Equilibria of Liquid Pig Iron of the System Fe-C-Si and Slags of the System SiO_2-CaO-Al_2O_3 under One Atomospheric Pressure of Carbon Monoxide

By

Hiroshi SAWAMURA and Jun SAWAMURA

Department of Metallurgy

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Introduction

In connection with the production of pig iron in a blast furnace or an electric furnace, it is very important to study the relationship between the compositions of the slag and those of the underlying pig iron which is in equilibrium with the former.

Now, consider the state of the hearth as shown in Fig. 1, where the liquid pig iron is of the system Fe–C–Si, the liquid slag is of the system SiO_2–CaO–Al_2O_3 containing 10 pct of Al_2O_3, and the partial pressure of carbon monoxide in the hearth atomosphere is 1 atomospheric pressure.

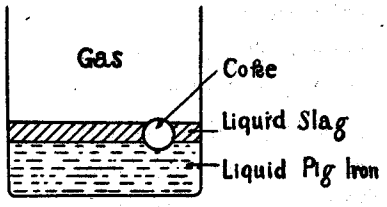

Fig. 1. State in hearth of blast furnace or electric furnace.

In this state, it is well known that the following reaction occurs:

$$(SiO_2)+2[C]=[Si]+2CO \qquad \cdots\cdots(1)$$

In equilibrium, Equation (1) should be revised as follows:

$$(SiO_2)+2[C]_s \rightleftarrows [Si]+2CO \qquad \cdots\cdots(2)$$

where $[C]_s$ represents carbon in the liquid pig iron saturated with carbon.

After the mass law,

$$K=\frac{f_3[Si]}{f_1(SiO_2)f_2^2[C]_s^2}P_{CO}^2 \qquad \cdots\cdots(3)$$

or

$$f_1(SiO_2)=\frac{1}{K}\cdot\frac{f_3[Si]}{f_2^2[C]_s^2}P_{CO}^2 \qquad \cdots\cdots(4)$$

where f_1, f_2 and f_3 are respectively the activity coefficients of (SiO_2), $[C]_s$ and [Si].

As $P_{CO}=1$,

$$f_1(SiO_2) = \frac{1}{K} \cdot \frac{f_3[Si]}{f_2^2[C]_s^2} \quad \text{.....(5)}$$

When equilibrium is attained, $[C]_s$ must also be in equilibrium with [Si] in the liquid pig iron. This equilibrium data were found by K. Schichtel and E. Piwowarsky[1] as shown in Fig. 2, which shows: (1) at a given temperature, when $[C]_s$ or [Si] is known, [Si] or $[C]_s$ is determined simultaneously, (2) [Si] becomes greater as $[C]_s$ decreases, and (3) consequently, $[Si]/[C]_s^2$ becomes greater as [Si] increases. Therefore, we see from Equation (5) that there exists a definite relation among $[C]_s$, [Si] and (SiO_2), and also among $[C]_s$, [Si] and the basicity of the slag $(\sum CaO)/(\sum SiO_2)$, because equilibrium should be attained in the slag containing Al_2O_3 of a constant content, and a definite relation must be found among (SiO_2), (CaO) and $(\sum CaO)/(\sum SiO_2)$.

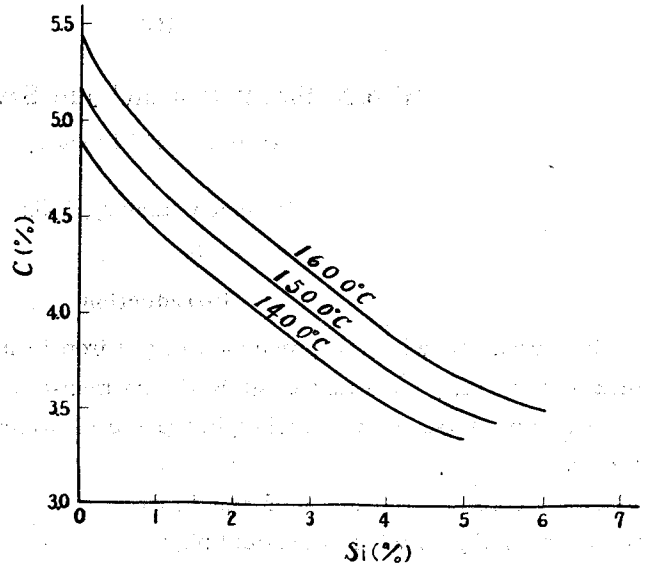

Fig. 2. Relationship among content of carbon saturated in pig iron, content of silicon in pig iron and temperature at equilibrium.
(K. Schichtel-E. Piwowarsky)

The authors first treated of the above relation theoretically,[2] and then tried to determine it experimentally at temperatures 1400°C., 1500°C. and 1600°C. in the present investigation.

Materials

The compositions of the materials used in the present investigation are given in Tables 1 and 3.

The high carbon white cast iron is a high-purity alloy made by melting the Kenjiho white pig iron covered with charcoal powder in a graphite crucible at about 1600°C. The Kenjiho white pig iron is a very pure alloy, its compositions being given below:

C=3.9%, Si=0.004%, Mn=trace, P=0.008%, S=0.007%, Cu=0.06%

Table 1. Compositions of Metals

	C(%)	Si(%)	Mn(%)	P(%)	S(%)
High Carbon White Pig Iron	5.03	0.010	0.007	0.009	0.011
Metallic Silicon		>97			

Table 2. Raw Materials used for Preparation of Synthetic Slags

	SiO_2(%)	CaO(%)	Al_2O_3(%)
Silica	95.55		
Calcium Carbonate	0.21	56.3	
Alumina			ca. 100

Table 3. Compositions of Synthetic Slags

SiO_2(%)	CaO(%)	Al_2O_3(%)	Basicity $(\Sigma CaO)/(\Sigma SiO_2)$
68.2	21.6	9.8	0.32
57.9	30.0	9.3	0.50
56.2	32.1	10.6	0.57
53.7	37.4	9.8	0.70
45.7	41.1	9.7	0.90
46.5	44.9	8.3	0.96
40.9	46.9	10.2	1.14
39.2	50.9	9.1	1.30
36.9	51.9	9.3	1.40

The synthetic slags were made by melting together the raw materials as given in Table 2 in a graphite crucible at about 1600°C. Each of them contains alumina of about 10 pct.

Experimental Work

The arrangement of the appratuses used in this investigation is shown in Fig. 3, where (z) is a high alumina reaction tube of German made (Staatliche Porzellan-Manufaktur Berlin-"*K*-Masse"), 30 mm. in inner diameter, and (p) is a carbon crucible used for melting charges, 19 mm. in inner diameter and 70 mm. long. The ash content of the crucible was 0.25 pct, and its sulphur content was 0.18 pct. Special attention was paid to the temperature measurement of the melt in the crucible throughout the present experiments. For this purpose, the following method was adopted:

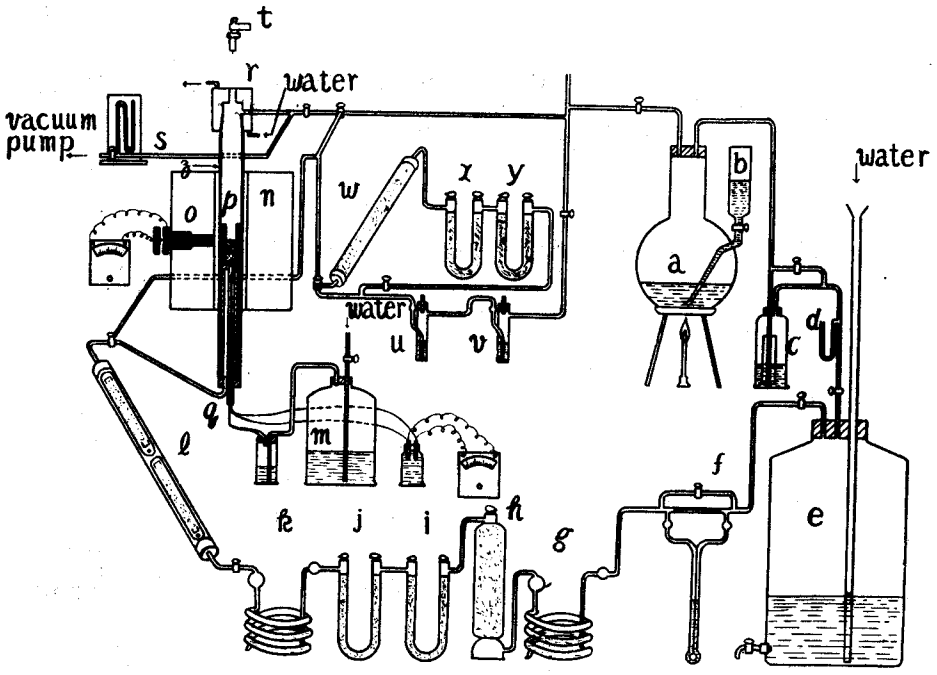

Fig 3. Arrangement of experimental apparatuses.

a, c, k:	conc. sulphuric acid	b:	formic acid	d, s:	manometer		
e:	gas reservoir	f:	flowmeter	g:	alkali solution of pyrogalol		
h, w:	soda lime	i, j:	calcium chloride	*l*:	phosphorus pentoxide		
m:	air reservoir	n:	Tamman furnace	o:	C-SiC thermo-couple		
p:	graphite crucible	q:	Pt-PtRh thermo-couple	r:	cap with water jacket		
t:	optical pyrometer	u, v:	barium hydroxide	x, y:	caustic potash		
z:	reaction tube						

In the first stage of heat experiments, the crucible charged with tin was brought into the reaction tube and heated at the rate of about 10°C./min. The temperature of molten tin was measured by a plutinum-plutinum rhodium thermo-couple dipped into the melt from the top side. The temperature of the bottom of the crucible was also measured with another plutinum-plutinum rhodium thermo-couple (q) at the same time. The air was introduced into a high alumina porcelain protecting tube used for this couple from an air reservoir (m) in order to hold the couple always in the oxidizing atomosphere. When the melt was heated up to about 800°C., the position of the crucible was so adjusted that the temperatures of two different parts became equal. Then the crucible with molten tin was quickly replaced in that position by another crucible, in which the metallic silicon, synthetic slag and the high carbon white cast iron were charged in succession. After the reaction tube was set with its cap (r), it was evacuated up to the pressure of 1 mm. Hg. Then pure carbon monoxide was introduced into the tube

at the rate of about 100 cc./min., and the contents of the crucible were heated up to a definitely determined temperature at the same rate as in the lower temperature range. A couple (o) and an optical pyrometer (t) were used for keeping a definitely determined temperature as constant as possible.

By the method above mentioned, the authors could regulate the temperature of the melt in the crucible in the range of 1500°C.±7°C. and 1600°C.±10°C.

Carbon monoxide was produced by dehydrating formic acid (b) with conc. sulphuric acid (a), and reserved in a bottle (e). In order to remove water vapour and carbon dioxide contained in crude carbon monoxide, the apparatuses (g), (h), (i), (j), (k) and (l) were arranged.

The reaction gases produced in the reaction tube were taken out in the open air through a glass tube dipped into water in a bottle at the hight of about 3 cm.

The purity of carbon monoxide was frequently examined by gas analysis before it was introduced into the reaction tube, and it was found that the quantity of impurities was trace. The content of carbon dioxide in the reaction gases was also analyzed several times while the melt was kept at a defintitely determined temperature, and its amount was confirmed to be about 0.0014 pct on the average. For this purpose the apparatuses (w), (x), (y), (u) and (v) were arranged.

The quantities of the high carbon white pig iron and the synthetic slags used in the experiments were respectively 15 gm. and 6 gm. at each heat. The metallic silicon of a different amount was added as shown later.

After the charges in the crucible were heated at a definitely determined temperature under the above-mentioned conditions, the crucible was taken out from the reaction tube as quickly as possible and quenched in water. The samples of the solidified pig iron specimens were secured after the skins of the specimens were removed at the thickness of about 2 mm. by a grinder.

The heat experiments were first carried out in order to determine the time allowed for attainment of equilibrium at 1400°C. For these experiments, the synthetic slag having the basicity of 0.9 and the metallic silicon of 0.51 gm. were used except the high carbon white pig iron. The time during which that temperature was kept was 15 min. to 4 hr. The results are shown in Fig. 4, which shows that the carbon and silicon concents of the pig iron were almost the same after 2 hr. and 30 min. elapsed. Hence, we can recognize that equilibrium was attained at that time.

The same experiments were carried out at 1500°C. The synthetic slags having the basicity of 0.57 and 1.14 were used, and the quantity of metallic silicon added was 0.7 gm. in the former case and 0.42 gm. in the latter case. The results are shown in Figs. 5 and 6, the former representing results obtained by using the

synthetic slag having the basicity of 0.57 and the latter those of another case. The time in question is known to be about 2 hr.

The synthetic slag having the basicity of 0.96 and the metallic silicon of 0.48 gm. were used in the experiments at 1600°C. The results are shown in Fig. 7.

The time in question is known also in this case to be about 2 hr.

The contents of sulphur and other impurities in the pig iron specimens, which were considered to be in equilibrium, were very small. Therefore, the influence of these impurities upon equilibrium of the present

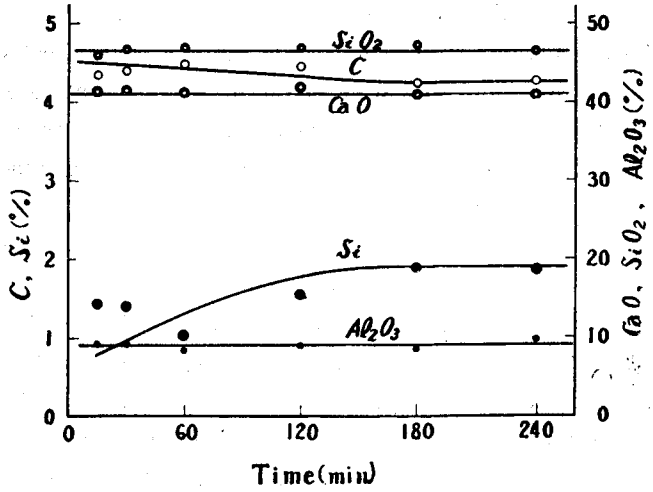

Fig. 4. Results of experiments made for determination of time allowed for attainment of equilibrium at 1400°C.

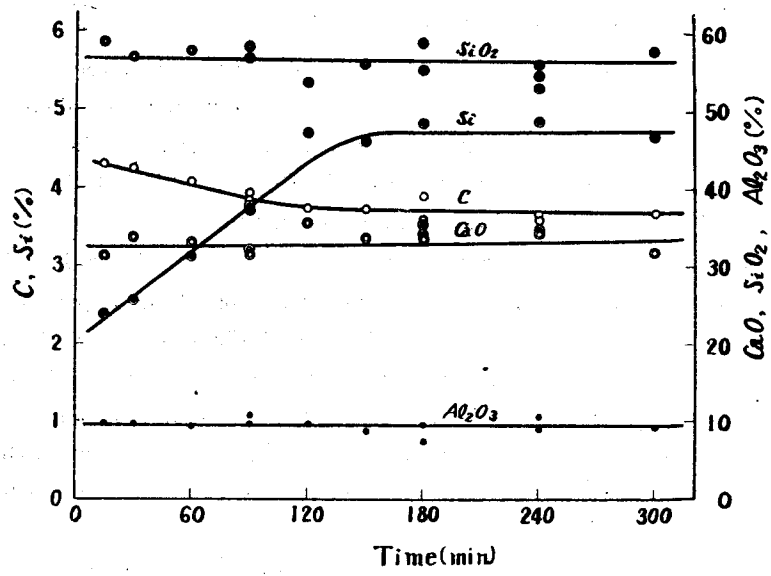

Fig. 5. Results of experiments made for determination of time allowed for attainment of equilibrium at 1500°C. (Basicity of synthetic slag used=0.57)

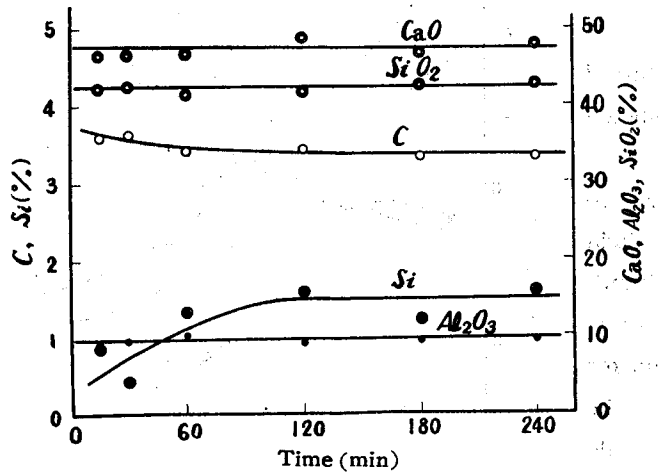

Fig. 6. Results of experiments made for determination of time allowed for attainment of equilibrium at 1500°C. (Basicity of Synthetic slag used=1.14)

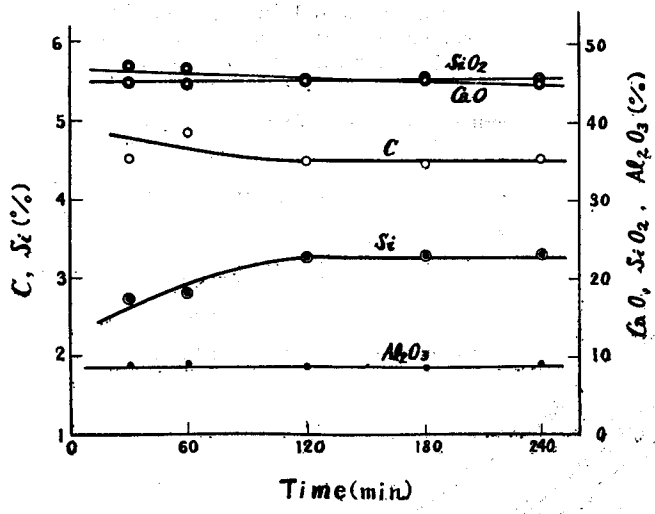

Fig. 7. Results of experiments made for determination of time allowed for attainment of equilibrium at 1600°C.

system can be ignored.

The relationship between the compositions of the pig iron and these of the slag which is in equilibrium with the former was examined at 1400°C., 1500°C. and 1600°C. in the second stage of heat experiments. The synthetic slags having varied basicities were used. The quantities of metallic silicon were respectively 0.8 gm. to 0.42 gm., 0.95 gm. to 0.35 gm. and 0.95 gm. to 0.36 gm. The time during which these temperatures were kept was 3 hr. The basicity of the slag specimens $(\sum CaO)/(\sum SiO_2)$ was calculated from the data obtained in the above experiments, and the relationship between this basicity and the composition of the pig iron was found as shown in Fig. 8.

We see that in equilibrium, (1) at a given temperature, the carbon content of the pig iron increases and its silicon content decreases as the basicity of the slag becomes greater, (2) at a given basicity of the slag, the silicon content of the pig iron increases remarkably and its carbon content remains almost constant as the temperature becomes higher, as far as the present experiments are concerned.

Now, the relationship in equilibrium between $[C]_s$ and [Si] is determined from the data obtained in the above experiments, as shown in Fig. 9.

The curves in this figure are drawn, assuming that the dada obtained by R. Ruer and J. Biren,[3] and K. Schichtel and E. Piwowarsky on the solubility of carbon for pure iron are accurate. The authors' curves do not coincide with those determined by K. Schichtel and E. Piwowarsky. The cause for this discrepancy should be farther studied.

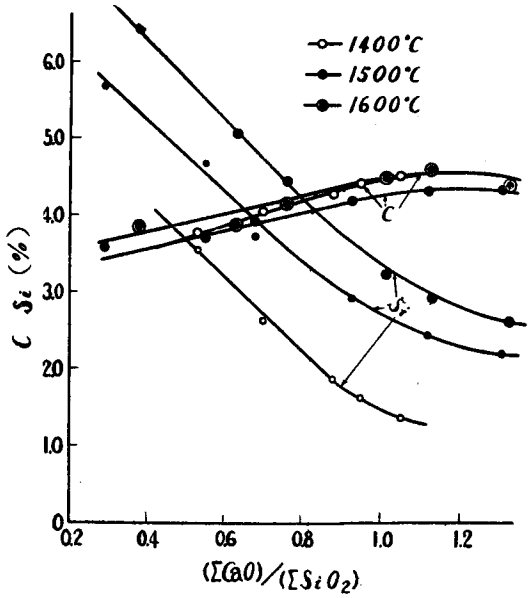

Fig. 8. Relationship among content of carbon saturated in pig iron, silicon content in pig iron, basicity of slag and temperature at equilibrium.

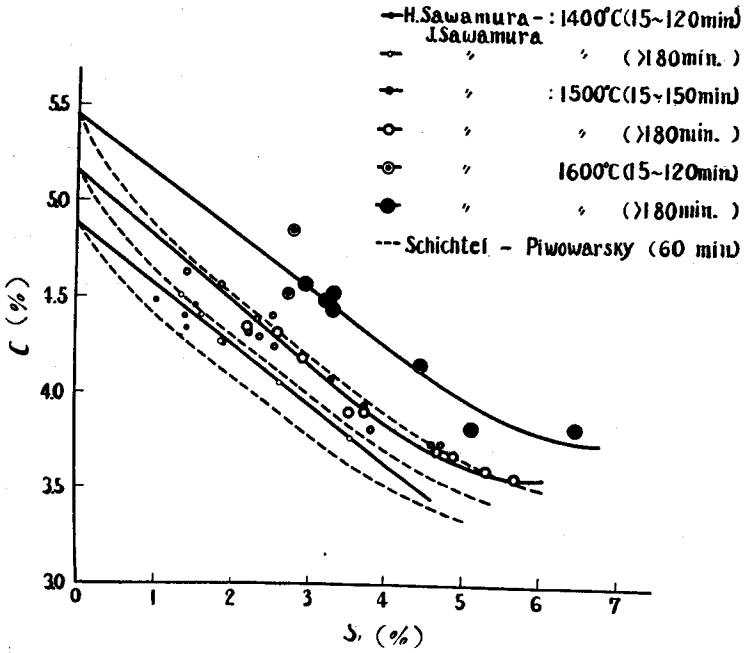

Fig. 9. Relationship among content of carbon saturated in pig iron, content of silicon in pig iron and temperature at equilibrium.

Summary

(1) This paper presents results of an experimental study of equilibrium between slags of the system SiO_2–CaO–Al_2O_3 and liquid pig iron of the system Fe–C–Si at temperatures accepted in pigmaking under the following conditions:

(a) The alumina content of the slags is constant, viz., 10 pct.

(b) The partial pressure of carbon monoxide in the gaseous phase is 1 atomospheric pressure.

(2) The carbon and silicon contents of metal in equilibrium with these slags were confirmed to depend upon temperature and the basicity of slags ($\sum$CaO)/($\sum SiO_2$). At a given temperature, the carbon content of metal increases and its silicon content decreases as the basicity of slags become greater. When the basicity of slags is constant, the influence of temperature upon the carbon content of metal is very small. The silicon content of metal, however, increases remarkably as temperature becomes higher.

(3) The relationship between the carbon content of metal and its silicon content in equilibrium was found. These results somewhat deviate from those reported by K. Schichtel and E. Piwowarsky.

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