

The System of Ferrous Oxide and Silica.

By

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INTRODUCTION.

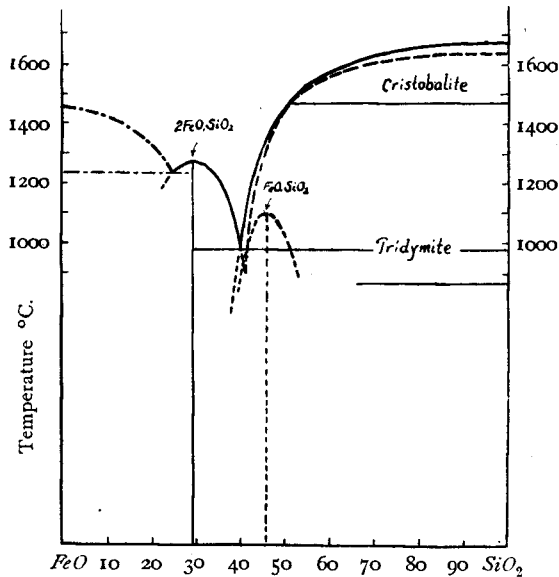
The precise investigation of the equilibrium of ferrous oxide and silica is an exceedingly difficult problem, because the preparation of pure ferrous oxide is very difficult and the atmosphere of the furnace must be controlled as well as the temperature and a proper container for the charge must be found which does not react with it at high temperature. Therefore, only a few papers on the investigation of this system have been published.

According to the investigation of *Whiteley* and *Hallimond*,⁽¹⁾ the equilibrium diagram of $FeO-SiO_2$ is as shown in Fig. 1. These investigators studied chemically as well as microscopically the formation of iron

(1) Journ. Iron & St. Inst., 99 (1919), 212.

Fig. 1.

Approximate Equilibrium Diagram of $FeO-SiO_2$
(Whiteley and Hallimond.)



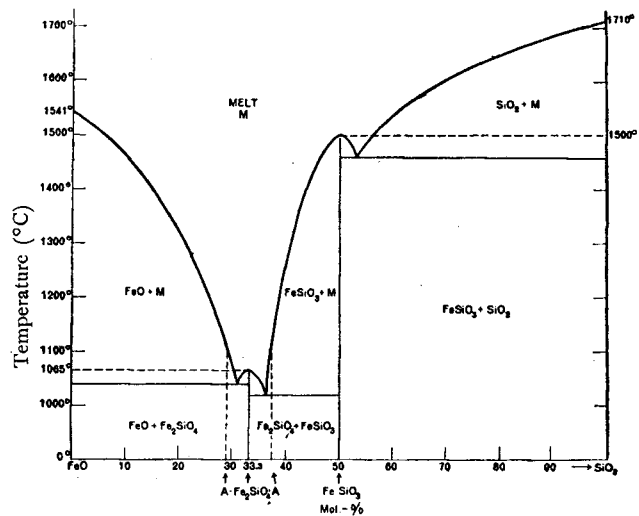
silicates in slags from acid open-hearth steel furnaces. This diagram shows the existence of two eutectics containing 24.5 and 40 per cent of silica, with eutectic points of 1240°C. and 980°C. respectively, and a compound of ferrous orthosilicate ($2FeOSiO_2$), with a maximum melting point of about 1280°C.. No evidence, however, was found of the presence of ferrous metasilicate ($FeOSiO_2$).

H. von Eckermann⁽²⁾

constructed a melting diagram of $FeO-SiO_2$, which is shown in Fig. 2. This diagram is not an outcome of his own experiments, but is simply based on the data collected from the published results of previous investigators. The diagram shows that there are two eutectics, containing respectively 27.4 and 32.2 per cent

Fig. 2

Equilibrium Diagram of $FeO-SiO_2$. (Eckermann.)

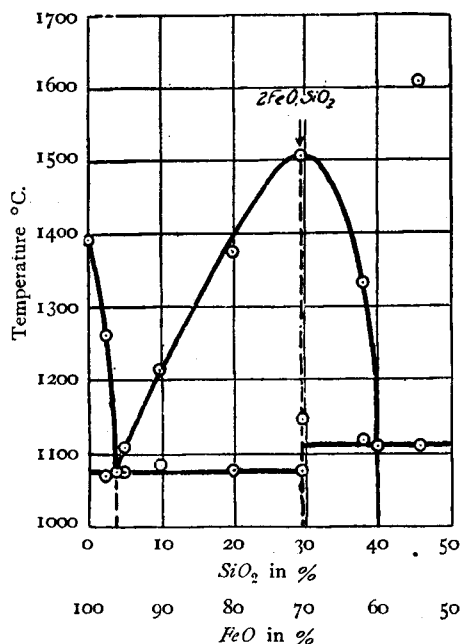


(2) Geologiska Foreningens, Stockholm Foerhandlingar, 44 (1922), 289.

silica with eutectic temperatures of about 1040°C. and 1020°C., and two compounds, $2FeOSiO_2$ and $FeOSiO_2$, with maximum melting temperatures of 1065°C. and 1500°C. respectively.

Fig. 3

Equilibrium Diagram of $FeO-SiO_2$
(Keil and Dammann).



Keil and Dammann⁽³⁾ studied the less silicious region of the system $FeO-SiO_2$, i. e. silica content of less than 45 per cent, by means of thermal analysis of mixtures of FeO and SiO_2 in a platinum crucible in a nitrogen atmosphere and their results are shown in Fig. 3. The FeO -rich eutectic is indicated at a region of where the SiO_2 content is 4 per cent, with the eutectic temperature of 1075°C., whereas $2FeOSiO_2$ is shown to melt at 1503°C.. The SiO_2 -rich eutectic (40 per cent SiO_2) is shown to have a minimum melting point of 1115°C..

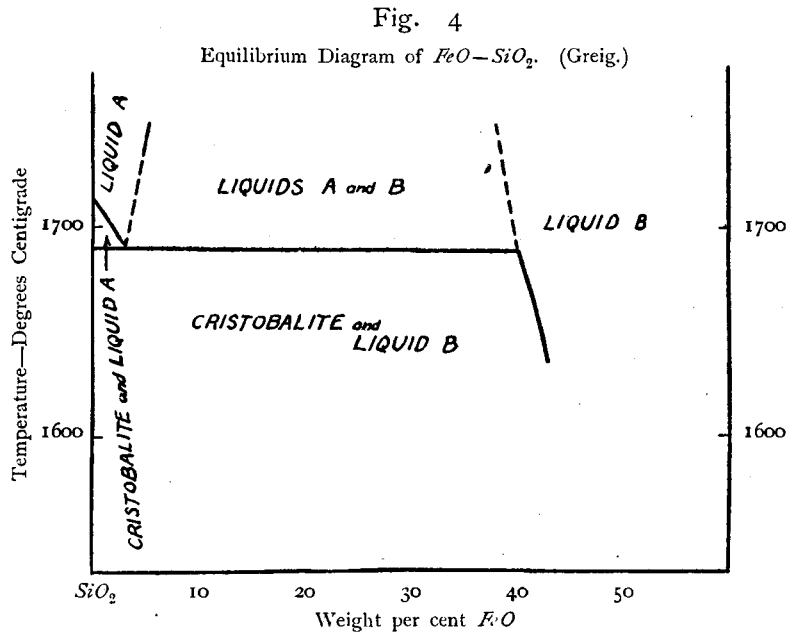
Greig⁽⁴⁾ studied the system, as shown in Fig. 4, from the standpoint of the immiscibility of the silicate melts at high temperatures, with regard to a high silicious region with an SiO_2 content of more than 50 per cent. His work determined the presence of two immiscible liquids A, rich in silica, and B, rich in ferrous oxide. The melts for the investigation were prepared by heating silica with ferrous oxalate or, in some cases, with ferrous oxide. The determination of immiscibility was effected by examining microscopically the samples quenched at 1700°C..

Herty and Filtner⁽⁵⁾ investigated the system by melting samples of

(3) Stahl u. Eisen, 45 (1925), 890.

(4) Am. Journ. Sci., 13 (1927), 133.

(5) Ind. and Eng. Chem., 21 (1929), 51.

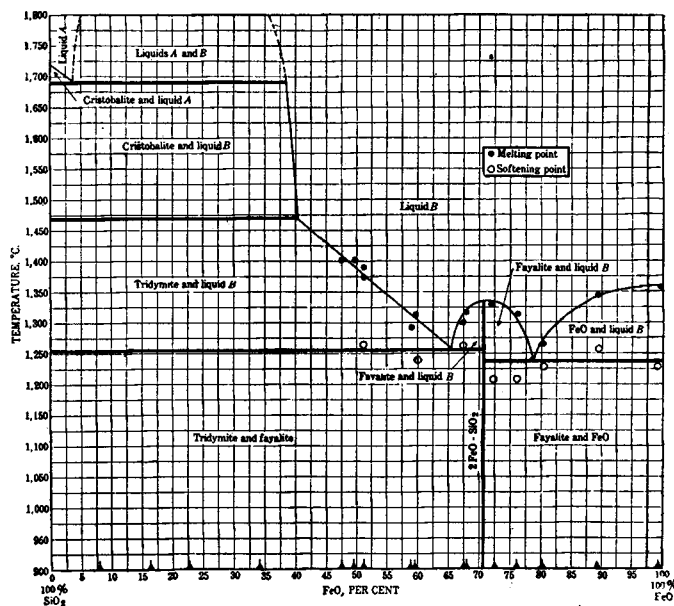


ferrous silicate slag in a nitrogen atmosphere and observing their softening and melting temperatures by means of the *Burgess* micropyrometer. The samples of ferrous silicate slag used were prepared by melting SiO_2 and Fe_2O_3 mixtures in a graphite crucible placed in a furnace of the electric register type or in a high frequency induction furnace at temperatures of about $1600^\circ C$.; each sample was then carefully analysed. The reduction of Fe_2O_3 into FeO was effected by the graphite of the crucible and some CO gas formed. They constructed an equilibrium diagram of the system $FeO-SiO_2$ as shown in Fig. 5. The FeO -rich eutectic is indicated at about 21.3 per cent of SiO_2 with a eutectic temperature of about $1235^\circ C$., whereas the ferrous orthosilicate has a melting point of about $1335^\circ C$.. The SiO_2 -rich eutectic has an SiO_2 content of about 34.5 per cent and a minimum melting temperature of about $1255^\circ C$..

According to my sintering experiment⁽⁶⁾ with powdered iron ore,

(6) Tr. World Eng. Congress, Tokyo, 1929, No. 436.
 Journ. Iron & St. Inst. Japan, 12 (1926), 431-452.
 Suiyokai-shi, (Tr. Min. & Met. Alumni Assoc.) Kyoto, 4, (1925), 1409-1424,
 " " " " 5, (1926), 134-144.

Fig. 5.

Equilibrium Diagram of $FeO-SiO_2$. (Herty and Fitterer.)

the apparent melting temperature of magnetite concentrate of Anshan, having about 14 per cent SiO_2 , is about $1150^{\circ}C$. in a reducing atmosphere, and it should correspond to the eutectic temperature of ferrous oxide and ferrous orthosilicate of the system $FeO-SiO_2$. I have found that there is a great discrepancy among the eutectic temperatures and also their compositions found by the above named investigators and the temperature of the FeO -rich eutectic does not coincide with the results of my experiments. Hence, I decided to pursue the system of $FeO-SiO_2$ in a less silicious region, i.e. with silica contents of less than 45.5 per cent, which corresponds to ferrous metasilicate.

Chapter I. PREPARATION OF FERROUS OXIDE.

One of the favorite early methods of preparing so-called FeO was to ignite ferrous oxalate. The usual end product was a material undoubtedly containing FeO , but also containing some metallic iron, magnetite and

carbon, usually as carbide, and their proportions were variable depending upon the conditions of ignition and cooling.

A ferrous oxide prepared from the oxalate by Kahlbaum was used by *Keil* and *Dammann*⁽³⁾ in their investigation of the system $FeO-SiO_2$.

I ordered and procured a few pounds of "ferrous oxide from oxalate" from Kahlbaum in Germany and analysed it: total *Fe*. 71.94%, metallic *Fe* 0.26%, ferrous *Fe* 27.53%, ferric *Fe* 44.15%, carbon 1.2%, or calculated to oxides, metallic *Fe*. 0.25%, *FeO* 6.69%, Fe_3O_4 91.52%, C 1.2%, total 99.67%, and it has a strong magnetic property. It was an oxidized product, almost to magnetite and could not be used for the purpose of investigating the system $FeO-SiO_2$.

Wöhler and *Günther*⁽⁷⁾ reduced a ferric oxide in a current of hydrogen-water vapor mixture at such temperatures and in such ratios that ferric oxide was reduced to magnetite and the latter to *FeO* in an atmosphere not sufficiently reducing to convert any *FeO* into metallic iron. They bubbled hydrogen gas through water at 74.1°-77.5°C. to saturate the former with water vapor, ($H_2O:H_2$ ratio, at 700°C. was 0.58 and at 800°C., 0.71) and for 0.1 gram of Fe_2O_3 , they passed 1 litre of the gas-mixture per hour, per square centimeter cross section of combustion tube. In 12 hours a product giving on analysis 99.9 per cent of *FeO* was prepared.

Groebler and *Oberhoffer*⁽⁸⁾ tried the *Hilpert* and *Beyer*⁽⁹⁾ method, thinking that it might be of value for the preparation of a large quantity of *FeO* of good purity. At about 800°C., using a gas consisting of 66 per cent of *CO* and 34 per cent of CO_2 , a 1-gram charge on a boat in a combustion tube could be reduced to a product which was 99.3 per cent pure. With 6-grams charge the best product obtained contained 95 per cent of *FeO* and had both magnetite and metallic iron as impurities. This latter charge required nearly 10 hours for preparation. The investigators concluded that small temperature variations are fatal and the material must all be kept at a constant temperature.

(7) Ztschr. Elektrochem., Jahrg. 29, (1923), 276-285.

(8) Stahl u. Eisen, Jahrg. 47, (1927), 1984-1988.

(9) Ber. Deut. chem. Gesell., Jahrg. 44 (1911), 1608-1619.

The samples of ferrous oxide used by *Wyckoff* and *Crittenden*⁽¹⁰⁾ were prepared by burning armco iron rods in an atmosphere of oxygen allowing the molten iron oxide product to drop into a receptacle at the bottom. This material was used as a raw material for the production of ferrous oxide. It contained mostly magnetite with some ferrous oxide and some metallic iron. It was broken up, mixed with more armco iron, and heated by resistance between two water-cooled iron electrodes, a puddle of the reaction product being formed in the midst of the unmelted raw materials and contamination with everything except the gases of the atmosphere being thus avoided. The product was broken up and remelted to encourage the reversible reaction $Fe_3O_4 + Fe = 4 FeO$ to proceed to completion and yield molten FeO of high purity. The material produced contained excess metallic iron which had to be separated by a strong electromagnet and the least magnetic portion of which was regarded as ferrous oxide. It was practically nonferromagnetic but contained 0.54 per cent of metallic iron which could not be separated. On chemical analysis by the *Sims* and *Larsen*⁽¹¹⁾ method it gave the following result: metallic Fe 0.54%, ferrous Fe 65.84%, ferric Fe 9.80%, total Fe 76.18%; or calculated for the oxides, metallic Fe 0.54%, FeO 78.40%, Fe_3O_4 20.32%, total 99.26%.

A similar attempt was made by *Tritton* and *Hanson*⁽¹²⁾, working under *W. Rosenhain* at the National Physical Laboratory, Teddington, England. Electrolytic iron was melted under ferric oxide in a high-frequency induction furnace in a magnesia crucible with specially glazed MgO lining, in the expectation that the molten iron would reduce the molten oxide to FeO , in order to determine the solubility of FeO in molten iron. The iron layer contained 0.21 per cent of O_2 , probably present as FeO , and the oxide layer had the following analysis: metallic Fe 0.99%, total FeO 80.6%, Fe_2O_3 14.0%, SiO_2 0.4%, MgO 3.0%; or recalculated, metallic Fe 1.03%, FeO 77.1%, Fe_3O_4 21.05%, total 99.18%.

(10) Jour. Am. chem. Soc., Vol. 47, (1925), 2876-2882.

(11) Ind. Eng. chem., Vol. 17 (1925), 86-88.

(12) Iron & St. Inst., Vol. 110 (1924), 85-143.

The present writer preferred the method adopted by *Groebler* and *Oberhoffer*. The ferrous oxide was prepared by the reduction of pure ferric oxide in a gas-mixture of CO and CO_2 , at a certain high temperature from 800° to $1000^\circ C.$, the relations between composition of gas and temperature being determined by means of the $Fe-FeO$ curve in the equilibrium diagram of $Fe-O_2-C$ already published by Prof. A. Matsubara⁽¹³⁾, and products containing about 88 to 93 per cent ferrous iron by chemical analysis were obtained. The details of the reduction process are described in a later section.

I regret, however, that the purity of the products was far inferior to that obtained by *Groebler* and *Oberhoffer* on account of a large quantity being prepared at a time. But there was no harm in this, because the purpose of this experiment was only to verify the result of investigation of the sintering of powdered iron ore.

Sec. 1. MATERIALS USED.

As ferric oxide for the preparation of ferrous oxide, a chemical "iron oxide" from Kahlbaum was preferred. It is classified into three sizes and analyzed as follows :

Kinds	Fe. %	Fe ₂ O ₃ . %
Iron oxide (Kahlbaum)	69.86	99.86
The same, over 100-mesh	69.99	100.19
The same, 100-150 mesh	69.86	99.88
The same, under 150 mesh	69.92	99.97
Iron oxide, for analysis (Kahlbaum)	69.94	99.99

Carbon dioxide is produced by the action of dilute sulphuric acid on calcium carbonate and is subsequently purified and dried by passing it through concentrated sulphuric acid and phosphoric oxide.

Carbon monoxide is prepared by the action of concentrated sulphuric acid on formic acid, and impurities are removed by passing it through

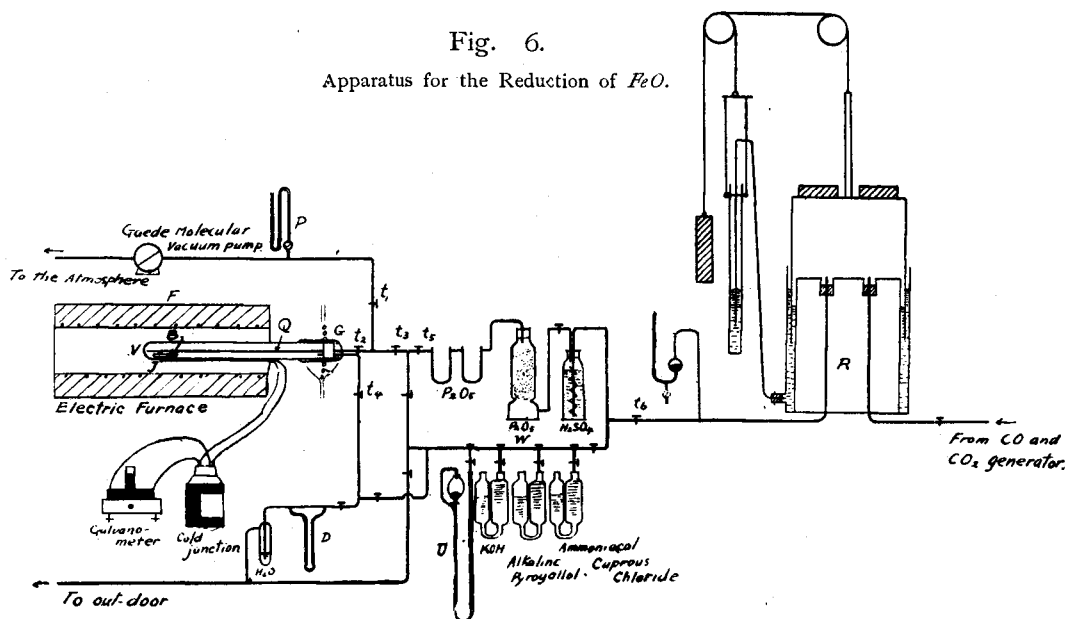
(13) Tr. Am. Inst. Min. Eng., Vol. 67, (1922), 3-55.

a series of gas-washers containing concentrated caustic potash solution with and without pyrogallol, and concentrated sulphuric acid, and it is finally dried over phosphoric oxide.

Sec. 2. ARRANGEMENT OF THE APPARATUS.

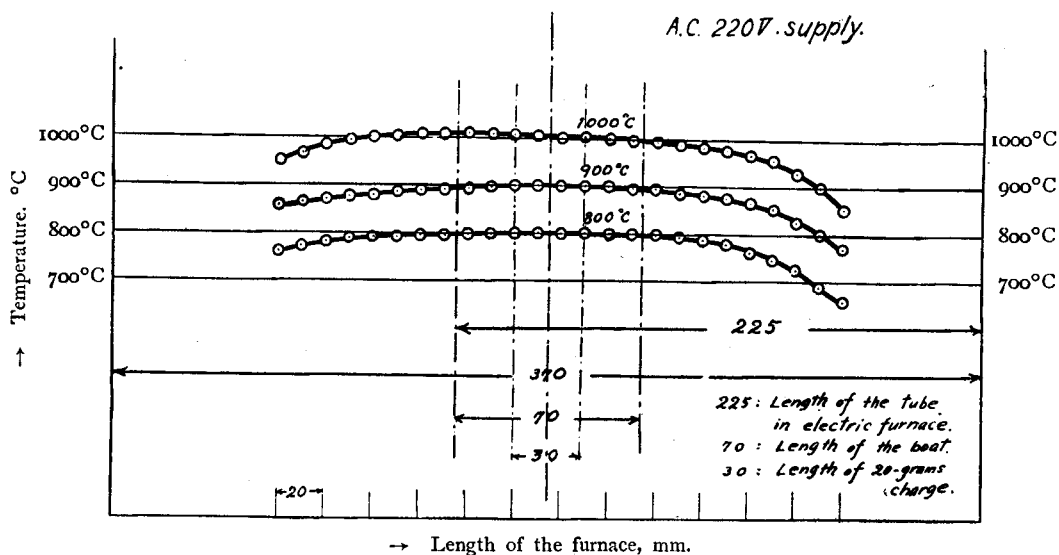
The apparatus is diagrammatically represented in Fig. 6. A porcelain tube *V*, 2.8 cms. inside diameter and 35 cms. long, sealed at one end and glazed both inside and outside, in which is placed a small porcelain boat *B* containing a weighed amount of ferric oxide, is inserted

Fig. 6.
Apparatus for the Reduction of FeO .



into an electric furnace of nichrome-wire resistance *F*, 6 cms. inside diameter and 37 cms. long (its temperature distribution is diagrammatically shown in Fig. 7) in such a position that the boat is in the middle of the furnace and heated uniformly with a difference of temperature of less than $\pm 5^{\circ}C$. A rubber stopper *G* closes the other end of the porcelain tube and is sealed with a sealing mixture, consisting of 3 parts of resin and 2 parts of yellow wax. During the experiments, the outside of this seal is cooled by circulating water.

Fig. 7.
Temperature Distribution in the Electric Furnace for the Reduction.



A thermo-junction J , of a platinum and platinum-rhodium couple, standardized for pure metals, is attached outside the tube V at the middle of the position of the boat. The other ends of the couple are connected in parallel with a galvanometer graduated for each 10°C . and a recording pyrometer. A temperature of the reduction is thus observed and recorded.

The porcelain tube is connected with a Gaede molecular vacuum pump by a glass tube and a rubber tube with a thick wall, having a cock at t_1 and a mercury manometer P .

The gas-mixture is stored in a reservoir R and introduced into the porcelain tube through the quartz tube Q and carried out to the open air through an exit-tube in the rubber stopper. The volume of gas flowing in the tube is measured by a pitots tube D , which was previously calibrated. The composition of the gas flowing into or out from the porcelain tube can be analyzed by the gas analysis apparatus W connected in the circuit.

Sec. 3. MANIPULATION OF THE REDUCTION.

After the boat has been loaded with a weighed amount of ferric oxide, the end of the porcelain tube *V* is sealed with the stopper *G* and the sealing mixture, cocks t_1 and t_2 being left open, cocks t_3 and t_4 are closed and the whole system is evacuated to about 5 mm. vacuum by the Gaede molecular vacuum pump. Cocks t_1 and t_2 are then closed and the temperature of the furnace is raised slowly to an appropriate reducing temperature. Any gas evolved during heating is pumped off from time to time. After the proper temperature has been attained, the gas-mixture in the reservoir is brought into the tube by passing through cocks t_6 , t_5 and t_2 , and the gas after reduction is carried outside the room.

The volume of gas flowing into the tube is regulated by cock t_4 and kept constant, about one litre per hour. It is measured by the pitots tube *D*, which was carefully standardized.

The temperature of the reduction is kept as constant as possible by applying a constant electric current from a storage battery having a capacity of 218 ampere-hours in a 10 hours-rate, and by using an electric furnace of very larger inner diameter than the porcelain tube. The temperature of the reduction is carefully observed by the galvanometer and recorded.

During the course of the reduction, gas at the outlet is drawn into the eudiometer *U* and analyzed for carbon dioxide constantly and sometimes for oxygen and carbon monoxide. By plotting the results of the gas-analysis in a diagram, the mode of the course of the reduction can be watched.

After the reduction have gone on for a certain time, the passage of the gas-mixture is stopped and the whole system is evacuated. Then, the electric current is cut off and the furnace is cooled down slowly, while pumping is continued. The cooling of the tube down to 600°C. is done slowly in the furnace, and at that temperature the tube is drawn out from the furnace and cooled to room temperature as quickly as possible.

The reason for this is that the ferrous oxide is metastable at

ordinary temperatures and has a critical point at 570°C .. It is stable only above 570°C ., the invariant point⁽¹⁴⁾, and below that it can split into two products according to the reaction:

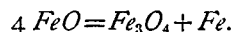
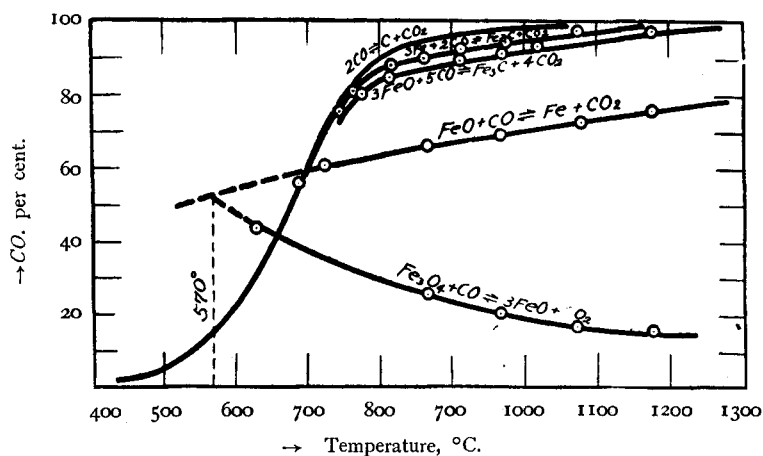


Fig. 8.

Temperature-CO per cent. Diagram. Pressure, 1 Atmosphere.
(A. Matsubara)



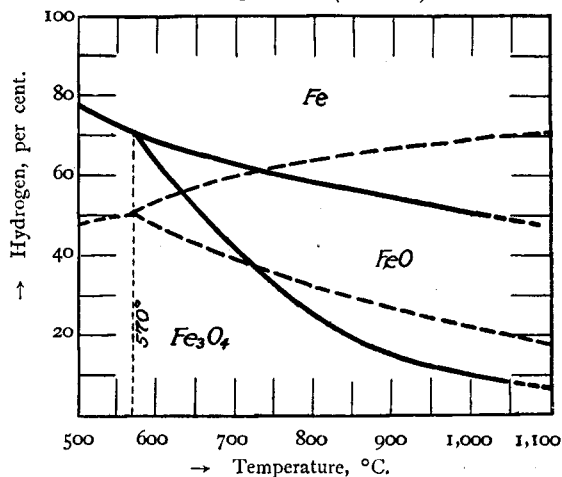
(14) O. C. Ralston, "Iron oxide reduction equilibria" Bull. 296, U. S. Bureau of Mines, 1929, pp. 96.

Extract from Ralston's monograph:

On the reduction-equilibrium diagrams Fig. 8 and 9 for both H_2 and CO used as reducing agents, ferrous oxide can be produced only at temperatures above the invariant point, 570°C ., whereas below that temperature ferrous oxide is metastable with respect to $\text{Fe}_3\text{O}_4 + \text{Fe}$, and instead of reducing Fe_3O_4 to FeO at these lower temperatures the tendency is to reduce Fe_3O_4 direct to Fe without any intermediate FeO step.

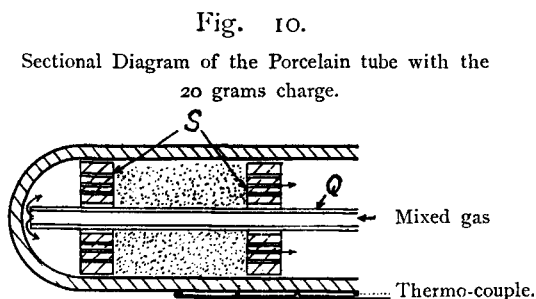
Fig. 9.

Temperature- H_2 per cent. Diagram. Dotted lines, CO equilibria. (Eastman)



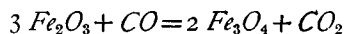
After cooling to the room temperature, the boat is removed from the porcelain tube and weighed and analyzed, so as to check the loss of weight by reduction with the result calculated from the percentage of ferrous oxide which was given by analysis.

After repeated reduction experiments, about 20 grams of ferric oxide, very fine powder of under 150 mesh being excluded, is placed directly in the porcelain tube between the perforated porcelain discs *S* as in Fig. 10, and a larger quantity of ferrous oxide is successfully prepared at one time with products of the same quality as in the case of the reduction in the boat.

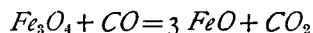


Sec. 4. RESULTS OF THE REDUCTION.

A typical example of a diagram showing the relation between composition of gas and time of reduction is given in Fig. 11. All the curves begin at a position of about 100 per cent, fall suddenly, become more or less horizontal, fall, again become horizontal and come gradually to the original composition of the gas. Each of the highest positions "A" corresponds to a practically irreversible reaction

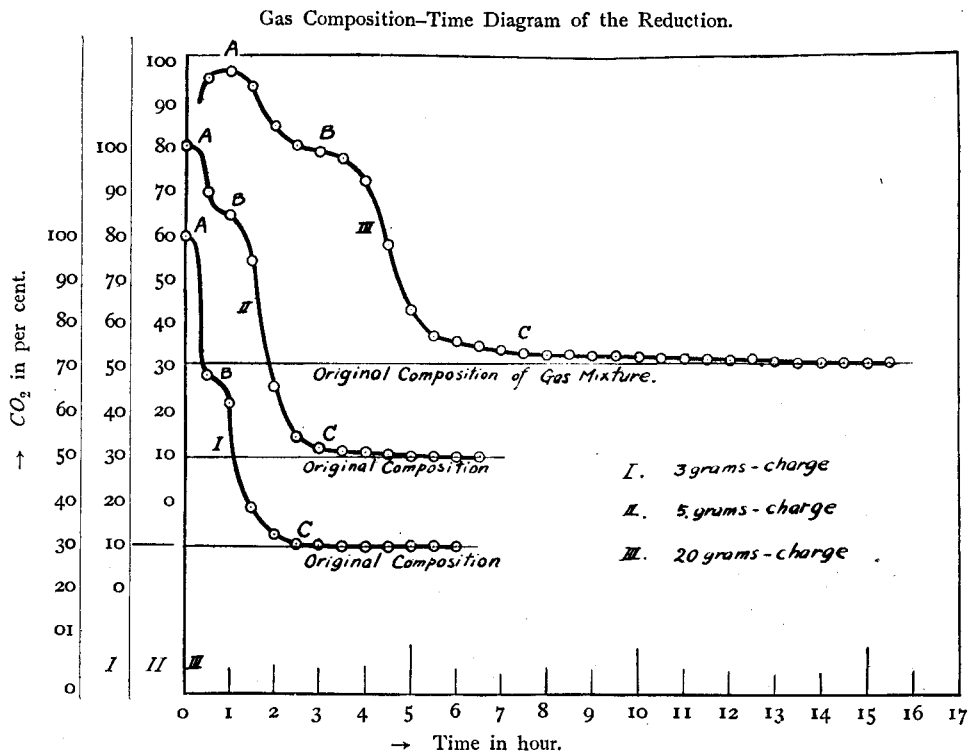


The second position "B" corresponds to the reaction



At the point "C", most of the samples are reduced to the ferrous oxide. Yet, it has a certain amount of Fe_3O_4 . Hence, the reduction must be continued a few hours more to eliminate this magnetite. Total time of reduction is about 5 to 8.5 hours when the sample taken is 3–5 grams, and 10 to 18 hours with samples of 20 to 25 grams.

Fig. II.



The results of reduction are collected in Table I.

Table 1. Results of the reduction.

No. of Reduction	Weight of Sample, in gms.	Composition of Reducing Gas.		Temp. of Reduction, °C.	Volume of Gas, Passed Litres	Time of Reduction, hrs.-mins.	Products of Reduction, (by chemical Analysis)		FeO, % Calculated by Weight loss.
		CO ₂ , %	CO, % (O ₂ , %)				FeO, %	Total Fe, %	
1	5.0000	38.6	61.4 (0.7)	800	7.5	7-45	—	—	92.41
2	3.0000	33.5	63.8 (0.4)	920	6.0	6-0	88.05	79.77	92.45
3	3.0000	32.5	67.1	950	5.5	5-30	87.35	79.23	91.98
4	3.0000	32.4	67.6	950	6.0	6-0	85.27	78.96	90.45
5	3.0000	32.2	67.8	950	7.5	7-30	88.29	79.50	93.29
6	3.0489	31.2	68.8	1000	5.0	5-0	89.87	76.89	92.00
7	5.0193	30.8	69.2	1000	5.0	5-0	89.23	76.49	92.20
8	5.0205	32.0	68.0	950	6.5	6-30	88.90	76.77	91.50
9	5.0113	30.8	69.2	980	6.0	6-0	90.20	76.61	—
10	5.0300	35.4	64.6	850	5.5	5-30	88.31	77.12	93.40

Table 1.

(Continued)

No. of Reduction	Weight of Sample, in gms.	Composition of Reducing Gas.		Temp. of Reduction, °C.	Volume of Gas, Passed Litres	Time of Reduction, hrs.-mins.	Products of Reduction, (by chemical Analysis)		FeO, % Calculated by Weight loss.
		CO ₂ , %	CO, % (O ₂ , %)				FeO, %	Total Fe, %	
11	5.0042	36.4	63.6	830	7.0	7-0	86.56	77.12	91.10
12	5.0037	32.4	67.6	950	6.0	6-0	89.63	78.78	92.00
13	5.0000	34.4	65.6	900	4.5	4-30	88.04	75.95	91.80
14	5.0017	33.6	66.4	900	7.5	7-30	89.65	76.12	91.60
15	5.0000	32.3	67.7	930	5.5	5-30	86.32	76.28	90.90
16	5.0000	35.5	64.5	900	8.5	12-0	87.40	76.20	100.56
17	5.0000	34.9	65.1 (2.3)	900	8.5	13-30	86.37	75.90	90.30
18	3.0000	35.0	62.7	850	8.5	10-0	83.67	75.08	80.50
19	3.0000	35.4	64.6	820	8.5	10-30	90.78	75.62	91.30
20	3.0000	32.1	67.3	950	8.5	14-45	90.30	76.08	92.20
21	3.0017	32.0	68.0	970	8.0	8-0	87.94	—	—
22	3.0328	33.1	66.9	900	7.0	7-0	93.74	—	—
23	3.0272	31.8	68.2	960	8.0	8-0	89.47	—	—
24	5.0090	35.1	64.9	860	6.5	6-30	90.56	—	—
25	5.0024	34.3	65.7	900	8.0	8-0	89.29	—	—
26	5.0004	34.6	65.4	880	7.0	7-0	Failed	—	—
27	5.0016	31.0	69.0	970	6.5	6-30	90.17	—	—
28	3.0028	32.0	68.0	950	6.0	6-0	91.35	—	—
29	3.0022	32.1	67.9	950	6.5	6-30	91.76	—	—
30	2.9999	33.2	66.8	960	7.0	7-0	89.36	—	—
31	3.0007	31.6	68.4	980	6.0	6-0	88.85	—	—
32	3.0012	34.1	65.9	900	7.0	7-0	88.62	—	—
33	4.0011	33.2	66.8	940	6.5	6-30	89.38	—	—
34	20.0000	35.8	64.2	900	14.0	14-0	88.62	—	—
35	20.0000	35.2	64.8	870	15.75	15-45	86.99	—	—
36	20.0000	31.8	68.2	970	12.75	12-45	89.12	—	—
37	25.0000	31.3	68.7	980	17.5	17-30	87.89	—	—
38	20.0000	33.0	67.0	950	9.5	9-30	89.89	—	—
39	20.00	32.2	67.8	950	12.0	11-40	87.64	—	—
40	20.00	31.0	69.0	970	18.0	18-0	90.54	—	—
41	20.00	30.0	70.0	1050	15.0	14-30	90.65	—	—
42	20.00	31.4	68.6	975	14.0	13-05	90.27	—	—
43	20.00	33.4	66.6	900	12.0	11-15	90.68	—	—
44	20.00	33.4	66.6	1000	15.0	15-0	91.02	—	—
45	20.00	33.4	66.6	900	16.0	16-0	90.73	—	—
46	20.00	32.3	67.7	950	15.0	14-20	91.88	—	—
47	20.00	33.4	66.6	900	14.0	13-10	91.68	76.59	—
48	20.00	29.0	71.0	1050	16.0	15-20	92.94	—	—
51	22.00	35.4	64.6	850	14.0	13-30	92.26	76.61	—
52	23.00	32.0	68.0	950	13.0	12-40	92.65	76.72	—
53	23.00	32.0	68.0	950	17.0	15-10	92.18	76.87	—

The reduction products, as given by chemical analysis, contained about 88 to 93 per cent FeO , including a small amount of metallic iron, say, about 0.5 per cent or less.

The content of FeO calculated from the loss of weight is always a little higher than that obtained by analysis. This is mostly owing to a flying loss of the sample on the evacuation and the introduction of the gas-mixture into the evacuated porcelain tube, and partly due to the formation of metallic iron.

The content of metallic iron, ferrous oxide and magnetic oxide in the products of reduction is shown in Table 2.

Table 2. Content of metallic Fe , FeO and Fe_3O_4 .⁽¹⁵⁾

No. of sample (No. of the Reduction)	FeO calculated approximately: from ferrous Fe . %	Complete analysis				
		Total Fe . %	Metallic Fe . %	FeO . %	Fe_3O_4 %	Total %
51	92.26	76.61	0.31	88.70	10.11	99.12
52	92.65	76.72	0.31	89.03	9.89	99.23
53	92.18	76.87	0.57	88.10	10.77	99.44

Chapter II. THERMAL ANALYSIS AND MICROSCOPIC STUDY.

Sec. I. MATERIALS USED.

Ferrous oxide is prepared as described in the preceding chapter and has an average composition of metallic Fe 0.3–0.5%, FeO 84–88.7%, and Fe_3O_4 9.9–16%.

Silica in the form of "Silicic acid precipitated" manufactured by Merke or "Silicic acid anhydride" from Kahlbaum are used after complete ignition in a platinum crucible and have the following composition:

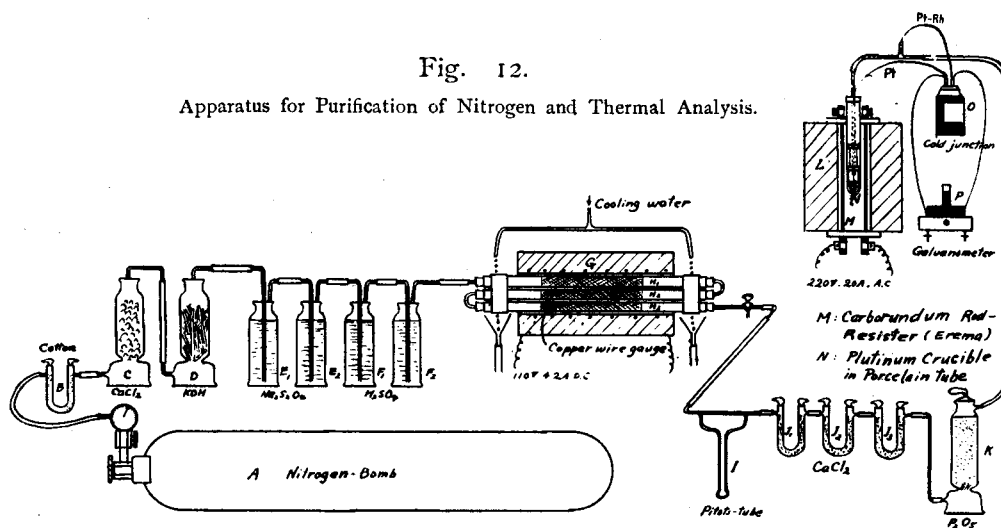
Kind	SiO_2 , %	$Al_2O_3 +$ Fe_2O_3 , %	Ignition loss, %
Silicic acid ppt. (Merke)	78.09	2.89	19.13
Silicic acid anhydride (Kahlbaum)	96.45	2.74	3.72

(15) The method of analysis employed for metallic Fe , ferrous Fe and ferric Fe was the $HgCl_2$ -method. Groebler & Oberhoffer. St. u. Eisen, 47 (1927), 1984–8. Ivar Bohm, chem. Abstr. 21. (1927), 1424.

Pure nitrogen is prepared by eliminating the impurities from the crude nitrogen manufactured by the fractional distillation of liquefied air and sold as bomb-nitrogen. The impurities⁽¹⁶⁾ are removed by passing the crude nitrogen through a series of gas-washers— calcium chloride, caustic potash, alkali-hydrosulphite solution, concentrated sulphuric acid—a glowing combustion tube with rolled copper wire-netting in it, again calcium chloride and phosphoric oxide.

Sec. 2. ARRANGEMENT OF THE APPARATUS AND MANIPULATION.

The apparatus is diagrammatically represented in Fig. 12. Crude nitrogen from a bomb *A* is passed through a series consisting of cotton-filter *B*, gas-washers with calcium chloride *C*, and caustic potash *D*, where



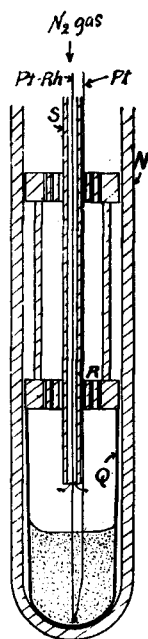
dust, moisture and a trace of CO_2 are removed. Absorption of the remaining O_2 is carried out in two ways, (1) by the wet method with alkaline sodium hydrosulphite ($Na_2 S_2 O_4$) solution $E_1 E_2$, and (2) the dry method with a roll of copper wire-netting $H_1 H_2 H_3$, heated to $800^\circ C$. in an electric furnace *G*. Then, the nitrogen is dried repeatedly with con-

(16) Moser, "Die Reindarstellung von Gasen." 1920, s. 78-81.

centrated sulphuric acid $F_1 F_2$, calcium chloride $J_1 J_2 J_3$ and phosphoric oxide K . Thus, pure and absolutely dry nitrogen, free from impurities except inactive raregases, such as argon etc., is prepared and a constant volume of it, about 1.5 litres per hour measured by means of a pitots tube I , is introduced into a platinum Tamman-crucible, in which the thermal analysis of the system $FeO-SiO_2$ is carried out.

Weighed amounts of ferrous oxide and silica totaling 5-10 grams are well mixed and placed in a platinum Tamman-crucible, having a diameter of 2.1 cms. tapering to a rounded bottom and a depth of 5 cms.,

Fig. 13.
Sectional Diagram
of Platinum Tam-
man-crucible with
the Charge.



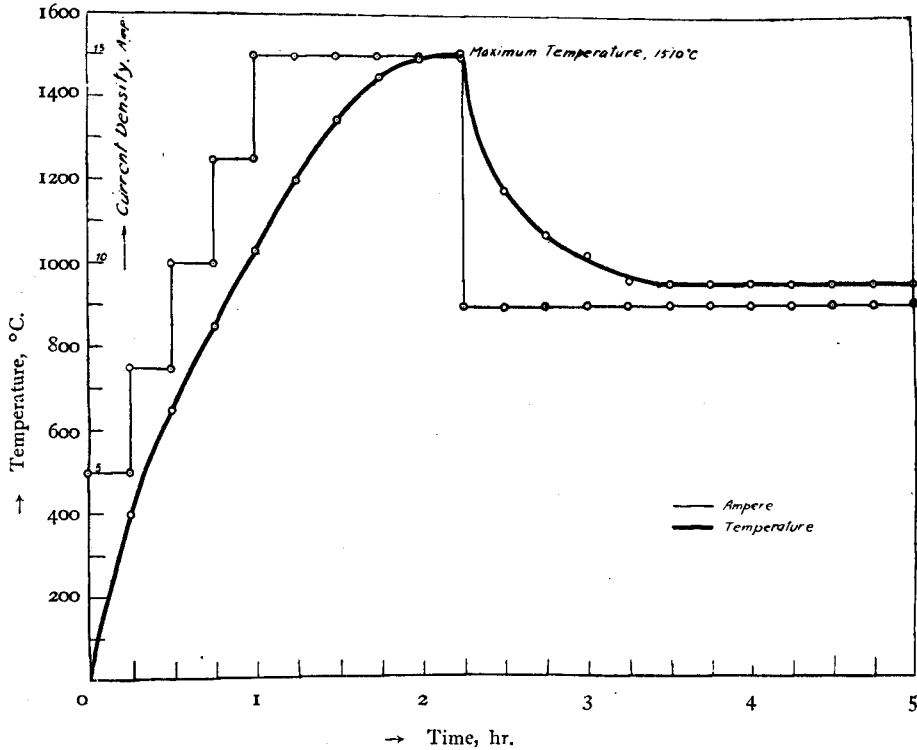
which is put into the bottom of a refractory porcelain tube sealed at the bottom N . A platinum thermo-couple junction is buried in the charge and arranged with a porcelain cover and a gas inlet-pipe, which simultaneously serves as insulating pipe for the couple, as shown in Fig. 13. The porcelain tube arranged as stated above is inserted into an electric furnace L with four carborundum rod-resistors M , 0.9 cms. in diameter and 35.5 cms. in length, with enlarged handles at both ends, called "Erema", and while a current of pure nitrogen is sent through, it is heated slowly up to a temperature suitable for melting down the charge, say, a maximum temperature of about $1550^{\circ}C.$. The maximum temperature is reached in about two hours by a supply of 15 amperes in 220 volts of $A. C.$ current to the four rod-resistors, two of which are connected in series.

As the furnace is heated up to such a high temperature as $1550^{\circ}C.$, the rate of cooling is very rapid when the electric current is cut off to zero, and it is pretty hard to find any transformation points except the eutectic. Therefore, the rate of cooling is controlled by leaving on a currents of from 7 to 9 amperes, according to the composition of the charge. A diagram of the rate of heating and cooling of the furnace is shown in Fig. 14.

The method of plotting the cooling curve is exclusively the inverse

Fig. 14.

Diagram of rates of heating and cooling of the furnace.



rate method, the rate of cooling being read every $10^{\circ}\text{C}.$ in the galvanometer by means of a metronome fixed for a pendulum at the graduation of 100.

Sec. 3. RESULTS OF THERMAL ANALYSIS.

Typical examples of a cooling curve obtained by the inverse rate method are shown in Fig. 15. Most of the curves have two "stops" corresponding to the transformation points of liquidus and of eutectic.

The composition of the charge is approximately calculated from the results of analysis shown in Table 1 and the analytical composition of Silica. For example: 5 grams of ferrous oxide of 90.54 per cent FeO are mixed with 0.679 gram of silica, containing 96.43 per cent SiO_2 , and placed

in the tube. The approximate percentage of Fe_2O_3 in this ferrous oxide is $100 - 90.54 = 9.46$. As all the ferric iron in the sample is present in the form of magnetic oxide, the percentage of Fe_3O_4 is $9.46 \times 1.451 = 13.72$. Therefore, the true percentage of FeO in the sample is calculated thus: $100 - 13.72 = 86.28$. The weight of true FeO in the charge is: $5 \times 86.28\% = 4.315$ grams and the weight of the SiO_2 is: $0.679 \times 96.43\% = 0.655$ gram. The ratio of true FeO to SiO_2 in percentage is 86.8 to 13.2. This result of calculation is not far from that of obtained by recalculation from the composition found by complete analysis shown in Table 2, as the metallic iron content is only a fraction of a per cent and the Fe_2O_3 content is a little overestimated.

This thermal analysis was carried about 45 times out in the range of the less silicious region of the system $FeO-SiO_2$, i.e. silica content of less than 45.5 per cent, which corresponds to ferrous metasilicate. Some of them failed, because the rate of cooling was not appropriate, although the heats of transformation is comparatively small.

The results of the thermal analysis collected together in an equilibrium diagram of the system $FeO-SiO_2$ are shown in Fig. 16.

The ferrous oxide has a melting point of $1378^\circ C.$ and the melting tem-

Fig. 15. Cooling Curves by the inverse rote Method.

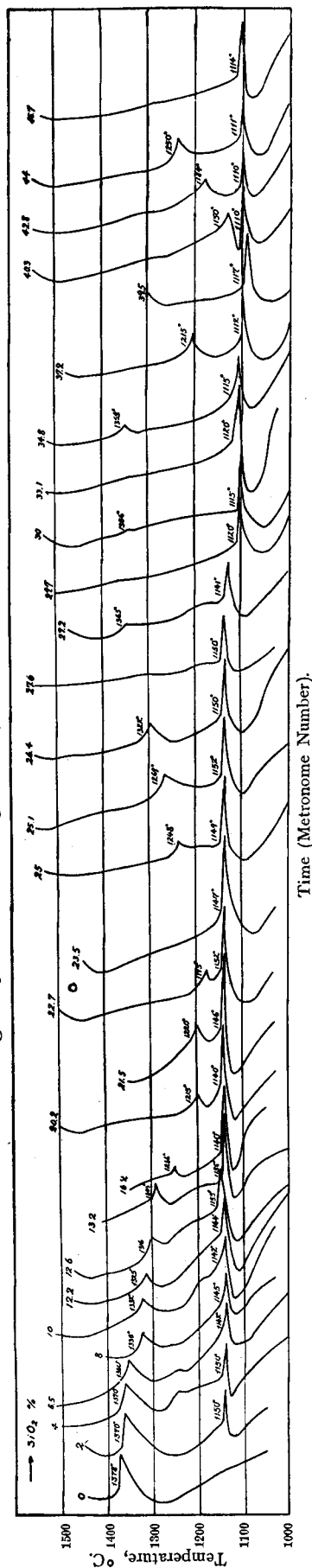
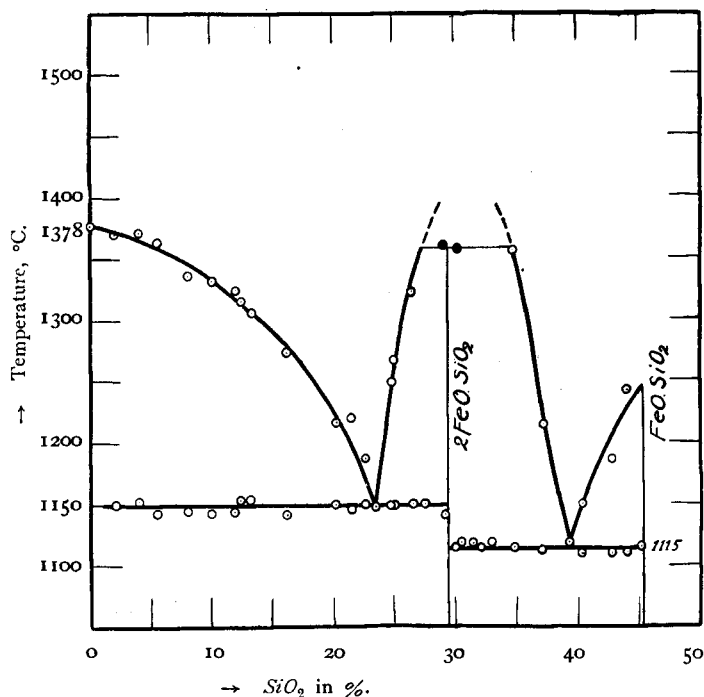


Fig. 16.

Equilibrium Diagram of the System $FeO-SiO_2$.

peratures of FeO decrease to the eutectic point, $1150^{\circ}C.$, as the SiO_2 content increases. The FeO -rich eutectic is presented at about 23.5 per cent of SiO_2 with the eutectic temperature of $1150^{\circ}C.$. The SiO_2 -rich eutectic contains about 39.5 per cent SiO_2 and has the minimum melting temperature of $1115^{\circ}C.$.

In my experiments on the thermal analysis of samples approaching ferrous orthosilicate in composition, about 29.5 per cent SiO_2 , none of the cooling curves has a distinct liquidus point in a range of temperatures as high as $1550^{\circ}C.$, but some of them have a minute "stop" or a deflection of the galvanometer needle at about $1360^{\circ}C.$ and the samples after cooling have an appearance of melt, even a crystal structure of regular polyhedral form. I explain this phenomenon as follows: Ferrous orthosilicate is unstable at temperatures higher than $1360^{\circ}C.$ and apparently melts at about $1360^{\circ}C.$.

Also, the cooling curve of a charge corresponding to ferrous metasilicate, about 45.5 per cent SiO_2 , has no distinct liquidus point.

On account of the small number of experiments and of further experiments with charges containing more than 45.5 per cent of SiO_2 , I am not certain whether ferrous metasilicate may be presented in the system or not.

I regret, however, that none of the runs of my experiments was equilibrium between the liquid and other substances, and also does not truly correspond to the system $FeO-SiO_2$, on account of the impurity of the materials used. Nevertheless I believe that the results of this work are substantially not far from what they should be, and in a general way the diagram holds good.

The composition and melting temperatures of FeO , eutectics and compounds in the system $FeO-SiO_2$, hitherto published by various investigators and the author are compared as follows:

Investigators. Kinds.	Whiteley and Hallimond. (1919)	Eckermann. (1922)	Keil and Dammann. (1925)	Herty and Fitterer. (1929)	The author (1930)
FeO -melting temp.	1450°C.	1540°C.	1395°C.	1370°C.	1378°C.
FeO -rich { Eutectic { -content, SiO_2 -melting temp.	24.5% 1240°C.	27.4% 1040°C.	4.0% 1075°C.	21.3% 1235°C.	23.5% 1150°C.
$2FeOSiO_2$ -melting temp.	1280°C.	1065°C.	1503°C.	1335°C.	unstable over 1360°C.
SiO_2 -rich { Eutectic { -content, SiO_2 -melting temp.	40.0% 980°C.	32.2% 1020°C.	40.0% 1115°C.	34.5% 1255°C.	39.5% 1115°C.
$FeOSiO_2$ -melting temp.	unstable (1100°C.)	1500°C.	unknown	not present	unknown

Sec. 4. MICROSCOPIC STRUCTURE.

After thermal analysis, the melt in the platinum crucible is taken away and studied under the microscope to check the results of thermal analysis. The microscopic structures of these melts are shown in Photo-

graphs Nos. 1-24.

It is to be noted first that it is always very difficult to take off melt from a platinum crucible; the melt is repeatedly treated with acid such as concentrated hydrochloric acid, or with fusing mixture and the whole is quenched in cold water, while the sample is quite hot. Hence, the samples are, as a rule, deeply corroded and the etched pits appear as dark spots in the photos. Second, the ferrous oxide used in thermal analysis is not quite pure, and contains about 10 per cent of magnetic oxide, and the latter in general may be present as a solid solution in ferrous oxide, because the ferrous oxide has the property of being able to dissolve approximately as much as 30 per cent of Fe_3O_4 at $300^\circ C.$ ⁽¹⁷⁾ Therefore, if the amount of ferrous oxide is less than that of the FeO -rich eutectic, a certain amount of magnetite may, in fact, appear as a primary segregation of cubic crystals in the photos.

Photos. No. 1 and 2 show the structure of the melt of ferrous oxide containing no SiO_2 . We observe that it is a homogeneous solution with irregular crystal boundaries.

Nos. 3-6 show the structures of melt with 2 and 4 per cent SiO_2 respectively. Large crystals of FeO and the dark eutectic segregated at their boundaries are clearly observed.

Nos. 7-12 show a similar structure, except that the field of the FeO -crystal decreases, while the eutectic as a ground mass gradually increases in proportion to the increase in the SiO_2 -content.

Nos. 8-10 represent the eutectic structures segregated at the boundaries of FeO -crystals, magnified 300 times.

Nos. 13 and 14 show the structure of the eutectic of $FeO-2FeOSiO_2$. Small dendrites of magnetite appear in Photo. No. 13, on account of the gradual decrease of FeO . The characteristic eutectic structure of the ground mass can be perfectly observed in Photo. 14.

Nos. 15-24 show the structures of melts in the order of increasing SiO_2 content.

(17) Ralston, O. C.; "Iron Oxide Reduction Equilibria", 1929, Bull. 296, U. S. Bureau of mines, pp. 91.

Nos. 17 and 18 represent the structure of a melt with 29.7 per cent SiO_2 , corresponding nearly to ferrous orthosilicate, $2FeOSiO_2$. No special features of structure can be found, except the small white crystals of magnetite and minute pores.

Typical cubic crystals of magnetite which look like "Eisenkreuz" can be seen in Photos. 15, 16, 19 and 20.

Photos. 21 and 22 show the structure of the second eutectic containing about 39.5 per cent SiO_2 . It is to be noticed that this eutectic structure is quite different from the first eutectic shown in Photo. 14.

CONCLUSIONS.

If the results obtained from the foregoing experiments are collated, the following conclusions may be drawn:

(1) The ferrous oxide has a melting point of $1378^\circ C$. which falls to the eutectic point, $1150^\circ C$. as the SiO_2 -content increases.

(2) The eutectic of FeO and $2FeOSiO_2$ in the system $FeO-SiO_2$ exists at about 23.5 per cent of SiO_2 content, with the eutectic temperature of $1150^\circ C$.

(3) The ferrous orthosilicate, $2FeOSiO_2$, is unstable at higher temperatures than $1360^\circ C$. and it looks like melt at about $1360^\circ C$.

(4) The SiO_2 -rich eutectic exists at about 39.5 per cent SiO_2 with a minimum melting temperature of $1115^\circ C$.

(5) It is not certain from the present experiments whether the ferrous metasilicate, $FeOSiO_2$, is presented or not, in the system $FeO-SiO_2$.

In conclusion, the writer wishes to express his hearty thanks to Professor D. Saito, for his kind guidance and valuable suggestions during the course of the present investigation. He is also greatly indebted to Mr. R. Osawa, Mr. E. Nishikawa, Mr. Y. Asada and Mr. S. Sato for their kind assistance in the experiments.

× 50



Photo. No. 1, 0% SiO₂.

× 300



Photo. No. 2, 0% SiO₂.

× 100

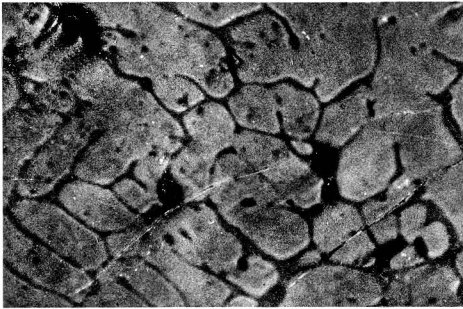


Photo. No. 3, 2% SiO₂.

× 300

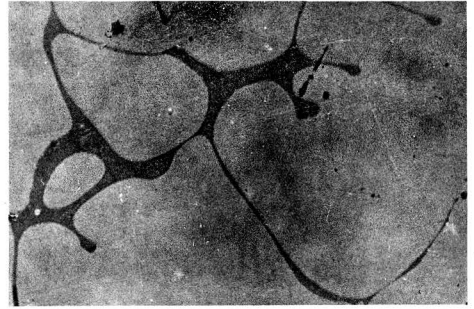


Photo. No. 4, 2% SiO₂.

× 100

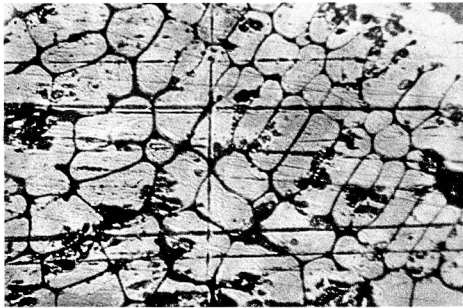


Photo. No. 5, 4% SiO₂.

× 300

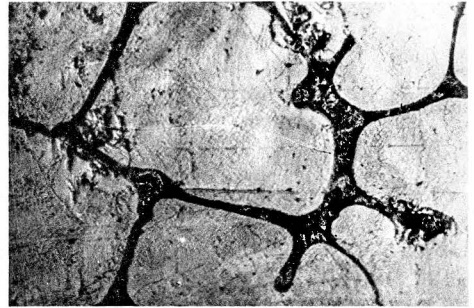


Photo. No. 6, 4% SiO₂.

× 100

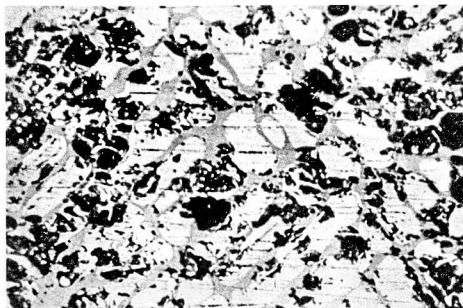


Photo. No. 7, 8% SiO₂.

× 300



Photo. No. 8, 8% SiO₂.

× 100

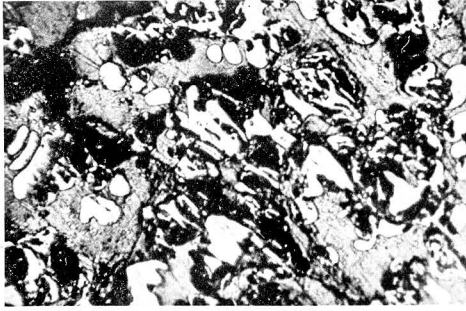


Photo. No. 9, 15% SiO₂.

× 300



Photo. No. 10, 15% SiO₂.

× 100

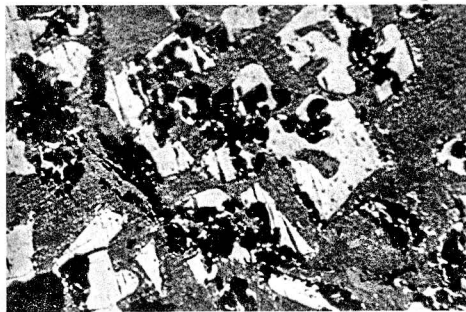


Photo. No. 11, 20.2% SiO₂.

× 300



Photo. No. 12, 20.2% SiO₂.

× 100

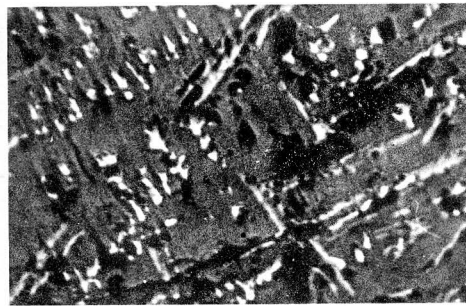


Photo. No. 13, 23.5% SiO₂.

× 300

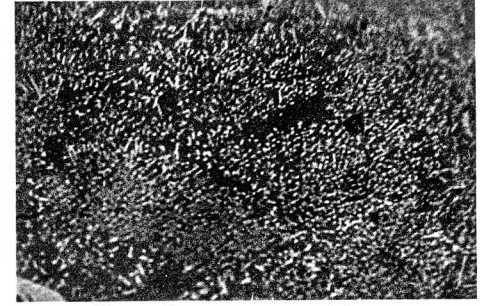


Photo. No. 14, 23.5% SiO₂.

× 100



Photo. No. 15, 25% SiO₂.

× 300

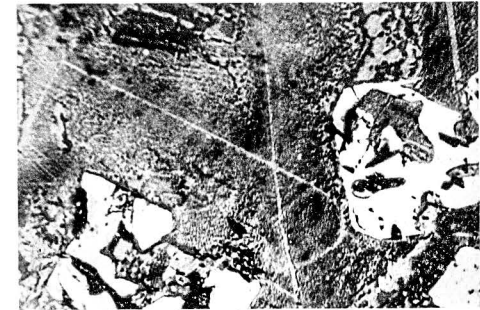


Photo. No. 16, 25% SiO₂.

X 100

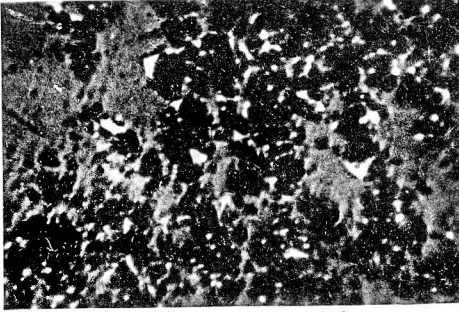


Photo. No. 17, 29.7% SiO₂.

X 300

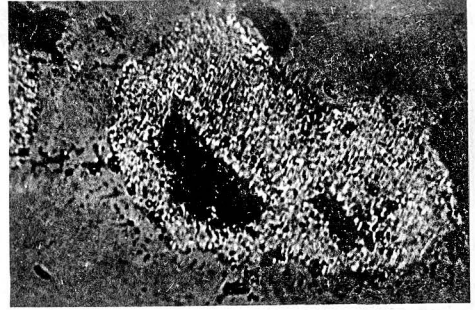


Photo. No. 18, 29.7% SiO₂.

X 100

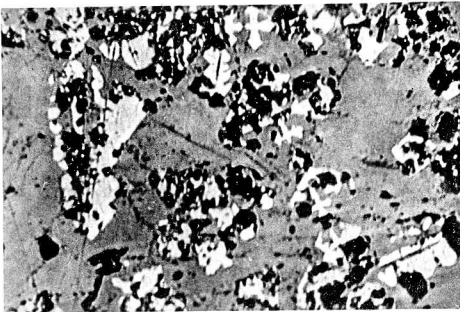


Photo. No. 19, 34.8% SiO₂.

X 300

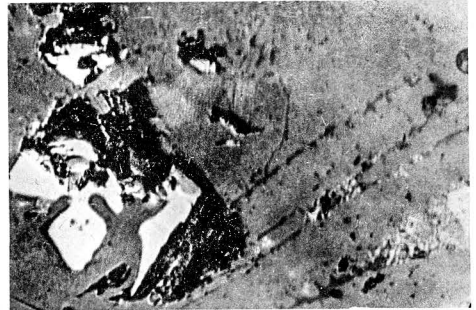


Photo. No. 20, 34.8% SiO₂.

X 100

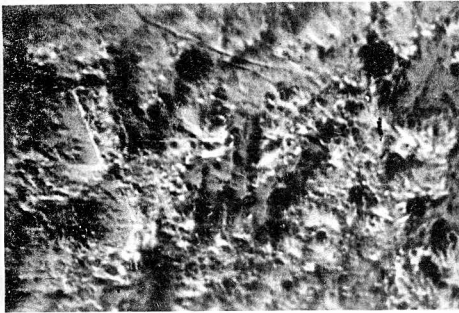


Photo. No. 21, 39.5% SiO₂.

X 300

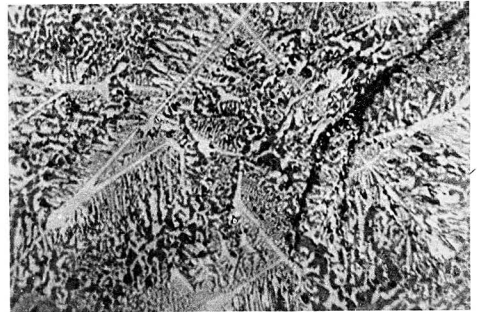


Photo. No. 22, 39.5% SiO₂.

X 100

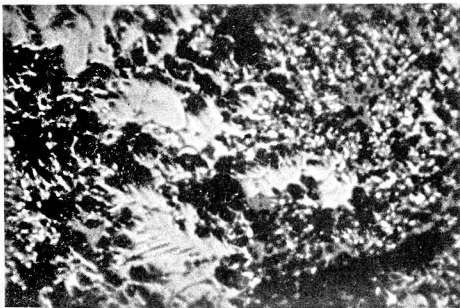


Photo. No. 23, 45.5% SiO₂.

X 300

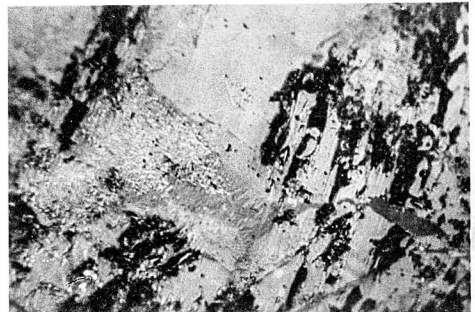


Photo. No. 24, 45.5% SiO₂.