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Rate of Desulfurization of Ferroalloys in Vacuum Melting*

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Synopsis

The rate-limiting process in the desulfurization of ferroalloys in vacuum melting was confirmed by a kinetic study. The increasing order of rate of desulfurization is as follows: Fe-S < Fe-C-S < Fe-C-Si-S. In Fe-Si-S alloy, the rate of desulfurization is well explained from the evaporation of SiS from the surface of the melt. It is suggested that the rate-limiting process is the evaporation of desulfurization products from the surface of molten iron.

I. Introduction

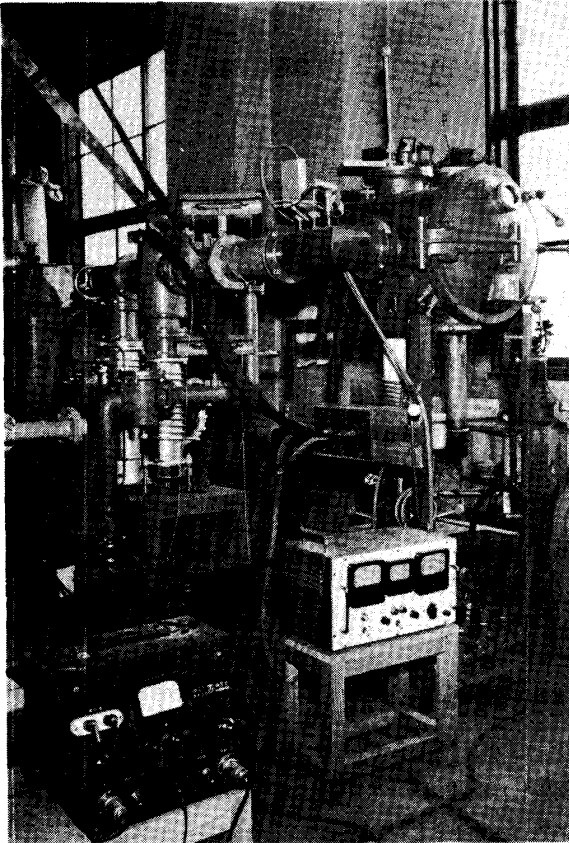
The desulfurization of ferroalloys in vacuum melting was studied by Fischer and Hoffmann⁽¹⁾⁽²⁾⁽³⁾, Jäniche and Bech⁽⁴⁾, Floridis⁽⁵⁾, Ohno⁽⁶⁾⁽⁷⁾, and Sehgal and Mitchell⁽⁸⁾. Ohno⁽⁶⁾⁽⁷⁾ obtained some interesting results in the vacuum melting of Fe-S, Fe-C-S, Fe-Si-S and Fe-C-Si-S alloys. In the presence of carbon and silicon, the rate of desulfurization is high compared with that of Fe-S alloy. Especially in the presence of silicon the rate of desulfurization is much higher than that of Fe-S alloy and desulfurization is strongly proceeded. The higher the equilibrium pressure of desulfurization products is, the lower the sulfur concentration attainable becomes and the higher the rate of desulfurization becomes. The former result was qualitatively explained from a thermodynamic standpoint. As to the rate of desulfurization a further investigation is desirable to examine a rate-limiting process. Therefore, the present investigation was carried out from a kinetic standpoint.

II. Experimental

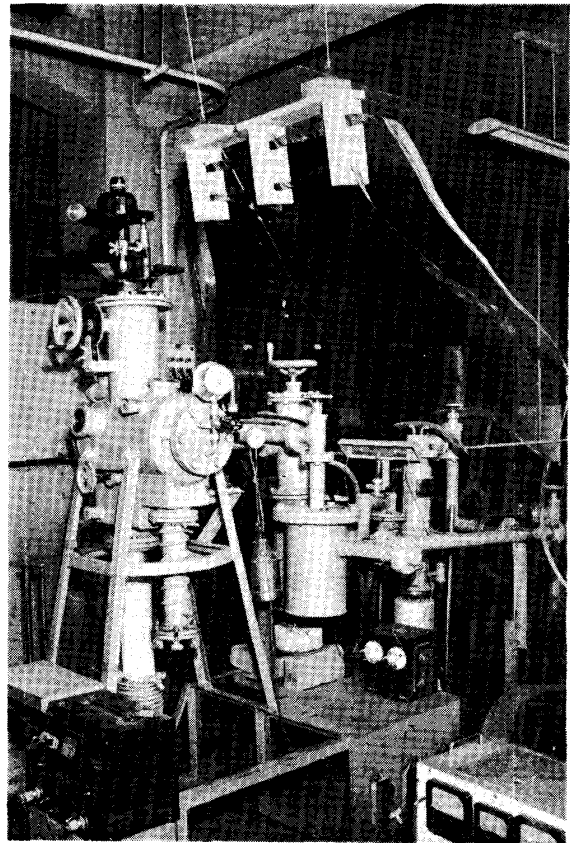
Vacuum induction furnaces (VIF-I and VIF-II) and a resistance furnace (Mo-F) were used for vacuum melting. In VIF-I, pumping system consisted of a rotary

* The 1131st report of the Research Institute for Iron, Steel and Other Metals.

- (1) W.A. Fischer und A. Hoffmann, Arch. Eisenhütt., **29** (1958), 339.
- (2) W.A. Fischer und A. Hoffmann, Arch. Eisenhütt., **31** (1960), 1.
- (3) W.A. Fischer and A. Hoffmann, Arch. Eisenhütt., **31** (1960), 411.
- (4) W. Jäniche und H. Bech, Arch. Eisenhütt., **29** (1958), 631.
- (5) T.P. Floridis, Trans. AIME, **215** (1959), 870.
- (6) R. Ohno, Sci. Rep. RITU, **A 12** (1960), 353.
- (7) R. Ohno, Sic. Rep. RITU, **A 15** (1963), 268.
- (8) V.D. Sehgal and A. Mitchell, J. Iron Steel Inst., **202** (1964), 216.



Phot. 1. Vacuum induction melting furnace (VIF-I)



Phot. 2. Vacuum induction melting furnace (VIF-II)

pump and an oil diffusion pump, and the rate of evacuation was 360 l/sec as a whole. A high frequency current of 450 KC was supplied by a generator. In VIF-II which was used in the previous experiments⁽⁶⁾⁽⁷⁾, pumping system consisted of a rotary pump of the capacity 450 l/min, an oil diffusion pump of the capacity 200 l/sec and an oil ejector of the capacity 50 l/sec. Power source was the same as that of VIF-I. The appearances of VIF-I and VIF-II are shown in Phots. 1 and 2, respectively.

Mo-F was a simple resistance furnace in which molybdenum wire was wound on an alumina tube placed in a silica tube. Evacuation was carried out by a rotary pump of the capacity 50 l/min.

(1) Method in VIF-I

In this case Fe-S (6311-31), Fe-C-S (6310-12), Fe-C-S (6310-16) and Fe-C-Si-S (6310-13) alloys were used, being synthesized in atmosphere from electrolytic iron, metallic silicon, graphite and iron sulfide. The chemical composition in percentage of the electrolytic iron was 0.005 C, 0.007 Si, 0.006 S, 0.004 Al, 0.010 Mn, 0.004 N and trace of P, and that of the metallic silicon was 98.81 Si, 0.56 Fe, 0.17 Al and 0.26 Ca. The iron sulfide was a commercial reagent synthesized from electrolytic iron and sulfur. For the syntheses of Fe-S and Fe-C-S alloys, the metallic silicon was not used. The chemical composition of the synthesized alloys is shown in Table 1.

Table 1. Chemical composition of alloys used.

Alloy	Alloy No.	% S	% C	% Si
Fe-S	6311-31	0.22	0.010	0.009
Fe-S	6310-14	0.22	0.006	0.009
Fe-C-S	6310-12	0.19	3.30	0.044
Fe-C-S	6310-16	0.19	4.10	0.009
Fe-C-Si-S	6310-13	0.19	4.08	1.62
Fe-C-Si-S	6312-13	0.18	3.66	2.68

A kilo-gram of each alloy was melted under vacuum within the temperature range 1500°~1600°C for 40 min after heating to 1600°C under argon at 1 atm. pressure. A small amount of each of molten alloys was cast into an iron mold every 10 min. The constant temperature of 1600°C could not be maintained because of discharge in the furnace for some time after evacuation. The measurement of temperature was made by an optical pyrometer. Vacuum pressure during melting was 10⁻³~10⁻⁴ mm Hg. An alumina crucible (CP-2), 52mm in internal diameter, 63 mm in external diameter and 160mm in height was used.

(2) Method in Mo-F

In this case were used Fe-C-S (6310-12), Fe-C-S (6310-16), Fe-C-Si-S (6310-13) and Fe-C-Si-S (6312-13), alloys. Their chemical compositions are shown in Table 1. Ten grams of each alloy was melted under vacuum at 1350°C for 5, 10 and 15 min after heating to 1350°C under argon at 1 atm. pressure. An alumina

crucible held in a graphite boat⁽⁶⁾ was used. The cooling of samples was carried out by transferring the graphite boat to a cold place in Mo-F. The relation of the reading of an optical pyrometer to the true temperature of the samples was obtained by measuring the apparent melting temperature of electrolytic copper, nickel and manganese according to the method of Fincham and Bergman⁽⁹⁾. Vacuum pressure during melting was of the order of 10^{-1} mm Hg.

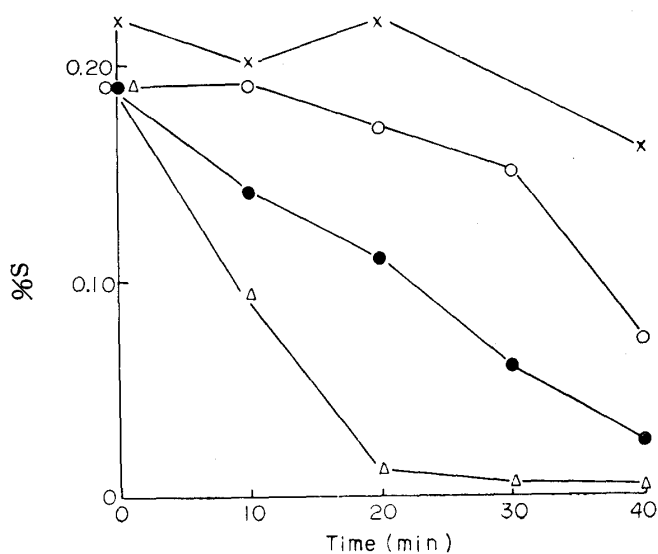
(3) Method in VIF-II

An Fe-S alloy (6310-14) was synthesized in atmosphere from electrolytic iron and iron sulfide. Its chemical composition is shown in Table 1. A hundred and fifty grams of the alloy was melted under vacuum at 1600°C for 5 to 60 min after heating to 1600°C under argon at 1 atm. pressure. Molten iron was entirely cast into an iron mold. The measurement of temperature was made by the same method as that in (1).

III. Experimental results

(1) Results in VIF-I

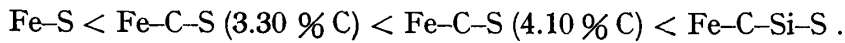
Experimental results are shown in Fig. 1. The increasing order of the rate of desulfurization is as follows:



Mark	Alloy	Alloy No.
x	Fe-S	6311-31
o	Fe-C-S	6310-12
●	Fe-C-S	6310-16
Δ	Fe-C-Si-S	6310-13

Fig. 1.

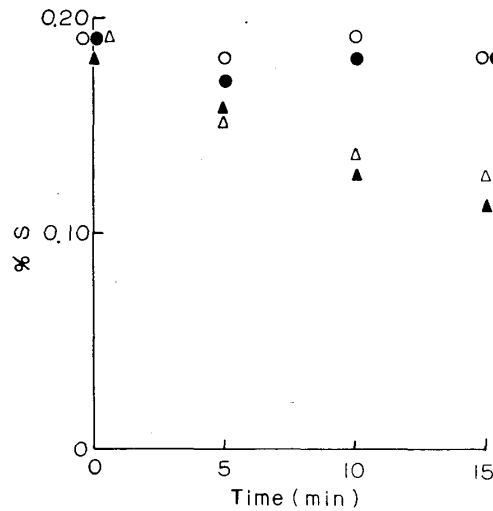
(9) C.J.B. Fincham and R.A. Bergman, *J. Metals*, **9** (1957), 690.



This increasing tendency is in accordance with the results in the previous experiments⁽⁶⁾ in which the entire heating was carried out under vacuum.

(2) Results in Mo-F

Experimental results are shown in Fig. 2. Though there is no clear difference in the rate of desulfurization between the alloys of the same kind, the rate of desulfurization of Fe-C-Si-S alloys is higher than that of Fe-C-S alloys. This result is the same as that in the previous experiments⁽⁶⁾ in which the entire heating was carried out under vacuum.



Mark	Alloy	Alloy No.
○	Fe-C-S	6310-12
●	Fe-C-S	6310-16
△	Fe-C-Si-S	6310-13
▲	Fe-C-Si-S	6312-13

Fig. 2.

(3) Results in VIF-II

Experimental results (mark ●) are shown in Fig. 3 together with those in the previous experiments⁽⁷⁾. The desulfurization proceeds with the increase of time in vacuum melting. All of the marks are identical with each other in experimental procedure.

IV. Considerations

According to the following model of the process of desulfurization, a consideration for the rate-limiting process was made.

- (1) Transport of S from a bulk liquid to the surface of liquid.
- (2) Desulfurization reaction at the surface.

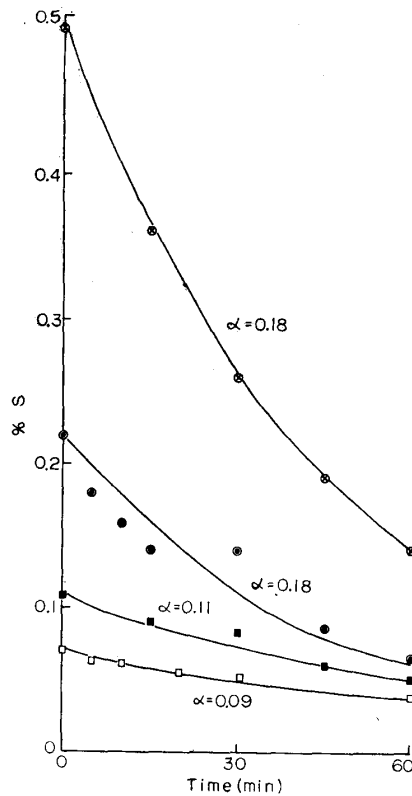


Fig. 3.

(3) Evaporation of desulfurization products from the surface.

The rate of chemical reaction at a phase boundary is strongly dependent (exponentially) on temperature. At the high temperatures characteristic of metallurgical processes the rate of almost all chemical reactions is so fast that the establishment of local equilibrium is possible⁽¹⁰⁾⁽¹¹⁾. Therefore, if it is assumed that the desulfurization reaction is in equilibrium at the surface, the transport of S to the surface (1) or the transport of desulfurization products away from the surface (3) becomes the rate-limiting process. The following examinations were made for the rate of desulfurization in the cases in which (1) or (3) is the rate-limiting process.

1. The rate of the transport of S to the surface from a bulk liquid

When several species are involved in a reaction, one of which is present at a much smaller concentration than the others, the transport of this species alone may control the over-all reaction rate⁽¹¹⁾⁽¹²⁾. Therefore, the rate of desulfurization is expressed by the following equation based on Fick's first law:

(10) L.S. Darken, *The Physical Chemistry of Steelmaking* (1958), 101, J.F. Elliot, Ed.

(11) T.B. King, *Thermodynamics and Kinetics in Vacuum Metallurgy* (1958), 51, R. Bunshaw, Ed.

(12) C. Wagner, *The Physical Chemistry of Steelmaking* (1958), 237, J.F. Elliott, Ed.

$$-\frac{d[\%S]}{dt} = \frac{A}{V} \cdot \frac{D_s}{\delta_s} \{ \%S \text{ (bulk)} - \%S \text{ (surface)} \} \quad (1)$$

where A is the boundary area, V the volume of iron melt, D_s the diffusion coefficient of sulfur and δ_s the effective thickness of diffusion boundary layer for sulfur. By integrating, Eq. (1) becomes

$$2.3 \log \left[\frac{\%S_0 \text{ (bulk)} - \%S \text{ (surface)}}{\%S \text{ (bulk)} - \%S \text{ (surface)}} \right] = \frac{A \cdot D_s}{V \cdot \delta_s} \cdot t, \quad (2)$$

where t is the time in second and $\%S_0$ (bulk) the initial bulk sulfur content. As described in the previous paper⁽⁷⁾, the rate of desulfurization of Fe-S alloys can be explained from Eq. (2) by taking δ_s to be of the order of 10^{-1} cm when D_s is 1×10^{-4} cm²/sec⁽¹³⁾. This value of δ_s is much larger than that for oxygen (0.003 cm)⁽¹⁴⁾ which was postulated for the explanation of the rate of carbon drop in an open hearth. In this respect, a question is raised about the applicability of Eq. (1). As may be seen from Eq. (1), if D_s/δ_s does not depend on the kind of alloy and if $\%S$ (bulk) is much larger than $\%S$ (surface), the rate of desulfurization should be constant independent of the kind of alloy. However, as shown in the previous papers⁽⁶⁾⁽⁷⁾ and Figs. 1 and 2, the rate of desulfurization obtained markedly depends on the concentrations of silicon and carbon. This result cannot be explained by Eq. (1) even though the change of $\%S$ (surface) due to the change of the concentrations of silicon and carbon is taken into consideration. Therefore, the following consideration was made for the effects of silicon and carbon on the value of D_s/δ_s .

It was first suggested by Einstein⁽¹⁵⁾ for ideal solutions and subsequently by many others including Hartley⁽¹⁶⁾ for nonideal solutions, that the virtual force acting on a diffusing atom or ion in a binary solution may be regarded as the negative gradient of the chemical potential or partial molal free energy. Fisher et al.⁽¹⁷⁾ expressed diffusion coefficient in interstitial diffusion by an equation containing $\partial a/\partial c$ in which a is the activity of a diffusing substance and c is its concentration.

Considering that it is more reasonable to use activity gradient $\partial a/\partial x$ instead of the concentration gradient $\partial c/\partial x$ in Fick's law, Iwase and Kachi⁽¹⁸⁾ have derived the following equation:

$$\frac{D}{D_0} = \frac{\partial a}{\partial c}, \quad (3)$$

where D_0 is the diffusion coefficient in a dilute solution.

(13) AIME, *Basic Open Hearth Steelmaking* (1951), 610.

(14) AIME, *Basic Open Hearth Steelmaking* (1951), 613.

(15) A. Einstein, *Ann. Physik*, **17** (1905), (4), 549.

(16) G.S. Hartley, *Trans. Faraday Soc.*, **27** (1931), 10.

(17) J.C. Fisher, J.H. Hollomon and D. Turnbull, *Trans. AIME*, **174** (1948), 202.

(18) K. Iwase and S. Kachi, *Nippon Kinzoku Gakkai-Shi*, **15** (1951), 189.

By applying Eq. (3) to the diffusion of sulfur in molten iron, the effects of silicon and carbon on the diffusion coefficient of sulfur D_s may be examined. In Eq. (3), D corresponds to the diffusion coefficient of sulfur in a multicomponent system, D_0 the diffusion coefficient of sulfur in a dilute solution of Fe-S alloy, a the activity of sulfur in the multicomponent system and c its concentration in the multicomponent system. Therefore, Eq. (3) is given as follows:

$$\frac{D_s}{D_0} = f_s + C \cdot \frac{\partial f_s}{\partial c}, \quad (4)$$

where f_s is the activity coefficient of sulfur. Because $C \cdot \partial f_s / \partial c$ is much smaller than f_s , the effects of silicon and carbon on the diffusion coefficient of sulfur may be examined by the effects of silicon and carbon on f_s , i.e. f_s^c and f_s^{Si} which are already known⁽¹⁹⁾.

As an example, a comparison between two experimental results in an Fe-S and an Fe-Si-S will be mentioned; the two experimental results are shown by the marks \odot and \circ in Figs. 3 and 4, respectively. The experimental results in Fig. 4 are those shown in the previous paper⁽⁷⁾. The experimental conditions are exactly the same in both cases. f_s in the Fe-Si-S alloy (2.70% Si) is 1.6 when f_s in Fe-S alloy containing the same amount of sulfur is unity. Therefore, the diffusion coefficient of sulfur D_s in the Fe-Si-S alloy should be about 1.6 times that in the Fe-S alloy when D_0 is taken to be the diffusion coefficient of sulfur in the Fe-S alloy. If δ_s equals each other in both alloys, the rate of desulfurization in the Fe-

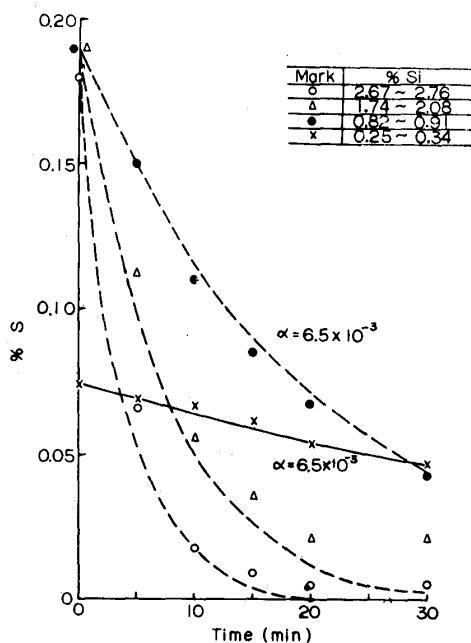


Fig. 4.

(19) AIME, *Basic Open Hearth Steelmaking* (1951), 680.

Si-S alloy should be about 1.6 times that in the Fe-S alloy. However, the rate of desulfurization in the Fe-Si-S alloy is much higher than 1.6 times that in the Fe-S alloy.

Similarly, the change of the rate of desulfurization in Fe-Si-S alloys due to the change of silicon concentration, which is shown in Fig. 4, cannot be explained by the effect of silicon on the diffusion coefficient of sulfur described above.

According to Wanger⁽¹²⁾, the following relation is expected:

When $D_s(\text{Fe-Si-S}) > D_s(\text{Fe-S}), \delta_s(\text{Fe-Si-S}) > \delta_s(\text{Fe-S})$.

Therefore, the explanation for the change of the rate of desulfurization by the change of D_s becomes more difficult.

Because f_s in Fe-C-S alloy is greater than that in Fe-Si-S alloy provided the same weight percentage of carbon and silicon, the rate of desulfurization of Fe-C-S alloy should be higher than that of Fe-Si-S alloy according to the above consideration. However, this is contradictory to the experimental results⁽⁶⁾⁽⁷⁾. According to Seghal and Mitchell⁽⁶⁾, the diffusion coefficient of sulfur is decreased by carbon, which decreases the rate of desulfurization in Eq. (1) contrary to the experimental results.

According to the above consideration, therefore, the change of the rate of desulfurization due to the change of the concentrations of silicon and carbon cannot be explained by Eq. (1). Hence, another rate-limiting process must be considered.

2. The rate of evaporation of desulfurization products from the surface

The rate of evaporation in vacuum is given by the following equation, which was developed by Hertz⁽²⁰⁾, Knudsen⁽²¹⁾ and Langmuir⁽²²⁾:

$$G = \alpha \sqrt{\frac{M}{2\pi RT}} \cdot P,$$

where G is given in $g/cm^2 \cdot sec$, α is the condensation coefficient, M the molecular weight of vaporizing substance, P its vapor pressure ($dyne/cm^2$), R the gas constant ($8.3 \times 10^7 \text{ ergs}/^\circ C \cdot \text{mole}$) and T the temperature ($^\circ K$).

As described in the previous paper⁽⁷⁾, when the desulfurization of Fe-S alloy is assumed to be made by the following reaction**:



the rate of desulfurization in the Fe-S alloy is given by the following equation derived from Eq. (5):

(20) H. Hertz, *Ann. Physik*, **17** (1882), 177.

(21) M. Knudsen, *Ann. Physik*, **47** (1915), 697.

(22) I. Langmuir, *J. Amer. Chem. Soc.*, **35** (1913), 931.

** This assumption is in accordance with the result of Sehgal and Mitchell⁽⁶⁾

$$-\frac{d[\%S]}{dt} = \alpha \frac{100A}{\rho V} \cdot \frac{\sqrt{M_s}}{\sqrt{2\pi RT}} \cdot P_s, \quad (7)$$

where A is the surface area of liquid Fe-S alloy, V its volume, ρ its density, M_s the atomic weight of sulfur and P_s the equilibrium vapor pressure of S. If the transport of S to the surface of the liquid alloy is fast enough to maintain its concentration uniform throughout, P_s is expressed as a function of % S (bulk) by the following equation⁽⁶⁾⁽⁷⁾:

$$\begin{aligned} P_s &= 4.07 \times 10^{-5} \times [\%S] \text{ atm} \\ &= 4.12 \times 10 \times [\%S] \text{ dynes/cm}^2, \end{aligned} \quad (8)$$

which is used in the concentration range in which Henry's law is applicable. Therefore, Eq. (7) becomes

$$2.3 \log \frac{[\%S]_0}{[\%S]} = \alpha \frac{100A}{\rho V} \cdot \frac{\sqrt{M_s}}{\sqrt{2\pi RT}} \cdot k_s \cdot t, \quad (9)$$

where k_s corresponds to 4.12×10 in Eq. (8). The curves in Fig. 3 were drawn according to Eq. (9). To explain the reason why α decreases with the decrease of sulfur concentration, further investigations are needed.

In Fe-Si-S alloy, when the desulfurization is made by the following reaction as described in the previous papers⁽⁶⁾⁽⁷⁾:



the rate of desulfurization is given by the following equation:

$$-\frac{d[\%S]}{dt} = \alpha \frac{100A}{\rho V} \cdot \frac{\sqrt{M_{SiS}}}{\sqrt{2\pi RT}} \cdot \frac{M_s}{M_{SiS}} \cdot P_{SiS} \quad (11)$$

where M_{SiS} is the molecular weight of SiS and P_{SiS} the equilibrium pressure of SiS. If the transport of S and Si to the surface of liquid Fe-Si-S alloy is fast enough to maintain their concentrations uniform throughout, P_{SiS} is given as a function of % S (bulk) in a constant silicon concentration by the following proportional expression:

$$P_{SiS} = C \cdot [\%S], \quad (12)$$

where C is a constant depending on silicon concentration. Eq. (12) is derived from the following relation:

$$\log P_{SiS} = \log a_{Si} + \log f_s [\%S] - \frac{\Delta F_{SiS}^\circ}{2.303 RT} \quad (13)$$

which was described in the previous paper⁽⁶⁾. Therefore, Eq. (11) becomes

$$2.3 \log \frac{[\%S]_0}{[\%S]} = \alpha \frac{100A}{\rho V} \cdot \frac{\sqrt{M_{SiS}}}{\sqrt{2\pi RT}} \cdot \frac{M_s}{M_{SiS}} \cdot k_{SiS} \cdot t \quad (14)$$

where $k_{SiS} = C \times 1.0132 \times 10^6$ dynes/cm².

All the curves in Fig. 4 were drawn according to Eq. (14) by taking α to be 6.5×10^{-3} and are very close to the experimental results.

The rate of evaporation of sulfur is simply expressed as follows:

$$-\frac{d[\%S]}{dt} = K_1 P_1 + K_2 P_2 + \dots, \quad (15)$$

where K_1 , K_2 and so forth are constants depending on the kind of desulfurization products, the concentrations of alloying elements and experimental condition, and P_1 , P_2 and so forth are the respective equilibrium pressures of the desulfurization products. The experimental results in the previous cases⁽⁶⁾⁽⁷⁾ and the present one show that the higher the equilibrium pressure of desulfurization products is, the higher the rate of desulfurization is***. This result may be understood according to Eq. (15) although the change in K must be considered.

It may be said from the above consideration that the rate-limiting process is the evaporation of desulfurization products from the surface of molten iron. The recent investigation of Sehgal and Mitchell⁽⁶⁾ shows that in Fe-S alloys (0.13~0.15% C) and Fe-C-S alloys (1.08~1.30% C), the rate of loss of sulfur is controlled by the rate of desorption of atomic sulfur from the surface, and that in Fe-Si-S alloys (0.96~0.99% Si) the desulfurization is made by the formation of evaporating molecules of SiS.

Summary

(1) Ferroalloys were melted under vacuum at temperatures 1500°~1600°C after heating to 1600°C in argon at 1 atm. pressure, by using a vacuum induction furnaces. It was shown that the increasing order of rate of desulfurization was as follows:



(2) Ferroalloys were melted under vacuum at 1350°C after heating to 1350°C under argon at 1 atm. pressure, by using a molybdenum furnace. It was shown that the rate of desulfurization of Fe-C-Si-S alloys was higher than that of Fe-C-S.

(3) The result that the higher the equilibrium pressure of desulfurization product is, the higher the rate of desulfurization is, may qualitatively be understood from an equation which expresses the rate of desulfurization when the evaporation is a rate-limiting process.

(4) Even though the effects of silicon and carbon on the diffusion coefficient of sulfur are considered, the rate of desulfurization cannot be explained by the transport of sulfur to the surface of molten iron.

*** The equilibrium pressures of desulfurization products over various ferroalloys were already reported⁽⁶⁾.

(5) The rate of desulfurization of Fe-Si-S alloys at 1600°C is well explained from the evaporation of SiS by taking the condensation coefficient α to be 6.5×10^{-3} . In Fe-S alloys, α is in the range of 0.09~0.18.

Acknowledgment

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