

PREPARATION OF PURE IRON AND IRON-CARBON ALLOYS

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I. INTRODUCTION

The fundamental importance of the iron-carbon thermal equilibrium diagram in the scientific metallurgy of iron and steel and its utility to practical workers have long been realized, and accordingly this subject has received attention from many points of view and from many investigators during the past two decades.

In view of this fact, it might seem superfluous to add to the existing literature except for the following considerations: Earlier workers have for the most part confined their attention to special portions of the diagram or to disputed questions of theory. Their thermal studies have not been carried out with the degree of accuracy now attainable. They have practically without exception employed commercial materials of varying degrees of purity. In two papers published in 1913¹ Prof. H. M. Howe, as a result of a thorough examination of the literature, has fixed the most probable position of the equilibrium lines. His net conclusions are that "this calculated line is not entitled to great weight because of the weakness of the evidence," and that "much better data are needed, reached with pure materials and with the many causes of error reduced to a minimum." In Table 1, compiled from Prof. Howe's papers, are given analyses of the materials used in some of the more important recent investigations. A glance at the table will show the justice of the conclusions quoted above. The analyses are incomplete even for the impurities ordinarily determined, and entirely ignore the possible presence of other impurities, such as Cu and Ni; but so far as they go, they indicate a very appreciable degree of contamination by S, Si, Mn, elements which we know exert a marked effect on the critical ranges. It may be said that the iron-carbon diagram has never been worked out with pure iron-carbon alloys. The present paper describes the preparation of a series of high degree of purity, to be used as the basis of a more accurate study of the equilibrium diagram than has heretofore been attempted.

¹ A₁, the Equilibrium Temperature for A₁ in Carbon Steel, *Bull. Am. Inst. Min. E.*, p. 1066; 1913.
A Discussion of the Existing Data as to the Position of A₂, *Bull. Am. Inst. Min. E.*, p. 1099.

TABLE 1

Composition of Iron-Carbon Alloys Used by Various Investigators in Determinations of Critical Points

No.	Authority	Date	Composition of specimens				
			C	Si	Mn	P	S
1	Carpenter and Keeling <i>a</i>	1904	0.38	0.06	Trace.	0.03	0.01
2	do		1.85	.09			
3	do		3.98				
4	do		4.50	.12			
5	do		2.63				
5A	do		2.85				
6	do		2.85		Trace?		
7	Heyn <i>b</i>	1904	.39	.04	.03		
8	do95	.04	.06		
9	Rosenhain <i>c</i> (on Brayshaw's steel A2)	1910	1.14	.09	.40	.014	.018
10	do						
11	Benedicks <i>d</i>	1908	1.00		.25		
12	Charpy and Grenet <i>e</i>	1903	.64				
13	do64				
14	do93				
15	do93				
16	do		1.50				
17	Brayshaw <i>f</i> No. W4	1910	1.15	.21	.31	.011±	.012±
18	Brayshaw No. W2	1910	1.16	.10	.37	.014	.023
19	Brayshaw No. A2		1.14	.09	.40	.014	.018
20	Levy <i>g</i>	1913	.23	.039	.05	.013	.010
21	Levy	1912	.92	.14	.123	.009	.011
22	Howe and Levy <i>h</i>	1913	.027		.26	.005	.024
23	do105	.013	.24	.015	.028
24	do214	.039	.05	.013	.010
25	do227	.039	.05	.013	.010
26	do235	.039	.05	.013	.010
27	do244	.050	Nil.	Nil.	.007
28	do382	.027	.22		.004
29	do40	.103	.16	.014	.012
30	do563	.18	.15	.013	.013
31	do59	.144	.17	.018	.013
32	do73	.141	.07	.012	.019
33	do92	.14	.123	.009	.011

a Carpenter and Keeling, Journal Iron and Steel Inst., 65, p. 244; 1904, No. 1; Collected Researches of the Nat'l Phys. Lab., 1, p. 227.

b Heyn, Verh. des Vereins zur Beförderung des Gewerbflusses, p. 371; 1904.

c Rosenhain, Proc. Inst. Mech. Engrs., p. 688; 1910, parts 1 and 2.

d Benedicks, Jour. Iron and Steel Inst., 77, p. 218; 1908, No. 2.

e Charpy and Grenet, Bulletin Soc. d'Encouragement pour l'Industrie Nationale, p. 480; 1903, No. 1.

f Brayshaw, Proc. Inst. Mech. Engrs., pp. 525, 537, 656, 670; 1910, parts 1 and 2.

g Howe, Bull. Amer. Inst. Min. Engrs., p. 1068; 1913, No. 1.

h Howe and Levy, Bull. Amer. Inst. Min. Engrs., p. 1076; 1913, No. 1.

For the production of pure iron on a fairly large scale, the electrolytic refining method was obviously most suitable and was therefore adopted in this work. Pure carbon was made by calcining in a Dixon graphite crucible the pure sugar used as stock for Bureau of Standards analyzed sample No. 17. The latter contains, as the only impurity of importance for present purposes, 0.003 per cent ash, and the carbon obtained from it has an ash content of 0.17 per cent.

II. MAKING THE ELECTROLYTIC IRON

The electrolytic method, using soluble anodes, has been frequently employed in similar investigations² and its essentials are well known, so that we give details only for the sake of completeness and because, in one respect, our method deviates from that usually followed, namely, in the use of porous anode compartments. The first iron was made on a small scale. The essential details of the bath are as follows: Two cylindrical anodes of ingot iron³ about 2 inches in diameter by 5 inches long, contained in porous clay cups; three cathodes of sheet iron, each 4 inches square; electrolyte, 25 to 30 per cent FeCl₂ solution (made by dissolving the ingot iron in chemically pure hydrochloric acid), prepared as nearly neutral as possible; current density about 0.5 to 0.7 ampere per square decimeter; temperature during electrolysis approximately that of the room. No attempt was made to determine the yield or to secure high current efficiency. Good adherent deposits were obtained, the greatest thickness being about 0.5 cm. Owing to the unfavorable current distribution when working with anodes and cathodes of such unequal sizes, the thickness of deposit was not uniform all over the plates. Qualitative tests of the sludge from the anode cells showed that there was an accumulation of manganese and copper derived from anodic impurities. The porous cups therefore seemed to be of service in preventing anode impurities from migrating to the cathodes, and they were accordingly used in one of the larger baths to be described later. In another similar tank the cups were omitted. Table 2 shows that the cathode deposits from the bath without the cups were a little higher in copper than the others but were otherwise of similar

² See bibliography at end of this paper.

³ Analysis as follows: C, 0.016; S, 0.022; Mn, 0.029; P, 0.001; Si, 0.002; and Cu, 0.15.

quality. It was found that there was much oxidation of the surface layers of electrolyte as the electrolysis went on, resulting in the production of basic salts of iron, which floated in the bath and which migrated to some extent to the cathodes. With the intention of avoiding or minimizing this oxidation, the small bath was provided with a hydraulically sealed cover having windows for observation and conduits for the current leads. The air in the space over the electrolyte was displaced with purified carbon dioxide and the electrolysis conducted as before. This method led to no marked improvement and it was abandoned, especially as there seemed to be a tendency toward higher percentages of carbon in the cathodic deposits. Although the greater part of the sediment settled to the bottom, the bath was never quite free from turbidity caused by these basic salts, and there is no doubt that the deposits were contaminated by them in slight degree. This was of no consequence, inasmuch as these impurities were either volatilized or were reduced to iron in subsequent melting operations. The analysis of the iron stripped from cathodes of the small electrolytic bath is given in Table 2. About 2 or 3 kg was made in this bath.

TABLE 2
Analyses of Electrolytic Iron from Various Sources

Source	C	S	P	Mn	Si	Cu	Ni and Co	Total impurity	Analysis by—
	Per cent	Per cent							
1 a, b.....	0.004	0.002	Trace	Trace	0.003	0.006	0.011	0.026	B. S.
2 c, b.....	.004	.003	Trace	Trace	.006	Trace	.011	.024	B. S.
3 a, b.....	.004	.006	Trace	Trace	.008	.006	.011	.035	B. S.
4 e.....	.004	.004	Trace	Trace	.005	.008	.011	.033	B. S.
5 f.....	.063	.002	0.005	0.009	.005084	Müller
6 g.....	.008	Trace	.002	.009	.014033	Stead
7 h.....	.008	.004	Trace	Trace	.006	.011029	B. S.
8 i.....	.009	.003	Trace	Trace	.006	.006024	B. S.

^a B. S. (with porous cups).

^b Bureau of Standards analysis of anodes from which this iron was made: C, 0.013 per cent; S, 0.020 per cent; P, 0.003 per cent; Mn, 0.025 per cent; Si, 0.003 per cent; Cu, 0.024 per cent; and Ni+Co, 0.021 per cent. (Cf. Burgess and Crowe, this Bulletin, 10, p. 342; 1914.

^c B. S. (with porous cups).

^d B. S. (without porous cups).

^e B. S. (from small tank).

^f A. Müller, Metallurgie, 6, p. 152; 1909.

^g H. C. H. Carpenter.

^h Langbein-Pfanhauser.

ⁱ C. F. Burgess.

The large electrolytic bath is shown in Fig. 1. The anode cups were molded from a mixture of equal parts by volume of alundum cement and of clean white Ottawa sand; after careful drying in an oven the cups were burned at a temperature of 1000° to 1100° and were then found to have a satisfactory degree of porosity. The current density during electrolysis varied from 0.3 to 0.4 amperes per square decimeter. The electrolyte contained 23.3 per cent FeCl_2 (made from the ingot iron previously

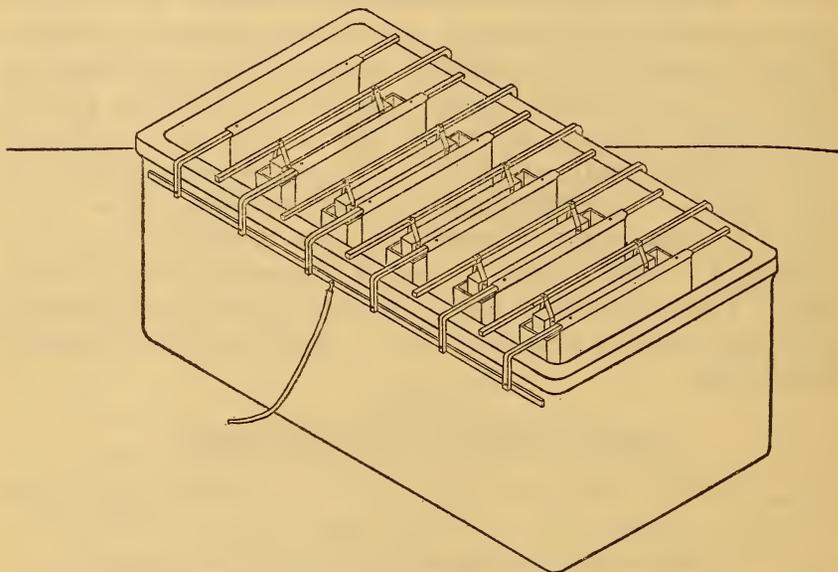


FIG. 1.—Tank for preparing electrolytic iron

described) and 10.3 per cent NaCl , and was nearly neutral. Analyses of electrolyte from the anode and cathode compartments made after a week's run were as follows:

	Anode compartment	Cathode compartment
Per cent iron, original.....	9.52	7.88
Per cent iron after one week's run.....	8.82	7.53

The character of the deposits is shown by Figs. 2, 3, and 4. Deposits of 5 to 7 mm thickness were obtained; the characteris-

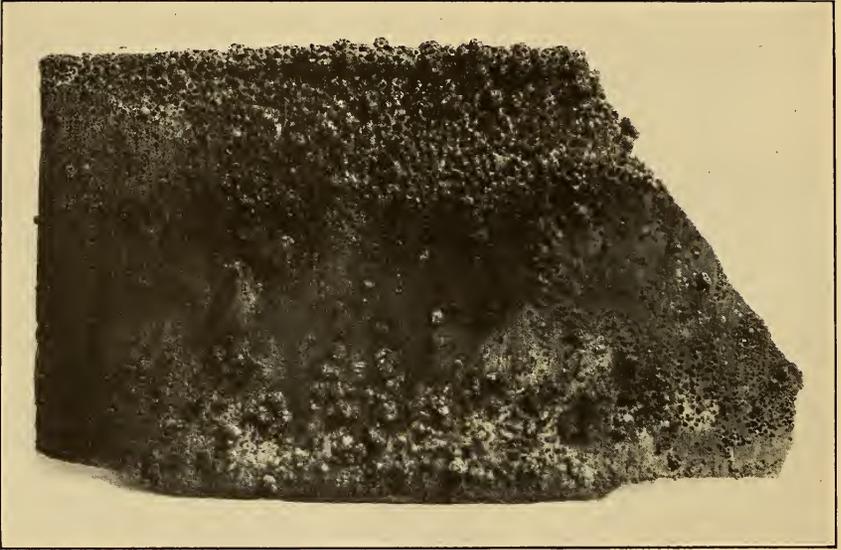


FIG. 2.—*Cathode deposit*

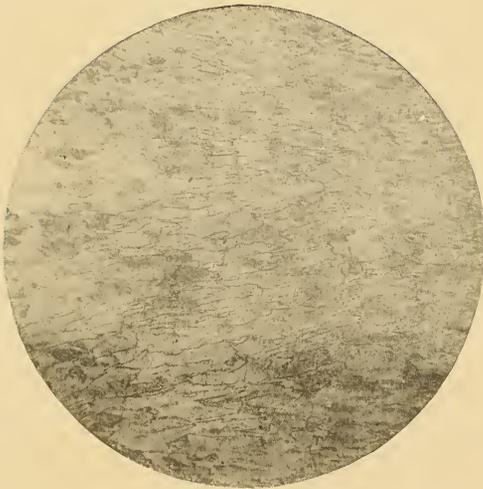


FIG. 3.—*Electrolytic iron as deposited. Section perpendicular to the electrode; 100 diameters*

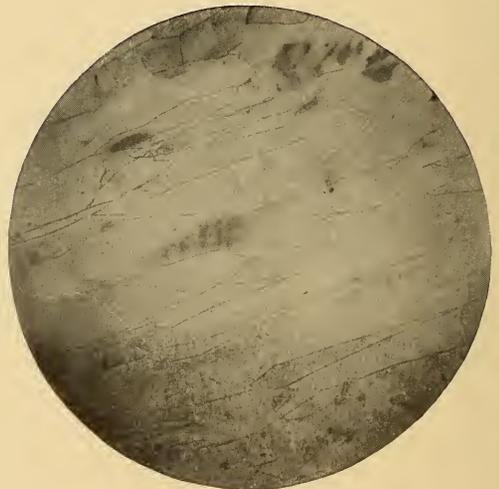


FIG. 4.—*Electrolytic iron as deposited. Section perpendicular to the electrode; 250 diameters*

tics of these were about the same as of those made in the smaller bath. They were very hard and brittle in consequence of contamination by hydrogen. On removal from the bath and after washing with distilled water they corroded rapidly in the air. No account was taken of this surface oxidation, inasmuch as the iron was to be used for making iron-carbon alloys in such a way that the oxidized compounds of iron would be reduced to metal and the hydrogen expelled. About 12 to 15 kg of iron was made for use in preparing the alloys. In Table 2 are given analyses of this iron made with and without the use of porous anode compartments, and for comparison analyses of electrolytic iron from other sources.

III. MELTING THE ELECTROLYTIC IRON

The next step for the further utilization of the electro-deposited iron is to melt it into ingots. As already stated, the material as taken from the bath is brittle and is contaminated with occluded chlorides from the electrolyte, with hydrogen, and with oxidized compounds of iron. Annealing at 600° to 800° suffices to remove most of the hydrogen and some of the chlorides; this renders the iron more malleable and resistant to corrosion, but to attain a still higher degree of purity and to simplify subsequent operations the iron must be fused, preferably in a reducing atmosphere, and held in a state of fusion for some minutes. Owing to the high melting point of iron (1530°), to its strong tendency to combine with or to be contaminated by substances likely to be present as vapors in electrically heated furnaces (Si, S, C, Pt, and the like), or as gases in the products of combustion of a fuel-fired furnace (CO, SO₂, SO₃, CO₂, H₂O), and especially because of the corrosive action on crucibles of molten oxides of iron, with resulting possible contamination of the melt by slags, etc., it is evident that great care must be taken in the choice of furnaces and crucibles for work of this kind. While it is true that iron in the molten condition containing as little as 0.1 to 0.2 per cent of the impurities ordinarily determined has been produced commercially for some time, the conditions of laboratory preparation on a small scale are entirely different and lead to new difficulties: (1) Contamination by the hearth, or crucible material, or by gases is less in

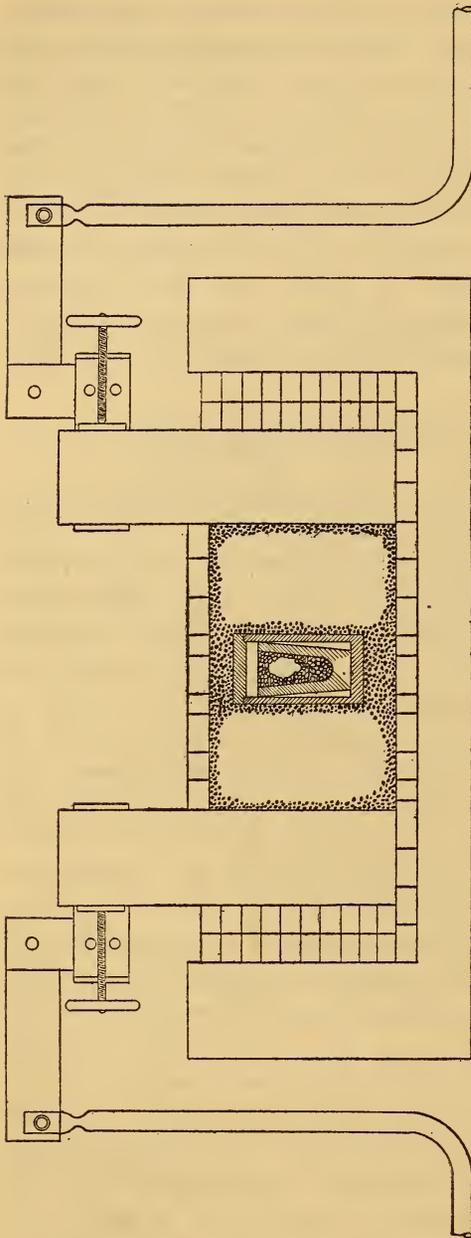


FIG. 5.—Kryptol furnace with crucible in position

large-scale operations, owing to the relatively smaller surface exposed compared with the weight of metal being handled; (2) additions, such as ferroalloys, aluminum, or titanium for purification of the melt, as used commercially, are not permissible in an investigation of this kind; (3) the use of slags for protection from the products of combustion or for eliminating impurities and controlling composition in desired ways is excluded. The importance of the conditions for melting pure iron and its alloys to secure products of very high purity does not seem to have been recognized sufficiently in the past, and we shall therefore give full details of our methods.

1. FURNACES

(a) ELECTRIC FURNACES.—For ease and convenience of manipulation a furnace used

for melting pure iron should maintain continuously a temperature of not less than 1600° . The temperature required eliminates furnaces wound with nickel or nichrome; molybdenum or platinum-wound furnaces are not desirable for work in high vacua, owing to volatilization of these metals with resulting contamination of the melt and destruction of the heater. Tungsten windings could no doubt be used, but no suitable furnace of this type was available at the Bureau. Our work with electric furnaces has been confined, therefore, to those employing carbon in some form as resistor. A furnace of the kryptol type, shown in Fig. 5, was constructed and has been found satisfactory. The Arsem vacuum furnace, shown in Fig. 6, was extensively used and is very suitable for work of this character.

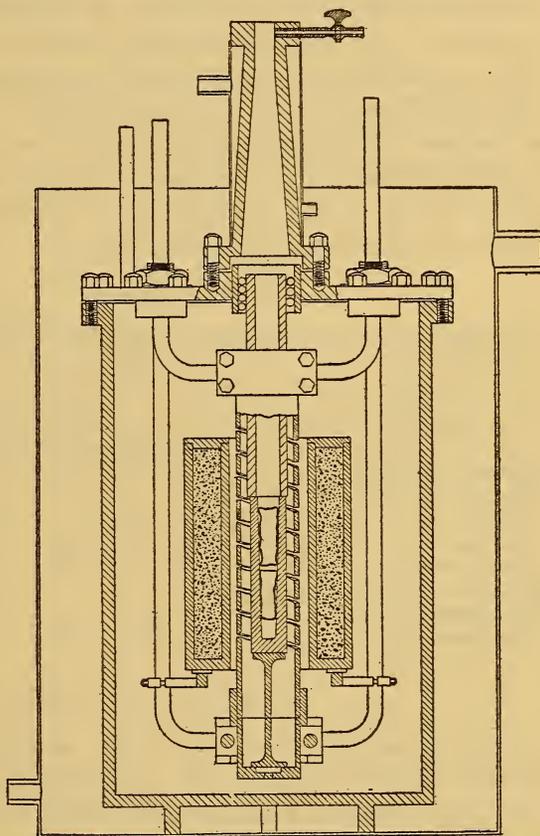


FIG. 6.—Arsem furnace with crucible and protecting tube in place

As this furnace has been described elsewhere⁴ we omit details here. The Helberger crucible furnace was used for melting some of our alloys. This furnace is intended to be used with conducting crucibles, but our work was done with amorphous carbon tubes as resistors. Because of the lack of protection of these from the oxidizing action of the air their life is incon-

⁴W. C. Arsem, Trans. Am. Electrochem. Soc., 9, p. 152; 1906.

veniently short. The resistance of Acheson graphite tubes was found to be too low to permit the desired temperatures to be reached. There were difficulties in securing good electrical contact between the terminals and the resistor so that this style of furnace as used by us is not to be recommended for work at 1600° or above. The difficulty common to all the types of electric furnaces used (unless the precautions mentioned later were observed) was that the melts were contaminated by volatile sulphur, silicon, or carbon derived from the resistors used. This contamination was least in the Arsem furnace when protecting the crucible, as shown in Fig. 6, and was greatest in the Helberger furnace and in the kryptol furnace when using amorphous carbon as resistors.

TABLE 3

Analyses of Bureau of Standards Electrolytic Iron after Melting in Various Furnaces

Manner of melting	C	Si	S	Mn	P	Cu
Original iron not melted	Per cent 0.004	Per cent 0.001	Per cent 0.004	Per cent Trace	Per cent Trace	Per cent
In kryptol furnace filled with Acheson graphite.....	.012	.01	.004	Trace	Trace
In Helberger furnace.....014	.024	Trace	Trace
In Arsem furnace.....	.010	.007	.007	Trace	Trace	0.012
In Helberger furnace and remelted in Arsem furnace.....	.009	.004	.005	Trace	Trace
In gas furnace.....	.012	.003	.02	Trace	Trace

Table 3 shows the amounts of contamination introduced by melting pure iron in various types of furnaces. An analysis of the amorphous carbon used as filling material in the kryptol furnace and for the resistor tubes of the Helberger furnace showed 0.75 per cent sulphur and 0.07 per cent silica. The high sulphur in the amorphous carbon resistors is due to the use of petroleum coke in their manufacture. Analyses of best grades of petroleum coke obtained by the Geological Survey showed percentages of sulphur ranging from 0.63 to 1.37 per cent. After having discovered these defects in amorphous carbon we discontinued its use, employing granular Acheson graphite of the best grade for the kryptol furnace and a graphite spiral for the Arsem furnace. A resistor from the Arsem furnace contained

0.02 per cent sulphur and 0.03 per cent silica. The results were satisfactory. It may be concluded that if carbon resistance furnaces are intended for making melts with minimum contamination by volatile substances from the heating element, the best material available at present is first-quality graphite; and that the resistors should be carefully analyzed to insure against impurity before installing them in the furnace. It is further evident that if the refractory walls of the furnace are in immediate contact with the heater, the former should be made of material not likely to react with the heated carbon.

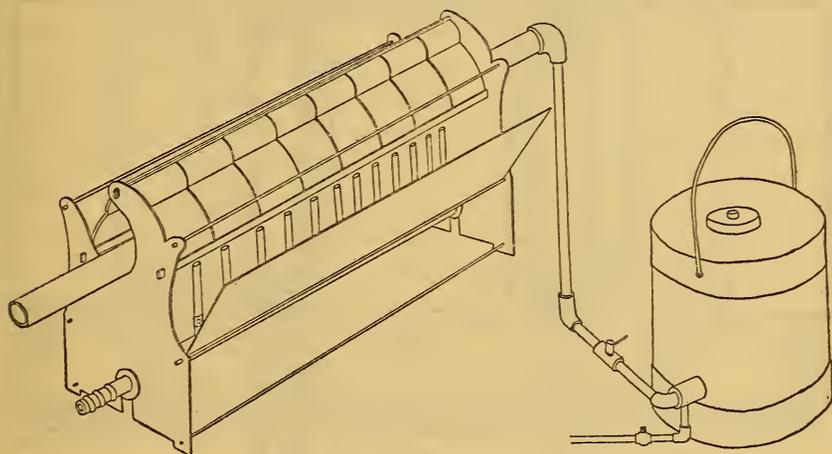


FIG. 7—Small gas furnace with preheater

Such reaction would cause not only possible contamination of the melt, but also irregularities in the working of the furnace. For this reason ordinary fire clay or silica bricks, or any others containing silica in considerable amount, are excluded. In our own kryptol furnace commercial magnesite bricks were used, and while they were not all that could be desired they proved serviceable, provided the resistor was renewed occasionally.

(b) GAS FURNACES.—Two types of gas furnace, shown in Figs. 7 and 8, were used and no difficulty was experienced in maintaining the necessary temperatures. The furnace shown in Fig. 7 was a standard type except in respect to the blowpipe, which is similar to that used in tool forges, or for brazing purposes.

A preheater raised the temperature of the necessary volume of air to about 350° . In some experiments made with this furnace pure platinum wire was melted, indicating that a temperature in excess of 1750° had been attained. The refractory lining supplied by the manufacturers was found to have a very short life

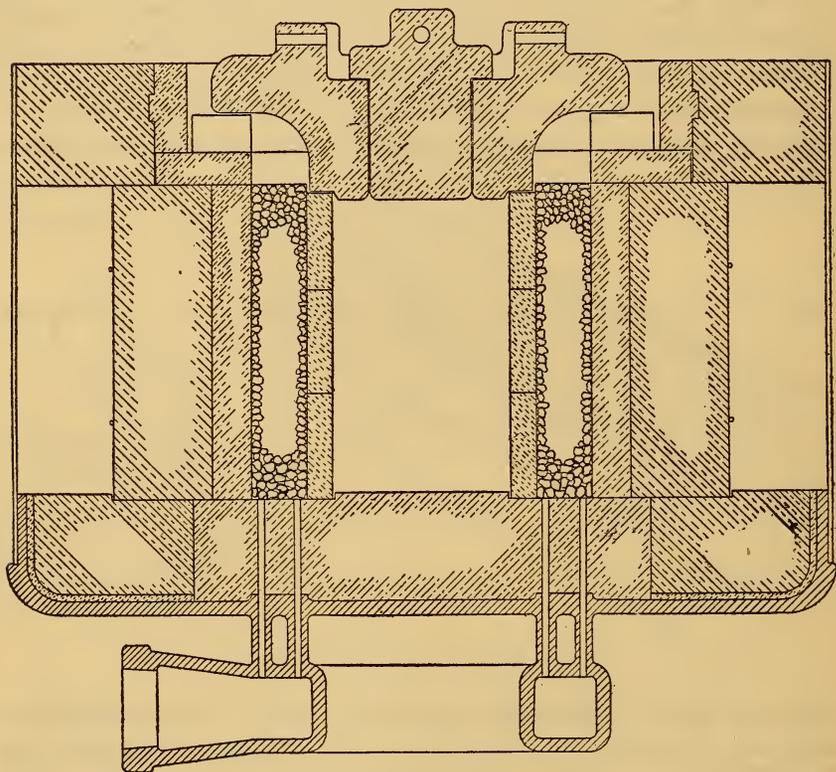


FIG. 8—Surface combustion crucible furnace

under these conditions, so that we later covered it with alundum cement, or with a mixture of alundum cement and clay, which prolonged the life. The surface combustion furnace (Fig. 8) proved to be very suitable. This furnace has already been illustrated and briefly described.⁵ The same trouble was experienced with the original refractory lining, and repairs were again made with alundum and clay. The highest temperature

⁵ Lucke, J. Ind. and Eng. Chem., 5, p. 801; 1913.

reached in this furnace, 1670°, was obtained when burning about 180 cubic feet of city gas per hour. In using this type of furnace for pure melts, the crucible must be protected from the large amount of very fine dust blown out of the contact material during operation.

2. CRUCIBLES

A few preliminary experiments with clay crucibles showed that it would be out of the question to use these for melting pure iron-carbon alloys. The clays used for making the crucibles which we tried were not sufficiently refractory and were badly corroded by the iron oxide which coats the surface of all melts made in gas-fired furnaces. This did not occur in the electric furnaces, but here the reducing atmosphere, which prevented oxidation, also caused the introduction of relatively large amounts of silicon from the clay. Alundum crucibles were tried, but gave the same trouble as those of clay. Crucibles made of electrically fused or sintered magnesia from two different sources were given a trial in the various types of furnaces, but with these also there was more contamination of the melts by silicon than seemed desirable. (See Table 4.)

TABLE 4

Alloys Made in Crucibles of Commercially Pure Magnesia

Designation	Method of melting	C	Si	S
P 27.....	Gas and vacuum furnaces.....	Per cent 0.584	Per cent 0.056	Per cent 0.004
P 28.....	do.....	.022	.029	.030
P 29.....	do.....	.367	.015	.029
P 41.....	Single melt in Helberger furnace.....	.886	.024	.013
P 39.....	Melted twice in Helberger furnace.....	.688	.054	.026
P 31.....	Helberger and vacuum furnaces.....	.210	.032	.020
P 32.....	do.....	.252	.022	.010
P 33.....	do.....	.094	.041	.024
P 35.....	do.....	.146	.050	.029
P 37.....	do.....	.088	.050	.039
P 40.....	do.....	.765	.033	.015
P 42.....	do.....	.058	.070	.016
P 36.....	Melted twice in kryptol furnace.....	.927	.045	.019

As it had become evident that the desired results could not be secured with any kind of crucible on the market, we began the

experiment of making our crucibles of various grades of chemically pure magnesia calcined in the electric furnace at 1600° to 1800°. Although our product contained usually not over 0.05 to 0.10 per cent silica the alloys melted in crucibles made from such magnesia still carried too much silicon. (See Table 4.) Because of the difficulty of securing from chemical dealers magnesia sufficiently low in silica, the high cost of a good grade of this material, and the need of large quantities for several contemplated investigations, we decided to prepare our own material. An endeavor was made to develop a method free from too many complicated manipulations. As raw material we used two or three grades of pharmaceutical manesium carbonate carrying 0.1 or 0.2 per cent silica, and later a calcined Grecian magnesite with about 3.5 per cent silica. Attempts to prepare silica-free magnesia from these sources by dissolving them in hydrochloric acid, evaporating the solutions to dryness and baking, followed by solution of the $MgCl_2$, filtration and precipitation of magnesium carbonate by ammonium carbonate were not very successful on the scale tried, for the technique was difficult and the product unsatisfactory, as well as expensive.

TABLE 5
Percentage of Silica in Magnesia from Different Sources

Source	SiO ₂	Source	SiO ₂
	Per cent		Per cent
Calcined Grecian magnesite.....	3.15	Bureau of Standards MgO, prepared from acetate.....	0.008
Do.....	4.61	Bureau of Standards MgO calcined in gas furnace.....	.013
University of Illinois electrically calcined MgO.....	1.99	Do.....	.017
Magnesium aluminate tube.....	5.39	Crucible made from Bureau of Standards calcined MgO.....	.025
MgO reagent (uncalcined) A.....	.03		
MgO reagent (uncalcined) B.....	.07		

After trials of several other methods we developed the following procedure, which has produced a magnesium oxide carrying usually not over 0.01 per cent silica, and at low cost.

The Grecian magnesite was dissolved in commercial acetic acid (70 per cent), using a slight excess of the latter; more of the magnesite was then added until the solution was alkaline to litmus paper, after which the solution was diluted with about twice its

volume of water, the whole thoroughly stirred and allowed to stand in barrels for a day or two; at the end of this time the clear solution was siphoned off into a large wrought-iron basin and rapidly evaporated over a large Fletcher burner, adding fresh liquid at intervals until a sufficient amount of the magnesium acetate had separated. The evaporation was then carried to the point where the solution solidified on cooling, after which the decomposition of the acetate into oxide was effected by directing the flame from a large Teclu burner over the surface of the separated salts. The magnesium oxide so obtained is contaminated by carbon, undecomposed acetate, and a little iron, but after calcining is quite suitable for use in making crucibles. The calcining was done in large gas furnaces which gave a temperature of approximately 1550° . The magnesia, as taken from the iron basin, was moistened slightly with water and made up into large balls, which were placed inside an ordinary No. 20 plumbago crucible coated on the inside with alundum cement, or lined with an Acheson graphite crucible. The crucible was carefully covered during the calcining operation, which lasted about two hours. As a result of this treatment the magnesia had shrunk to about one-third its original volume, all the carbon had burned out, and the silica content was very slightly increased. We found it important to blow air through the furnace for several minutes after shutting off the gas, in order to remove the last traces of products of combustion carrying sulphur. If these are allowed to remain in the furnace during the cooling period, the magnesia takes up some sulphur; our best material contained less than 0.01 per cent of this element. Calcining in the gas furnace at the temperature named gives a product which still shrinks a little when used in crucibles heated to higher temperatures, but we had no serious trouble with crucible failures on this account.

Two sizes of crucibles were used which, together with the molds employed for making them, are shown in Fig. 9. The calcined material was mixed with about 10 per cent by weight of uncalcined magnesia and the whole wet with water until it formed a pasty mass. The thin brass cups used for lining the molds were put in place and there was introduced into the mold a sufficient

amount of the material (ascertained by preliminary trials); a pressure of 5000 to 10 000 pounds per square inch was applied to the head of the plunger and kept there a minute or two after the plunger had been driven down as far as it would go. The mold was then opened by removing the rings, the brass cup carrying the crucible removed, and the plunger taken out. The crucibles were dried at 100° to 120° for a day and the brass cups stripped off by melting the solder from the joints. They were then either used directly for melts, or after heating to 1200° to

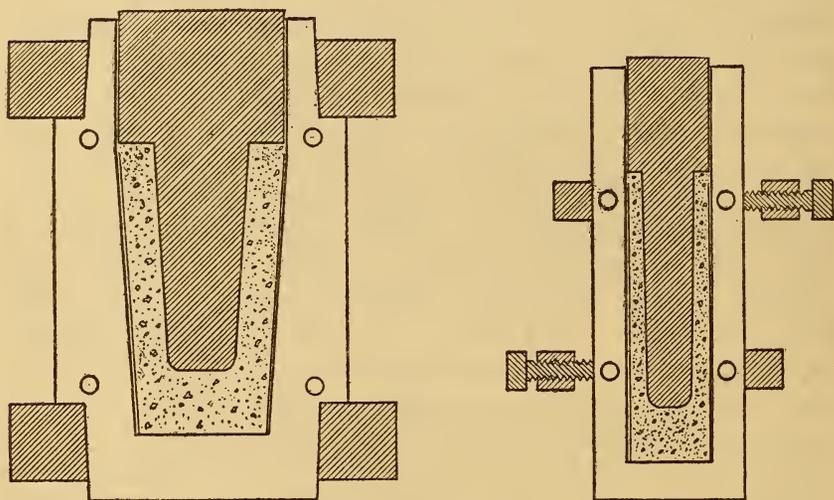


FIG. 9.—Crucible molds

1600° in a gas or electric furnace. The latter procedure is necessary for all crucibles that are to be used in vacuum furnaces.

IV. PROCEDURE IN MAKING ALLOYS

We first attempted to make ingots in the following manner:

The iron as stripped from the cathodes was dried, broken into small pieces, and placed in the larger magnesia crucibles (Fig. 9), together with a suitable quantity of carbon. These were brought gradually to temperatures above the melting point of iron and left in the furnace for 10 or 15 minutes. After cooling, the crucibles were removed and broken away from the ingots. This procedure, while apparently wasteful, was necessary for several

reasons: (1) Magnesia crucibles are extremely fragile at high temperatures and any attempt to handle them results in breakage with resultant loss of melts; (2) with the small mass of metal which we used (100 g) it would be impossible to pour successfully; and (3) even if it could be accomplished, pouring would be objectionable because of the added danger of contamination. Moreover, the loss of the crucible is not serious, since the material can be recovered and worked up into new crucibles repeatedly.

The ingots obtained in the manner above described were found to be very unsound and full of blowholes; in this respect there was little difference between those made in the various furnaces. This seemed surprising in view of the difference in atmosphere over the melt in a gas furnace, where the conditions are oxidizing to iron, and in an electric furnace, where carbon dioxide, water vapor, or oxygen—the gases which would oxidize iron at high temperatures—are present only in very small amounts. It would thus appear that the blowholes in iron may be caused by carbon monoxide as well as by any or all of the other gases named, and that the maintenance of a reducing atmosphere is no guarantee of freedom from blowholes. That the melts made in the kryptol furnace were made under reducing conditions is evident from Fig. 5, which shows that the crucibles are completely covered with carbon at all times; this is further evident from an oxygen determination made on drillings from an ingot melted in the kryptol furnace. The percentage of oxygen in this ingot, notwithstanding the fact that no deoxidizer had been used, was 0.03.⁶ The weight of these ingots was about 100 g. Fig. 10 (a) is a photograph of a split ingot, showing the unsound structure.

The introduction of a regulated amount of carbon into the alloys gave a good deal of trouble. In the gas furnace the amount of oxidizing gases was so great, relative to the weight of carbon introduced, that the latter was all burned out before the melting operation was completed, even when special precautions were taken to protect the crucibles. These difficulties were finally overcome by using the following procedure, which has been fairly satisfactory: The electrolytic iron was first melted down in the larger crucibles in a gas or electric furnace. The ingots of pure

⁶ We are indebted to J. A. Aupperle, metallurgist of the American Rolling Mill Co., for this analysis.

iron so made were sawed into longitudinal strips of convenient size for insertion into the smaller magnesia crucibles (Fig. 9) and the necessary amount of carbon was added. The crucible was placed in the vacuum furnace with the protecting chimney in place, as shown in Fig. 6. The furnace was evacuated to 0.2 mm, and the current through the heater was increased gradually until the iron had melted and dissolved the carbon; this point was determined by observation through the window. As soon as this stage was reached a violent ebullition took place; sometimes the contents of the crucible were ejected. We attribute this principally to the expulsion of gases from the cavities in the ingots. In 10 or 15 minutes the surface of the melt became quiescent and the operation was ended. After cooling, the ingots were removed by breaking the crucibles.

Fig. 10*b* shows the sound structure of these ingots, which were usually entirely or nearly free from blowholes. After discarding the surface down to clean metal, the ingots were turned down to the size required for the thermal test specimens (Fig. 10*c*), retaining the chips for analysis. Complete analyses of typical samples are given in Table 6. For comparison, Table 7 is given, showing the results of attempts by two earlier workers to make pure iron-carbon alloys.

We are now building a larger vacuum furnace for producing large ingots of pure iron and iron-carbon alloys, which will be examined either as made or after forging, rolling, and application of heat treatment as to physical properties, magnetic and electrical characteristics, resistance to corrosion, and related properties. Reports of progress in this work will be issued as they are justified. Later we shall deal with the effect of alloying elements other than carbon on the properties of iron.

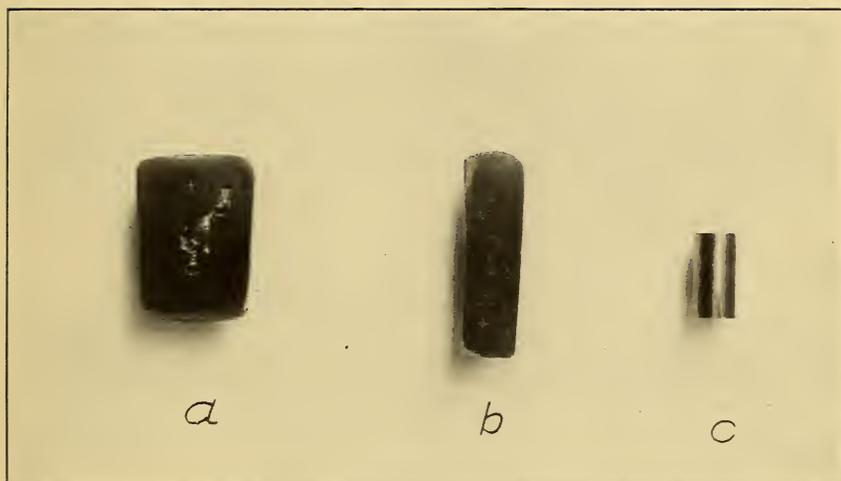


FIG. 10.—*Split ingots and test specimen*

TABLE 6

Analyses of Typical Bureau of Standards Iron-Carbon Alloys

C	Si	S	P	Mn	Cu	Ni and Co	Total Im- purities
Per cent	Per cent						
0.084	0.007	0.009	Trace	Trace	0.020	a 0.011	0.047
.376	.013	.009	Trace	Trace	.005	a 0.11	.038
.395	.008	.013	Trace	Trace	.012	a .011	.044
.597	.010	.008	Trace	Trace	.004	a .011	.033
.624	.004	.010	Trace	Trace	.008	a .011	.033
.692	.006	.011	Trace	Trace	.008	a .011	.036
.860	.006	.006	Trace	Trace	.007	a .011	.030
1.087	.006	.006	Trace	Trace	.013	a .011	.036
1.797	.010	.005	Trace	Trace	.018	a .011	.044
2.240	.005	.005	Trace	Trace	.020	a .011	.041
2.560	.005	.005	Trace	Trace	.014	a .011	.035
3.27	.006	.006	Trace	Trace	.016	a .011	.039

^a The figures given for nickel and cobalt do not represent individual determinations for each specimen, since the amount of sample was insufficient to allow of these being carried out. Four representative analyses on pure iron and iron-carbon alloys having given the result indicated, it was assumed that these elements were present in that amount in all the samples.

TABLE 7

Degree of Contamination of Iron Melts Made by Others

	C	Si	P	S	Mn
	Per cent				
Müller's electrolytic iron.....	0.0630	0.0053	0.0045	0.0024	0.0090
Müller's electrolytic iron after remelting in vacuo in "pure MgO crucible" ^a017	.089	.028	.037	.025
C. F. Burgess' electrolytic iron.....	.009	.006	<.001	.010	Trace
C. F. Burgess' electrolytic iron melted with sugar carbon in magnesia crucible by Howe ^b	2.954	.040	.050	.035	None

^a A. Müller, *Metallurgie*, 6, p. 159; 1909.

^b Howe, *Bull. Am. Inst. Min. Eng.*, p. 1118; 1913, No. 1.

V. DISCUSSION OF THE SOURCES OF CONTAMINATION

1. SILICON

In our earlier experiments, where we were obliged to make crucibles of magnesia higher in silica than that produced by the acetate method already described, we noted that occasionally an alloy of very low silicon content would result from a melt made in a crucible relatively high in silica. The use of our purified

magnesia had eliminated all trouble from silicon contamination of melts, but we later decided to make some experiments to determine the relationship between the introduction of silicon and temperature of melting. For this purpose a series of runs was made in the vacuum furnace varying independently the temperature of melting and the silica content of crucibles. One per cent of carbon was added to all these melts since in the presence of carbon there is additional likelihood of contamination due to reduction of silica at high temperatures. The results in Table 8 show that if the temperature is not allowed to rise much above 1600°, crucibles containing as much as 0.9 per cent silica may be used safely. This is of importance when a great deal of work is being done, for it enables one to use repeatedly old crucible material until the silica becomes dangerously high.

TABLE 8
Factors Governing Contamination of Melts by Silicon

Temperature of melting (degrees)	SiO ₂ in crucible	Si in melt	Temperature of melting (degrees)	SiO ₂ in crucible	Si in melt
	Per cent	Per cent		Per cent	Per cent
1610	0.57	0.007	1720	1.27	0.040
161067	.007	1780	1.20	.042
161075	.007	177019	.007
161091	.006	172024	.006
1610	1.14	.015	176031	.021
1610	1.66	.023	174060	.031
1650	1.35	.032			

2. SULPHUR

As has been shown, contamination by sulphur may result from the use of gas furnaces or of petroleum coke carbon in electric furnaces. On abandoning the use of gas furnaces and employing Acheson graphite as resistor material this difficulty disappeared, as is apparent from a comparison of Tables 5 and 7.

3. MANGANESE AND PHOSPHORUS

Both these elements have been reduced to mere traces (less than 0.001 per cent) in all our alloys.

4. COPPER

This impurity, one of the most difficult to guard against, is present in objectionable quantities in some of our melts and to some extent in all. The ingot iron used for anodes contains copper which is not completely removed in the electrolytic refining process, so that our deposits contain about 0.005 per cent of this element. This Cu persists through the melting operation, and unless great care is taken, more is introduced owing to the use of copper connections in furnaces. In particular, the copper blocks used in the vacuum furnace must be smooth and make good contact with the graphite heater, since any arcing causes the vaporization of considerable quantities of Cu with resulting contamination of the melt.

5. NICKEL AND COBALT

Our anode iron contains 0.02 per cent Ni + Co; in the electrolytic refining this is reduced to 0.01 per cent which persists through the melting operations.

6. MAGNESIUM

As all our melting was done in magnesia crucibles it was thought desirable to look for this element as a possible impurity. Several analyses of ingots made in the regular way showed that Mg was not present in any determinable quantity. A rather interesting result, however, was obtained on analyzing some ingots which had been melted at high temperatures (over 1700°). It was found that these contained appreciable amounts of Mg (from 0.005 to 0.01 per cent). Furthermore, the samples were so brittle that the pieces broke while turning in the lathe. It appears at least possible that there may be a direct connection between the two circumstances, though our present data are not sufficient to justify a definite conclusion to that effect.

7. OXYGEN

Unfortunately, the Bureau is not at present prepared to make accurate oxygen determinations on this class of material, but it is hoped later to publish analyses of some of the alloys for this element, if it is found to be present. In our method of prepara-

tion, starting with an ingot already low in oxygen (see p. 17) and carburizing in a vacuum furnace where the carbon monoxide resulting from interaction of oxides or oxygen with carbon would be removed as formed, the deoxidation would tend toward completion, and accordingly the alloys should contain but small residual amounts of oxides and oxygen.

VI. SPECTROSCOPIC EXAMINATION

In order to confirm the results of the chemical analyses for small quantities of impurities, the arc spectra of a number of samples of iron and iron-carbon alloys were studied by Dr. K. Burns⁷ of this Bureau, to whom we are indebted for the data given below:

MAGNESIUM.—The spectra fully confirmed the chemical tests. Line 2851.1A showed strong in two samples containing 0.007 and 0.010 per cent mg while it was very faint or absent in unfused irons and in alloys which failed to give magnesium by the chemical method.

SILICON.—Line 2881.5A showed presence of silicon in the alloys, but unfused iron showed no traces.

MANGANESE.—Several manganese lines show in various samples of electrolytic iron that have been melted. These lines are absent from the spectrum of unmelted electrolytic iron. The faintness of the manganese lines as compared with those given by a specimen containing 0.01 per cent of this metal indicate a very low manganese content.

CHROMIUM.—The statements made in regard to manganese also apply to chromium.

COPPER.—Lines 3247.7 and 3274.1A are always present though so faint as to be questionable in unmelted specimens.

NICKEL AND COBALT.—Several nickel and cobalt lines show faintly in the various samples.

In the course of the examination of the arc spectrum of pure iron several faulty identifications have been corrected:

- 2795.542 ascribed to magnesium is iron;
- 3369.555 ascribed to nickel is iron and nickel;
- 3412.347 ascribed to iron is probably cobalt; and
- 3443.645 ascribed to iron is no doubt cobalt.

No attempt has as yet been made to clear up all the doubtful identifications in the iron spectrum; the above list is given to show the possibilities in this direction which may be realized by means of the use of pure iron.

VII. METHODS OF CHEMICAL ANALYSIS

The analyses recorded in this paper were carried out according to well-known principles with suitable precautions, and the methods are given below merely for reference.

⁷ For an account of the methods used, c. f. K. Burns, *Bull. Bur. Standards*, 12, pp. 179-196; 1916.

The chips obtained when making the thermal test specimens were thoroughly mixed before weighing portions for analysis. Chips from high-carbon alloys which contained admixed graphite were finely ground and mixed before weighing.

1. CARBON

Carbon was determined by the barium-carbonate titration method devised by one of the authors.⁸ The chips (1 to 5 g) were burned in purified oxygen, passing the products of combustion into a solution of barium hydroxide; the barium carbonate was filtered and washed in an atmosphere free from carbon dioxide (see the original for details of apparatus used), and the barium carbonate was titrated against standard hydrochloric acid, using methyl orange as indicator.

2. SULPHUR

Sulphur was determined by dissolving 5 g of the metal, contained in an appropriate evolution apparatus having all ground-glass connections, in concentrated hydrochloric acid, the gases given off being passed into an ammoniacal solution of hydrogen peroxide. After complete solution of the metal the contents of the evolution flask were boiled for 10 minutes while a slow current of purified hydrogen was passed through the solution. The ammoniacal peroxide solution was transferred to a beaker and boiled a few minutes, then the solution was slightly overneutralized with hydrochloric acid and the sulphur precipitated at boiling temperature as barium sulphate. After digestion for a sufficient length of time the precipitate was filtered, washed, ignited and weighed, and the percentage of sulphur calculated.

3. SILICON

Five to 10 g of metal were dissolved in an Erlenmeyer flask in hydrochloric acid (equal volumes of water and hydrochloric acid of specific gravity 1.20), the solution evaporated to dryness and the flask heated on the hot plate at about 200° for an hour. The residue was digested with hydrochloric acid of the same strength as that used for dissolving, the insoluble matter containing the

⁸ J. R. Cain, Determination of Carbon in Steel and Iron by the Barium Carbonate Titration Method. Bur. Stand. Technologic Paper No. 33.

silica was filtered off, washed with dilute hydrochloric acid and water, ignited in a platinum crucible and weighed, after which the silica was volatilized with hydrofluoric acid and its amount determined from the change in weight of the crucible after again igniting. The results were then calculated to silicon.

4. PHOSPHORUS

The usual method of precipitation as ammonium phosphomolybdate was employed, and the phosphorus estimated by comparing the volume of the precipitate with that produced by treating a standard steel in the same way.

5. MANGANESE

The sodium bismuthate method was used.

6. COPPER

Ten to 20 g of metal were dissolved in a slight excess of hydrochloric or sulphuric acid, and hydrogen sulphide passed into the hot solution until all the copper was precipitated. The precipitate was filtered off, and, after washing the paper carrying it, was transferred to a porcelain crucible, and the whole ignited until all the carbon was burned off. A little potassium bisulphate was added and the copper oxide brought into solution by fusion, following by leaching with water and filtration. The solution was compared with a standard solution colorimetrically, either by the ammonia or ferrocyanide method, or by both.

7. MAGNESIUM

Ten to 20 g of metal were dissolved in aqua regia, the solution evaporated to dryness, and dehydrated. The residue was dissolved in 1:1 HCl and silica removed by filtration. The iron was extracted by the ether method. After the removal of the iron, hydrogen sulphide was passed through the solution (acidified with acetic acid) to precipitate copper, etc. Manganese and residual iron were removed from the filtrate by bromine and ammonia and the magnesium was precipitated as magnesium-ammonium phosphate. The accuracy of the above procedure was checked by running duplicates to which small amounts of a magnesium salt had been added.

8. NICKEL AND COBALT

The solution of 10 g in $\text{HNO}_3 + \text{HCl}$ was evaporated to dryness, dehydrated, taken up with HCl of 1.1 specific gravity, filtered, the filtrate evaporated to a small volume, and the iron removed by the ether method. Copper was precipitated with hydrogen sulphide, and the iron and manganese in the filtrate were precipitated by ammonia and bromine. The filtrate was acidified with acetic acid, and nickel and cobalt were precipitated as sulphides from the boiling solution. The two metals were either weighed as oxides or deposited electrolytically from ammoniacal solution, the two methods giving concordant results. The oxides (or metals) were dissolved in hydrochloric acid, the solution was neutralized, and finally made acid with acetic acid and the cobalt precipitated as $\text{K}_3\text{Co}(\text{NO}_2)_6$. After filtering and igniting this precipitate at a low temperature, the cobalt was dissolved, reprecipitated with hydrogen sulphide, and finally weighed as CoSO_4 . The nickel was determined by the dimethylglyoxime method in the filtrate from the cobalt. The sum of these determinations checked very closely with the total nickel + cobalt found directly.

VIII. SUMMARY

Methods have been developed for producing laboratory samples of iron-carbon alloys, of a very high degree of purity; sources of contamination of melts and means of eliminating them have been described; a method for producing magnesia of a satisfactory degree of purity for making crucibles to be used in work of this kind has been developed; a procedure for making small ingots, which are sound and free from blowholes, without the use of deoxidizers has been worked out. A series of iron-carbon alloys containing 99.96 per cent of the two elements has been prepared, to serve as a basis for the redetermination of the iron-carbon equilibrium diagram.

WASHINGTON, November 11, 1915.

BIBLIOGRAPHY

PREPARATION OF ELECTROLYTIC IRON

- LENZ, J. f. prakt. Chem., **108**, p. 438; 1869.
CAILLETET, Comptes Rendus, **80**, p. 319; 1875.
ROBERTS-AUSTEN, J. Iron and Steel Inst., **1**, p. 71; 1887.
ARNOLD AND HADFIELD, Stahl u. Eisen, p. 526; 1894.
HICKS AND O'SHEA, Electrician, p. 843; 1895.
WINTELER, Z. f. Elektrochem., **4**, p. 338; 1898.
HABER, Z. f. Elektrochem., **4**, p. 410; 1898.
ABEGG, Stahl u. Eisen, p. 736; 1901 (II).
SKRABAL, Z. f. Elektrochem., **10**, p. 749; 1904.
C. F. BURGESS AND HAMBUECHEN, Trans. Amer. Electrochem. Soc., **5**, p. 201; 1904.
MAXIMOWITSCH, Z. f. Elektrochem., **11**, p. 52; 1905.
RYSS AND BOGOMOLNY, Z. f. Elektrochem., **12**, p. 697; 1906.
COWPER-COWLES, C. A., **3**, p. 1371; **5**, p. 3013; **8**, p. 3648.
C. F. BURGESS AND WATTS, Trans. Amer. Electrochem. Soc., **9**, p. 229; 1906.
AMBERG, Z. f. Elektrochem., **14**, p. 326; 1908.
KERN, Trans. Amer. Electrochem. Soc., **3**, p. 103; 1908.
MÜLLER, Metallurgie, **6**, p. 145; 1909 (contains bibliography).
PFAFF, Z. f. Elektrochem., **16**, p. 217; 1910.
TUCKER AND SCHRAMM, J. Ind. and Eng. Chem., **2**, p. 237; 1910.
WATTS AND LI, Trans. Amer. Electrochem. Soc., **25**, p. 529; 1914.
YENSEN, University of Illinois Bulletin No. 72, 1914.