Influence of Silicon, Manganese, Nickel and Chromium on the Determination· of Oxygen in Iron and Steel by the Ledebur Method.

By Hiroshi Sawamura and Hironori Momata.

Synopsis.

Experimental equipment, similar to that adopted by Petersen but somewhat modified, was used for this investigation. The sample was a cylindrical block having about 10 g. As alloying metal, tin or gold was used. The reduction temperature and the temperature of the nickel-thoria catalyst was kept at 1,200°C and 250°C respectively. The blank value to be reduced from the observed value obtained in the usual analysis was as follows: In the first weighing tube, 0.074 mg. per hour at 1,200°C. In the second weighing tube, 0.080 mg. per hour at 250°C. Armco iron was first accurately analyzed for its oxygen to be used as the standard sample for the following experiments. Silicon, manganese, nickel and chromium in the state of metal or ferro-alloy were then melted together with the standard sample. From the results of this investigation, it was confirmed that nickel has no influence, but silicon, manganese and chromium have a great influence on the results of the Ledebur method adopted here. It was also found that the complete reduction of the deoxidation products such as SiO_2, MnO or Cr_2O_3 by hydrogen in this process is not imp·ssible, although it requires a very prolonged time. This phenomenon was explained theoretically.

Introduction.

As the behavior of the oxygen in iron and steel has become better known, the necessity for the combination of the analysis of this element in iron and steel with the daily practice in steel works has been greatly increased. In the authors' opinion, the Ledebur method is most practicable among the various methods[1] for the determination of the oxygen in iron and steel known at the present time, if its results are reliable.

The other impurities contained in carbon steels are carbon, manganese, sulphur, phosphorus, silicon, copper and nitrogen: the influence of carbon, sulphur, phosphorus and nitrogen upon the result of the Ledebur method was found by Bardenheuer and Müller[2] and Brower, Larsen and Shenk[3] to be very small or negligible when they are contained in steels in usual quantity. It is also unnecessary here to take the influence of copper into consideration, because its oxides are reducible by hydrogen far more easily than iron oxides. As to the investigation on the influence of silicon and manganese by former investigators,[4] the results do

Fig. 1.
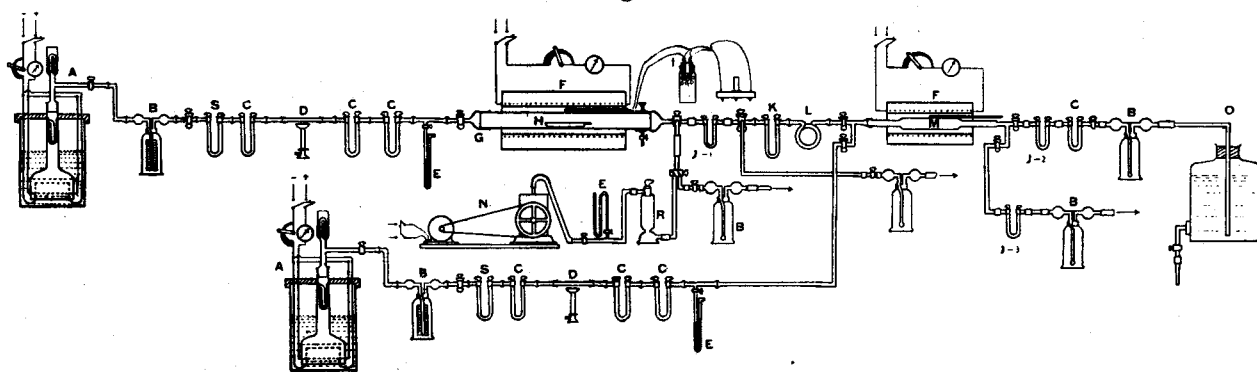
A:	H_2-generater	G:	Reduction tube	L:	Glass coil
B:	Conc. SO_4H_2	H:	Boat	M:	Catalyst (Ni-ThO_2)
C:	P_2O_5	I:	Pyrometer	N:	Vacuum pump
D:	Pd-asbestos	J–1:	First weighing tube (P_2O_5)	O:	Aspirator
E:	Manometer	J–2:	Second weighing tube (P_2O_5)	S:	Soda lime
F:	Electric furnace	K:	SH_2-absorber (SO_4Cu)		

1) Special Rep., No. 9 (Ir. St. Inst.) (1935) 91.
2) Arch. Eisenhüttenw., 1 (1928) 707.
3) Ir. St. Div. (A. I. M. E), (1934) 61.
4) Cain and Pettijohn, United States Bureau of Standards, Technical Paper (1919) No. 118.
Chauldron and Blanc, Comptes Rendus, 175 (1922) 885.
Oberhoffer, St. E., 40 (1926) 1045.
Thanheiser ·and Müller, Mit. Kaiser Wilh. Inst. Eisen Forsch., 9 (1927) 211.
Czermak and Keil, Arch. Eisenhüttenw., 6 (1932) 145.
Brower, Larsen and Shenk, Loc. cit.

not necessarily agree.

In the present investigation, the influence of nickel and chromium besides the last two elements was confirmed by an entirely different methnd of investigation, from that used by former investigators.

Description of experimental equipment.

The arrangement of the experimental equipment used by the authors is shown in Fig. 1, which is analogous to that used by Petersen[1] but somewhat modified. In the figure, G is a reduction tube, 27 m.m. in diameter and 700 m.m. in length, made of " *K*-Masse " of the Staatliche Porzellan-Manufactur Berlin in Germany. Its ends are connected with glass cup by grinding. The left connection in the figure is never removed, but the other connection is opened whenever a sample in the boat H is set in the tube. In order to make this connection completely air-tight, mercury is used for seal as shown in Fig. 2. The first branch

Fig. 2.
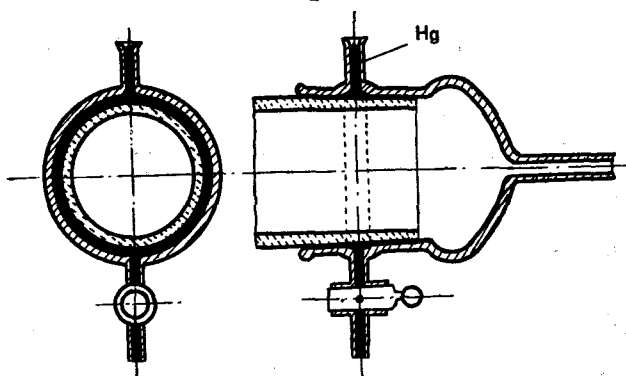
connection is used only when the oxides on the surface of the sample are reduced and also for the evacuation of the reduction tube. The second branch connection is for removing the minute quantity of the air in the side tubes of the first weighing tube which may reoxidize the catalyst. The third and forth branch connections are for reduction and cooling of the nickel-thoria catalyst M packed in a pyrex tube. Special care is paid not to allow the gas to come in contact with gum

Fig. 3.
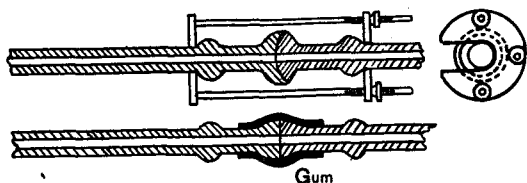
used in the main path of the equipment by the direct glass connection as shown in Fig. 3.

Catalyst and absorber for hydrogen-sulphide.— The method of preparation of these reagents was the same as that adopted by Petersen[2] and Larsen and Brower[3].

Sample.—The sample was in the form of a cylindrical block, 10 m.m. in diameter and 17 m.m. in length, its weight being about 10 g. It was polished with a No. 2 polishing paper just before use.

Alloying metal.—Electrolytic tin was usually adopted, which was previously purified in the current of hydrogen at 1,200°C for 2 hours. The purified tin was added to the sample in the proportion of 1 : 1. In the experiment on the influence of chromium, the authors were compelled to use gold instead of tin. It was also purified carefully before use by the above method.

Reduction temperature and the temperature of catalyst.—1,200°C was adopted for reduction. According to Edwards and Preace[4], the alloy of iron and tin with 50 per cent. of tin is in a completely molten state at 1,110°C.

The catalyst was kept at 250°C.

Manipulation of experimental equipment.

After the entire free space of the apparatus was completely replaced by hydrogen, the sample with the same weight of tin was set in the reduction tube. The reduction tube was evacuated under a pressure below 1 m.m. of mercury, and then it was gradually filled with hydrogen. In order to exhaust air and moisture from the reduction tube as completely as possible, the above operation was repeated five times successively. Then the continuous introduction of hydrogen through the main path of the equipment was begun at the constant rate of flow of 40 c.c. per minute. Thirty minutes later, heating of the catalyst was begun and continued up to the predetermined temperature, while the weighing tubes were weighed and set in position again. The gas was then allowed to flow through the second branch connection for about 30 minutes. The direction of gas flow was changed to the first branch tube and the electric current for the reduction tube was closed. The latter tube was then heated up to 500°C and this temperature was kept constant for 1 hour to reduce the oxides which might have been produced on the surface of the sample while it was being prepared and also to remove any moisture which might have remained on the inner surface of the reduction tube. In the next step, the direction of the gas flow was rever-

1) Arch. Eisenhüttenw., 3 (1930) 459.
2) Loc. cit.

3) Ir. St. Div. (A. I. M. E), (1932) 211.
4) Jl. Ir. St. Inst., (1931) No. II, 41.

sed to the weighing tubes, and the reduction tube was further heated up to the predetermined reduction temperature—1,200°C.

After a desired interval of time when it was kept at 1,200°C, the reduction tube was allowed to be cooled by shutting the current circuit of the furnace. It took about 30 minutes before the weighing tubes were taken out of their position to be weighed. One cycle of the analytical operation is graphically shown in Fig. 4.

Fig. 4.
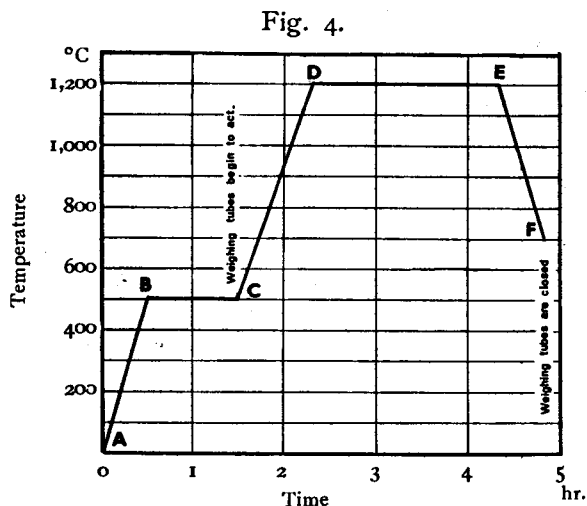
At the period A–B–C : Oxygen on the surface of sample and water vapour in reduction tube are abstracted out of the experimental equipment.
At the period C–D–E–F : Oxygen contained in sample is absorbed in weighing tubes as water.

For the weight determination of the weighing tubes, a microbalance was adopted which has a sensibility of 0.02 mg. Before it was carried out, the free space of the weighing tube was completely filled with hydrogen and hung to the balance after it had been held in a desiccator for 15 minutes. The observation was taken 3 minutes later after the weighing tube was hung to the balance.

Preliminary experiments.

The following preliminary tests were carried out under the same conditions as in the analysis of the iron sample.

Blank test for reduction tube.—The blank value in question for 1 hour heating at 1,200°C was smaller than the weight indicated by the sensibility of the balance.

Blank test for boat.—The kinds of boat here tested were as follows : (1) porous porcelain boat without glaze, (2) compact porcelain boat without glaze, (3) compact porcelain boat with glaze, (4) magnesia boat and (5) " Sinterkorund " boat of the Siemens-Schuckert Co. in Germany. The blank values of the former three kinds of boat were very large and out of the question. It was very small

in the magnesia boat, being 0.05 mg. for 1 hour heating at 1,200°C. But this boat was very porous and the solidified sample adhered to it too tightly to be taken off. In the present investigation, the " Sinterkorund " boat was adopted as it is very compact and also very satisfactory in its blank value which was found to be 0 015 mg. for 1 hour heating at 1,200°C.

Blank test for alloying metal.—The received electrolytic tin was first melted in a graphite crucible, and cast in an iron mould into rods, each 10 m.m. in diameter and 100 m.m. in length. The tests were then carried out to find proper conditions necessary for obtaining the metal which contains oxygen in as small a quantity as possible. For this purpose, the oxygen in the crude tin was determined by melting it in a " Sinterkorund " boat under the same conditions as in the analysis of the iron sample. The weight of tin melted was 10 or 20 gs. The weight increase of the first weighing tube was measured each 1 hour after the heating of the tin sample began. The results of this experiment are graphically shown in Fig. 5. As seen in this figure, the rate of weight increase after 2 hours reduction at 1,200°C is very small, being 0.074 mg. per hour on the verage.

Fig. 5.
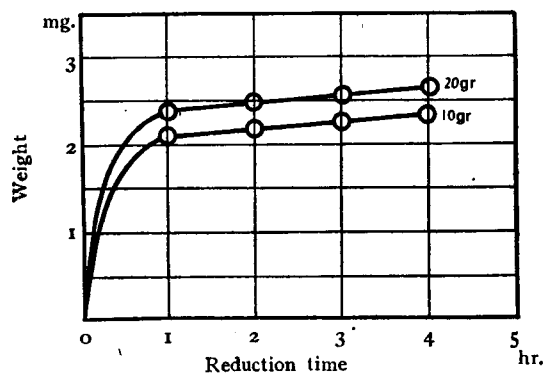
Consequently it was determined to refine the crude tin by reduction at 1,200°C for 2 hours in hydrogen before using it as an alloying metal.

Gold was also treated in the same manner when it was adopted as an alloying metal.

Blank test for the alloy, consisting of iron and tin, which contains a negligible quantity of oxygen.— The sample was prepared by heating the alloy, consisting of 10 gs. of Armco iron and 10 gs. of refined tin, in a " Sinterkorund " boat at 1,200°C for 8 hours in a hydrogen current. The blank tests for this alloy were carried out in the same manner as for tin. The results are graphically shown in Fig. 6. The average value of the weight increase of the first weighing tube was 0.074 mg. per hour after the temperature of the reduction furnace reached 1,200°C.

Fig. 6.
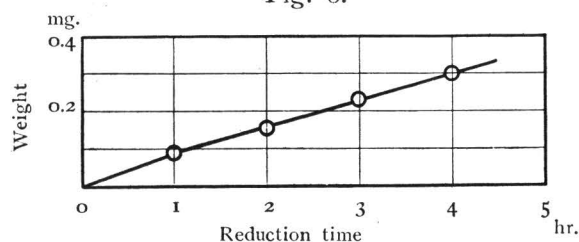
Blank test for catalyst.—The blank value for the catalyst was determined under the same conditions as in the usual analysis. The rate of weight increase of the second weighing tube was found to be 0.08 mg. per hour.

From the results of experiments for various blank tests as before mentioned, the blank value to be reduced from the observed value obtained in the usual analysis was determined as follows :

In the first weighing tube......

0.074 mg. per hour at 1,200°C.

In the second weighing tube......

0.080 mg. per hour at 250°C.

Tests for determining the activity of the catalyst.—The activity of the catalyst was determined after the method of Larsen and Brower[1]. About 0.05 g. of dry pure calcium carbonate was heated slowly up to 1,200°C in the reduction tube of the equipment. The temperature of the catalyst and the rate of flow of hydrogen was the same as in the usual analysis. The results were very satisfactory as shown in two extreme examples in Table I.

Table I.

	1	2
Weight of $CaCO_3$, g.	0.0501	0.0503
H_2O in first tube, mg.	7.4	7.3
H_2O in second tube, mg.	11.9	11.2
Total weight H_2O, mg.	19.3	18.5
Blank correction, mg.	0.4	0.4
Net weight H_2O, mg.	18.9	18 1
Theoretical H_2O, mg.	18.0	18.0

Determination of oxygen in Armco iron.

In the following experiments, Armco iron was adopted as the standard sample. The received iron was a bar, 25 m.m. in diameter, and machined into a cylindrical block having the predetermined dimensions before it was used for analysis. Its
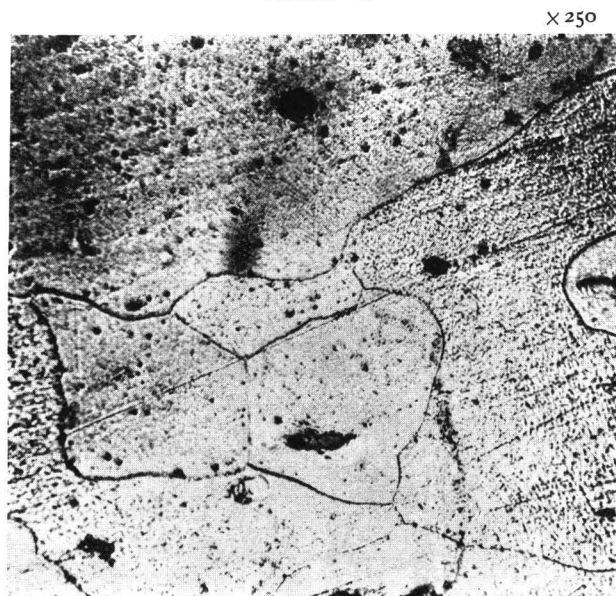
Table II.

C	Si	Mn	P	S	Cu	N_2
0.016%	0.030%	0.040%	0.003%	0.011%	0 035%	0.002%

1) Loc. cit.

composition is given in Table II.

The impurities partly exist in the form of inclusions as shown in Photo. 1.

Photo. 1.

Armco iron

The analysis was repeated several times. The results, however, were almost in agreement quantitatively. One example is shown in Fig. 7, where the abscissa represents the reduction time measured from the time at which the temperature of the reduction tube reaches 1,200°C (point D in Fig. 4), and the ordinate represents the cumulative weight of oxygen abstracted in per cent. of the sample.

In this curve, it is shown conclusively that the oxygen contained in the Armco iron adopted in this investigation can be quantitatively reduced in 2 hours at 1,200°C, its value being 0.067 per cent. As the quantity of other impurities is very small

Fig. 7.
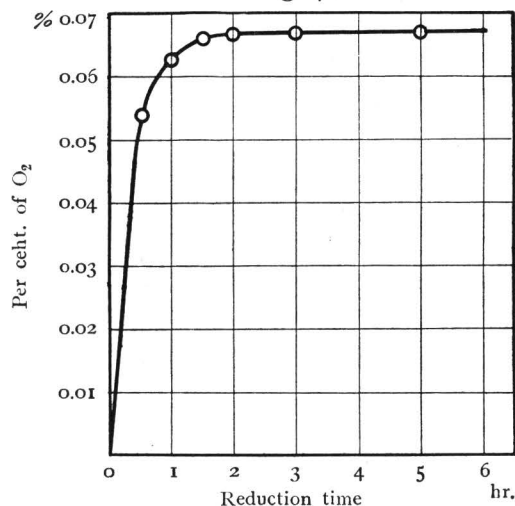
in this iron, almost the total amount of oxygen above obtained is believed to exist in the state of a solid solution of FeO in a- or γ-iron in the temperature range between room temperature and 1,200°C, according to the equilibrium diagram[1] of iron and oxygen.

Influence of silicon.

In the following experiments, in which the influence of various elements was investigated, a small hole was bored on the back of the standard sample of Armco iron and a predetermined quantity of the element in question was buried in this hole before it was melted. The standard sample was set in the boat in such a way as to keep the back with hole upwards.

In the first experiment, pure silica obtained from cast iron was added to the standard sample. The results of analysis were just the same as in the analysis of the Armco iron without the addition of silica. The experiment was further carried out on a standard sample to which the particles of metallic silicon containing 99.2 per cent. of silicon instead of pure silica was added. The quantity of silicon added is given in Table III.

Table III.

Weight of standard sample (g.)	Weight of refined tin added (g.)	Weight of metallic silicon added (g.)	Per cent. of Si added for standard sample (%)
11.0961	11.1007	0.0564	0.51
10.3421	10.3394	0.1072	1.03

The results are graphically shown in Fig. 8.
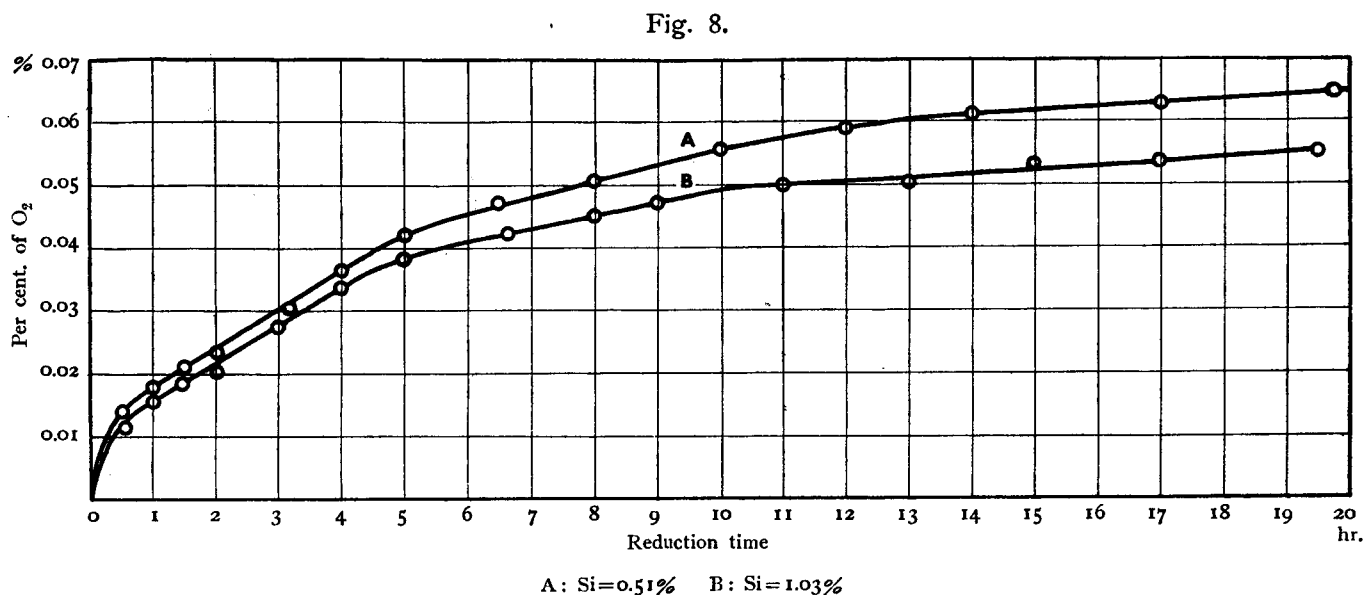
The rate of reduction is somewhat high in the first 2 hours of reduction time, but afterwards, it becomes slower and slower. Consequently, the time required for complete reduction of the oxygen in the sample is very prolonged : in the first sample it is about 20 hours and is still longer in the second one.

Influence of manganese.

The standard sample was fused with a Mn-Sn alloy containing 20 per cent. of manganese which was prepared by melting metallic manganese (Fe = 1.55%) together with refined tin in a hydrogen current at 1,200°C. This alloy melts at about 750°C. The quantity of manganese added is given in Table IV.
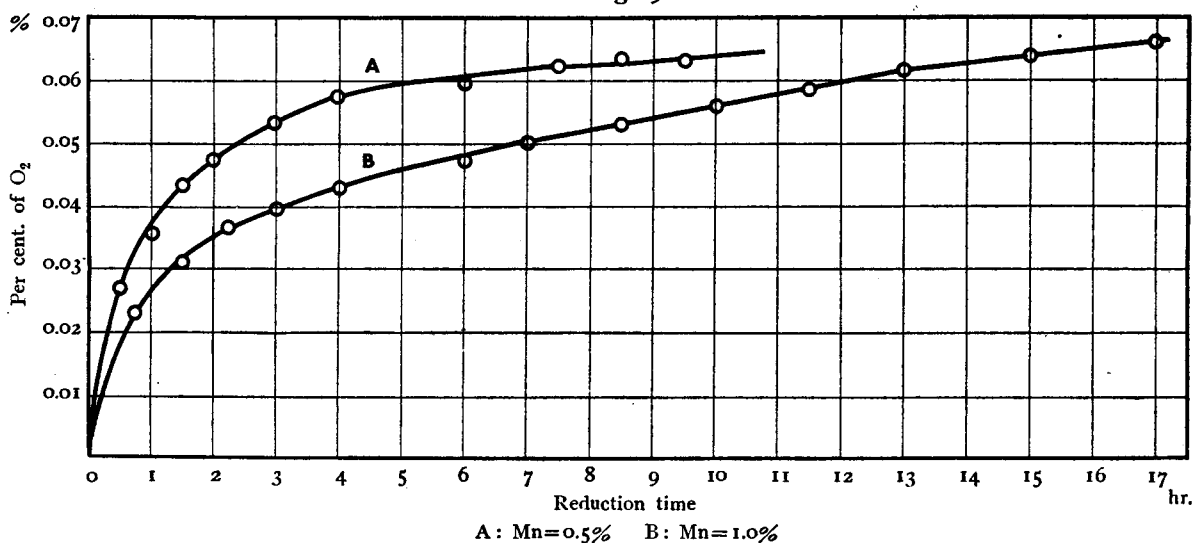
Table IV.

Weight of standard sample (g.)	Weight of Mn-Sn alloy added			Weight of Sn added		Per cent. of Mn added for standard sample (%)
	Total (g.)	Mn in alloy (g.)	Sn in alloy (g.)	From alloy (g.)	Total (g.)	
11.7499	0.2952	0.0590	0.2362	0.2362	11.7400	0.50
11.5211	0.5795	0.1159	0.4636	0.4636	11.5222	1.00

The results are graphically shown in Fig. 9. These curves show that the total oxygen contained in the standard sample can be reduced even when it contains 1 per cent. of manganese. In this case, however, the time required for complete reduction of the total oxygen is far longer than in the analysis of the standard sample itself, and far shorter than in the analysis of the standard sample with silicon added.

Fig. 8.

A: Si = 0.51% B: Si = 1.03%

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1) Schenck, Physikalische Chemie der Eisenhüttenprozesse (1932) 131.

Fig. 9.

A: Mn=0.5%   B: Mn=1.0%

It is a noticeable fact that the results obtained by the authors are considerably different from those of Oberhoffer and his collaborator[1] and Thanheiser and Müller[2] who investigated the same problem by melting steel samples with MnO and confirmed the fact that the latter oxide is quantitatively reduced by hydrogen by the Ledebur method.

Influence of nickel.

Nickel was added in the form of the Ni-Sn alloy containing 20 per cent. of nickel. The procedure of its preparation was just the same as in the preparation of this kind of alloy. It is in a completely molten state at about 1,000°C.

The quantity of nickel added is given in Table V.

The results are graphically shown in Fig. 10. As presumed from the chemical affinity of nickel for oxygen, the time required to abstract the total oxygen in the standard sample is independent of the presence of nickel.
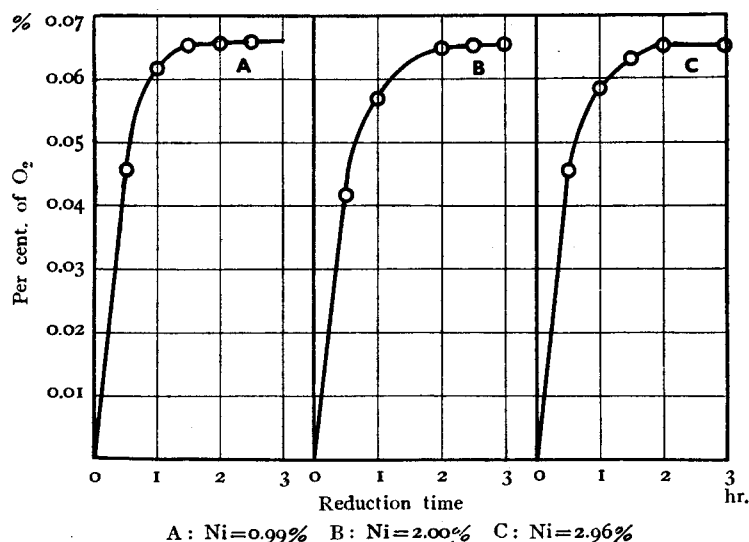
Influence of chromium.

As chromium does not melt with tin below 1,200°C, and the melting temperature of the Fe-Cr alloy is also above the same temperature, tin can not be used as alloying metal in this case as used in the preceeding experiments. The authors decided to adopt here gold instead of tin because of the following reasons: (1) We can easily prepare Fe-Au and Cr-Au alloys which melt at a temperature below 1,200°C. (2) Chemical affinity

Table V.

Weight of standard sample (g.)	Weight of Ni-Sn alloy added			Weight of Sn added		Per cent. of Ni added for standard sample (%)
	Total (g.)	Ni in alloy (g.)	Sn in alloy (g.)	From alloy (g.)	Total (g.)	
12.3008	0.6015	0.1228	0.4787	0.4787	12.2962	0.99
11.7723	1.1769	0.2405	0.9369	0.9369	11.7752	2.00
12.0150	1.7892	0.3661	1.4231	1.4231	12.0159	2.96

Fig. 10.

A: Ni=0.99%   B: Ni=2.00%   C: Ni=2.96%

of oxygen for gold is far smaller than for iron. (3) The vapour tension of gold is low at such a temperature as 1,200°C.

As preliminary experiments, the analysis of the standard sample with gold added instead of tin in the proportion of 1 part of the standard sample for 4 parts of gold was carried out and the fact was confirmed that the time required to reduce total oxygen was just the same as in the analysis
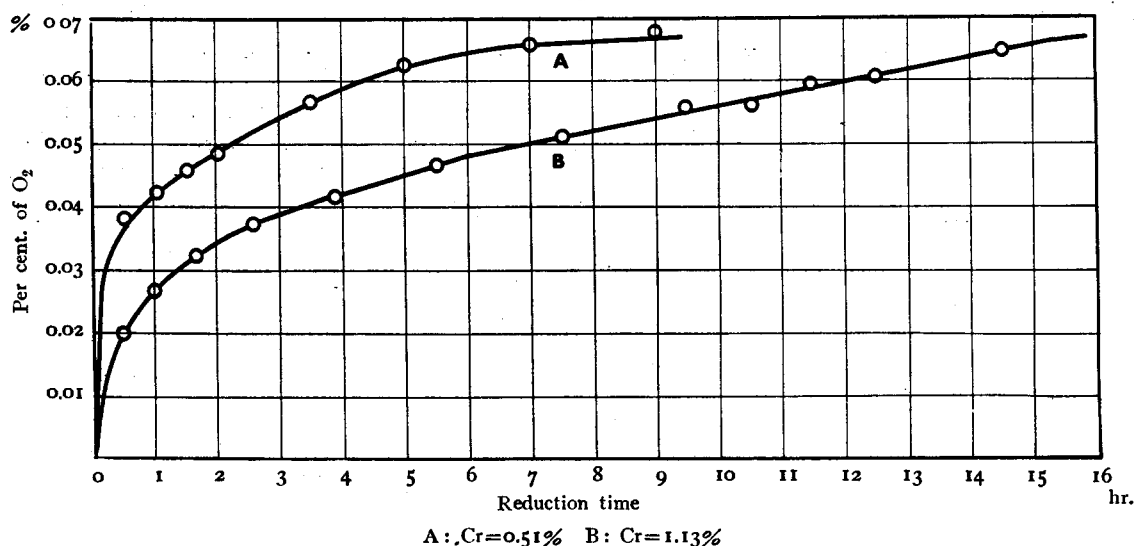
1) Loc. cit.   2) Loc. cit.

Table VI.

Weight of standard sample (g.)	Weight of alloy added				Weight of Au added		Per cent. of Cr added for standard sample (%)
	Total (g.)	Au in alloy (g.)	Cr in alloy (g.)	Fe in alloy (g.)	From alloy (g.)	Total (g.)	
10.3140	0.7648	0.6818	0.0523	0.0307	0.6818	41.3663	0.507
8.9582	1.4762	1.3160	0.1010	0.0592	1.3160	40.0359	1.13

Fig. 11.

A: Cr=0.51%   B: Cr=1.13%

of the standard sample with tin added at the ratio of 1 : 1.

The alloy was prepared by melting together in a hydrogen current at 1,200°C about 10.5 gs. of refined electrolytic gold and about 1.3 gs. of ferro-chromium containing 36.4 per cent. of iron, 0.8 per cent. of silicon and below 0.1 per cent. of carbon. The composition of the alloy thus made was as follows :

Au = 89.15%   Cr = 6.84%

Fe = 4.01%   Si = 0.09%

The quantity of chromium added to the standard sample is given in Table VI.

The results are graphically shown in Fig. 11.

The form of the curves here obtained is very similar to that obtained on the sample with manganese added, and the time required to abstract the total oxygen is almost the same in both cases.

Consideration of experimental results.

From the results of these experiments, it is confirmed that nickel has no influence and silicon, manganese and chromium have a great influence on the results of the Ledebur method which was adopted by the authors. When the standard sample containing the latter 3 elements is heated at 1,200°C, a great quantity of oxygen is abstracted in the first 2 hours, and the remainder of the oxygen is reduced at a very slow rate during a long time.

It is not impossible, however, to abstract total oxygen from these sample.

When silicon, manganese or chromium is dissolved in molten Armco iron, the latter must be deoxidized by these elements. The reversible reactions among molten iron, and FeO and deoxidation products— SiO_2, MnO and Cr_2O_3— which are dissolved in molten iron may be expressed by the following formulae :

$$2\,FeO + Si \rightleftarrows SiO_2 + 2Fe$$

$$FeO + Mn \rightleftarrows MnO + Fe$$

$$3\,FeO + 2\,Cr \rightleftarrows Cr_2O_3 + 3\,Fe$$
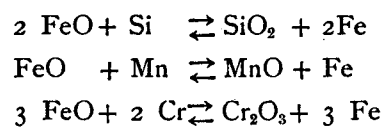
As the saturation value for these deoxidation products is very small, the excessive deoxidation products have to appear as a solid phase in molten iron at the case of our experiments. Of course, this solid phase will flux the dissolved FeO with the formation of a ferrous slag. As, in the course of analysis, the molten bath in the boat comes in contact with hydrogen which reduces dissolved FeO and the reduction product H_2O is removed by hydrogen as it is produced, the above reactions must proceed to the left as far as the deoxidation products exist, after the law of mass action. Therefore, the concentration of the dissolved deoxidation products decrease below their saturation value, accompanying the dissolution of these substances from the same substances in solid phase or the ferrous slag.

Consequently, it is theoretically acceptable that total oxygen may be abstracted from the sample even though it contains an active deoxidizer such as silicon, manganese or chromium.

The rate of reduction, however, depends greatly on the chemical and physical nature of deoxidation products, probably particularly on the area of the contact surface between iron and the deoxidation products.

In practical analysis, tin or gold is used as alloying metal. But the chemical affinity of oxygen for these metals is smaller than for iron. Then the presence of these alloying metals was neglected in the above discussion.

Summary.

The results of the present investigation may be summarized as follows:

(1) In the Ledebur method adopted by the authors, the total oxygen contained in Armco iron was determined with a satisfactory accuracy.

(2) The influence of silicon, manganese, nickel and chromium upon the determination of oxygen in Armco iron was confirmed.

(3) The reduction of the total oxygen in Armco iron is not impossible even when silicon is contained in the iron. But the reduction time is remarkably prolonged when it is rich in silicon and the analysis of such iron can not be practically accomplished by this method.

(4) The reduction of oxygen in the iron containing manganese takes place slowly, but faster than in the analysis of the iron containing silicon. The total oxygen in Armco iron can be determined by this method unless it is not rich in manganese.

(5) The time required to reduce total oxygen in Armco iron containing nickel is almost the same as in the analysis of Armco iron itself.

(6) The rate of reduction of oxygen in the iron containing chromium is almost the same as in the analysis of the iron containing manganese.

(7) The experimental fact that the deoxidation products such as SiO_2, MnO or Cr_2O_3 are reduced by hydrogen when they exist with iron was theoretically explained.

Appendex.

Analysis of the steel samples taken during smelting in an electric furnace.

Samples were taken from a basic Snyder electric furnace having a capacity of about 3 tons at the Army Arsenal in Osaka during the smelting of carbon cast steel. Table VII gives the data about charge and time when the samples were taken.

They were cast in a metal mould into a small ingot having the dimension, 50 m.m. × 35 m.m. × 35 m.m.

Table VII.

Time	Kind of charge	Weight of charge (Kg.)	Remarks
	Purchased steel scrap	800	
	Misellaneous steel scrap	1,200	
	Lime	200	
P.M. 12–10			Current closed
A.M. 2–20	Turnings in Arsenal	1,000	
4–10			Sample A taken
	Coke	1	
	Ferro-manganese	12	
	Mixed lime	100	
4–50	Fluorspar	8	
5–20			Sample B taken
	Ferro-manganese	11	
	Ferro-aluminium	7	
	Mixed lime	10	
5–30			Sample C taken
5–35	Ferro-silicon	12	
5–40	Ferro-aluminium	8	
	Mixed lime	10	
5–45			Sample D taken
5–50			Tapped
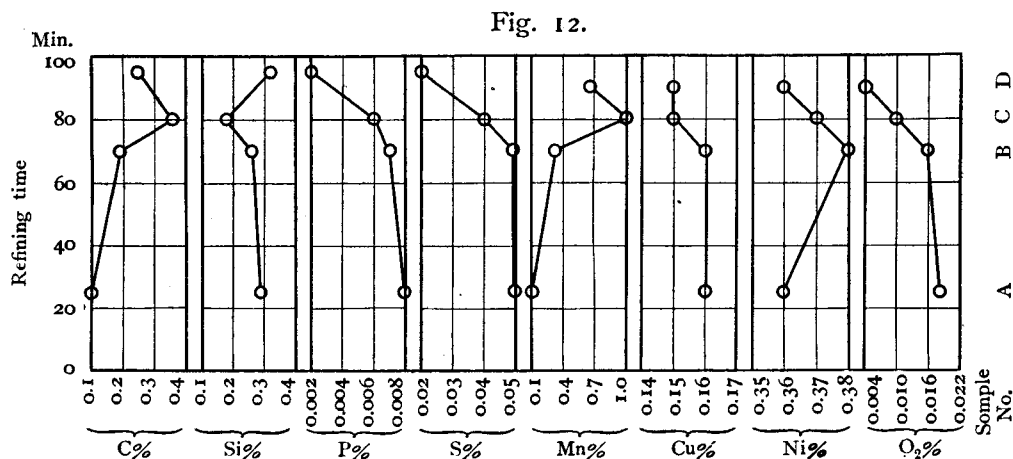
Fig. 12.

The content of oxygen as well as other impurities in these samples was determined, as graphically shown in Fig. 12.

In the analysis of oxygen, the reduction time was 2 hours at 1,200°C for all samples. Consequently, the values obtained from Sample A and B, containing lower content of manganese, will be near total oxygen, but the reduction time here adopted may be too short to abstract all oxygen contained in Sample C and D in which manganese is richer.

Though the results may be not very accurate, we can estimate that the oxygen content in the melt was decreased as smelting proceeded.

Acknowledgement.