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著者	YAGIHASHI Tetsuo, SHIBATA Zen-ichi
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On the Equilibrium Reaction among Aluminium, Oxygen and Carbon in Molten Iron*

Tetsuo YAGIHASHI and the late Zen-ichi SHIBATA**

The Research Institute for Iron, Steel and Other Metals

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Synopsis

As the direct measurement of the reaction of the deoxidation by aluminium in steel making was very difficult, an indirect measurement was carried out by using a pure carbon crucible in the atmosphere of CO gas at the temperature ranging over from 1650 to 2060°C. Then, combining the equilibrium constant of the above reaction with that of the reaction among CO gas, oxygen and carbon in molten iron, the equilibrium relation between oxygen and aluminium was obtained.

Further, the ternary deoxidation diagram of oxygen, carbon and aluminium in molten iron was discussed.

I. Introduction

F. Körber and W. Oelsen⁽¹⁾ have already studied the deoxidations with manganese and silicon from the standpoint of chemical thermodynamics, but reports on the researches in aluminium as a deoxidizer are small in number and, results are considerably different from one another. As aluminium has a strong affinity for oxygen, it has been used greatly in the ladle or casting in steel-making and has a great influence on steel thus produced. The theoretical consideration from specific heat and heat toning and the experimental result were first reported by C. H. Herty, Fittler and Byrnse⁽²⁾. Judkins⁽³⁾ also performed some experiments and H. Schenck⁽⁴⁾ reported the deoxidation force of aluminium calculated from the dissociation pressure of Al_2O_3 by utilizing the experimental results obtained by D. W. Murphy and co-workers⁽⁵⁾. Schumacher⁽⁶⁾ carried out experiments with 0.6 per cent aluminium and 50 per cent Al_2O_3 at 1,700°C. As the direct method was difficult, J. Chipman⁽⁷⁾ searched after the equilibrium constant from the partition law of aluminium between iron and silver in order to see the activity of aluminium in iron. H. Wentrup and G. Hieber⁽⁸⁾ performed experiments by

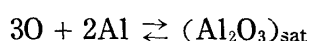
* The 741st report of the Research Institute for Iron, Steel and Other Metals.

** Professor of Hokkaido University and of the Research Institute of Mineral Dressing and Metallurgy, Tohoku University.

- (1) F. Körber and W. Oelsen, Mitt-K-Wihl-Inst. Eisenforsch., **15** (1933), 271; **14** (1932), 181.
- (2) C. H. Herty, Fittler and Byrnse, Min. Met. Invest. Bull., **46** (1942), 24; Stahl und Eisen, **50** (1930), 1230.
- (3) Judkins, *Gmelins Handbuch*, system No. 59 Eisen. T. I. A. Lfg., (1933), 952.
- (4) H. Schenck, *Physikalische Chemie der Eisenhüttenprozess*, Bd. 1, S. 213~294.
- (5) D. W. Murphy, W. P. Wood, and W. E. Joming, Trans. Amer. Soc. Steel Treat, **19** (1923), 1.
- (6) W. Schumacher, Dissert Berlin J.H. (1933),
- (7) J. Chipman, Trans. Amer. Soc. Metals, **22** (1934), 385.
- (8) H. Wentrup and G. Hieber, Arch. Eisen, **13** (1939/40), 15.

vacuum melting with an induction furnace and made chemical analyses of Al, Al₂O₃ and oxygen content in iron cast into a copper mould. It was made clear from the experiments by Herty⁽²⁾, Judkins⁽³⁾ and Schumacher⁽⁶⁾ that the deoxidizing power of aluminium would become weak, being almost equal to that of silicon. According to the results of H. Schenck⁽⁴⁾ and J. Chipman⁽⁷⁾, it has, on the contrary, a very strong deoxidizing power. The value determined by H. Wentrup was just between these two and has been considered to be the most reliable one. As mentioned above, there was a remarkable difference between the experimental values and the theoretical ones, and hence, to get more satisfactory results, the present experiment was done by an indirect method.

When aluminium is added to molten iron containing oxygen, the following reaction takes place :



$$K_{\text{Al-O}} = \frac{(\text{Al}_2\text{O}_3)_{\text{sat}}}{[\% \text{O}]^3 [\% \text{Al}]^2}$$

in which

$$(\text{Al}_2\text{O}_3)_{\text{sat}} = 1$$

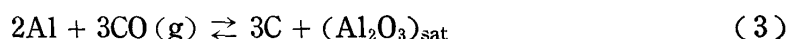
or

$$K'_{\text{Al-O}} = [\% \text{O}]^3 \cdot [\% \text{Al}]^2$$

The direct measurement of the equilibrium constant cannot be made with satisfactory accuracy, because an extremely small amount of oxygen in molten iron will cause a large error in analytical results, as actually shown by the experiment of H. Wentrup. Therefore, instead of Eq. (1), the following reaction was first assumed :



the equilibrium constant being $K_{\text{C}} = P_{\text{CO}}/[\% \text{O}] \cdot [\% \text{C}]$. From Eqs. (1) and (2),



The equilibrium constant of the above reaction is given by

$$K_{\text{Al-C}} = \frac{[\% \text{C}]^3 (\text{Al}_2\text{O}_3)_{\text{sat}}}{[\% \text{Al}]^2 P_{\text{CO}}^3},$$

in which Al₂O₃ is assumed to be saturated. In order to obtain a saturated state of carbon, a pure carbon crucible was used so that the partial pressure P_{CO_2} might be ignored, because the partial pressure P_{CO_2} was always detected when carbon in molten iron was not saturated. Therefore, the purest CO gas was used for P_{CO} . Then, the value of $K_{\text{Al-C}}$ could be given by

$$K_{\text{Al-C}} = [\% \text{C}]^3 / [\% \text{Al}]^2,$$

where

$$(\text{Al}_2\text{O}_3)_{\text{sat}} = 1$$

and

$$P_{\text{CO}} = 1 \text{ atmosphere.}$$

The equilibrium relation (3) can be obtained by adding carbon and aluminium to molten iron in the atmosphere of CO at a certain temperature and finally analyzing carbon and aluminium in the sample. Then, it follows that the equilibrium constant of the deoxidation equilibrium of (1) can be obtained reversely

* O and Al respectively means oxygen and aluminium in molten iron.

at every temperature from Eqs. (3) and (2). After the publication of this report in Japanese, a study on the deoxidation equilibrium of aluminium was reported by W. Geller and K. Dicke⁽⁹⁾, using an alumina crucible in the atmosphere of CO gas. Their experimental values, however, are considerably scattered, which may be attributed to their ignorance of the partial pressure of CO₂ gas. In the present paper, the values by Geller and Dicke will be discussed in comparison with our own.

II. Experimental procedure

(1) Experimental apparatus

Fig. 1 is a schematic diagram of the apparatus used in the present experiment. To produce CO gas, formic acid was dropped from the top of the tube into heated concentrated sulphuric acid and CO gas thus generated was first made to escape

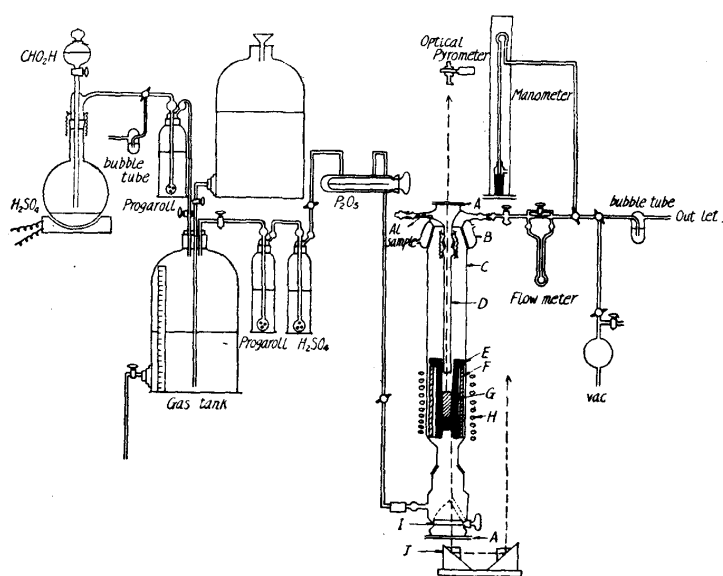


Fig. 1. Experimental apparatus.

A : Glass-window	E : Graphite Crucible
B : Water-cooled Glass head	F : Heat insulation alumundum
C : Quartz tube	G : Molten iron
D : Sample inlet Quartz tube	H : Induction Coil
	I : Pivoted-Window
	J : Glass Prism

through the bubble tube containing concentrated sulphuric acid to replace inside air. Then, the gas was passed through the tower of pyrogallol solution to take away free oxygen and was led into the gas tank containing water saturated with sodium chloride. This vessel is capable of containing 20 l. In carrying out the experiment, the free oxygen remaining still in CO gas was absorbed by the progallol solution, and the water vapour in it was dehydrated through the tower of concentrated sulphuric acid and phosphoric acid anhydrous tube and was led to the reaction tube through the hole of the lower cap. The gas outlet from the furnace was passed through the hole of the upper cap, the flow meter and the bubble tube. Before the experiment, the apparatus was evacuated, the vacuum degree being ascertained every minute with both the mercury manometer and the flow meter. The reaction tube is a glazed silica tube, 500 mm in length and 35 mm in diameter, its lower part being 25 mm in diameter. They are both connected with a water-cooled Terex glass cap. The former cap is equipped with a glass window to read temperature and with a side tube for gas

(9) W. Geller and K. Dicke, Arch. Eisenhüttenw., 16 (1943), 431.

out-let and sample in-let. As the leading tube for deoxidizer inlet, the opaque quartz is connected with the central tube of the cap. The latter cap has the same glass window and the pivoted glass window to read temperature, which is operated by a vacuum cock to prevent graphite powder from dropping. This cap is equipped with the gas-inlet tube connected with the rubber tube to keep vacuum. The crucible used was made of graphite sticks of Acheson Company containing very small amount of ash. It was protected by the sintered alumina sheath, so that it might not directly touch the quartz tube. The sheath and the graphite tube must be placed sufficiently far from each other, except their upper parts of contact. Temperatures were measured at molten iron and the graphite crucible with an optical pyrometer by using two prisms.

(2) Experimental procedure

The sample was electrolytic iron of very high purity. It was cut into pieces of 24~26 g and polished with sand paper before it was put in the graphite crucible. The amount of aluminium was about 2 per cent of iron, that is, 0.5~0.6 g was inserted in the side tube of the upper cap. After the whole apparatus was sufficiently evacuated, CO gas was introduced at a certain flow rate. The equilibrium state among CO gas, molten iron and carbon was kept at a desired temperature for half an hour, during which the temperature of the graphite crucible was carefully controlled, because the temperature of the melt gradually varied as the iron approached the saturation state with carbon. Then, aluminium was dropped to the melt from the side tube of the cap through the sample inlet tube. As the oxide film was immediately formed on the surface of melt, the temperature observed by the optical pyrometer was from 50 to 60°C higher than that of molten iron. This film, however, gradually broke and the molten surface usually appeared within 15 to 20 mins. After the charge of aluminium, it took 1 to 1.5 hrs to form the equilibrium between the gas and the melt. At the end of the run, the power of the induction furnace was shut off under the passing of CO gas throughout the apparatus and the melt was quenched as rapidly as possible, the solidification time never exceeding 15 sec. The calibration of the optical pyrometer was frequently made by referring to the melting points of metals Ni, Cu, Fe and to platinum thermocouple. To calibrate the temperature, the value $E = 0.37$ was used as the emission.

(3) Analysis of aluminium in sample

After quenching, the surface entrapment of impurities of the ingot was mechanically removed. Whenever possible, an entire sample was shaved to pieces to eliminate errors due to segregation, and about 2~3 g was used for the chemical analysis. Aluminium analysis was made by the standard gravimetric method. Insoluble inclusion Al_2O_3 was sufficiently separated from soluble aluminium.

(4) Analysis of carbon in sample

Carbon analysis was performed by the combustion method with an apparatus improved considerably for the present investigation. The outline of analytical apparatus is shown in Fig. 2. The analytical procedure was made in the

following way: CO_2 gas was first produced in the reaction tube by the reaction between oxygen gas and carbon in the sample at $1,100^\circ\text{C}$. CO_2 in gas mixtures was caught by the trap which had previously been evacuated and cooled by liquid air.

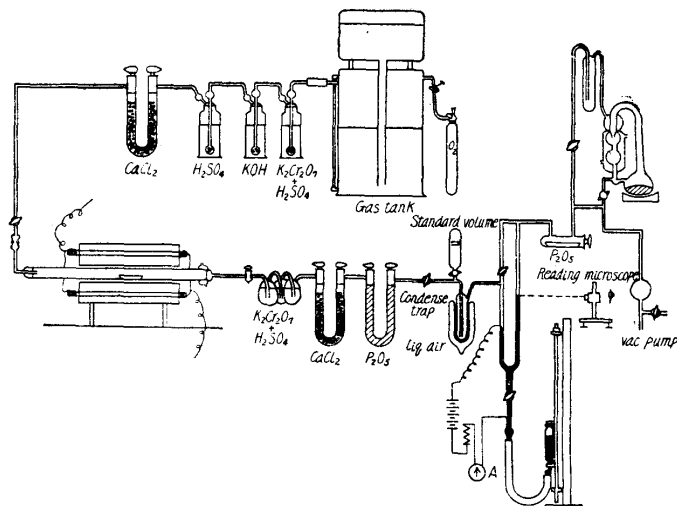


Fig. 3. Experimental apparatus of carbon analysis.

precisely the height of mercury column, that is, when the needle was out of contact with mercury, the electric current was spontaneously cut down. The adjustment of a minute difference of pressure could be made by means of microsliding. Thus, the amount of carbon contained in the sample could be determined by the pressure of CO_2 gas.

III. Results of experiment and their discussion

The results of the experiment at the temperature range $1,650\sim 2,060^\circ\text{C}$ are summarized in Table 1. Heats 1~20, in each of which about 2 per cent of aluminium were charged, showed oxidizing reaction after the equilibrium had been attained. Heats 22~25, each containing about 1.4 per cent of aluminium, showed the reducing reaction of Al_2O_3 by carbon in the atmosphere of CO gas. In this case, an ampoule made from the electrolytic iron was used. In it about 1~0.5 g of the mixture of Al_2O_3 , carbon and iron powder was charged. From the results of this experiment, it was confirmed that the reducing reaction took place on account of greater content of aluminium in the sample than that in the initial charge. Such a method had already been proved to be reliable by Ziegler⁽¹⁰⁾, who succeeded in the reduction of the inclusion Al_2O_3 in molten iron by mixing the powder of carbon with Al_2O_3 . Columns 6 and 7 in the table respectively show the actual analytical results of carbon and aluminium in the sample and Columns 9 and 11 the experimental value of the equilibrium constant $K_{\text{Al-C}}$ in the reaction (3) and $\log K_{\text{Al-C}}$. In Fig. 3, observed values of $\log K_{\text{Al-C}}$ are plotted against the reciprocal of the absolute temperature, in which signs \otimes and \bullet respectively indicate the oxidizing reaction and the reducing reaction of aluminium. In view of the fact that they seem to be almost in a straight line,

(10) Ziegler, Trans. Electro. Chem. Soc., 62 (1932), 109.

liquid air. Then, all the oxygen gas was removed with a vacuum pump, only solidified CO_2 gas being left. When the liquid air was removed and the temperature of the trap was raised up to room temperature, the solidified CO_2 again expanded in gas state. The pressure difference in the mercury manometer was accurately observed by a microscope. In this case, a platinum needle was used to indicate

Table 1. Experimental Results.

Heating No.	Experimental condition		Absolute temperature	Reciprocal of Abs temp.	Analysis of ter Experiment			O * wt. %	KAl-C = $\frac{[\%C]^3}{[\%Al]^2}$	KAl-O = $\frac{1}{[\%O]^3[\%Al]^2}$	log KAl-C	log KAl-O	$\zeta'_{Al-O} = \frac{[\%O]^3[\%Al]^2}{[\%Al-O]}$
	Reaction	Heating C° temperature			C wt. %	Al wt. %							
1		2060	2333	42.86	4.4299	2.6599	0.000949	12.287	1.653×10^8	1.0894	8.2182	0.604×10^{-8}	
2		1917	2190	45.66	5.0506	2.4967	0.000723	20.210	4.243×10^8	1.3152	8.6276	0.235×10^{-8}	
3		1840	2113	47.32	5.0131	1.9670	0.000669	32.561	8.608×10^8	1.5127	8.9349	0.116×10^{-8}	
4		1805	2078	48.12	5.390	1.8587	0.000598	37.92	1.351×10^9	1.6560	9.1303	0.740×10^{-8}	
5		1800	2073	48.23	4.647	1.8981	0.000689	27.853	8.452×10^8	1.4451	8.9269	0.118×10^{-8}	
6		1782	2055	48.65	4.753	1.9363	0.000646	28.639	9.866×10^8	1.4570	8.9941	0.113×10^{-8}	
7		1780	2053	48.70	4.816	1.5326	0.000650	37.09	1.549×10^9	1.6770	9.1549	0.645×10^{-9}	
8		1770	2043	48.94	4.605	1.5454	0.000671	43.42	1.382×10^9	1.6118	9.1405	0.723×10^{-9}	
9		1760	2033	49.18	4.584	1.9944	0.000666	24.216	8.487×10^8	1.3841	8.9287	0.117×10^{-8}	
10	CO Atmosphere	1758	2031	49.23	5.786	2.4605	0.000526	31.995	1.129×10^9	1.5051	9.0526	0.885×10^{-9}	
11		1740	2013	49.67	4.381	1.4890	0.000680	70.58	1.4306×10^9	1.5789	9.1553	0.698×10^{-9}	
12	2Al + 3CO(g)	1735	2008	49.79	4.535	1.5563	0.000653	35.80	1.477×10^9	1.5857	9.1693	0.676×10^{-9}	
13		1725	1998	50.04	4.831	1.8538	0.000605	30.62	1.310×10^9	1.5160	9.1172	0.763×10^{-9}	
14	$\rightarrow 3C + Al_2O_3(s)$	1720	1993	50.17	4.362	1.7374	0.000666	27.495	1.118×10^9	1.4395	9.0484	0.894×10^{-9}	
15		1725	1998	50.04	4.935	1.6636	0.000592	59.85	1.733×10^9	1.6377	9.2388	0.576×10^{-9}	
16		1716	1989	50.27	4.887	1.9510	0.000591	58.93	1.266×10^9	1.4860	9.1031	0.789×10^{-9}	
17		1710	1983	50.42	4.7380	1.8185	0.000608	33.91	1.345×10^9	1.5076	9.1287	0.743×10^{-9}	
18		1700	1973	50.68	4.2341	1.3897	0.000669	39.304	1.728×10^9	1.5944	9.2375	0.578×10^{-9}	
19		1680	1953	51.20	4.4139	1.2720	0.000625	53.147	2.528×10^9	1.7254	9.4027	0.395×10^{-9}	
20		1670	1943	51.46	4.3873	1.1238	0.000620	66.867	3.308×10^9	1.8251	9.5195	0.302×10^{-9}	
21		1650	1923	52.00	4.8381	1.3344	0.000547	63.599	3.413×10^9	1.8034	9.5331	0.292×10^{-9}	
22	CO Atmosphere	1818	2091	47.82	4.926	1.6359	0.000664	43.06	1.272×10^9	1.6341	9.1044	0.785×10^{-9}	
23		1770	2041	48.94	5.066	1.6753	0.000609	36.45	1.576×10^9	1.5637	9.1975	0.634×10^{-9}	
24	3C + Al ₂ O ₃ (s)	1710	1983	50.42	4.572	1.7319	0.000627	33.48	1.346×10^9	1.5341	9.1290	0.742×10^{-9}	
25	$\rightarrow 2Al + 3CO(g)$	1670	1943	51.46	4.436	1.5919	0.000614	46.33	1.704×10^9	1.6659	9.2314	0.586×10^{-9}	

* Oxygen in molten iron calculated according to following equation $\log K_C = \log \frac{P_{CO}}{[\%O][\%C]} = \frac{2193.4}{T} + 1.436$.

these constants can also be expressed by the following equation:

$$\log K_{\text{Al-C}} = \log \frac{[\%C]^3}{[\%Al]} = \frac{6094.9}{T} - 1.452 \quad (4)$$

The calculated values from Eqs. (4) are shown in the figure by the symbol \circ . The same figure also shows the results obtained by Geller and Dicke⁽⁹⁾,

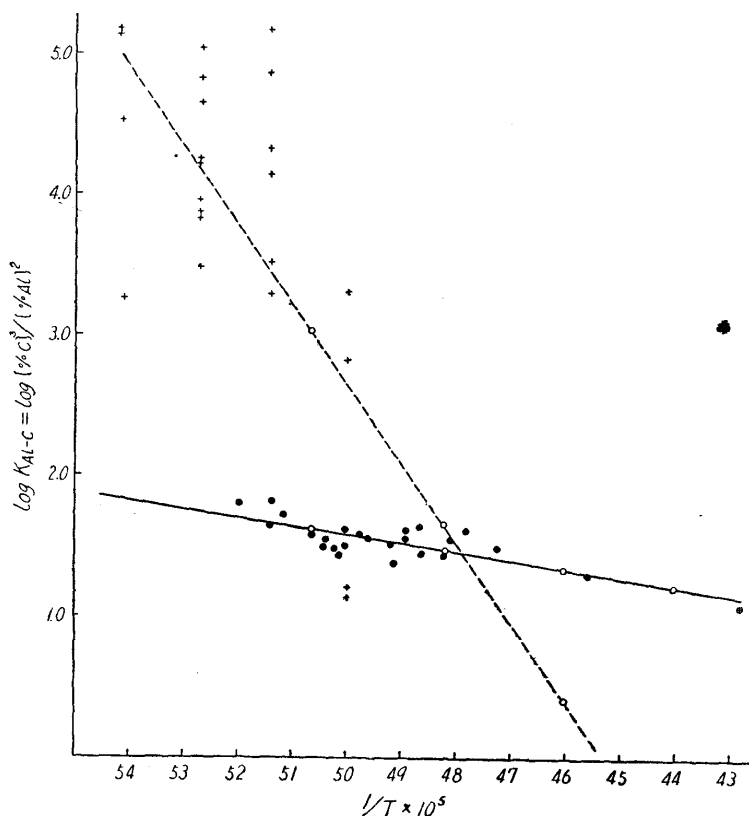


Fig. 3. Relation between $\log \frac{[\%C]^3}{[\%Al]^2}$ and reciprocal of temperature.

Yagihashi

— \circ — Cal value $\log \frac{[\%C]^3}{[\%Al]^2} = \frac{6094.9}{T} - 1.452$ (1942)

\oplus Al high side } Experimental value.
 \bullet Al low side }

Geller, Dicke

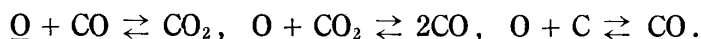
{ — \circ — $\log \frac{[\%C]^3}{[\%Al]^2} = \frac{56230}{T} - 25.45$ (1943)

{ + Experimental value.

as ours except that they used an alumina crucible and that the melts were not saturated with carbon in CO atmosphere. It was reported in detail by Vacher and Hamilton⁽¹¹⁾, S. Matoba⁽¹²⁾, and Z. Shibata and Ichihara⁽¹³⁾ that the partial pressure of CO_2 must, in this case, be taken into consideration because of the simultaneous occurrence of the following three reactions:

- (11) H. C. Vacher and E. H. Hamilton, *Trans. A. I. M. E.*, **95** (1931), 124. H. C. Vacher, *Bar. Stds Jnl of Research*, **11** (1933), 541.
 (12) S. Matoba, *Tetsu to Hagane* (in Japanese), **20** (1935), 837; **21** (1936), 875.
 (13) Z. Shibata and Ichihara, Not yet published.

which were reported after the publication of the present study as already mentioned. Their experimental values indicated by the symbol + show such a remarkable irregular distribution that they seem very difficult to lead to an equation of straight line, though the straight line determined by them is given in the figure for reference. It will be seen that these two lines intersect in the neighbourhood of $1,820^\circ\text{C}$ and that the values of their equilibrium constant and the temperature gradient are generally large as compared with ours. Their experiment was carried out in the same way



In Geller's measurement at 1,625°C, the carbon content was in the range 0.5~1.1 per cent, while Vacher's experimental values showed that the partial pressure of CO₂ became 1~2 per cent, when 0.5~0.9 per cent of carbon was contained in the melt. Therefore, CO gas (of 100 per cent) may undergo a partial decomposition and carbon in the melt may somewhat be increased without reaching actual equilibrium. This may be the reason why the above-mentioned irregularity appeared in the observed values. Another reason may be that they considered the sum of aluminium and alumina to be the analytical value of aluminium, because the separation of both elements was ambiguous in a sample containing small amount of aluminium. Further, we cannot agree with their opinion that aluminium in the melt transforms into Al₂O₃ during solidification. To confirm this point, a complete separation must be made between aluminium and alumina, which is possible, because the melt can be quenched in case the induction furnace is used. In the present experiment, a carbon crucible was used and the molten iron was saturated with the carbon in CO atmosphere and, hence, the partial pressure of CO₂ might completely be ignored. Accordingly, the experimental values might almost be

represented by a straight line. The equilibrium relation between carbon and aluminium at various temperatures were calculated by Eq.(4) and the results are shown in Fig. 4. From this figure, it will be seen that the equilibrium amount of aluminium in the melt increases with the increase of carbon content at a constant temperature and with the rise of temperature at a constant carbon content. Accordingly, a great attention must be

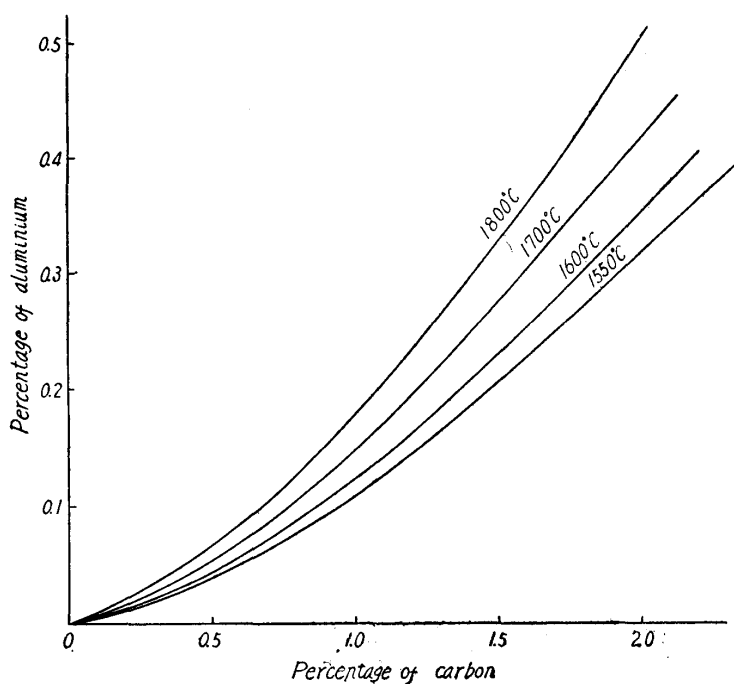
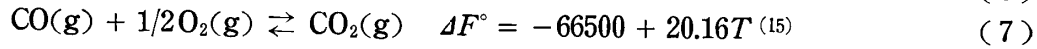
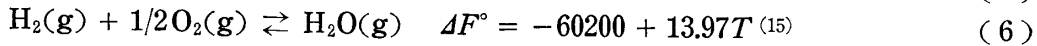
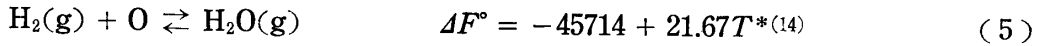


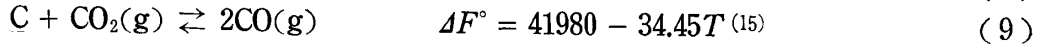
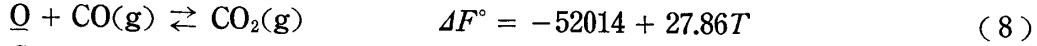
Fig. 4. Equilibrium relation of carbon and aluminium at various temperature.

paid to these problems in practical steelmaking. It was, therefore, concluded that aluminium should not be used as a deoxidizer at comparatively high temperatures.

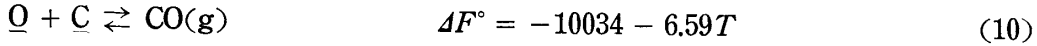
Next, the experimental values concerning the fundamental reaction (2) will be compared with the present results computed from the data obtained by the indirect method.



$$(5) + (7) - (6)$$



$$(8) + (9)$$



From Eq. (10), the equilibrium constant of Eq. (2) will be obtained as follows:

$$\log K_C = \log \frac{P_{\text{CO}}}{[\% \text{O}][\% \text{C}]} = \frac{2193.4}{T} + 1.436 \quad (11)$$

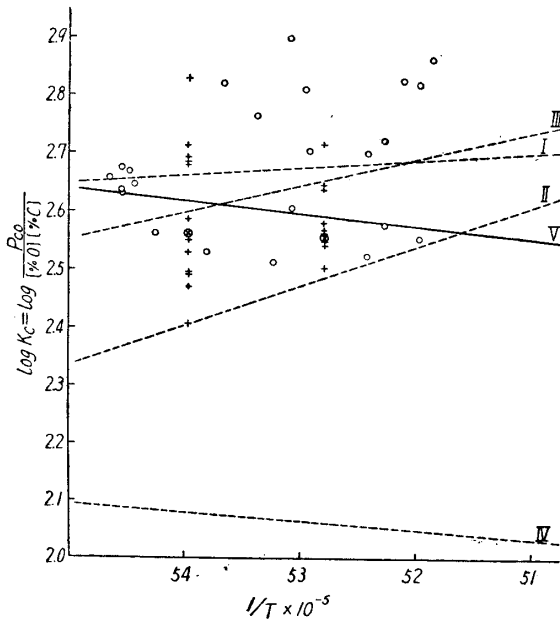


Fig. 5. Relation between $\log \frac{P_{\text{CO}}}{[\% \text{O}][\% \text{C}]}$ and reciprocal of temperature.

I $\log K_C = \frac{-1350}{T} + 3.392$ U. Matoba (1934) Experi

II $\log K_C = \frac{-6883}{T} + 6.123$ Z. Sibata (1935) Experi

III $\log K_C = \frac{-4586}{T} + 5.075$ Sibata & Ichihara (1945) Experi

IV $\log K_C = \frac{1758}{T} + 1.138$ Geller & Dicke (1942) Experi

V $\log K_C = \frac{2193.4}{T} + 1.436$ T. Yagihashi & Sibata Calcu

o U. Matoba

+ mean value } Vacher & Hamilton (1931~1933) Experi

(14) T. Yagihashi, Journal and Japan Institute of Metals, Tokyo Meeting (1946).

(15) J. Chipman and A. M. Samarin, A. I. M. E., 125 (1937), 338, 340.

* This measurement was made during 1933 to 1944 in the laboratory of J. Chipman and Z. Shibata and the most reliable 38 experimental values were selected from these results. Then, the authors obtained the following equation by the method of least squares.

$$\log K_H = \log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}[\% \text{O}]} = \frac{9992.2}{T} - 4.738. \text{ From the above constant, the value of } \Delta F^\circ \text{ was calculated.}$$

Fig. 5 shows the results calculated from the above equation and the experimental results. It will be seen that the latter are irregularly distributed due probably to the difficulty of measurement. Although the gradients of the lines I, II and III are reverse to those of the calculated value and of Geller and Dicke, the average value of the experimental results obtained by Vacher and Hamilton seems to be represented by our straight line. In this case, the values of Geller and Dicke are so different from the others that their measurement may be considered to be the least reliable. From these results, it was concluded that Eq. (11), which was obtained by combining a few thermodynamical data with the experimental value of $\text{H}_2\text{-H}_2\text{O-Fe}$ system having no sub-reaction, was most adaptable to the present study. The calculation of the

equilibrium constant K_{Al-O} is as follows :

$$\begin{aligned}
 2Al + 3CO(g) &\rightleftharpoons 3C + Al_2O_3(s)_{sat} \\
 \log K_{Al-C} &= \frac{6094.9}{T} - 1.452 \\
 3O + 3C &\rightleftharpoons 3CO(g) \\
 3 \log K_C &= \frac{6580.2}{T} + 4.308 \\
 \therefore 3O + 2Al &\rightleftharpoons Al_2O_3(s)_{sat} \\
 \log K_{Al-O} &= \log \frac{1}{[\%O]^3[\%Al]^2} = \frac{12675}{T} + 2.85 \quad (12)
 \end{aligned}$$

The above reaction shows the deoxidizing equilibrium of molten iron by aluminium metal. From the equation, the free energy change in the above reaction is given by

$$\Delta F^\circ = -57988 - 13.03T \quad (13)$$

The equilibrium of Eq. (1) was studied first thermodynamically and then experimentally by the direct or indirect method. To calculate K_{Al-O} thermodynamically, J. Chipman first established the partition law of aluminium between molten iron and silver and then calculated the activity coefficient of aluminium in iron and finally obtained the following equation by combining some thermodynamical values as to aluminium and alumina :

$$\log K_{Al-O} = \frac{62700}{T} - 19.39.$$

W. Schumacher⁽⁶⁾ investigated this reaction with the sample containing 0.6 per cent of aluminium in metal and 60 per cent of alumina in slag at 1,700°C by the direct method and obtained the following results :

$$\log K_{Al-O} = \frac{40390}{T} - 14.71.$$

Geller and Dicke⁽⁹⁾ studied it in the same way as the present writers except that the value of the oxygen in molten iron was determined not from the actual analysis but from the following expressions :

$$\begin{aligned}
 O + C &\rightleftharpoons CO(g) \\
 \log \frac{P_{CO}}{[\%O][\%C]} &= \frac{1758}{T} + 1.138',
 \end{aligned}$$

from which the following equation resulted :

$$\log K_{Al-O} = \frac{58600}{T} - 18.9.$$

On the other hand, H. Wentrup and G. Hieber reported the most reliable results by the direct method. They melted the sample in an induction furnace by means of the vacuum fusion method under the mercury pressure of 8 to 10 mm at the given temperature for 15 min. and then added aluminium to it and poured part of it into the mould after 10 min., the rest being cooled in the crucible. They made the oxygen analysis of the sample by the vacuum fusion method and

obtained the analytical values of aluminium and alumina in the same way as we did, but their experimental values were scattered within the following extent :

1,700°C	1,600°C
$K'_{\text{Al-O max}} = 1.9 \times 10^{-8}$	$K'_{\text{Al-O max}} = 2.8 \times 10^{-10}$
$K'_{\text{Al-O mean}} = 7.5 \times 10^{-9}$	$K'_{\text{Al-O mean}} = 9.0 \times 10^{-11}$
$K'_{\text{Al-O min}} = 3.0 \times 10^{-9}$	$K'_{\text{Al-O min}} = 3.0 \times 10^{-11}$,

in which all $K'_{\text{Al-O}}$ are the reciprocal of the equilibrium constant $K_{\text{Al-O}}$. It seems that the cause of these scatterings may be attributed to the error in oxygen analysis. From these values, the equilibrium constant $K_{\text{Al-O}}$ can be expressed by

$$\log K_{\text{Al-O}} = \frac{71200}{T} - 27.78$$

The values of $\log K_{\text{Al-O}}$ at various temperatures calculated by the above equations

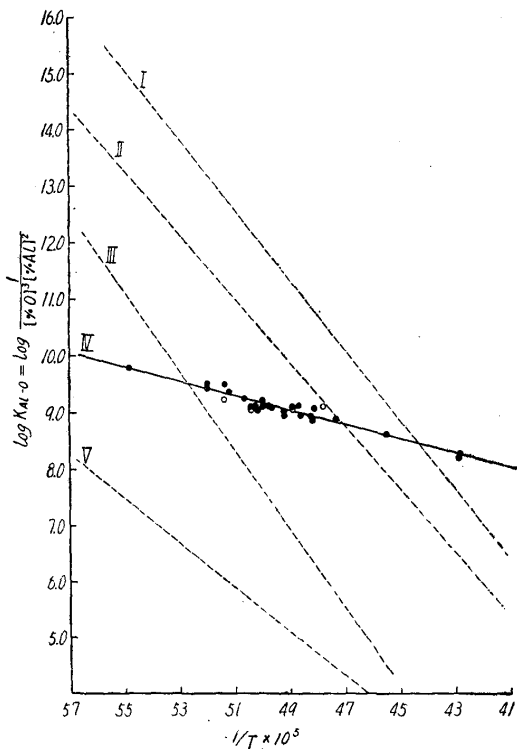


Fig. 6. Relation between $\log 1/[\%O]^3[\%Al]^2$ and reciprocal of temperature.

- I $\log K_{\text{Al-O}} = \frac{62700}{T} - 19.39$ (Chipman 1934
Calculation)
- II $\log K_{\text{Al-O}} = \frac{58600}{T} - 18.9$ (Geller, Dicke 1943
Experiment)
- III $\log K_{\text{Al-O}} = \frac{71200}{T} - 27.98$ (Wentup Hieber 1939
Experiment)
- IV $\log K_{\text{Al-O}} = \frac{12675}{T} + 2.85$ (T. Yagihashi 1942
Experiment)
- V $\log K_{\text{Al-O}} = \frac{40390}{T} - 14.71$ (W. Schmacher 1953
Experiment)

—⊗— Calculated value
● Al high side } Experimental Value
○ Al low side }

are plotted in Fig. 6. It seems that Chipman's values are the largest of all, while Schumacher's results are small, both being less reliable. The present authors experimental values agree with those of Wentrup and Hieber at the temperature near 1,630°C, but the equilibrium constant becomes considerably small in the case of higher temperature. Also, our values fairly agree with those of Geller and Dicke at about 1860°C, though the latter is generally higher than the former. Although the results of the above three studies show almost the same temperature gradients, the present authors' results are somewhat smaller. So, it may be said that the deoxidizing power of aluminium is not strongly affected by the change in temperature. In Fig. 6, the values of $\log K_{\text{Al-O}}$ shown in Column 12 of Table 1 are plotted, which were calculated from the analytical value of aluminium in column 7 and that of oxygen in column 8 obtained by Eq. (11). It will be seen that they are distributed almost in a straight line, in which symbols ● and ○ indicate respectively the oxidizing reaction

results of Judkin⁽³⁾ almost agreed with those of C. H. Herty. Their results, however, seem to be less reliable due to the inaccuracy of experimental method. H. Schenck obtained $K'_{\text{Al-O}}$ from the dissociation pressure of the oxygen in FeO and Al_2O_3 by using the following equation:

$$K'_{\text{Al-O}} = \frac{P_{\text{O}_2}^{3/2}/\text{Al}_2\text{O}_3 \cdot [\text{Al}]^2_{\text{max}}}{D_{\text{FeO}}^{3/2}}$$

Moreover, he reported the values calculated on the basis of the experimental values of D. W. Murphy and co-workers, which are also shown in Table 2. The summary of these results is illustrated in Fig. 7, in which the respective values obtained by Wentrup and Hieber and Geller and Dicke besides ours are shown for the comparison of the accuracy of experimental method with one another. From the above results, it will be seen that the results of Geller and Dicke show the largest irregularity, the range being from $K'_{\text{Al-O max}} = 5.4 \times 10^{-12}$ to $K'_{\text{Al-O min}} = 1.4 \times 10^{-12}$ at $1,620^\circ\text{C}$, and that Wentrup's values at $1,600^\circ\text{C}$ lie in the range $K'_{\text{Al-O max}} = 2.8 \times 10^{-10} \sim K'_{\text{Al-O min}} = 3.0 \times 10^{-11}$, which is still of a considerable irregularity, showing the difficulty of the direct method. On the other hand, the present authors' results converge in the range $K'_{\text{Al-O max}} = 9 \times 10^{-10} \sim K'_{\text{Al-O min}} = 4 \times 10^{-10}$ in the neighborhood of $1,700^\circ\text{C}$. The figure also shows the calculated value of $K'_{\text{Al-O}}$ based on the experimental values of P. Bardenheuer and A. Ranfft⁽¹⁶⁾ in the actual open hearth process. In their experiment, the molten steel was left in the ladle for a while after having been tapped, and the steel was sampled at the opening of the ladle or in the neighbourhood of the boundary surface between the molten steel and slag at the time just before casting. The time from the complete tapping to the sampling is recorded in the subsequent table. This steel, however, was slightly deoxidized by aluminium and silicon. These results are shown in Table 3. Judging from the rapid reaction rate of aluminium, these values mostly seem to have reached the equilibrium and to have had enough time for almost perfect separation of Al_2O_3 . Though the considerable lowness of casting temperature appears to be a defect of this experiment, it seems generally to be excellent standard data in the actual operation. The theoretical values by H. Schenck and J. Chipman are considerably different from the experimental values due to some hypothesis in the theory. The calculated values of deoxidizing isotherms at various temperatures obtained from the expression $K'_{\text{Al-O}} = [\% \text{O}]^3 [\% \text{Al}]^2$ are shown in Fig. 8, in which the values of

Table 3. Results of Open Hearth steel obtained by P. Bardenheuer and A. Ranfft.

Temperature C°	Absolute Temperature	Reciprocal of Abs. Temp. $\times 10^5$	Time (min)	[O%]	[Al%]	Al_2O_3 (s)	$K'_{\text{Al-O}}$ $= [\% \text{O}]^3 [\% \text{Al}]^2$
1490	1763	56.80	46	0.00149	0.09	0.0063	0.272×10^{-10}
1470	1743	57.40	82	0.00250	0.05	0.0095	0.390×10^{-10}
1430	1703	58.80	92	0.0090	0.02	0.0317	0.2905×10^{-9}

(16) P. Bardenheuer and A. Ranfft, Mitt. K. W. I. Eisenforsch., 13 (1931), 291.

silicon at 1,600°C by Körber and Oelsen are taken together with those by several other workers. Results of Wentrup and Hieber and of the present authors showed approximate deoxidizing isotherms and it was found that this metal was far better than silicon as a deoxidizer. In the present case, for example, the amount of oxygen equivalent to 0.014 per cent of aluminium was only 0.01 per cent, but, when silicon was used as a deoxidizer, 0.35 per cent of silicon was necessary.

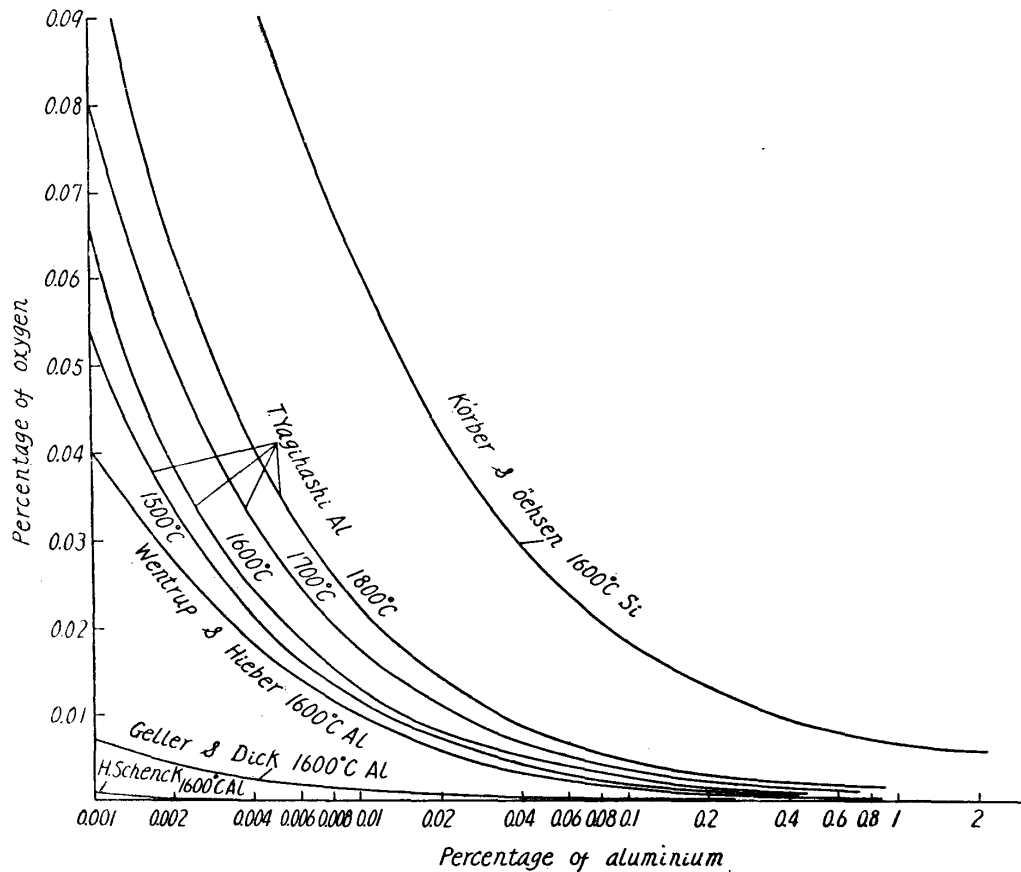


Fig. 8. Equilibrium relation of oxygen and aluminium at various temperature.

The values by Geller and Dicke as well as the calculated values by H. Schenck, which show a stronger deoxidizing power than ours seem to be less reliable. Concerning the influence of temperature, it can be shown that the deoxidizing power of aluminium becomes stronger proportionally to the fall of temperature. According to the experiment of Wentrup, the amount of the inclusion Al_2O_3 in molten iron decreases with the fall of temperature and such an operation must be carried out at as low temperature as possible. It is commonly recognized that when a large amount of deoxidizer is used, the quantity of residual oxygen in steel may fairly be decreased. For example, from the deoxidizing isotherms of aluminium in Fig. 8, it will be seen that the residual oxygen will be decreased almost to zero, in case a large amount of aluminium is used. On the contrary, it was found from our experimental results that aluminium could not completely take away residual oxygen in molten steel, when some amounts of carbon still existed in the metal. Therefore, when the amount of carbon in it is determined,

that of aluminium may necessarily be limited by it. The calculated values of the equilibrium relation concerning the ternary system O-C-Al in molten iron at various temperatures and its space diagram are shown in Fig. 9. From this diagram, the following problems may be considered:

- (1) The change of aluminium along an isothermal line
(A)

For example, it can be seen from Fig. 9 that at 1,600°C the metal in equilibrium with 0.6 per cent of carbon contains 0.06 per cent of aluminium and 0.00425 per cent of oxygen. When the melt contains 0.6 per cent of carbon and 0.05 per cent of aluminium, the decaobonization is carried out by the reaction $C + O \rightarrow CO$ and this reaction is made to proceed with the content of 0.55 per cent of carbon, which is in equilibrium with aluminium content. Therefore, the amount of oxygen to be in equilibrium with aluminium naturally becomes higher than 0.0045 per cent.

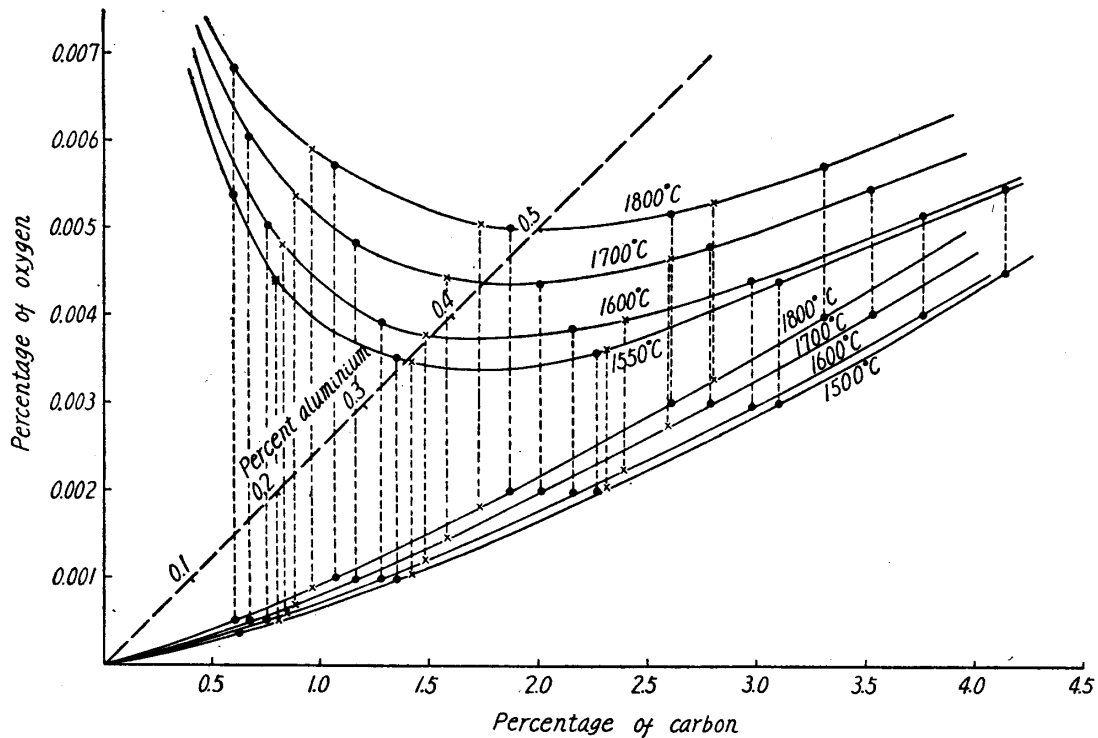


Fig. 9. Ternary equilibrium diagram of aluminium-carbon-oxygen in molten iron.

- (B)

When the melt contains larger amount of aluminium than that in the equilibrium, say, 0.07 per cent, this metal will be carbonized by the reaction $CO \rightarrow C + O$ up to 0.68 per cent carbon which is in equilibrium with the above amount of aluminium, while the amount of residual oxygen decreases to 0.00375 per cent in proportion to the increase of aluminium.

- (2) The deoxidizing phenomena outside the furnace

When the steel deoxidized by aluminium is tapped from an open hearth or an electric furnace into a ladle, it is always exposed to the oxidation of air. In

such a case, to manufacture a standard steel of 0.6 per cent of carbon content not oxidized by air at 1,600°C, the amount of aluminium in equilibrium with the carbon must be greater than 0.06 per cent. It may, however, not be less than the equilibrium quantity of 0.00425 per cent of oxygen.

(3) Influence of temperature

(A)

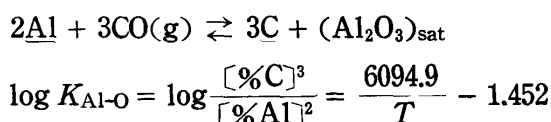
When the temperature of the melt was raised from 1550° to 1800°C with the same amount of carbon as that shown in Fig. 9, the amounts of aluminium and oxygen in equilibrium with carbon both increased. Therefore, in order to decrease the oxygen in steel and to economize the amount of aluminium, the deoxidizing operation must be done at a low temperature sufficient to float easily deoxidation products.

(B)

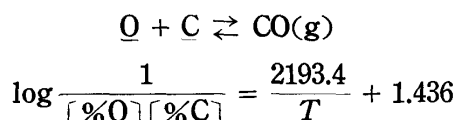
When the temperature was raised from 1,550° to 1,800°C with the same amount of aluminium, the amount of carbon in equilibrium with aluminium decreased, while that of oxygen in the melt increased. Accordingly, the decrease of carbon content in proportion to the rise of temperature make it difficult to keep the desired amount of carbon in the steel and at the same time it gives an unfavorable influence due to the increase of oxygen. Thus, the present authors have improved the old conception on the deoxidation and proposed a new notion based on the experimental results.

Summary

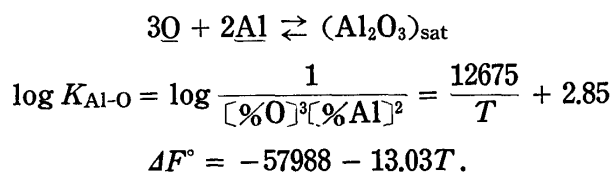
The equilibrium among aluminium, oxygen and carbon in molten iron was studied by an indirect method. Using a carbon crucible, the equilibrium of the following reaction was studied under a saturated condition of carbon in the temperature range from 1,650° to 2,000°C :



Then, by combining the expression deduced from the basic study of the H₂-H₂O-Fe system in molten iron with some thermodynamical data, the following equation was obtained :



By combining these equations, the so-called equation of the deoxidation equilibrium was deduced as a function of temperature, namely,



From the above equation, it was found that the present experimental values were between those of Geller and Dicke and those of Wentrup and Hieber, having small temperature gradients in comparison with others. Next, by comparing the present results with those of the deoxidation by aluminium in the actual open hearth operation, it was seen that they agreed fairly well with the actual data. Further, from the consideration of the space diagram of the ternary system Al-C-O in molten iron, it was concluded that the deoxidizing power of aluminium was not so great as usually supposed in case a certain amount of carbon is given, and that the amounts of aluminium and residual oxygen in equilibrium with carbon must be limited. Therefore, the molten metal must be deoxidized at a properly low temperature, because the rise of temperature causes undesirable increases of both aluminium, as the deoxidizer, and the residual oxygen in metal.

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