1942	0.0121	0.0070	0.567	−0.246	4.3	
★112	1,400→1,500	20→60	0.40	5.05	1.87	0.229	0.1982	0.0034	0.0036	0.428	−0.369	4.6	Desulphurized by Fe-Mn addition at 1,400° C and attained to equilibrium at 1,500° C.
★113	〃	〃	0.40	5.02	1.04	0.433	0.1972	0.0064	0.0043	0.452	−0.345	4.6	
30	1,400	40	0.31	4.96	4.72	0.046	0.1952	0.0007	0.0000	0.217	−0.664	3.8	
34	〃	90	0.53	4.79	1.24	0.196	0.1894	0.0029	0.0040	0.243	−0.614	4.2	
36	〃	60	0.28	4.78	1.98	0.117	0.1891	0.0017	0.0045	0.241	−0.618	4.0	
37	〃	〃	0.36	4.91	2.92	0.092	0.1935	0.0014	0.0006	0.269	−0.570	4.1	
38	〃	〃	0.28	4.82	1.74	0.153	0.1905	0.0023	0.0030	0.266	−0.575	4.1	
39	〃	50	0.65	4.89	2.07	0.123	0.1928	0.0018	0.0009	0.257	−0.590	4.2	
40	〃	〃	0.96	4.72	0.79	0.369	0.1869	0.0055	0.0061	0.288	−0.540	4.1	
41	〃	〃	0.96	4.80	1.13	0.210	0.1898	0.0030	0.0033	0.237	−0.625	4.3	
42	1,400	60	0.68	4.89	2.25	0.081	0.1929	0.0012	0.0009	0.183	−0.738	4.2	
44	〃	〃	0.68	4.93	2.96	0.078	0.1951	0.0012	(−0.0009)	0.232	−0.635	4.1	
46	〃	〃	0.63	4.84	1.85	0.114	0.1921	0.0017	0.0023	0.211	−0.676	4.2	
50	〃	〃	0.94	4.72	0.34	0.611	0.1866	0.0090	0.0061	0.209	−0.680	4.1	
51	〃	〃	0.27	4.95	3.53	0.062	0.1949	0.0009	(−0.0004)	0.218	−0.662	4.1	
★54	1,300→1,400	20→60	0.32	4.87	2.40	0.094	0.1931	0.0014	0.0007	0.226	−0.646	4.1	Desulphurized by Fe-Mn addition at 1,300° C and attained to equilibrium at 1,400° C.
★55	〃	〃	0.30	4.85	1.75	0.122	0.1919	0.0018	0.0016	0.214	−0.670	4.2	
★56	〃	〃	0.28	4.85	1.54	0.165	0.1919	0.0024	0.0015	0.254	−0.595	4.3	
86	1,400	60	0.65	4.94	3.12	0.073	0.1956	0.0011	(−0.0014)	0.229	−0.640	4.1	
87	〃	〃	0.30	4.98	5.12	0.050	0.1958	0.0007	(−0.0005)	0.257	−0.590	3.8	
88	〃	〃	0.35	4.92	4.12	0.055	0.1939	0.0008	0.0009	0.225	−0.648	3.9	
★89	1,300→1,400	20→70	0.50	4.78	0.99	0.239	0.1890	0.0035	0.0041	0.237	−0.625	4.2	Desulphurized by Fe-Mn addition at 1,300° C and attained to equilibrium at 1,400° C.
91	1,400	60	0.40	4.95	3.82	0.062	0.1949	0.0009	(−0.0003)	0.237	−0.625	4.0	
11	〃	〃		4.71	0.40	0.607	0.1863	0.0089	0.0064	0.243	−0.614	4.1	

TABLE 7. (*Continued*)

Melt No.	Temp. (°C)	Time (min.)	Initial (S %)	Metal pct. at equilibrium C	Mn	S	Mole fraction N_C	N_S	$-\Delta N_C^S$	$K''=[S\%][Mn\%]$	log K''	f_S	Remarks
2-a	1,300	20	0.38	4.46	0.58	0.164	—	—	—	0.0950	−1.022	3.7	
-b	〃	〃		4.46	0.79	0.100	—	—	—	0.0789	−1.103	3.7	
-c	〃	〃		4.58	1.27	0.065	—	—	—	0.0817	−1.088	3.8	
3-a	〃	30	0.38	4.55	0.75	0.108	—	—	—	0.0806	−1.094	3.8	
-b	〃	〃		4.58	1.29	0.058	—	—	—	0.0747	−1.127	3.9	
-c	〃	〃		4.65	2.20	0.042	—	—	—	0.0921	−1.036	3.8	
4-a	〃	〃	04.0	4.54	0.57	0.150	—	—	—	0.0860	−1.065	3.8	
-b	〃	〃		4.59	1.42	0.064	—	—	—	0.0908	−1.042	3.8	
-c	〃	〃		4.61	2.48	0.040	—	—	—	0.1004	−1.000	3.7	
5-a	〃	〃	0.40	4.51	1.47	0.059	—	—	—	0.0870	−1.060	3.7	
-b	〃	〃		4.56	1.62	0.042	—	—	—	0.0682	−1.166	3.7	
-c	〃	〃		4.69	2.58	0.031	—	—	—	0.0795	−1.100	3.8	
6-a	〃	〃	0.35	4.50	0.37	0.194	—	—	—	0.0726	−1.139	3.8	
-c	〃	〃		4.61	1.15	0.075	—	—	—	0.0830	−1.080	3.9	
7-a	〃	〃	Mn: 2.36		1.48	0.062	—	—	—	0.0917	−1.038	—	Demanganesed by Fe-C-S alloy addition.
-b	〃	〃			0.81	0.112	—	—	—	0.0909	−1.041	—	
-c	〃	〃			0.44	0.166	—	—	—	0.0722	−1.141	—	
14-a	〃	〃	Mn: 2.12		1.38	0.069	—	—	—	0.0955	−1.020	—	
-b	〃	〃		—	1.17	0.072	—	—	—	0.0848	−1.072	—	
-c	〃	〃		—	1.04	0.086	—	—	—	0.0895	−1.048	—	
16-a	〃	〃	0.59	4.51	0.33	0.249	—	—	—	0.0819	−1.087	3.8	
-b	〃	〃		4.50	0.70	0.105	—	—	—	0.0732	−1.135	3.8	
-c	〃	〃		4.58	1.04	0.074	—	—	—	0.0723	−1.141	3.8	
9-a	1,200	20	0.58	4.29	0.15	0.252	—	—	—	0.0373	−1.428	3.6	
-b	〃	〃		4.33	0.44	0.100	—	—	—	0.0437	−1.360	3.6	
-c	〃	〃		—	0.84	0.057	—	—	—	0.0475	−1.323	—	
10-a	〃	30	0.58	—	0.13	0.281	—	—	—	0.0377	−1.424	—	
-b	〃	〃		4.34	0.49	0.081	—	—	—	0.0395	−1.403	3.6	
-c	〃	20		—	0.92	0.040	—	—	—	0.0368	−1.434	—	
11-a	〃	30	0.58	4.39	1.38	0.028	—	—	—	0.0380	−1.420	3.5	
-b	〃	〃		4.41	1.71	0.022	—	—	—	0.0370	−1·432	3.5	
12-a	〃	〃	0.23	4.40	0.61	0.074	—	—	—	0.0447	−1.350	3.7	
-b	〃	〃		4.36	0.78	0.048	—	—	—	0.0376	−1.425	3.6	
-c	〃	〃		—	1.03	0.045	—	—	—	0.0457	−1.340	—	
13-a	〃	35	0.28	4.38	0.76	0.068	—	—	—	0.0510	−1.292	3.6	
-b	〃	30		4.40	1.23	0.040	—	—	—	0.0490	−1.310	3.5	
-c	〃	〃		4.46	1.47	0.033	—	—	—	0.0482	−1.317	3.5	
27-a	〃	40	0.32	4.34	1.31	0.030	—	—	—	0.0396	−1.402	3.4	
-b	〃	35		4.35	1.85	0.021	—	—	—	0.0379	−1.432	3.4	
81-a	〃	60	0.20	4.45	2.25	0.025	—	—	—	0.0562	−1.250	3.5	
-b	〃	45		4.59	3.39	0.018	—	—	—	0.0623	−1.206	3.5	
-c	〃	45		4.64	4.27	0.012	—	—	—	0.0525	−1.280	3.4	
82-a	〃	60	0.20	4.51	2.65	0.014	—	—	—	0.0366	−1.437	3.5	
-b	〃	40		4.49	3.82	0.019	—	—	—	0.0726	−1.139	3.3	
-c	〃	30		4.58	4.04	0.011	—	—	—	0.0445	−1.352	3.4	

be recognized that manganese and sulphur in these melts were attained to equilibrium with each other. The reverse reaction was not undertaken at 1,200° C and 1,300° C, but the measurements might prove equilibrium. The points marked ⦶ at 1,300° C represent the demanganesed melts by Fe-S addition but they were not reverse reactions. Those data as marked -a, -b, -c in Table 1 were obtained in the same run by adding Fe-Mn continuously.

The results show clearely that at the higher temperature as in the blast furnace, the desulphurization by manganese does not proceed even if under the carbon saturation, but when the temperature lowers to about 1,200° C, the desulphurization may be remarkable and so it may be said that manganese is effective in spite of its thermodynamically weak desulphurizing power. For example, if the open hearth pig iron containing 1～2% manganese lowers its temperature to about 1,200° C, it can be expected that the sulphur content will be below 0.04% without any desulphurization technique. It must be mentioned that this value is suitable for steelmaking.

Table 8 shows the desulphurization limits obtained from the present work with those which have been recognized in literature.

TABLE 8. Limits of Desulphurization by Manganese at Various Temperatures

Temp. (°C)	Mn pct.	Limits of desulphurization, S pct.			
		Authors	Oelsen	*Wentrup	†Schenck
1,200	0.5	0.088	0.100	—	—
	1.0	0.044	0.052	—	—
	1.5	0.027	0.027	—	—
	2.0	0.022	0.023	—	—
	2.5	0.017	0.018	—	—
1,300	0.5	0.165	0.205	0.38	—
	1.0	0.080	0.105	0.10	—
	1.5	0.060	0.070	0.07	—
	2.0	0.045	0.055	0.07	—
	2.5	0.037	—	—	—
1,400	0.5	0.465	0.47	0.55	1.08
	1.0	0.240	0.25	0.31	0.63
	1.5	0.162	0.17	0.17	0.39
	2.0	0.120	0.13	0.12	0.27
	2.5	0.095	0.11		0.20
1,500	0.5	—	0.75	1.10	—
	1.0	0.500	0.42	0.60	—
	1.5	0.338	0.30	—	—
	2.0	0.254	0.25	—	—
	2.5	0.205	0.18	—	—

*: Unsaturated, by carbon contained 2.1% silicon.
†: Contained 2.9～5.4% carbon.

Since many of the early works were not systematic, the equilibrium curves between manganese and sulphur could be compared only among a few experiments. Moreover, as they were far from carbon saturation or contained silicon or phosphorus, it is difficult to compare the present results with them strictly. However, those of the recent work of Oelsen[19] which have been quoted from the literature may be the most reliable, although his original papers have not been available. The results of the present work are in good agreement with those of Oelsen. Some of Wentrup's data[16] are also fairly agreed, but the comparison seems to be unsuitable since most of them are as of unsaturation by carbon or contained some silicon or phosphorus.

The results of H. Schenk's work[14] at 1,400° C are far apart from our data, but their melts were made in wide ranges for carbon and moreover the contents of other components are not described.

Comparing these equilibrium curves with those obtained from thermodynamical calculation as shown previously in Fig. 14, it may be recognized that a fairly good agreement is found among them especially at higher temperature. Some discrepancies found in lower temperature may be resulted from uncertainties of thermodynamical values extraporated to that temperature.

Fig. 18 shows the carbon solubility in liquid iron under the equilibrium between manganese and sulphur. It is well known that the carbon solubility decreases with sulphur addition and increases with manganese. In the case that manganese and sulphur are in equilibrium with each other, the additional effects of them increase the carbon solubility consequently with manganese content and then approach the solubility line of Fe-C-Mn system.

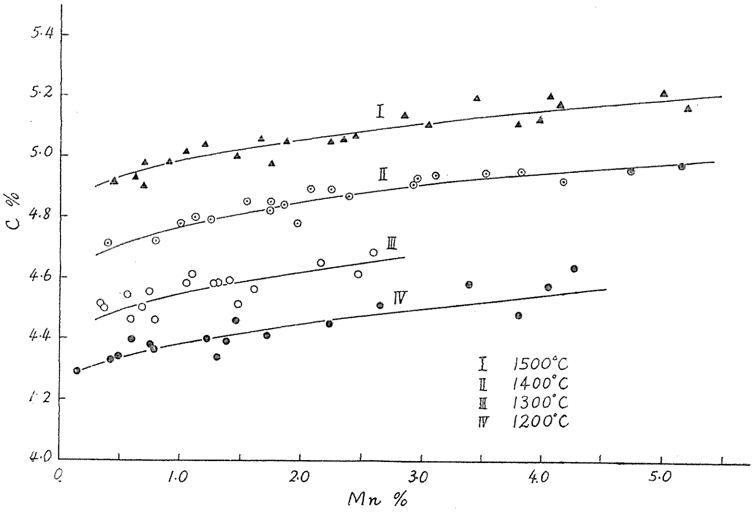

FIG. 18. Carbon solubility in liquid iron under the equilibrium between manganese and sulphur at 1,200 ~ 1,500° C.

5. Discussions

(1) *Desulphurization limit by manganese*

As above mentioned, the desulphurization limit by manganese determined by the present work is somewhat lower than those described in the literature. While those data of many investigators seems to be obtained disregarding carbon saturation, the present results show the desulphurization limit under carbon saturation.

It is necessary to obtain the most effective desulphurization by manganese that the iron melt should be saturated with carbon and also attained to equilibrium at temperature as lower as possible. The pig iron containing 1 to 2 per cent manganese may lower its sulphur content below 0.04 per cent which may be useful for the steel-making without any desulphurizing procedure. The experimental results by Oelsen[19] which are in good agreement with the present work may be effected under carbon saturation. The effects of added elements such as silicon, phosphorus will be discussed later. Strictly speaking, since the present experiment was carried out under 1 atmosphere of carbon monoxide, the results might be brought out by dissolved oxygen in the melts; nevertheless this effect was neglected because of extremely lower oxygen potential.

(2) *Activity coefficient of sulphur and manganese-sulphur equilibrium*

It is suggested that the desulphurization limit may be mainly affected by the difference of the activity of sulphur in the melts, by comparing the present results with those of many investigators. Then, the activity of sulphur in the present work is discussed. Now, those melts of this work can be written as Fe-$C^{sat.}$-Mn-S system. It is well known that the activity coefficient of sulphur in such a multi-component system was investigated by Sherman and Chipman.[27] Namely, the activity coefficient of sulphur in Fe-X-S ternary iron melts (X=C, Si, Mn, P, Al etc.) at 1,600° C is shown in Fig. 12. If the activity coefficient of sulphur $f_S^{(X)}$ in these ternary system is known, the simultaneous effects of two or more alloying elements on the activity coefficient of sulphur can be shown by a simple relation as given by Wagner[37] in their dilute solutions. Now, applying this relation to the present system the activity coeffecient of sulphur f_S can be obtained as follows:

$$\log f_S = \log f'_S + \log f_S^{(C)} + \log f_S^{Mn} \qquad (3.8)$$

where f'_S, $f_S^{(C)}$ and $f_S^{(Mn)}$ are the activity coefficient of sulphur in Fe-S binary solution, Fe-C-S ternary solution and Fe-Mn-S ternary solution respectively. This procedure utilizes the infinitely dilute solution as the reference state as usually. Sherman and Chipman mentioned that at 1,600° C the agreement between observed and calculated values was very good in their lower concentrations. Strictly speaking, the application of each term in Eq. (3.8) should be limited to 1,600° C, and it is clearly recognized that carbon has the most definite effect on the activity coefficient of sulphur in this system. According to the experimental results by Morris and Buehl[35] who determined $f_S^{(C)}$, the effect of temperature on the activity coefficient of sulphur was extremely small near carbon saturation and it may be able to apply the data of $f_S^{(C)}$ at 1,600° C to the present experimental results at any temperature. On the other hand, considering the interaction between solute atoms, f'_S and $f_S^{(Mn)}$ may vary with temperature since the interactions between sulphur atoms each other or sulphur and manganese atoms may become stronger with decreasing temperature. Nevertheless f'_S is nearly equal to unity in those lower sulphur ranges and then the effect of temperature may be neglected. On the other hand, comparing the values of $f_S^{(Mn)}$ which have been recently determined at 1,200° C on the γ-Iron[42] of Fe-Mn-S system with those obtained at 1,600° C on liquid iron, no large discrepancy can be recognized as shown in Fig. 19. Therefore, it may be able to apply the values at 1,600° C to the present results approximately

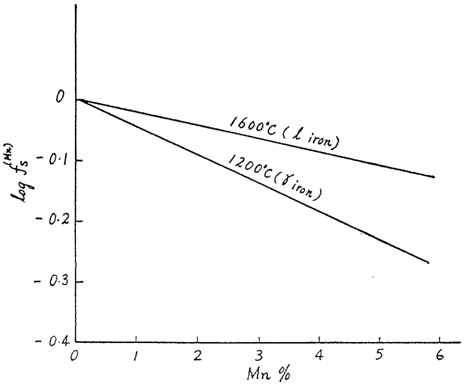

FIG. 19. log γ_S^{Mn} plotted against manganese per cent at 1,600° C (Sherman, Chipman) and at 1,200° C (γ, Turkdogan *et al.*).

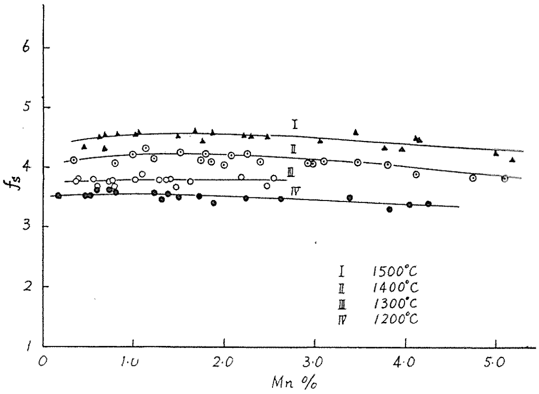

FIG. 20. Activity coefficient of sulphur estimated at equilibrium between manganese and sulphur in carbon saturated iron.

even if the temperature descends.

Now, applying the above equation (3.8) to the present results the activity coefficient of sulphur under the equilibrium was calculated as the 9th column in the Table 7 and plotted against manganese content as in Fig. 20. It is observed that at constant temperature the activity coefficient of sulphur tends to decrease gradually with increasing of manganese content, according to the effect of $f_S^{(Mn)}$ rather than $f_S^{(C)}$ in the equation (3.8). In the ordinary pig iron, however, the values of f_S may be practically constant in their composition. The values of f_S in those equilibrium will increase with temperature because of the increase of carbon solubility.

Now, the equilibrium between manganese and sulphur in liquid iron is shown as the following relations:

$$\underline{S} + \underline{Mn} = (MnS)$$

$$K = \frac{a_{MnS}}{a_S \cdot a_{Mn}} = \frac{a_{MnS}}{f_S[\%S] \cdot f_{Mn}[\%Mn]}. \tag{3.9}$$

If the desulphurization product can be regarded as pure MnS, a_{MnS} will be unity and the following relation is given,

$$K' = f_S[\%S] \cdot f_{Mn}[\%Mn]. \tag{3.10}$$

Then, as above mentioned, in the composition range of the ordinary pig iron the values of f_S are constant and furthermore if the values of f_{Mn} are also assumed to be constant, the above equilibrium may be written more simply as follows:

$$K'' = [\%S][\%Mn]. \tag{3.11}$$

Here, f_{Mn} is shown by Eq. (3.12) as the case of f_S

$$\log f_{Mn} = \log f'_{Mn} + \log f_{Mn}^{(S)} + \log f_{Mn}^{(C)} \tag{3.12}$$

where f'_{Mn}, $f^{(\mathrm{S})}_{\mathrm{Mn}}$ and $f^{(\mathrm{C})}_{\mathrm{Mn}}$ are the activity coefficients of manganese in Fe-Mn binary solution, Fe-S-Mn ternary and Fe-C-Mn ternary solution.

Since it is well known that manganese behaves as ideal solution in Fe-Mn binary solution, then f'_{Mn} may be equal to unity. In the lower sulphur concentrations $f^{(\mathrm{S})}_{\mathrm{Mn}}$ may also be nearly equal to unity.

On the other hand, $f^{(\mathrm{C})}_{\mathrm{Mn}}$ was not known in the literature before the work of Ohtani.[33] Considering the value of the atomic interaction between manganese and carbon in liquid iron $\varepsilon_{\mathrm{C}}^{(\mathrm{Mn})} = -0.5$[43] and the ideal behavior of manganese in high concentration of iron, the effect of carbon on f_{Mn} seems to be small and it may be considered that under carbon saturation $f^{(\mathrm{C})}_{\mathrm{Mn}}$ is regarded as at least nearly constant. The recent study by Ohtani[33] on the activity of manganese in Fe-C-Mn melts proves this consideration to be correct. Therefore, as far as the desulphurization product can be regarded as nearly manganese sulphide the equilibrium constant of the reaction can be shown as Eq. (3.11). The value of K'' in Eq. (3.11) is not the true equilibrium constant but the apparent equilibrium constant. Now, taking the experimental values of $\log K''$ against the manganese content, Fig. 21 is obtained. While the values of K'' are not necessarily constant in whole ranges, they seem to be constant in the ordinary pig iron which contains manganese 0.5~2.5% and the equilibrium is shown as Eq. (3.11). Therefore, the denominator of Eq. (3.9) becomes constant and it may be recognized that the desulphurization product is MnS in the composition ranges. On the other hand, as temperature increases K'' becomes lower in especially lower manganese range and this fact shows the lowering of the activity of MnS in desulphurization product. This will be discussed later. Up to this time the desulphurization equilibrium has been taken as K'', this representation is, however, recognized only under the above conditions.

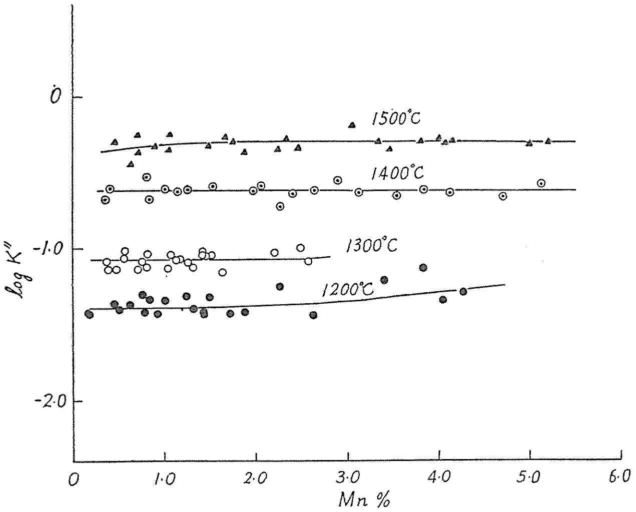

FIG. 21. Variation of apparent equilibrium constant K'' with concentration of manganese at various temperatures.

(3) *Calculation of thermodynamical values*

As above mentioned, in those considerably lower temperatures Eq. (3.11) represents the apparent equilibrium constant and plotting $\log K''$ against the reciprocal of absolute temperature, the lenear relation was obtained as shown in Fig. 22. Calculating this relation by the least square, the following Eq. (3.13) was established.

$$\log K'' = -9{,}763/T + 5.197 \qquad (3.13)$$

Since the values of f_S are taken as constant except higher manganese range, the activity of sulphur $a_S = f_S[\%\,S]$ at every temperature may be determined at the range of manganese content of 1 to 2 pct, taking the mean values of f_S.

Assuming that the behavior of manganese in those melts is ideal, the temperature dependence of K' may be similarily calculated as the following Eq. (3.14)

$$\log K' = -10{,}435/T + 6.227 \qquad (3.14)$$

This equation is also represented in Fig. 22.

From Eq. (3.14), the equation for the free energy of the desulphurization by manganese is obtained as shown by Eq. (3.15).

$$\underline{S} + \underline{Mn} = (MnS) \quad \Delta F^\circ = -47{,}741 + 28.49\,T \quad (3.15)$$

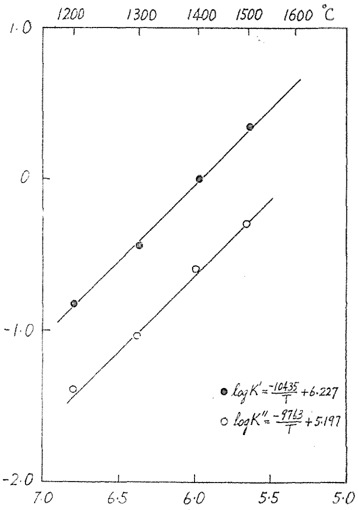

FIG. 22. Effect of temperature on equilibrium constant $K' = a_S \cdot a_{Mn}$ and $K'' = [\%S][\%Mn]$.

Equations (3.14) and (3.15) are generally available independent of the carbon saturation, assuming MnS for the desulphurization product.

Hence, combining the known thermodynamical data with the Eq. (3.15), the equation for the free energy of formation of manganese sulphide at higher temperature is obtained. Namely, introducing the known data of the following Eq. (3.16) and Eq. (3.17),

$$1/2\,S_2(g) = \underline{S} \qquad \Delta F^\circ = -31{,}520 + 5.27\,T \qquad (3.16)$$

$$Mn(l) = \underline{Mn}\ (\text{in l Fe}) \qquad \Delta F^\circ = -9.11\,T \qquad (3.17)$$

it follows from Eq. (3.15) that

$$Mn(l) + 1/2\,S_2(g) = MnS(s) \qquad \Delta F^\circ = -79{,}261 + 24.65\,T \qquad (3.18)$$

The corresponding value which was written in "*Basic Open Hearth Steel-making*" showed $\Delta F^\circ = -68{,}700 + 19.1\,T$[44] and these calculated values at several temperatures were in good agreement with those calculated by Eq. (3.18), especially at higher temperatures as follows.

	Present work Eq. (3.18)	B.O.H.S.
$\Delta F^\circ_{1,573}$	40,487 cal	38,656 cal
$\Delta F^\circ_{1,673}$	38,022 〃	36,746 〃
$\Delta F^\circ_{1,773}$	35,557 〃	34,836 〃
$\Delta F^\circ_{1,873}$	33,092 〃	32,926 〃

These are also illustrated in Fig. 23.

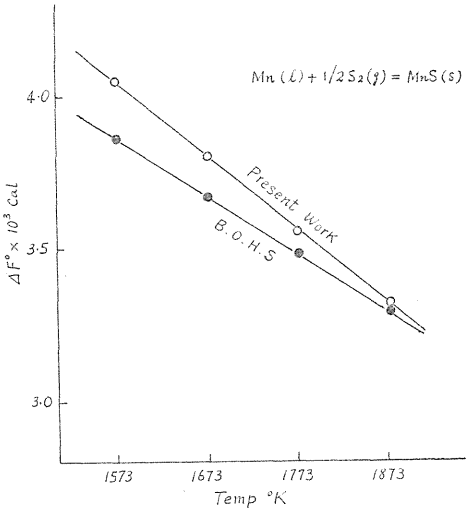

FIG. 23. Free energy of formation of MnS; comparison of the data obtained by the present work with those found in "B.O.H.S.".

(4) *Carbon Solubility of Fe-C-S system and Fe-C-Mn system*

As is generally known, the carbon solubility in liquid iron is increased or decreased by addition of a third element. The investigations published on the effect of those elements such as silicon, manganese and phosphorus are found to be nearly in good agreement, though the effect of sulphur has not yet been established. The question still remains for solution why the recent results given by Kitchener[45] and Turkdogan[46] are in high disagreement. Hence, the authors attempted to find the effect of sulphur on the carbon solubility from the present equilibrium data. Since the solubility of carbon in Fe-C-Mn melts has not yet been determined in lower manganese range, the measurement of the solubility was undertaken in the carbon monoxide or Argon atmosphere. The apparatus used was the same as in the experiment of manganese-sulphur equilibrium. The solubility was determined by quenching the samples taken by the suction in a silica tube, after the saturation by the graphite crucible. The materials used for this purpose were the Fe-C alloy as used previously and sublimed metallic manganese. The results at 1,400° C and 1,500° C are shown as Fig. 24. It is found that the solubility of carbon increases linearly with increasing manganese up to 10 per cent. Approximately the difference of the solubility of carbon between the lines shown in Fig. 18 and Fig. 24 may be ascribed to the decrease of the solubility by the presence of sulphur, and then the relation between sulphur per cent and carbon solubility was determined as shown in Fig. 25. In this Figure the experimental data at 1,500° C by Turkdogan and Leake and some data near 1,500° C by Kitchener *et al.* and the calculated solubility line by their experiment are also described. The results of the present work nearly agree with those of Turkdogan *et al.*

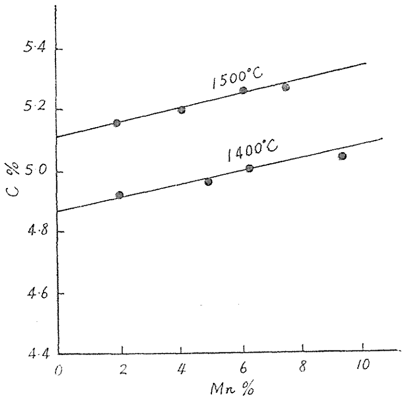

FIG. 24. Solubility of graphite in Fe-C-Mn melts.

Turkdogan *et al.*[46] showed that generally in Fe-C-X solutions the values of ΔN_C^X were independent of the temperature, where ΔN_C^X was shown as the difference of the carbon solubility between in Fe-C binary and Fe-C-X ternary solutions denoted by atom fraction. For example, they also showed those solutions such as Fe-C-Si, Fe-C-Mn and Fe-C-P systems in which the above value were nearly linear with each atom fraction of the third element. However, the similar relationship was not found in the Fe-C-S solution, perhaps because of the complex liquid structure of this solution. Now, taking the experimental data of the present work at 1,500° C and 1,400° C the relationship between ΔN_O^S and N_S as atom fraction was obtained as shown in Fig. 26. In considerably lower concentrations of sulphur the relationship is found to give a parabollic curve and moreover in extremely lower consentrations of sulphur as below 0.005 N_S (about 0.35% S) it may be regarded as linear and then the following equation (3.19) established by Turkdogan *et al.*[33] is valid.

$$\Delta N_C^S = -N_S \qquad (N_S < 0.005). \qquad (3.19)$$

This was also independent of the temperature as shown in Fig. 25.

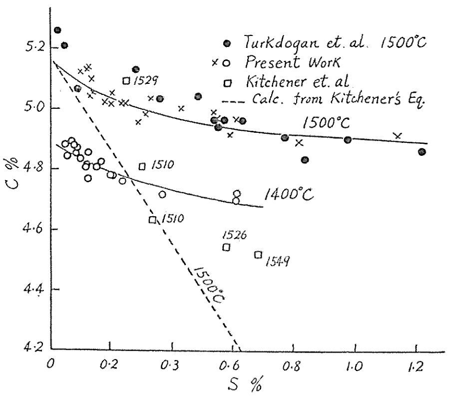

FIG. 25. Effect of sulphur on solubility of graphite in molten iron; dotted line represents the experimental equation by Kitchener *et al.* at 1,500° C.

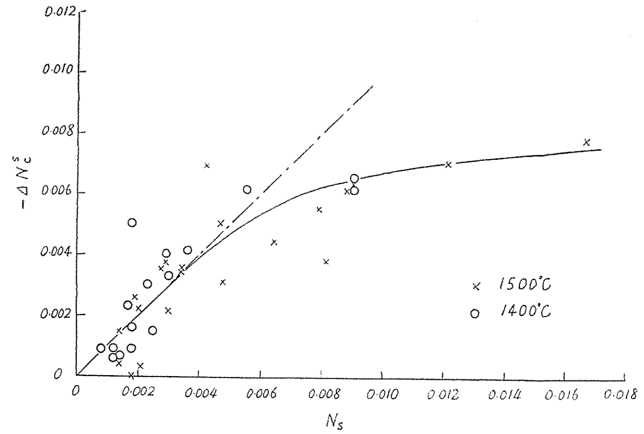

FIG. 26. Relationship between $-\Delta N_S^C$ and sulphur concentration.

6. Conclusion

(1) In recent years, it has become evident that the activity coefficient of sulphur in liquid iron as a function of the ability for the desulphurization is affected

by coexisting with other elements. Thus, in order to study how the so-called natural desulphurization of pig iron by manganese is affected by its composition, the equilibrium between manganese and sulphur in the carbon saturated molten iron was determined under the atmosphere of 1 atm carbon monoxide.

(2) In the temperature range between 1,200° C and 1,500° C, the established desulphurization limit by manganese was in good agreement with those of Oelsen. It goes without saying that the desulphurization proceeds as temperature decreases. Though the sulphur content of the pig iron used for the steel-making containing 1~2 per cent manganese becomes lower so as to be useful for steel-making at about 1,200° C without any further treatment, such effective desulphurization can't be expected considering from the thermodynamical values on the desulphurizing power of manganese. This suggests the high sulphur activity in liquid iron.

(3) Calculating the activity coefficient of sulphur, f_S, by the semi-empirical method as shown by Sherman and Chipman using the present solubility data of carbon at the manganese-sulphur equilibrium, it is found that the values of f_S are inclined to decrease as manganese increases. However, they are also regarded as constant in the ordinary compositions of pig iron at definite temperature. Furthermore, since the activity coefficient of manganese f_{Mn} is unvaried under such iron melts such as carbon-saturated solution and low sulphur content, the apparent equilibrium constant $K''=[\%\,S][\%\,Mn]$ is substituted for the equilibrium constant $K=a_{MnS}/a_S\cdot a_{Mn}$, if the desulphurization product is regarded as manganese sulphide.

(4) The relation between $\log K''$ and reciprocal of the absolute temperature is linear as followings:

$$\log K''=-9{,}763/T+5.197.$$

From this the following thermodynamical values are obtained.

$$\underline{S}+\underline{Mn}=(MnS) \qquad \Delta F^\circ=-47{,}741+28.49\,T$$
$$Mn(l)+1/2\,S_2(g)=MnS(s) \qquad \Delta F^\circ=-79{,}261+24.65\,T.$$

(5) The effect of sulphur on the solubility of carbon in liquid iron is obtained from the present equilibrium data and the measured data on the solubility of carbon in Fe-C-Mn melts. The results at 1,500° C nearly agree with those of Turkdogan *et al.*

Chapter IV. The Effect of Silicon on the Equilibrium between Manganese and Sulphur in Carbon Saturated Iron

1. Introduction

In a previous chapter the experimental results were shown on the equilibrium between manganese and sulphur in carbon saturated iron melts. It was clarified that the higher sulphur potential in carbon saturated iron melts results in the effective desulphurization by manganese as decreasing temperature, although the desulphurizing power of manganese may be weak considering from the thermodynamical values. Since silicon increases the activity coefficient of sulphur in liquid iron as well as carbon and is generally contained more or less in liquid iron during the blast furnace operation, it may be necessary to find the effect on the desulphurization by manganese. There has not yet been seen literature on this subject except the some data of Wentrup.[16] He has recognized that the presence of silicon improves the desulphurization by manganese, but he has not given the effect at carbon saturation. While silicon increases the activity coefficient of sulphur, it decreases the carbon solubility in liquid iron and consequently decreased carbon lowers the activity coefficient of sulphur. Therefore, the effect of the presence of silicon on the activity coefficient of sulphur may be somewhat cancelled. Namely, the desulphurization limit may be determined by those summarizing effects and this will be discussed in the following paragraph.

In the present chapter, the authors try to clarify the effect of silicon on the desulphurization by manganese at carbon saturated iron melts.

2. Some considerations on the reactivity for the desulphurization of carbon saturated iron containing silicon

Before begining the experiment, the reactivity for the desulphurization of carbon saturated iron containing silicon is considered from calculation of the activity coefficient of sulphur in those melts.

As mentioned in the previous chapter, the activity coefficient of sulphur in multicomponent system generally can be estimated by a simple relation given by Wagner,[37] if $f_S^{(X)}$ is known in ternary Fe-X-S system. Now, applying to Fe-C-Si-S system, the activity coefficient of sulphur is calculated by Eq. (4.1).

$$\log f_S = \log f'_S + \log f_S^{(C)} + \log f_S^{(Mn)}. \quad (4.1)$$

Then considering the carbon saturated iron melts, it must be known how much the carbon solubility decreases by the presence of silicon. The carbon solubility in the Fe-C-Si system has been studied by many authors such as Piwowarsky,[47] Chipman and coworkers,[48] Turkdogan and co-wokers,[46] Matoba and Banya[49] and also Ohtani.[50] They are in fairely good agreement and now taking the data of Chipman *et al.*, their data were corrected to 1,400° C as shown in Fig. 27 (a), from which f_S at any silicon per cent at carbon saturation was calculated by Eq. (4.1) and plotted as Fig. 27 (b). It is obvious that the activity coefficient of sulphur will increase with silicon addition to carbon saturated iron melts. Accordingly this fact suggests that the desulphurization limit by manganese may lower with silicon addition in carbon saturated iron melts.

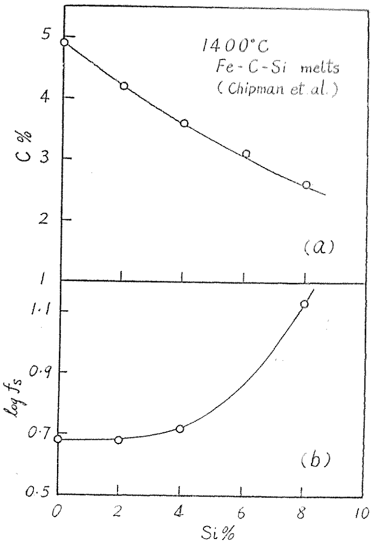

FIG. 27. (a) Carbon solubility in liquid Fe-C-Si system at 1,400° C and (b) estimated $\log f_S$ related to Si per cent at carbon saturation.

3. Experimental apparatus and procedure

(*1*) *Apparatus.*—The present experimental apparatus is the same as described in the previous chapter, namely, on the experiment of Fe-C^{sat}-Mn-S system.

(2) *Materials.*—They are almost the same as used in the previous experiment. Moreover, synthesized Fe-Si alloy (50% Si) and commercial ferrosilicon (75% Si) were used to give silicon to the melt. The synthesized Fe-Si alloy was produced by adding metallic silicon (98% Si) to molten electrolytic iron in an alumina crucible under Argon atmosphere.

(3) *Experimental procedure.*—The procedure employed in these experiments was quite similar to that employed in the previous investigation. The determination of equilibrium was undertaken from the direction of desulphurizing high sulphur iron melt by adding manganese. Silicon addition was aimed at 2 per cent, 4 per cent and 8 per cent at 1,400° C. The initial charge consisted of electrolytic iron, Fe-C alloy and Fe-Si alloy. It was heated gradually in a graphite crucible and melted in vacuum for 20 to 30 minutes at the temperature which was higher by 50 to 100° C than the experimental temperature. After degassing as much as possible, this Fe-C-Si alloy was solidified in the crucible. Then carbon monoxide was introduced in the reaction tube and the solidified alloy was melted again. Some amount of the Fe-C-S alloy previously inserted in the side branch of the glass head on the reaction tube was fallen into the melt by a magnet. The whole melt was then brought to the desired temperature and ferro-manganese was added similary. By holding the constant temperature for about 60 to 90 minutes, the equilibrium was attained. Samples for chemical analysis were sucked by inserting a narrow silica tube into the melt and quenched into cold water. Chemical analysis of C, Mn and S was carried out by the same methods as in the previous work. Since these samples having higher silicon as 8% Si in the metal could not be dissolved completely in nitric acid at sulphur analysis, the residue was filtered and fused with alkali in a platinum crucible and then leached in dilute hydrochloric acid. This solution was added to main solution and the whole solution was treated as usually. Besides, those samples were not easily combustioned at carbon analysis, so the combustion temperature was taken as 1,200 to 1,250° C and thus satisfactory results were obtained. Silicon analysis was taken as standard method as JIS.*

4. Experimental results

The equilibrium was determined at 1,400° C under 1 atm. carbon monoxide. The results are shown in Table 9 and also plotted in Fig. 28 in the three groups. The curves I, II and III represent the equilibrium between manganese and sulphur in carbon saturated iron melts containing 2%, 4% and 8% silicon respectively. The marks ↑ and ↓ at some observed points mean that silicon content is too high or low for the desired value. The mark ◑ represents the first group containing $2.0 \pm 0.15\%$ Si, ⊙ represents the second group containing $4.0 \pm 0.15\%$ Si and ● represents the third group containing $8.0 \pm 0.20\%$ Si. For comparison the observed data of the Fe-C^{sat}-Mn-S system ($\text{Si} < 0.2\%$) are plotted as the mark ○.

It is clearly observed that the effect of silicon addition to the manganese-sulphur equilibrium is negligibly small up to 2% silicon. The curve I entirely

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* Japanese industrial standards.

TABLE 9. Equilibrium Data at 1,400° C

Melt No.	Temp. (°C)	Time (min.)	Initial (S%)	Metal pct. at equilibrium				Mole fraction				$K''=[\mathrm{Mn}\%][\mathrm{S}\%]$	f_S	Remarks
				C	Si	Mn	S	N_C	N_{Si}	N_{Mn}	N_S			
Series I														
S-30	1,400	80	0.63	4.18	2.07	0.57	0.497	0.165	0.035	0.005	0.0074	0.283	4.1	
S-31	〃	90	〃	4.17	1.99	0.66	0.378	0.165	0.034	0.006	0.0056	0.248	4.4	
S-32	〃	60	0.58	3.97	2.01	0.76	0.318	0.159	0.034	0.007	0.0047	0.241	4.1	
S-33	〃	70	〃	4.20	1.98	0.98	0.276	0.167	0.034	0.009	0.0041	0.270	4.4	
S-36	〃	60	0.56	4.29	2.05	1.63	0.152	0.170	0.035	0.014	0.0023	0.248	4.5	
S-37	〃	60	0.47	4.40	1.96	2.08	0.104	0.174	0.033	0.018	0.0015	0.216	4.5	
S-39	〃	60	0.39	4.19	2.10	2.84	0.087	0.167	0.036	0.024	0.0013	0.246	4.1	
S-40	〃	60	〃	4.34	2.01	2.98	0.067	0.172	0.034	0.026	0.0008	0.199	4.2	
S-41	〃	60	—	4.36	2.38	3.67	0.059	0.169	0.039	0.031	0.0008	0.216	4.4	
S-44	〃	60	0.58	4.22	2.26	0.98	0.218	0.167	0.038	0.009	0.0032	0.214	4.5	
S-45	〃	60	0.65	4.17	2.04	0.41	0.478	0.165	0.035	0.004	0.0071	0.196	4.5	
S-46	〃	60	0.42	4.24	1.97	1.45	0.158	0.168	0.033	0.013	0.0023	0.230	4·4	
Series II														
S- 1	1,400	60	0.35	3.53	3.91	2.81	0.072	0.140	0.066	0.024	0.0011	0.201	4.6	
S- 2	〃	70	0.50	3.59	4.01	0.598	0.260	0.143	0.068	0.005	0.0039	0.156	5.1	
S- 3	〃	60	〃	3.43	4.24	0.42	0.367	0.133	0.070	0.004	0.0053	0.154	5.1	
S- 6	〃	60	0.31	3.61	4.12	1.37	0.138	0.143	0.070	0.012	0.0021	0.188	5.1	
S- 7	〃	70	0.30	3.78	3.98	1.74	0.097	0.148	0.067	0.015	0.0014	0.171	5.1	
S- 8	〃	60	〃	3.70	4.04	2.32	0.087	0.145	0.069	0.020	0.0013	0.202	5.0	
S- 9	〃	〃	0.25	3.84	3.86	2.56	0.098	0.152	0.066	0.022	0.0015	0.250	4.9	
S-10	〃	〃	〃	3.74	4.12	3.30	0.057	0.148	0.071	0.031	0.0008	0.188	4.8	
S-11	〃	〃	〃	3.79	4.01	3.65	0.050	0.148	0.067	0.032	0.0008	0.183	4.9	
S-13	〃	〃	0.56	3.52	3.64	0.66	0.274	0.141	0.062	0.006	0.0040	0.181	4.5	
S-15	〃	80	0.47	3.49	4.01	1.06	0.176	0.139	0.069	0.009	0.0026	0.187	4.8	
S-16	〃	60	0.61	3.37	3.99	0.496	0.343	0.133	0.067	0.004	0.0051	0.170	4.7	
Series III														
S-20	1,400	60	0.35	2.30	8.19	0.69	0.148	0.092	0.140	0.006	0.0022	0.101	9.6	
S-21	〃	90	0.53	2.45	7.92	0.91	0.156	0.018	0.137	0.008	0.0024	0.142	9.2	
S-22	〃	90	0.48	2.61	8.00	1.14	0.141	0.104	0.136	0.009	0.0021	0.161	9.5	
S-23	〃	60	0.47	2.50	8.15	1.50	0.091	0.099	0.138	0.013	0.0014	0.135	9.6	
S-24	〃	60	〃	2.69	8.15	1.46	0.103	0.107	0.138	0.013	0.0015	0.150	10.0	
S-26	〃	60	0.50	2.72	8.10	2.42	0.068	0.108	0.137	0.021	0.0010	0.165	9.7	
S-27	〃	60	0.62	2.33	8.08	0.51	0.264	0.093	0.138	0.004	0.0039	0.135	8.9	
S-29	〃	90	0.36	2.55	8.20	3.20	0.067	0.100	0.138	0.021	0.0010	0.216	9.2	
S-50	〃	90	0.25	2.61	8.20	3.68	0.056	0.111	0.138	0.037	0.0008	0.206	9.2	
S-51	〃	90	0.40	2.38	8.26	0.80	0.214	0.095	0.141	0.007	0.0032	0.172	9.8	
S-52	〃	90	〃	2.60	7.87	1.50	0.113	0.104	0.134	0.013	0.0017	0.169	9.1	
S-53	〃	90	〃	2.55	8.00	0.54	0.193	0.100	0.136	0.005	0.0029	0.104	9.6	
S-54	〃	60	0.33	2.33	8.60	0.89	0.147	0.093	0.147	0.008	0.0021	0.130	10.1	
S-56	〃	60	0.23	2.85	7.54	3.24	0.052	0.111	0.126	0.027	0.0008	0.168	8.4	
S-57	〃	60	〃	2.62	8.07	2.56	0.052	0.102	0.135	0.022	0.0008	0.133	9.2	
S-58	〃	90	0.26	2.60	7.78	2.90	0.048	0.102	0.131	0.025	0.0007	0.139	8.4	
S-59	〃	90	0.23	2.56	8.40	3.97	0.037	0.100	0.141	0.033	0.0006	0.147	9.4	

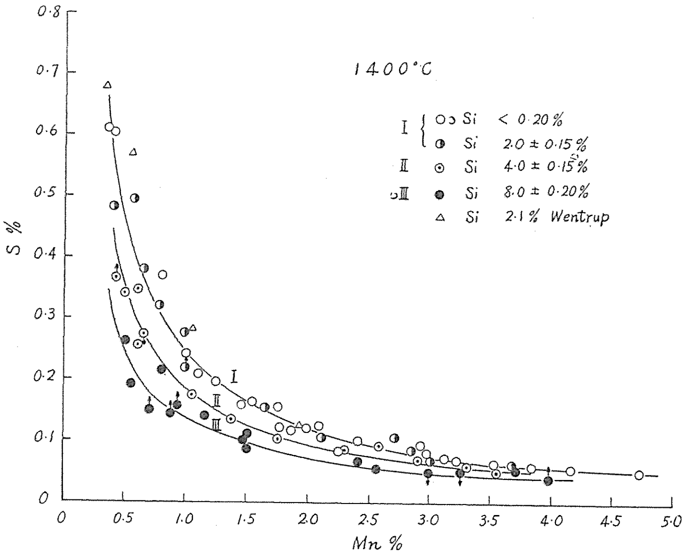


FIG. 28. Equilibrium between manganese and sulphur in carbon saturated iron containing various silicon contents at 1,400° C.

agrees with the equilibrium curve of Fe-C^{sat}-Mn-S system as previously determined. However, more silicon addition brings about lowering effect on the desulphurization limit. This may be attributed to the fact that the increasing effect of silicon itself on the activity coefficient of sulphur is stronger than the decreasing effect owing to the decrease of carbon solubility by silicon addition. This fact agrees well with the considerations of the previous section. Some observed points marked △ in Fig. 28 represent the data obtained by Wentrup,[16] which are as of 2.1% silicon at 1,400° C, and nearly agree with the present work. Further experimental data on the effect of silicon have not been found, especially in higher silicon range. There were some difficulties with those melts of the third group in sampling for analysis, since some of them were viscous at the experimental temperature.

These experimental results come to the conclusion that in carbon saturated iron melts the effect of substituting silicon for carbon shows the tendency of improving the desulphurization of manganese but it is practically negligibly small in the lower range of silicon such as the ordinary pig iron used for steel-making, and the desulphurization limit depends wholly on the carbon saturation. Furthermore, at the higher range of silicon the effect of silicon addition tends to be lowered with increasing manganese concentrations. Namely, assuming that the apparent equilibrium constant K'' is valid

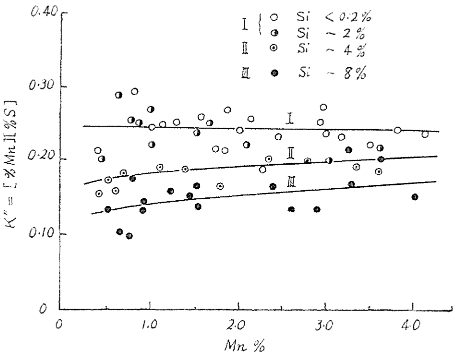


FIG. 29. Apparent equilibrium constant K'' plotted against Mn per cent in Fe-C^{sat}-Si-Mn-S melts at 1,400° C.

in this system and plotted against manganese concentration, it is found that the values of K'' are not constant, but tend to increase with manganese concentration in higher silicon melts, as shown in Fig. 29. Further considerations will be discussed later.

The solubility of carbon in these melts is shown in Fig. 30, Where the equilibrium between manganese and sulphur is attained. The curves are quite similar to those obtained in Fe-C^{sat}-Mn-S system and suggest that the effects of manganese and sulphur on the solubility of carbon are not varied by the presence of silicon, as will be discussed later.

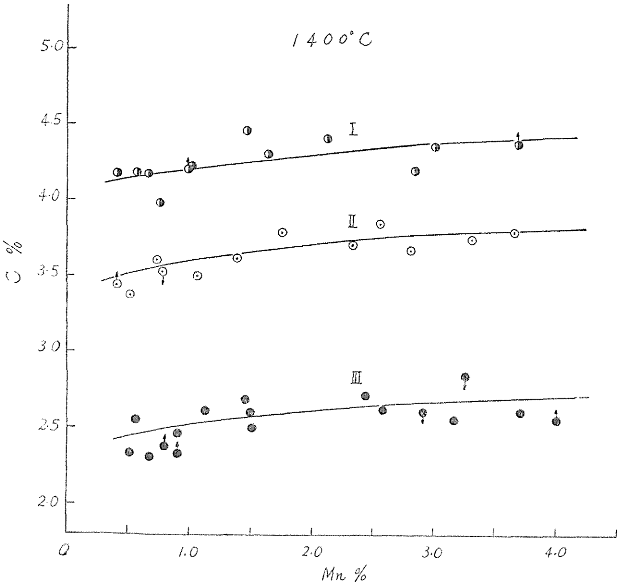


FIG. 30. Carbon solubility in liquid Fe-C-Si melts varies with Mn-S equilibrium at 1,400° C.

5. Discussions

(1) Relations between the desulphurization limit of molten pig iron by manganese and the presence of silicon

Although some investigators described that the desulphurization by manganese is further improved by the presence of silicon, it is found from the present results that in the carbon saturation the desulphurization limit is not effected by the presence of silicon up to 2%, but is wholly dependent on the carbon saturation.

Since those pig irons used for steel-making such as the basic open hearth pig iron or the thomas pig iron are generally restricted in the silicon content below 1.5%, it is important to obtain the carbon saturation in the melts in order to decrease the sulphur content as low as possible. Furthermore, it is noted that more silicon would be reduced from slags which are produced in the acid slag operation of blast furnace, but it would never be injurious to the desulphurization of manganese at least referring to the present equilibrium data.

(2) *Effect of silicon on the activity coefficient of sulphur under Mn-S equilibrium*

As previously mentioned, it is estimated that the activity coefficient of sulphur will increase with silicon as substituting carbon for silicon in carbon saturated iron melts. The assumption seems to be acertained by the present experimental results. Hence, taking the results, the effect of silicon on the activity coefficient of sulphur in the Fe-C^{sat}-Mn-S-Si system will be further discussed.

From the experimental data, the activity coefficient of sulphur f_S under the equilibrium between manganese and sulphur may be estimatable using the curves of $\log f_S$ vs X concentration of Fe-X-S melts determined by Sherman and Chipman. Now, applying the Wagner's relation to those melts, it follows

$$\log f_S = \log f'_S + \log f_S^{(C)} + \log f_S^{(Si)} + \log f_S^{(Mn)} \tag{4.2}$$

and the values of f_S calculated were shown in Table 9 and also plotted against manganese per cent as shown in Fig. 31. It is found that in those carbon saturated melts containing silicon the activity coefficient of sulphur under the equilibrium between manganese and sulphur increases with silicon content, but slightly tends to decrease with manganese content. Nevertheless, it may be practically regarded as constant in the ordinary pig iron such as the basic open hearth pig iron or the thomas pig iron produced by the blast furnace. This is the same as in the case of the carbon-saturated iron melt as previously mentioned. On the other hand, it seems doubtful whether the Wagner's relation may be valid in those melts containing so much amounts of silicon and carbon which are found to show a strong interaction to f_S, since the equation is valid only for dilute solution. It is suggested[51] that the activity coefficient of sulphur in those melts may be also found by a graphical method using the curves shown in Fig. 12 but it is not always useful for the present case.

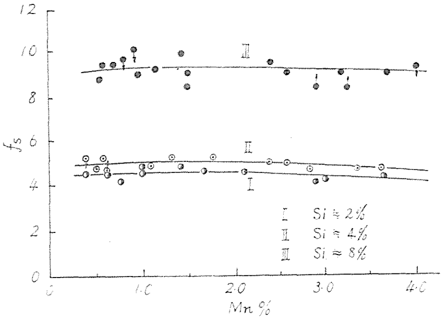


FIG. 31. Activity coefficient of sulphur in liquid Fe-C-Si melts at Mn-S equilibrium related to Mn per cent (1,400° C).

Anyway calculating the values of f_S by Eq. (4.2) tentatively and plotting against silicon concentration, the curve I is obtained as shown in Fig. 32. The curve is in fairely good agreement with that of Fig. 27 (b) predicted in Fe-C^{sat}-Si system. It is found that the activity coefficient of sulphur rapidly increases with silicon content above 4% silicon in the carbon saturated melts.

As already mentioned, the following description by Eq. (4.3) may be used regarding the desulphurization product as MnS,

$$K' = f_S[\%S] \cdot f_{Mn}[\%Mn]. \tag{4.3}$$

Assuming that this equation is valid in the present case and manganese is also ideal, the following relation may be written, referring to the equilibrium curves of manganese and sulphur,

$$\frac{f_S}{f_{S_0}} = \frac{[S_0]}{[S]} \tag{4.4}$$

where f_{S_0} and $[S_0]$ represent the activity coefficient of sulphur and sulphur concentration of the standard F-C^{sat}-Mn-S melts, and then f_S and $[S]$ represent those of the corresponding Fe-C^{sat}-Si-Mn-S melts at any manganese concentration. Taking the values of f_{S_0} as already obtained, the activity coefficient of sulphur f_S is determined from the equilibrium curves in Fig. 28. Those calculated values of f_S are shown in Table 10 together with the desulphurization limits at any silicon content and also plotted against silicon concentration as shown in Fig. 32. The results are expressed as the curves II, III, IV respectively. Compared the present results with the curve calculated by Eq. (4.2), there are approximately agreement among them in lower silicon concentration, but rather discrepancies are found as increasing silicon concentration. Moreover, f_S becomes lower as manganese increases at higher silicon concentration. This seems to be attributed to negative deviation from ideality of manganese. The interaction between manganese atom and silicon atom in liquid iron has never been acertained, but some interaction power may exist since silicon behaves similarly to carbon in liquid iron.[52] Thus, the activity coefficient of manganese may tend to lower as silicon and manganese increase. Now assuming that the interaction between manganese and silicon is the same as of manganese and carbon, the activity coefficient of manganese in those melts will be considered.

TABLE 10. Desulphurization Limit and Activity Coefficient in Fe-C^{sat}-Si-Mn-S Melts at 1,400° C

Si %	Mn = 0.5%		Mn = 1.0%		Mn = 2.0%		Mn = 3.0%	
	S %	f_S	S %	f_S	S %	f_S	S %	f_S
0.2	0.46	4.2	0.24	4.2	0.12	4.2	0.075	4.1
2	0.46	4.2	0.24	4.2	0.12	4.2	0.075	4.1
4	0.35	5.5	0.19	5.3	0.095	5.3	0.065	4.8
8	0.25	7.7	0.13	7.5	0.075	6.7	0.055	5.6

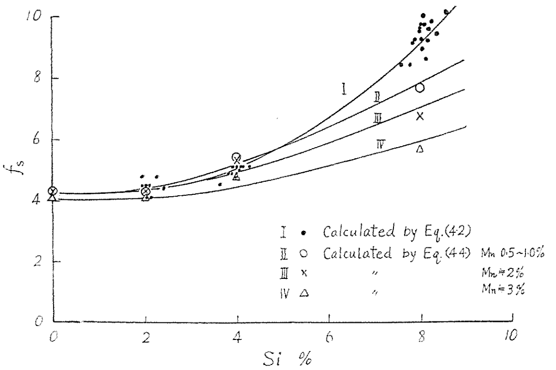


FIG. 32. Effect of silicon addition on activity coefficient of sulphur in C-saturated iron at Mn-S equilibrium.

Recently, Ohtani[38] has determined the activities of Fe-Mn-C ternery melts and showed the effect of carbon on the activity coefficient of manganese γ^{C}_{Mn} as

Eq. (4.5)

$$\log \gamma_{Mn}^{C} = -3 N_{Mn} \cdot N_C/(1-N_C)^2 \tag{4.5}$$

where γ_{Mn}^{C} represents the activity coefficient based on the Raoult's law and N_{Mn}, N_C are atom fractions of manganese and carbon respectively. Now, applying this equation to those melts which was substituted some of carbon for silicon, the activity coefficient of manganese γ_{Mn}^{C+Si} becomes

$$\log \gamma_{Mn}^{C+Si} = -3 N_{Mn} \cdot (N_C + N_{Si})/(1-N_C-N_{Si})^2. \tag{4.6}$$

The results calculated by this equation are shown in Table 11 at 1 and 3 per cent manganese. It is found that the effect of the sum of carbon and silicon on the activity coefficient of manganese is negligibly small in lower manganese range even at higher silicon content, therefore manganese behaves ideal as predictedly. As manganese increases, it deviates negatively from Raoult's law and the activity coefficient becomes $\gamma_{Mn}^{C+Si} = 0.93$ at 8 per cent silicon and 3 per cent manganese. This deviation seems to be very small and the discrepancies between the curves II, III and IV may not be caused by the lowering of the activity coefficient of manganese. Although the propriety of the above calculation leaves some questions, manganese may be regarded as ideal also at the presence of silicon in lower manganese range at least. Then, the curve II in the figure representing f_S in lower manganese melts may be reliable and also in those silicon concentrations as seen in the ordinary blast furnace pig iron, the activity coefficient of sulphur is calculated from the Wagner's relation as previously shown by Eq. (4.2).

TABLE 11. Activity Coefficient of Manganese in Fe-C^{sat}-Si-Mn-S Melts Calculated by Eq. (4.5)

Si %	N_{Si}	C %	N_C	Mn %	N_{Mn}	$N_{Si}+N_C$	$\log \gamma_{Mn}^{Si+C}$	γ_{Mn}^{Si+C}
2	0.0340	4.2	0.1665	1	0.0087	0.2005	−0.008	0.98
4	0.0681	3.6	0.1430	1	0.0087	0.2111	−0.009	0.98
8	0.1368	2.5	0.0995	1	0.0086	0.2363	−0.010	0.98
2	0.0338	4.4	0.1733	3	0.0258	0.2071	−0.026	0.94
4	0.0676	3.8	0.1499	3	0.0259	0.2175	−0.028	0.94
8	0.1356	2.7	0.1068	3	0.0258	0.2424	−0.033	0.93

(3) *Effect of sulphur on the carbon solubility of Fe-C-Si system*

The carbon solubility in the Fe-C-Si system has been well recognized and if $-\Delta N_C^{Si}$ is defined as carbon atom fraction decreased by adding 1 atom fraction of silicon, it is nearely independent of the temperature. Hence, the carbon solubility in the Fe-C-Si system at 1,400° C was obtained from the results of Chipman *et al.*[48] and plotted in the N_C-N_{Si} diagram as shown in Fig. 33. This is shown by the chain line and is observed as nearely straight line up to 0.08 N_{Si}, but gradually deviates as increasing of N_{Si}. The effect of addition of manganese in this system was investigated by Sanbongi, Ohtani and Toita.[50] They found that the degree of increase of carbon solubility in the presence of manganese is not influenced by silicon concentration in considerably lower silicon range. The results obtained about 2.3% manganese at 1,400° C are observed in Fig. 33 as marks □. Hence, from the equilibrium data in the present work, the effect of sulphur on the carbon solubility in Fe-C-Si system may be found substracting the effect of the presence of manganese. Then, the data of the carbon solubility obtained in the present work were classified into 3 groups, namely, $N_S<0.001$, N_S 0.002~0.003, $N_S\approx0.005$ and plotted against atom fraction of silicon as shown in Fig. 33. It is generally recognized that the effect of sulphur is similar to that of the Fe-C-S system, at least below 0.08 atom fraction of silicon. However, the degree of decrease of carbon solubility by the presence of sulphur seems to increase gradually as increasing of silicon, but the conclusion is not yet attained since the present data are somewhat at random.

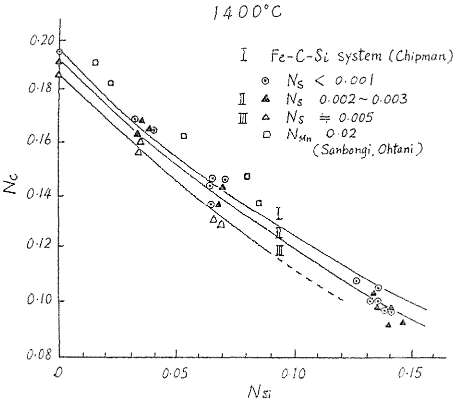


FIG. 33. Carbon solubility in liquid Fe-C-Si melts at various sulphur contents at 1,400° C. Chain line represents solubility of Fe-C-Si melts by Chipman *et al.*

6. Conclusion

The effect of the presence of silicon in the carbon saturated iron melts on the equilibrium between manganese and sulphur was investigated, in order to ascertain the effect on the desulphurization of manganese. The experimental procedure was similar to the previous work and the results were as follows.

(1) In the carbon saturation the desulphurization limit is not effected by the presence of silicon up to 2%, but is lowered as increasing of silicon. In the ordinary blast furnace pig iron the effect of silicon may be negligible and it is important to obtain the carbon saturation in the melts in order to decrease the sulphur content as low as possible.

(2) The activity coefficient of sulphur does not increase by silicon addition because of decrease of the carbon solubility. This will be confirmed by comparing the equilibrium curves between manganese and sulphur in those melts and those of Fe-C^{sat}-Mn-S system. The values of f_S found by this procedure are in nearly good agreement with those calculated by Wagner's relation below 4% silicon.

(3) The effect of sulphur on the carbon solubility in the Fe-C-Si system was discussed. The degree of decreasing of carbon solubility by the presence of sulphur is independent of the silicon concentration up to 4% silicon at least.

Chapter V. The Effect of Phosphorus on the Equilibrium between Manganese and Sulphur in Carbon Saturated Iron

1. Introduction

Generally phosphorus is also contained in pig iron as silicon and sometimes its content amounts to two or three per cent as in the thomas pig iron. It has been recognized that phosphorus increases the activity coefficient of sulphur in liquid iron as silicon, but on the other hand it decreases the carbon solubility. Therefore, it may be necessary to confirm the effect on the desulphurization of manganese as previously discussed on the effect of silicon. However, little literature is yet known on this confirmation. Wentrup[16] mentioned that the presence of phosphorus also improves the desulphurization by manganese, but his data was not obtained at carbon saturation.

In this chapter, the authors try to examine the effect of phosphorus on the desulphurization by manganese at carbon saturation, considering the changes of the activity coefficient of sulphur in those melts.

2. Some considerations on the reactivity for the desulphurization of carbon saturated iron containing phoshorus

As mentioned in the previous chapter, some thermodynamical considerations on the reactivity for the desulphurization can be taken using the activity coefficient of sulphur in the present system.

The activity coefficient of sulphur f_S becomes approximately

$$\log f_S = \log f'_S + \log f_S^{(O)} + \log f_S^{(P)} \tag{5.1}$$

where f'_S and $f_S^{(C)}$ are the same as in the previous system and $f_S^{(P)}$ denotes interaction coefficient of phosphorus.

The effect of the addition of phosphorus on the carbon solubility has been recently studied by Turkdogan *et al.*[46] up to a considerally higher phosphorus range. Taking the mean values of their data at 1,490° C and 1,290° C, the solubility curve at 1,390° C is obtained and then the activity coefficient of sulphur is calculated by Eq. (5.1) as shown in Fig. 34 (a), (b). It is recognized that in contrast with the case of silicon the activity coefficient of sulphur decreases with addition of phosphorus in the carbon saturated melts. This tendency will be resulted from the fact that phosphorus has stronger effect on the lowering of carbon solubility than silicon and furthermore its interaction coefficient for sulphur is rather small.[36] From this viewpoint on the behavior of sulphur, it is suggested that phosphorus addition may result in worse effect on the desulphurization by manganese. Since this conclusion has not yet been attained from the literature, the authors try to acertain it by the following experiments.

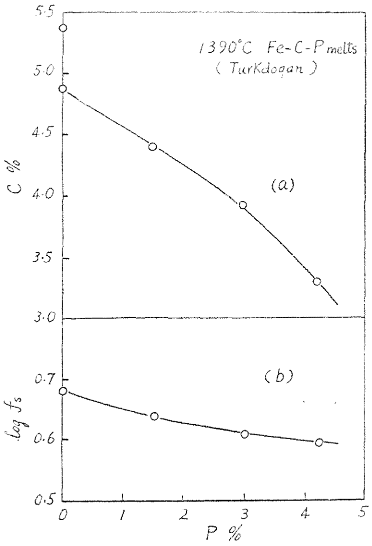


FIG. 34. (a) Carbon solubility in liquid Fe-C-P system at 1,390° C and (b) estimated $\log f_S$ related to P per cent at carbon saturation.

3. Experimental apparatus and procedure

(*1*) *Experimental apparatus and materials used.* The apparatus used in this system is the same as already mentioned. Moreover, the materials for the experimental melts are also the same as in the previous investigation, except the ferrophosphor (C: 0.079%, Si: 0.537%, Mn: 0.259%, P: 23.42%, Fe: 74.40%, Ti: 0.983%, Cu: 0.198%).

(2) *Experimental procedure.* The procedure was essentially the same as in the previous investigation of the effect of silicon. Phosphorus was added as ferrophosphor in each charge so as to contain 2 per cent and 4 per cent respectively. The equilibrium between manganese and sulphur was obtained at 1,370° C by quite the similar procedure as mentioned previously. Determination of phosphorus was made by the electrophotometric method and others were the same as previously.

4. Experimental results

The results obtained at 1,370° C are shown in Table 12 and also plotted in Fig. 35 in two groups. The curve I and II represent the equilibrium between manganese and sulphur in carbon saturated melts containing 2% and 4% phosphorus respectively. The marked point ↑ indicates that phosphorus content is too low for the desired value. The broken line in the figure represents the equilibrium curve of the $\text{Fe-C}^{\text{sat}}\text{-Mn-S}$ system at 1,370° C, calculated by the Eq. (3.13) as previously mentioned. It is clearly observed that the presence of phosphorus in carbon saturated melts has not improving effect on the desulphurization by manganese, but rather reverse effect as previously suggested. In consequence, large amounts of phosphorus may be undesirable for the effective desulphurization. However, it may be recognized that in considerably lower phosphorus range as in the practical Thomas pig iron, the desulphurization limit is entirely dependent on the carbon saturation.

The marked points Δ in the Fig. 35 represent the data of Wentrup at 1,350° C containing 2.1% phosphorus. They are not agreed with the present work, and this may be ascribed to the fact that his samples were not saturated with carbon. For example, they contained 3.2~3.3% carbon at 1,350° C and 2.1% phosphorus.

TABLE 12. Equilibrium Data at 1370° C

Melt No.	Temp. (°C)	Time (min.)	Initial (S%)	Metal pct. at equilibrium				Mole fraction				$K'' = [\text{Mn}\%][\text{S}\%]$	f_S	Remarks
				C	P	Mn	S	N_C	N_P	N_{Mn}	N_S			
P- 1	1370	90		4.28	1.96	2.72	0.071	0.170	0.030	0.024	0.0011	0.194	3.8	
P- 2	〃	60	0.84	4.01	2.09	0.54	0.343	0.160	0.032	0.005	0.0051	0.185	3.9	
P- 3	〃	〃	0.81	4.09	2.16	0.68	0.321	0.163	0.033	0.006	0.0048	0.219	4.0	
P- 4	〃	〃	〃	4.05	2.00	0.88	0.246	0.162	0.031	0.008	0.0037	0.217	3.9	
P- 5	〃	90	0.74	4.22	2.02	1.19	0.161	0.168	0.031	0.010	0.0040	0.192	3.9	
P- 6	〃	70	0.68	4.07	2.11	1.59	0.145	0.163	0.033	0.014	0.0021	0.230	3.8	
P- 7	〃	〃	〃	4.16	2.17	1.75	0.118	0.166	0.033	0.015	0.0018	0.207	3.9	
P- 8	〃	〃	0.41	4.15	2.07	2.19	0.085	0.166	0.032	0.019	0.0013	0.185	3.8	
P-10	〃	〃	0.34	4.20	2.10	2.73	0.068	0.167	0.032	0.024	0.0010	0.186	3.8	
P-13	〃	〃	〃	4.25	2.07	3.12	0.054	0.169	0.032	0.027	0.0008	0.169	3.7	
P-14	〃	90	0.48	4.32	2.05	4.06	0.044	0.171	0.032	0.035	0.0007	0.180	3.6	
P-15	〃	〃	0.42	4.36	2.08	3.95	0.054	0.173	0.032	0.034	0.0008	0.212	3.7	
P-16	〃	〃	0.56	4.18	2.01	1.52	0.143	0.167	0.031	0.013	0.0021	0.218	3.9	
P-17	〃	〃	0.89	4.13	2.04	0.54	0.370	0.165	0.032	0.005	0.0055	0.200	3.9	
P-31	〃	65	0.59	3.59	3.71	0.92	0.236	0.144	0.058	0.008	0.0036	0.217	3.8	
P-32	〃	〃	0.46	3.44	4.00	1.17	0.162	0.139	0.062	0.010	0.0025	0.190	3.7	
P-33	〃	60	0.46	3.53	4.06	1.65	0.151	0.141	0.063	0.014	0.0023	0.249	3.8	
P-34	〃	70	0.37	3.65	4.09	2.05	0.103	0.146	0.063	0.018	0.0015	0.211	3.8	
P-35	〃	60	0.37	3.62	3.95	2.36	0.094	0.144	0.061	0.021	0.0014	0.222	3.7	
P-36	〃	〃	0.70	3.43	3.81	0.56	0.412	0.138	0.059	0.005	0.0062	0.234	3.7	
P-38	〃	〃	0.55	3.59	3.85	0.70	0.327	0.144	0.060	0.006	0.0049	0.230	3.9	
P-39	〃	〃	0.55	3.49	3.91	0.99	0.271	0.140	0.061	0.009	0.0041	0.268	3.7	
P-40	〃	90	0.27	3.58	3.85	3.80	0.057	0.144	0.060	0.033	0.0009	0.217	3.4	
P-42	〃	〃	0.35	3.70	3.85	3.74	0.064	0.148	0.060	0.033	0.0010	0.239	3.5	
P-43	〃	〃	0.89	3.43	4.14	0.51	0.518	0.138	0.065	0.005	0.0078	0.265	3.8	

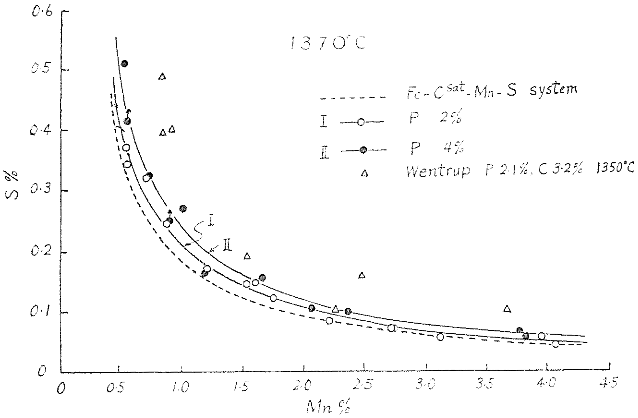


FIG. 35. Equilibrium between manganese and sulphur in carbon saturated iron containing various phosphorus contents at 1,370° C.

Since the pig iron containing some phosphorus is very fluid, it may easily attain to equilibrium even at lower temperaturs which are favorable for the desulphurization by manganese. Fig. 36 shows the relationship between apparent equilibrium constant K'' and manganese per cent and then it may be sure that the values of K'' are nearly constant for each phosphorus concentration in the present experimental range. The carbon solubility in those melts under the equilibrium was measured and plotted against manganese per cent as shown in Fig. 37. The relations obtained are nearly similar to the previous data, obtained in the Fe-C^{sat}-Mn-S system or in the Fe-C^{sat}-Si-Mn-S system.

All the melts contained some small quantities of silicon which was dissolved in the melts from ferro-phosphorus: for example, 0.08% silicon in 2% phosphorus series and 0.11% silicon in 4% phosphorus series were found. However, as already

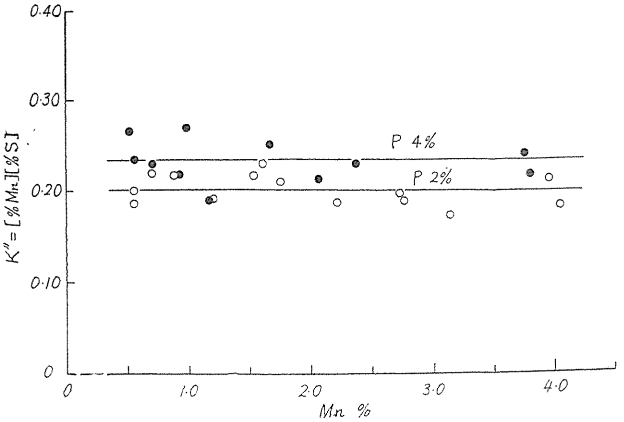


FIG. 36. Apparent equilibrium constant K'' plotted against Mn per cent in Fe-C^{sat}-P-Mn-S melts at 1,370° C.

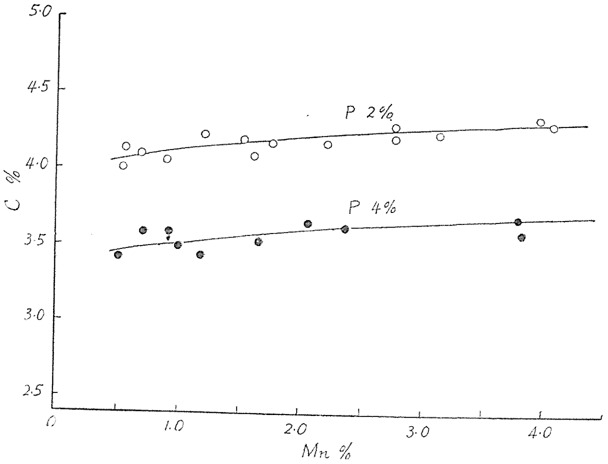


FIG. 37. Carbon solubility in liquid Fe-C-P melts varies with Mn-S equilibrium at 1,370° C.

determined, the effect of these presence of silicon is negligible for the determination of the equilibrium.

5. Discussions

(1) *Effect of phosphorus on the desulphurization limit by manganese*

On the contrary to the results obtained by Wentrup,[16] it is concluded from the present work that the improvement of the desulphurization by manganese is not achieved by the presence of phosphorus but rather disturbed reversely. It is, however, recognized that the desulphurization by manganese may be practically independant of the phosphorus content in such a range as in the Thomas pig iron. The desulphurization limit of this pig iron may be attained wholly under the condition of carbon saturation. Apart from the discussions on the equilibrium, the high phosphorus iron melts, such as the Thomas pig iron, may be favorable for desulphurization, since they easily attain to equilibrium even at lower temperature because of their good fluidity.

(2) *Effect of phosphorus on the activity coefficient of sulphur*

As described in the previous chapter, the activity coefficient of sulphur in such a multi-component system may be obtained from the observed equilibrium data.

Taking the similar relation on the present system, it follows:

$$\log f_S = \log f'_S + \log f_S^{(O)} + \log f_S^{(P)} + \log f_S^{(Mn)} \tag{5.2}$$

the calculated values of f_S by Eq. (5.2) are shown in Table 12 and represented in Fig. 38. It seems that the values of f_S tend to slightly lower as manganese increases, but they are almost constant at any phosphorus content in the range of the ordinary pig iron. Furthermore, they are plotted against phosphorus content and shown as the curve I in Fig. 39, which is nearly similar to that shown in Fig. 32 (b). On the other hand, assuming that the behavior of manganese is also ideal in phosphorus containing melts, the values of f_S in those melts were estimated by comparing the manganese-sulphur equilibrium curves with the standard curve of Fe-C^{sat}-Mn-S system.

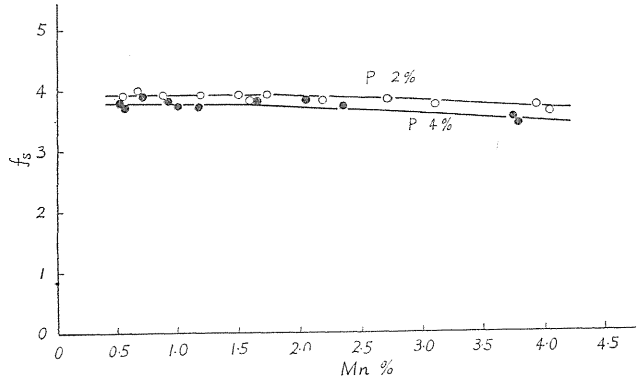


FIG. 38. Activity coefficient of sulphur in liquid Fe-C-P melts at Mn-S equilibrium related to Mn per cent (1,370° C).

Namely, the following Eq. (5.3) was used,

$$\frac{f_S}{f_{S_0}} = \frac{[S_0]}{[S]} \tag{5.3}$$

where f_{S_0} and $[S_0]$ were the same as Eq. (4.4), and f_S and $[S]$ were those of Fe-C^{sat}-P-Mn-S melts.

The results are shown in Table 13 and plotted against phosphorus as shown by the curve II in Fig. 39. Referring this curve to the curve I calculated previously (by Wagners' relation), both curves approximately agree in th elower phosphorus range.

Since the curve II is not nearly effected by manganese, the interaction between manganese and phosphorus seems to be negligibly small in the experimental range, and the behavior of manganese may be also regarded as ideal.

TABLE 13. The Effects of Phosphorus on the Desulphurization Limit of Manganese at Carbon Saturation and the Estimated Activity Coefficient of Sulphur (1370° C)

P%	Mn=0.5%		Mn=1%		Mn=2%		Mn=3%	
	S%	f_S	S%	f_S	S%	f_S	S%	f_S
0	0.36	4.2*	0.18	4.2*	0.090	4.2*	0.060	4.1*
2	0.41	3.7	0.21	3.6	0.105	3.6	0.067	3.7
4	0.48	3.2	0.24	3.2	0.115	3.3	0.075	3.3

* Represents the values at 1,400° C.

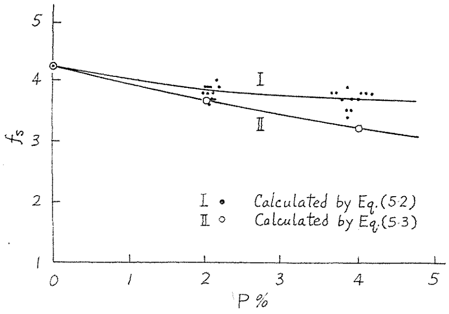


FIG. 39. Effect of phosphorus addition on activity coefficient of sulphur in C-saturated iron at Mn-S equilibrium.

(3) *Effect of sulphur on the carbon solubility of Fe-C-P system*

The carbon solubility of Fe-C-P system has been recently studied by Turkdogan *et al.*[46] up to 4% phosphorus. Similarly as the case of Fe-C-Si system, if $-\Delta N_C^P$ is defined as carbon atom fraction decreased by adding 1 atom fraction of silicon, it is also regarded as nearly independent of the temperature. Then, the carbon solubility at 1,390° C was determined from their observed data and plotted as marked point ○ in the N_C-N_P diagram as shown by Fig. 40. They are found on a straight line approximately below 0.050 N_P.

Now, substracting the effect of manganese from the present equilibrium data, the effect of sulphur on the carbon solubility in the Fe-C-P system will be obtained. The experimental results were devided into two groups according to their sulphur contents, namely $N_S < 0.001$ and $N_S = 0.004 \sim 0.006$, and plotted carbon atom fraction N_C against phosphorus atom fraction N_P. As shown in Fig. 40, the two parallel straight lines were obtained and so in the range of the present measurement, the degree of decreasing of carbon solubility by the presence of sulphur seems to be independent of phosphorus content. The carbon solubility of the extremely lower sulphur melts shown by the curve I approximately agrees with the data of Turkdogan *et al.* below 0.005 N_P, which were obtained at a temperature higher about 20° C.

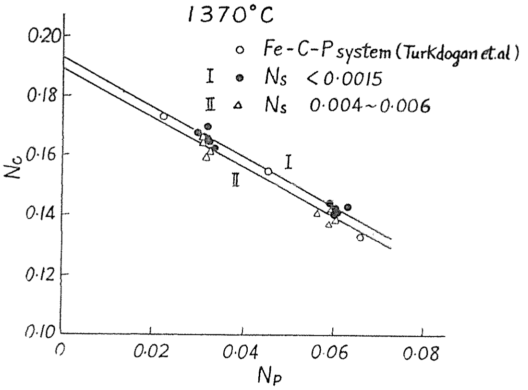


FIG. 40. Carbon solubility in liquid Fe-C-P melts at various sulphur contents at 1,370° C.

6. Conclusion

The effect of the presence of phosphorus in the carbon saturated iron melts on the equilibrium between manganese and sulphur was investigated, in order to ascertain the effect on the desulphurization by manganese. The results obtained at 1,370° C are as follows.

(1) In the carbon saturation, the presence of phosphorus does not give the improving effect on the desulphurization by manganese, but gives rather reverse

effect. However, since this effect is considerably weak in lower phosphorus content, it may be concluded that the desulphurization by manganese in the practical Thomas pig iron is wholly dependent on the carbon saturation, neglecting the effect of the presence of phosphorus.

(2) As is well known, phosphorus lowers carbon solubility more than silicon and somewhat cancells the increasing effect on the activity coefficient of sulphur by carbon. The values of activity coefficient of sulphur estimated from the present equilibrium data tend to slightly lower as manganese increases and also slightly lower as phosphorus increases. Approximately they are regarded as constant in the range of the ordinary pig iron.

(3) The effect of sulphur on the carbon solubility of Fe-C-P system has been discussed from the observed data of carbon solubility under the equilibrium between manganese and sulphur. The degree of decreasing of carbon solubility by the presence of sulphur seems to be independent of phosphorus content.

Chapter VI. Studies on the Desulphurization Product by Manganese

1. Introduction

The mechanism of the desulphurization by manganese is now interpreted as the process of the precipitation and the separation of sulphide phase consisting of mainly manganese sulphide from iron melts. As previously described, if the desulphurization product formed in this way is regarded as manganese sulphide, the equilibrium constant of the desulphurization reaction by manganese can be expressed as $K_1' = a_S \cdot a_{Mn}$ or furthermore approximately $K'' = [\%S][\%Mn]$. Moreover, it was clarified that in the carbon saturated iron melts the apparent equilibrium constant $K'' = [\%S][\%Mn]$ is approximately valid in the range of manganese content between 0.4 and 5 per cent at the temperature range of 1,200 to 1,500° C. However, in higher temperature, the observed values of K'' are not always constant, but decrease as manganese lowers, as shown at 1,500° C. In such case, K'' can't represent the equilibrium at least lower than 1 per cent manganese.

A cause of this fact may be attributed to the lowering of the activity of manganese sulphide in desulphurization product, and then it will be necessary to clarify the compositions of such desulphurization products.

Even though the manganese sulphide has been assumed to precipitate and separate from molten iron as the desulphurization product, it is obvious from the FeS-MnS phase diagram[53] (cf. Fig. 44), that the manganese sulphide itself dissolves a large amount of ferrous sulphide, and it is also well known that the FeS-MnS solid solution is often found as sulphide inclusion in many steels. Therefore, the desulphurization product which is regarded as manganese sulphide is considered to be dissolved at least by FeS or some other materials. From this viewpoint the authors try to determine the composition of desulphurization product directly, in order to understand the desulphurization reaction of manganese more precisely.

2. Preparation of slags as desulphurization product

The experimental studies on the slags as the desulphurization product by manganese have been made by Wentrup,[16] Oelsen,[17] and Meyer and Schulte.[15] The most precise and systematic study was followed by Meyer and Schulte on the equilibrium $FeS+Mn \rightleftharpoons MnS+Fe$. They determined the slag phase equilibrated with liquid metal. The experimental method used by them was that the mixtures of electrolytic iron (or armco iron), metallic manganese and synthetic manganese sulphide or ferrous sulphide were melted in atmosphere of nitrogen and hydrogen and attained to equilibrium after maintaining several minutes at a definite temperature, and then solidified samples were seperated into metal and slag phase for chemical analysis. Wentrup also tried a similar experiment. In spite of their precise studies, it is difficult to make the reactions between slag and metal reversible, if the slag is viscous or solid at the temperature. It is doubtful whether slags obtained by their technique show the correct slags which should be formed at that temperature, and whether the slags and metals are completely separated from each other under such conditions. In a similar preliminary experiment made by the authors, it was very difficult to seperate the both phases after solidification. Considering that the data of Meyer and Schulte are extremely higher compared with the present equilibrium values, it is to be pointed out that some slags were included in metal phase, inspite of their careful analysis of the metal phase. Thus, the authors try to examine the desulphurization products which are in equilibrium of manganese and sulphur in molten iron by the following method. The remarkable point of the method is that the slags are formed by mixing molten Fe-C-Mn alloy and molten ferrous sulphide which are previously maintained at the same temperature, while the equilibrium between manganese and sulphur in the metal phase are attained in the same time. This procedure will be useful to obtain the object in comparatively short time if the both molten alloys are mixed and reacted together at a definite temperature.

3. Experimental apparatus and method

(1) *Experimental apparatus*

On constructing apparatus, special attention was paid to produce the desulphurization product at the temperature as intended. For this purpose the sulphur rich iron (ferrous sulphide) and the manganese rich iron were melted separately in two graphite crucibles and then mixed at the desired temperature. The main part of the apparatus is shown as Fig. 41.

A silica tube (40 mm I.D., 500 mm Height and bottom closed) was used as the reaction tube, in which two graphite crucibles were set up and down, protected by a alumina crucible. The upper graphite crucible is shown as Fig. 42. In the bottom of this crucible there was a tapping hole of 4 mm diameter accompanied by a graphite stopper so as to fall the molten metal into the lower crucible as desired. The graphite stopper had a hole drilled into it as 5 mm inner diameter and connected to a silica tube, which was spread at the head and was wound round by a thin silicon steel band. The silica tube connected with graphite stopper can be raised by moving the silicon steel band by a magnet outside the glass cap in order to fall the molten metal.

The temperature was measured by a disappearing-filament optical pyrometer, sighting into the hole of graphite stopper through the inner silica tube from the window of the glass cap. For the purpose of maintaining the reaction chamber vacuum or carbon-monoxide or argon atmosphere, the reaction tube was connected with vacuum system or gas purification system of carbon monoxide or argon.

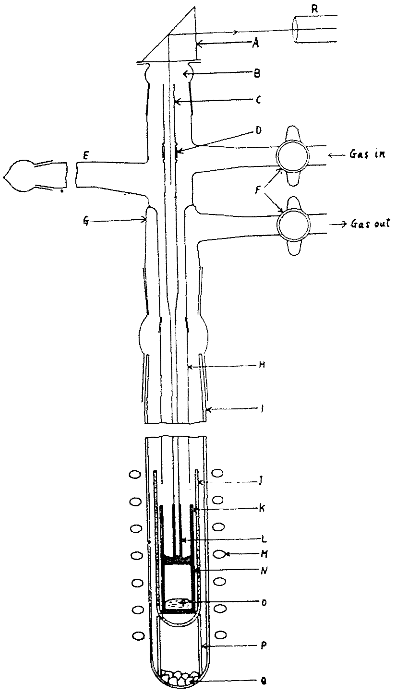


FIG. 41

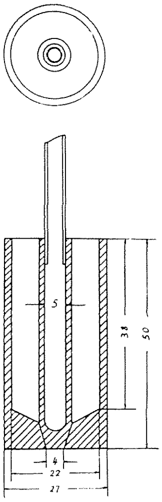


FIG. 42

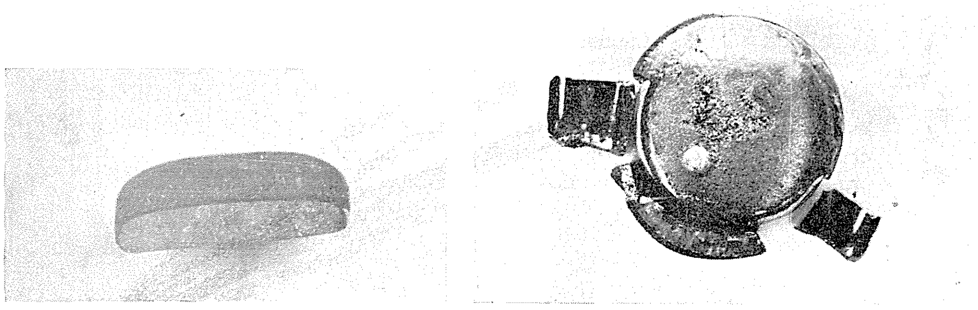
FIG. 41. Furnace assembly. FIG. 42. Upper graphite crucible. *A*: Glass prism. *B*: Glass window. *C*: Silica tube. *D*: Silicon steel band. *E*: Side branch. *F*: Cock. *G*: Glass cap. *H*: Gas inlet tube (silica tube). *I*: Silica tube. *J*: Alumina crucible. *K*: Upper graphite crucible. *L*: Graphite stopper. *M*: Induction coil. *N*: Lower graphite crucible. *O*: Liquid metal. *P*: Alumina tube. *Q*: Silica pieces. *R*: Optical pyrometer.

(2) *Experimental method*

Almost experiments were carried out at 1,500° C. For the temperature measurment the optical reading was taken through the silica tube on the bottom of graphite stopper and calibrated by Pt-PtRh thermocouple which was inserted into the molten metal through the stopper nozzle of the upper graphite crucible. The temperature difference between molten metal and the stopper end was only 20~25° C and this value may be negligible.

The experimental procedure was as follows: the two graphite crucibles were preliminary degassed in vacuum. Then about 15 grams of Fe-C-Mn alloy (Mn 10~20%) was charged in the lower crucible and 4~5 grams of pure synthesized ferrous sulphide in the upper crucible as shown in Fig. 41. After replacing the atmosphere of the reaction chamber by carbon-monoxide or Argon, both samples were melted by induction heating. Then, both melts were maintained at the desired temperature and molten ferrous sulphide in the upper crucible was fallen down into the lower crucible at once by raising the graphite stopper with the silica tube by a magnet. Molten ferrous sulphide is not viscous at the experimental temperature and seemed to drop into the lower crucible easily through the stopper nozzle.

Dropped molten ferrous sulphide was mixed and reacted with Fe-C-Mn melt immediately by induction stirring at a definite temperature. After 1 to 3 hours electric power was cut off and they were solidified in the reaction chamber. Solidified samples were separated into two phases, such as metal and slag by hammering. Photo 1 shows the example of the two separated phases of the solidified sample, and Example (a) shows: the slag was entirely fluid as in the case of extremely lower manganese content. On the other hand, Example (b) shows: the slag was not fluid or solid and generally sticked to the inner surface of the crucible. Such case was seen in those melts which have manganese higher than 1 per cent in the metal. Thus, both phases which seemed to be almost separated may contain some small parts of the another phase as inclusions and therefore careful sampling must be needed for analysis. The slag phase was easily crushed to powder and enclosed metallic iron was eliminated carefully by a magnet before sampling for analysis. However, dispersed sulphide slag in the metal phase could not be separated mechanically. After removing the slag adhered on the surface of solidified metal as much as possible, the metal lump was remelted in graphite crucible in the same condition and thus dispersed slag in the metal could be mostly floated and removed. The metal samples for analysis were sucked by silica tube and quenched in water.



(*a*) (*b*)

PHOTO 1. Solidified samples.

The analytical procedure used was as follows: sulphur in the metal was determined by the gravimetric method and that in the slag by ion exchange acidimetric method.*[54] Manganese in both phase was determined by spectrophotometry.

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* Ref. The ion exchange acidimetric method was already applied to determination of sulphur in sulphide ore successfully by Hirano and Kurobe. This method is as follows: Sample is fused with sodium peroxide and dissolved in water. This solution is passed through a glass column packed with "Amberlite IR 120", and H_2SO_4 formed by ion exchange in the filtrate is titrated with the standard sodium hydroxide solution.

4. Experimental results

(1) Relation between Mn-S equilibrium and desulphurization product

The experimental results at 1,500° C are shown in Table 14. Fig. 43 (a) shows the slag composition and (b) shows the Mn-S relationship in metal phase. The curve shown in Fig. 43 (b) is the equilibrium curve at 1,500° C as previously determined. Since the present values are almost distributed on this equilibrium curve, manganese and sulphur in these melts may be in equilibrium. Some values which are markedly apart from the curve mean containing of the dispersed slags as inclusions and therefore will be neglected in the following discussion. The appearance of slags equilibrated with iron melts below 0.5% manganese showed that they were almost fluid and distinctly separated from metal phase as another phase. The apparent color of slags was generally dark grey, but those powders of higher manganese content were tinted with green. The slags could not be regarded as the pure manganese sulphide, since they contained some iron perhaps as sulphide even in higher manganese range. In due consideration of enclosed graphite in the slag phase, analytical values of each element were corrected taking (Fe%)+(Mn%)+(S%)=100%, as shown in Table 14. Plotting the manganese per cent in the slag against the corresponding in the metal, it is recognized from Fig. 43 (a) that the manganese content in the slag becomes almost constant value above about 3 per cent manganese in the metal, but decreases rapidly below 1 per cent. On the contrary the iron content increases rapidly. Plotting the slag compositions on the Fe-Mn-S ternary diagram, the present values are recognized as nearly on the line connecting FeS and MnS, as shown by c-d line in Fig. 44. The curve a-b represents the equilibrium curve between manganese and sulphur in the corresponding molten iron. Those slags equilibrated with iron melts containing extremely lower manganese content somewhat tend to deviate from the

TABLE 14. Equilibrium Data on the C-saturated Melts and Slags

Melt No.	Temp. (°C)	Metal %			$K''=$ [Mn][S]	$\log K''$	Slag %				(Fe)+(Mn)+(S)=100			(MnS) %	Remarks
		C	Mn	S			(Fe)	(Mn)	(S)	Σ=(Fe)+(Mn)+(S)	Fe %	Mn %	S %		
SG 6	1,500	5.10	2.68	0.32	0.813	−0.090	5.46	55.1	32.7	93.3	5.85	59.1	35.1	93.6	Ar atmos. 1 h
SG 9	〃		0.03	1.18	0.0354	−1.451	53.3	13.6	31.5	98.4	54.2	13.8	32.0	21.9	〃
SG10	〃	4.90	0.05	1.01	0.0505	−1.297	46.6	18.5	32.2	97.3	47.9	19.0	33.1	30.1	〃
SG11	〃		0.08	0.92	0.0735	−1.134	43.8	22.2	31.6	97.6	44.9	22.7	32.4	36.0	〃
SG12	〃	5.04	0.39	0.99	0.386	−0.413	22.0	41.2	34.1	97.3	22.6	42.3	35.1	67.1	〃
△SG14	〃	5.26	1.00	0.92	0.920	−0.036	16.2	48.4	34.5	99.1	16.3	48.8	34.9	77.4	〃
SG15	〃		0.40	0.84	0.336	−0.474	24.2	40 1	34.5	98.8	24.5	40.6	34.9	64.4	〃
SG16	〃	5.25	6.52	0.092	0.600	−0.222	3.22	56.7	30.9	90.8	3.54	62.5	34.0	99.0	〃
SG17	〃	5.45	5.83	0.16	0.939	−0.027	3.97	54.3	34.0	92.3	4.30	58.9	36.8	93.3	CO atmos. 1 h
SG18	〃	5.24	1.93	0.32	0.618	−0.209	6.94	52.5	33.9	93.3	7.44	56.3	36.3	89.3	〃
△SG19	〃	5.15	1.07	0.94	1.005	0.002	19.5	39.8	34.4	93.7	20.8	42.5	36.7	67.4	〃
SG20	〃	5.08	3.17	0.14	0.442	−0.355	4.90	52.6	32.1	89.6	5.47	58.7	35.8	93.0	〃
SG21	〃	5.20	4.38	0.19	0.832	−0.080	3.90	53.5	31.5	88.9	4.39	60.2	35.4	95.5	〃
SG22	〃	5.05	1.75	0.32	0.563	−0.249	10.7	45.5	33.8	90.0	11.9	50.5	37.6	80.0	Ar atmos. 1 h
△SG23	〃	5.11	0.55	1.44	0.792	−0.101	25.5	32.5	35.2	93.2	27.4	34.9	37.7	55.3	〃
SG24	〃	5.20	5.60	0.076	0.426	−0.371	5.52	52.5	33.6	91.6	6.02	57.3	36.7	90.8	〃
SG25	〃	5.01	0.76	0.69	0.524	−0.281	15.2	34.8	29.1	79.1	19.2	44.0	36.8	69.7	1 h
SG26	〃	4.96	0.84	0.52	0.437	−0.360	11.3	43.8	33.6	88.7	12.7	49.4	37.9	78.3	3 h
SG28	〃	5.12	5.82	0.094	0.547	−0.262	2.86	54.2	36.0	93.1	3.07	58.2	38.7	92.3	3 h
SG29	〃	5.16	1.10	0.55	0.605	−0.218	10.9	47.0	35.0	92.9	11.7	50.6	37.7	80.2	1 h

Remarks: △ Some slags contained in the metal phase.

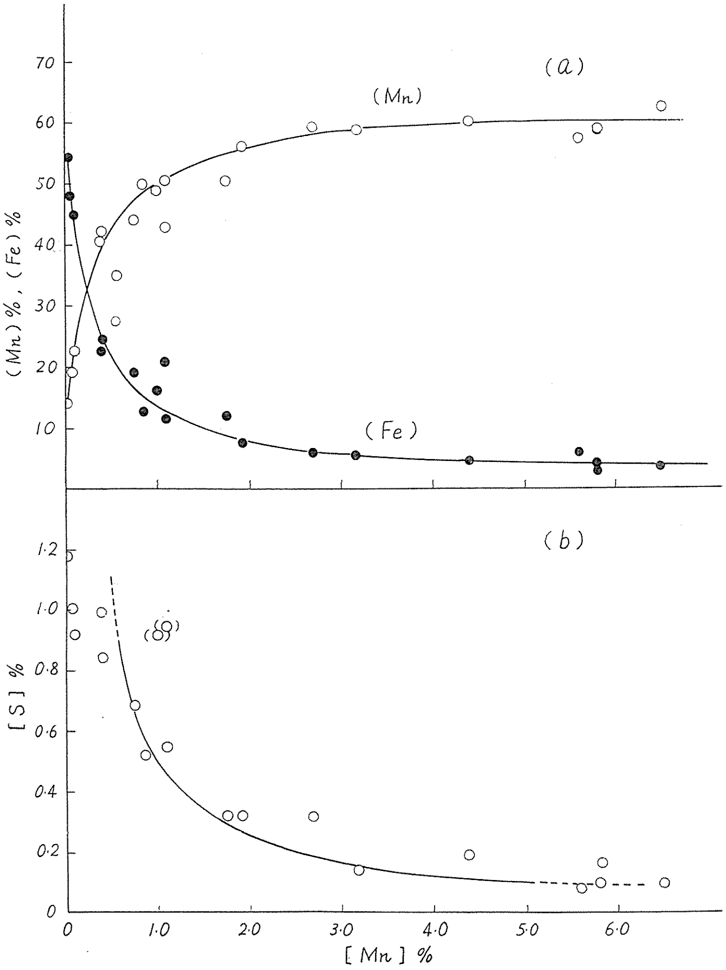

FIG. 43. (a) Composition of desulphurization product related to Mn per cent in C-saturated iron melt, and (b) corresponding Mn-S equilibrium in the metal at 1,500°C. The line represents the equilibrium curve as previously determined.

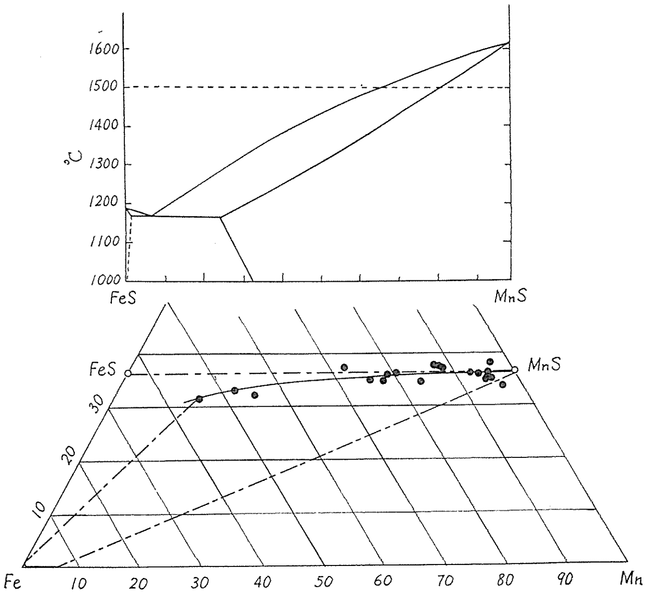

FIG. 44. Composition of desulphurization product on the Fe-S-Mn diagram referring to the FeS-MnS diagram.

FeS-MnS line to the iron side. Nevertheless, the desulphurization products, for the most part, may be represented by FeS-MnS system. Referring to the FeS-MnS diagram established by Shibata,[53] the desulphurization products of the present experiment are mostly such solid or liquid solutions that FeS dissolved into MnS. This will be further clarified by X-ray analysis.

(2) *X-ray analysis of desulphurization Products*

Considering from the results of the present experiment, it is recognized that the desulphurization products may be such solutions that FeS dissolved into MnS. However, there is no definite conclusion only from the analytical data that manganese or iron in slags combines as a sulphide and also some quantities of graphite are mixed besides iron, manganese and sulphur. Then, taking several samples of slags according to manganese content, the X-ray analysis was carried out by Norelco Geiger Counter X-ray spectrometer. The diffraction patterns were obtained using Cu-target. Since there were no remarkable points except those peaks corresponding to manganese sulphide and graphite, precise examination was concentrated on the range concluding the above points. The diffraction patterns shown in Fig. 45 (a)～(f) represent several typical slags. Referring to the A.S.T.M. index of X-ray diffraction data card, precise data of manganese sulphide was obtained and was compared with the present data. The main peaks in these patterns were recognized to correspond to those of manganese sulphide and these peaks at about 26° showed the existence of graphite precipitated in molten iron. The interatomic distance of the maximum peak corresponding to manganese sulphide

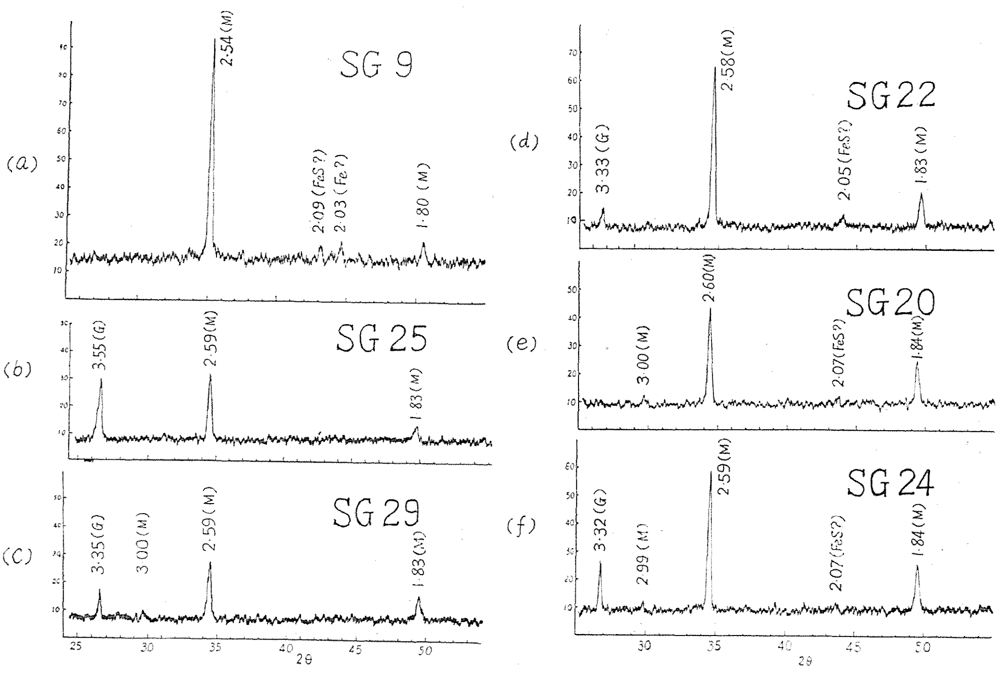

FIG. 45. X-ray diffraction patterns of slags.
(M···MnS, G···Graphite.)

was in the range of 2.60~2.54 Å and decreased slightly from the standard value $d=2.61$, as manganese in the metal decreased. Therefore, strictly speaking, desulphurization products can not be regarded as pure manganese sulphide. Nevertheless, even in the case of a extremely lower manganese melt such as SG 9, it is clearly observed from the diffraction patterns that the desulphurization product consists maninly of manganese sulphide. Thus, as suggested from the analytical results, the desulphurization products can be regarded as solid or liquid solutions where manganese sulphide is solvent, and approach to manganese sulphide with increasing of manganese in the metal.

Now, regarding manganese in those slags entirely combined with sulphur, MnS per cent was calculated from analytical data and plotted against manganese per cent in the metal as shown in Fig. 46. The percentage of manganese sulphide in the slag approaches nearly constant such as 94% when manganese in the metal increases above 3%.

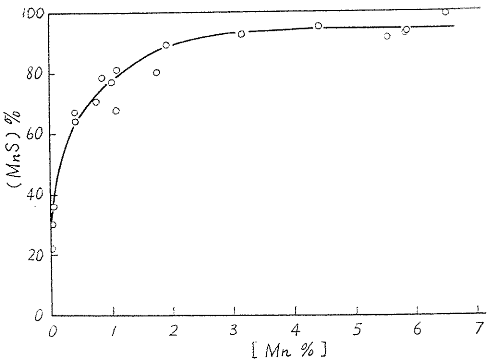

FIG. 46. MnS per cent in desulphurization product related to Mn per cent in metal.

5. Discussions

As already mentioned, the apparent equilibrium constant $K''=[\%\mathrm{S}][\%\mathrm{Mn}]$ of the desulphurization reaction of manganese in carbon-saturated molten iron can be applied to those melts more than 3 per cent manganese at 1,500° C, since the desulphurization product is nearly manganese sulphide and then it follows that a_{MnS} may be constant. However, it must be taken into account that the effect of decreasing of a_{MnS} in lower manganese melts is considerably large.

Regarding the slags, namely desulphurization products, as being solid or liquid FeS-MnS solutions and regarding activity of manganese sulphide as equal to its mole fraction in the range of MnS side of FeS-MnS diagram, the equilibrium constant K of the desulphurization reaction of manganese was obtained as 0.428 at 1,500° C, since the value of N_{MnS} was 0.94 (const.) at more than 3% manganese, and it was written: $K=a_{\mathrm{MnS}}/a_{\mathrm{S}}\cdot a_{\mathrm{Mn}}=N_{\mathrm{MnS}}/f_{\mathrm{S}}[\%\mathrm{S}]\cdot f_{\mathrm{Mn}}[\%\mathrm{Mn}]$. Taking the obtained value of K as a standard, the equilibrium may be determined at lower manganese range. From the Fig. 46, taking the values of N_{MnS} according to the manganese content in the metal and the given values of f_{S}, K'' was calculated and compared with experimental results as shown in Table 15 where f_{Mn} was taken as constant. The relation between $\log K''$ and manganese per cent in iron melts in the range of lower than 3 per cent manganese is shown in Fig. 47 where the mark △ represents the former experimental data and the mark ○ represents the present data. These are found approximately on the curve I and clearly K'' is not constant, but decreases rapidly at lower than 1 per cent manganese. The curve II was gained from the calculated values, $\log K''$ (calc.) in the Table 15, but it should be corrected for $f^{(\mathrm{S})}_{\mathrm{Mn}}$ as those lower manganese melts contain necessarily higher sulphur contents.

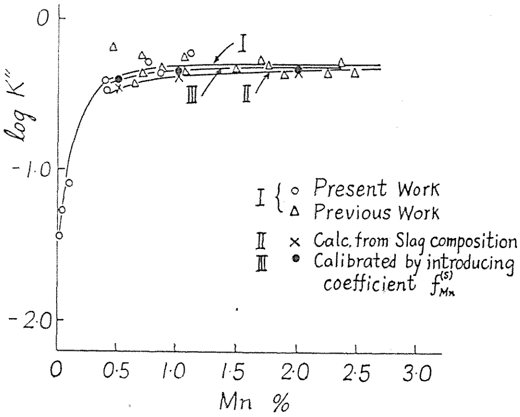

FIG. 47. Relation between log K'' and Mn per cent in C-saturated iron melts at 1,500° C.

The value of $f_{Mn}^{(S)}$ has not yet been determined, and then it will be calculated from the known value $f_S^{(Mn)}$, applying the relation obtained by Wagner.[36) 37)] He has shown that a simple relation exists between the effect of component i on f_j and the effect of component j on f_i, namely

$$\varepsilon_i^{(j)} = \varepsilon_j^{(i)}.$$

These relations between e and ε for two elements of atomic weights M_i and M_j in the solvent metal, iron, are

$$e_i^{(j)} = \frac{M_i}{M_j} e_j^{(i)}.$$

The value of $e_S^{(Mn)}$ has been obtained as -0.025 and then it follows

$$\log f_{Mn}^{(S)} = -0.045[S\,\%].$$

Taking the calculated values of $\log f_{Mn}^{(S)}$, $\log K''$ (calc.) was corrected as shown in Table 15 and in the Fig. 47 Curve III was obtained, which is in good agreement with experimental results.

TABLE 15. Comparison of the Apparent Equilibrium Constant K'' Calculated by the Slag Clmposition with Those Observed at 1,500° C

Mn%	f_S	N_{MnS}	K''(obs.)	log K''(obs.)	K''(calc.)	log K''(calc.)	$\log f_{Mn}^{(S)}$	log K''(calc.) corr.
2.0	4.5	0.90	0.50	−0.30	0.468	−0.330	−0.010	−0.320
1.0	4.5	0.80	0.48	−0.31	0.413	−0.375	−0.023	−0.352
0.5	4.4	0.67	0.43	−0.38	0.354	−0.450	−0.045	−0.405

Consequently, in lower manganese range in the metal the activity of manganese sulphide in the slag must be taken into account to explain the equilibrium between manganese and sulphur.

6. Conclusion

The composition of desulphurization product by manganese in carbon saturated iron melts was clarified and its relationship to the manganese-sulphur equilibrium was discussed. For this purpose a suitable experimental apparatus was deviced so as to mix molten ferrous sulphide and Fe-C-Mn solution at the temperature as intended and a tolerable success was attained.

(1) The main component of desulphurization product as sulphide slag consists of Mn, Fe and S, and manganese content in the slag increases with manganese in molten iron in equilibrium with the slag and approaches to nearely constant value at more than 3 per cent manganese in the metal.

(2) From X-ray diffraction patterns of the slags, it is considered that the main constituent of desulphurization product is manganese sulphide, and gradually ferrous sulphide dissolves into it as manganese content decreases. However, even in lower manganese melts, the formed slags are regarded as manganese sulphide in their main constituent.

(3) Considering manganese in the slags entirely combined with sulphur, MnS per cent was calculated from the analytical data and plotted against manganese per cent in the metal. It is almost constant at more than 3 per cent manganese in the metal but rapidly decreass at lower per cent than that.

(4) Regarding the slags as solid or liquid FeS-MnS solutions and regarding the activity of manganese sulphide as equal to its mole fraction in the range of MnS side of the FeS-MnS diagram, the equilibrium constant K of the desulphurization reaction of manganese was obtained as 0.428 at 1,500° C. Taking this value as a standard, the apparent equilibrium constant $K''=[\%S][\%Mn]$ was calculated in lower manganese range and is found to agree with the experimental value.

Summary

It has been well recognized that the desulphurization is one of the most important problem throughout the iron- and steel-making processes. On the desulphurization by manganese more fundamental knowledge may be required to establish the reasonable desulphurization practice. If raw materials for the blast furnace were to become inferior in quality, it will be difficult to obtain the low sulphur pig iron as produced by the present blast furnace. Therefore, in such a case some desulphurization practice should be desired after tapping from the furnace. Since manganese is generally contained in those pig irons used for steel-making, it is desirable to utilize its desulphurizing power as much as possible.

Although many investigations on the desulphurization of manganese are found in the literature, there are large disagreements among them and moreover the desulphurization degree at a definite temperature has not yet fully determined. Recently, Oelsen has published a detailed research on the carbon saturated iron, but he did not examine the effects of coexisting elements.

Then, summarizing the results obtained to this day, it becomes evident that the chemical reactivity of molten pig iron is predominating for the desulphurization and the lack of this knowledge resulted in the above disagreement. From this viewpoint, the authors tried to study the desulphurization of manganese to ascertain experimentally what conditions are the most efficient for the desulphurization and moreover how lower limit the sulphur content of pig iron can be attained in practical works.

The results obtained are summarized as follows.

(1) From the viewpoint of the molten pig iron, the desulphurization limit by manganese depends wholly on the activity coeffecient of sulphur in liquid iron. Now, for the iron-carbon binary liquid, the carbon saturation is the limit of lowering sulphur.

(2) The results of thermodynamical calculation show that the desulphurization limit by manganese lowers with lowering temperature and also suggest that 1 to 2% manganese in the carbon saturated iron is sufficient to lower sulphur content useful for steel-making at 1,200° C.

(3) The equilibrium constant of the desulphurization reaction is shown by $K'' = [\% S][\% Mn]$, assuming the desulphurization product as manganese sulphide. The approximation is nearly valid at lower temperatures within the manganese content of the practical pig iron. However, the apparent equilibrium constant K'' tends to decrease with lowering of manganese at the temperatures over 1,500° C. This represents the decrease of activity of MnS as the desulphurization product.

(4) In the carbon saturated iron the presence of silicon or phosphorus up to 2% has no effect on the desulphurization limit, and then, the practical pig iron is generally recognized that its desulphurization limit is wholly dependent on the carbon saturation. Namely, though silicon or phosphorus increases the activity coefficient of sulphur, yet they decrease the carbon solubility. Therefore, the effects of silicon or phosphorus on the activity coefficient of sulphur are somewhat canceled under carbon saturation. A considerably much addition of silicon or phosphorus effects remarkably on the desulphurization. While silicon tends to increase the activity coefficient of sulphur at carbon saturation, on the contrary phosphorus tends to decrease.

(5) The desulphurization product by manganese in carbon saturated iron was examined at 1,500° C. From the chemical and X-ray analysis its main constituent is observed as manganese sulphide. Generally it is considered that the desulphurization product is a liquid or solid solution of ferrous sulphide dissolved into manganese sulphide. The activity of MnS in the desulphurization product is approximately 0.94 as constant at 1,500° C when the equilibrated molten iron contains more than 3% manganese. It, however, becomes lower when manganese in liquid iron decreases below 2%. This explains the fact that the apparent equilibrium constant decreases with manganese in such lower manganese range. In conclusion, the practical pig iron may be generally controlled its desulphurization limit by manganese content and temperature if only carbon is saturated. Furthermore, more possible desulphurization limit may be expected when the manganese content in pig iron is known.

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