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PREPARATION OF HIGH-PURITY IRON

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ABSTRACT

Iron of high purity, in the form of 1-lb ingots, has been prepared by reducing purified iron oxide to sponge iron, melting the sponge iron, and remelting under hydrogen and in vacuo. The ingots were examined by spectroscopic and chemical methods for the presence of 55 possible impurities; the number of impurities that could be identified in individual ingots ranges from 6 to 9. The total of impurities in each ingot in most cases is less than 0.010 percent. The major impurities are nonmetallic, chiefly oxygen and sulfur, with traces of carbon, phosphorus, nitrogen, and hydrogen. Copper is the only metallic impurity in seven of the ingots; others contain small amounts of silicon and occasional traces of aluminum or beryllium from the refractories.

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I. INTRODUCTION

The preparation of metals of the utmost possible purity has ever been a matter of interest to metallurgists, primarily because the fundamental properties of a metal can be ascertained with accuracy only by direct determinations made on samples that are free from significant amounts of impurities. What constitutes a significant amount of an impurity depends both on the nature of the impurity and on the metal which it contaminates, as well as on the purpose for which the metal is to be used. It has been known for a long time that some properties of certain metals, for example, the ductility of gold and the electric conductivity of copper, are seriously affected by the presence of very small amounts of impurities. Consequently, a high degree of purity with respect to particular impurities has been demanded in such metals when they are to be used for special purposes. On the other hand, mechanical properties such as strength, hardness, and load-carrying capacity, for which the common metals are valued, are

less sensitive to the presence of impurities; in fact these properties in iron are improved by increasing the amount of certain constituents, such as carbon, which are normally present in small amounts as "impurities." For these reasons, the definition of "purity" in metals has varied with the metal and with the intended use; in general the requirements of purity were more rigid for the noble and precious metals than for the common ones. However, in recent years the preparation of common metals such as aluminum and zinc, in higher states of purity than had been previously obtained, has shown that certain properties of common metals may be materially affected by amounts of impurities so small that they were formerly considered insignificant. Furthermore, intensive investigation of the magnetic properties of iron revealed outstanding examples of the significance of minute amounts, 0.001 or 0.002 percent, of impurities such as carbon, oxygen, and sulfur. Such observations naturally lead to speculation regarding the effect of small amounts of these and other impurities on the properties of iron, and the degree of purity with respect to various constituents which must be attained to permit measurements of properties that will not be significantly affected by the inevitably remaining traces of contaminating substances.

Attempts to prepare metallic iron of the utmost possible purity have been made from time to time throughout the past one hundred years, but the elimination of impurities with which iron is associated in its ores and the avoidance of contamination from other sources are matters of extreme difficulty. Previous investigations of the preparation of high-purity iron and the varying properties that have been observed in the products of these investigations were reviewed in previous publications [1, 2],¹ the preparation of which constituted the first phase of the current investigation. A critical review of the previous work led to the conclusion that the best possibilities for the preparation of iron of very high purity lay in the chemical methods, that is, in the preparation of a purified compound of iron and its subsequent conversion to metallic iron. Experimental work indicated that recrystallization of ferric nitrate offered promise for the production of a purified compound of iron, and a description of the preparation of a quantity of recrystallized nitrate and the conversion of this material to high-purity iron oxide has been published [3]. The present paper describes attempts to convert the purified iron oxide to metallic iron of equally high or superior purity.

II. MATERIALS

Four lots of purified iron oxide were available, representing two purification processes applied to each of two lots of ferric nitrate. The only impurities that could be identified by spectroscopic and chemical methods are listed in table 1. The presence of silicon, aluminum, calcium, magnesium, and copper was revealed by spectrochemical examination, and the numerical values for the silicon contents were determined by chemical analysis. Sulfur and phosphorus could not be detected in any of the oxide samples, using chemical methods that were sensitive to 0.001 percent of sulfur and 0.0005 percent of phosphorus. Examination of the spectra failed to reveal the presence of sensitive lines of any of the following elements: Antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, cerium, chro-

¹ Numbers in brackets indicate the literature references at the end of this paper.

mium, cobalt, columbium, gallium, germanium, gold, hafnium, indium, iridium, lead, lithium, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, potassium, rhodium, ruthenium, scandium, silver, sodium, strontium, tantalum, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, yttrium, zinc, and zirconium.

TABLE 1.—*Impurities in purified iron oxide*

Elements	Oxide			
	A	B	C	D
Silicon.....	0.016%.....	0.009%.....	0.006%.....	0.005%.....
Aluminum.....	Trace.....	Faint trace.....	Faint trace.....	Faint trace.....
Calcium.....	do.....	do.....	do.....	Do.....
Magnesium.....	do.....	do.....	do.....	Do.....
Copper.....	Faint trace.....	do.....	do.....	Do.....

III. CONVERSION OF PURIFIED OXIDE TO SPONGE IRON

Iron oxide may be converted to metallic iron by several means. In commercial operations iron ores are reduced with carbon or carbonaceous compounds, but the iron thus produced is always contaminated by carbon. Metallic reducing agents—calcium [4], aluminum [5], zinc [6], and sodium [7]—have been suggested for the production of carbon-free iron, but these reagents also are open to the objection of contamination of the iron by the products of deoxidation and by the excess of reducing agent that is necessary to insure complete reduction. Reduction by hydrogen offers the least possibility of contaminating the reduced iron, either by the products of the reduction reaction or by an excess of the reducing agent. The product of the reduction reaction is water vapor which is removed by the stream of hydrogen. Contamination by an excess of the reducing agent is minimized because the solubility of hydrogen in iron is only 0.0005 percent [8, 9] at 1,000° C and atmospheric pressure, and is even less at lower temperatures.

The reduction of iron oxide by hydrogen begins at low temperatures, about 370° C according to Tammann and Nikitin [10] and only a little above 300° C according to Kamura [11], but at these temperatures the reaction proceeds slowly and is difficult to carry to completion. The rate of the reaction increases with increasing temperature until an optimum temperature for rapid and complete reduction is reached, between 500° and 600° C [11, 12, 13]. With increasing temperature above the optimum range there is an increasing tendency to sinter the surface of the particles of partially reduced oxide, which hinders the penetration of hydrogen to the center of the particles and thus increases the time required to complete the reduction.

Another factor to be considered, in addition to the speed and completeness of the reduction, is that iron reduced at low temperatures is pyrophoric, that is, subject to spontaneous reoxidation upon exposure to the air. Pyrophoric iron results from reduction at any temperature below 530° C, according to Tammann and Nikitin [10], and even up to 710° C, according to Smits and Wallagh [14]; but the tendency towards pyrophoric behavior can be overcome by heating the reduced iron to still higher temperatures.

The procedure adopted for the reduction of iron oxide to sponge iron in the present investigation comprised two steps, (a) maintenance

of the material at about 500° C until the reduction was practically complete, followed by (b) raising the temperature to about 1,000° C to sinter the surface of the particles and destroy the tendency towards pyrophoricity. This procedure is similar to the one successfully employed on a small scale by Baxter and Hoover [13] in their classic determination of the atomic weight of iron.

The hydrogen used in the reduction was a commercial product, compressed in cylinders and containing up to 0.5 percent of oxygen as the principal impurity. The hydrogen was purified by passing it through Ascarite to remove any hydrogen sulfide and carbon dioxide that might be present, then through platinized silica at 750° C to convert the oxygen to water, which was absorbed by anhydrous magnesium perchlorate.

Preliminary experiments indicated that a charge of iron oxide could be reduced, sintered, and cooled in the furnace within 7 hours. Under these conditions of operation, only about 10 percent of the hydrogen was utilized in the reduction of the iron oxide, the remainder serving merely to flush the reaction product (water vapor) out of the furnace and thus permit the reaction to go to completion within the allotted time. However, the use of two furnaces in series, with provision for repurifying the gas between furnaces, doubled both the rate of production of sponge iron and the efficiency of the utilization of hydrogen. The reaction chamber in each furnace was the central portion, about 40 cm in length, of a fused silica tube 5 cm in inside diameter. Each reaction chamber was lined with a sheet of electrolytic iron to protect the iron oxide and sponge iron from contamination during the reduction. The inlet end of each silica tube was sealed to the hydrogen supply line; the outlet ends were closed by removable stoppers, to facilitate charging and discharging the furnaces. Perforated porcelain disks near the ends of the silica tubes served as radiation shields, and the extreme ends of the tubes were further protected by water cooling.

The schedule of operation of the apparatus shown in figure 1 was as follows: Reduction furnaces *A* and *B* were each loaded with 300 g of iron oxide, equivalent to 200 g of sponge iron, contained in a boat that was made from a thin sheet of electrolytic iron. The apparatus was flushed with purified hydrogen from one of two cylinders connected in parallel, the furnaces were heated to 500° C, and the rate of flow of the hydrogen was adjusted to about 2 liters per minute. These conditions were maintained for about 3½ hours, until the reduction was practically completed as indicated by the disappearance of condensed water in the outlet tubes of the furnaces. The hydrogen flow was then reduced to about 300 ml per minute; the temperature was raised to 1,000° C and maintained there for 1 hour, after which the power was cut off, the rate of flow of the hydrogen was further reduced to 100 ml or less per minute, the split furnaces were opened, and the silica tubes and contents were cooled with streams of air from electric fans. The catalyst furnace in the hydrogen purification train was then allowed to cool, after which the hydrogen flow was stopped. The following morning the condensate was drained from the water and vapor traps located between the two furnaces, the boats were removed from the furnaces, the sponge iron was transferred to storage containers, the boats were refilled with iron oxide and replaced in the furnaces, and another run was started.

The sponge iron was easily removed from the boats and was readily granulated, but the boats frequently stuck to the electrolytic-iron sleeve. The oxygen content of the sponge iron was not determined, in fact an oxygen-free sponge iron was not desired because, as described in the ensuing paragraphs, the presence of FeO was found to facilitate the removal of silica. Examination of the sponge iron indicated that no new impurities had been introduced and that the impurities other than oxygen were the same as in the four lots of iron oxide. However, because of the decrease in weight that accompanied the reduction, the concentration of each impurity in the sponge iron was about one-third greater than it had been in the oxide. Silicon or silica was still the principal impurity, ranging from 0.024 percent of Si in sponge iron *A* to 0.008 percent of Si in sponge iron *D*.

IV. REMOVAL OF SILICA FROM SPONGE IRON

Two processes, (a) sintering and (b) melting, were considered for converting the sponge iron to solid metal. Sintering at temperatures below the melting point of iron is, perhaps, less apt to introduce new impurities but offers no possibility of reducing the content of impurities already present in the sponge iron. On the other hand, previous work in this laboratory has demonstrated the feasibility of melting, without contamination, high-purity metals, such as platinum and its alloys, which melt at temperatures appreciably higher than the melting point of iron. Furthermore, there was a possibility that the content of silica, and perhaps of other impurities in the sponge iron, could be reduced by slagging during a melting operation, as was indicated by the work of Adcock and Bristow [15]. Also, a dense, coherent structure is more readily obtained by melting than by sintering. For these reasons a melting process was preferred for the conversion of the sponge iron to solid metal.

The sponge iron, prepared as described in the preceding section of this report, was granular and bulky, with an apparent density of about 2 g/cm³. This material was compressed under approximately 2,000 lb/in.² in a steel mold, to form briquettes 4 cm in diameter and 2 to 3 cm thick, with densities slightly less than 6 g/cm³. Briquetted sponge iron was melted in alumina, magnesia, and beryllia crucibles to determine the relative merits of the three refractories with respect to contamination of the melt as well as to elimination of silica. The alumina was purified oxide prepared commercially for the production of metallic aluminum and contained sodium salts as its principal impurities. The magnesia and beryllia were of "chemically pure" grades. Crucibles were formed by the methods of pressing or tamping that had been previously used for the preparation of small crucibles [16], but difficulty was encountered in preparing crucibles, in the larger sizes desired in this work, with satisfactorily smooth walls and bottoms. Better crucibles were obtained by a slip-casting process, based on the results of Turner [17] and of Partridge and Lait [18]. The slip-cast crucibles had excellent inner surfaces, and, consequently, there was a minimum possibility of contaminating the melt with particles or flakes of the refractory. Ingots melted in slip-cast crucibles were smooth surfaced and seldom required cleaning, in contrast to the rough-surfaced, refractory-contaminated ingots from the tamped crucibles. For these reasons, slip-cast crucibles were used in most of this work, particularly in the later stages.

Spectrochemical examination of ingots melted in alumina and magnesia revealed contamination from the refractories either by inclusions of minute particles of refractory oxides or by partial reduction of the refractory and solution of the reduced metal in the molten iron. However, ingots melted in beryllia, in these preliminary experiments, were not contaminated. From the point of view of possible contamination of high-purity iron by the refractory, beryllia was preferable to magnesia or alumina.

Beryllia was also found to be preferable to the other two in the removal of silica during melting. The silicon content of some sponge iron was reduced from 0.027 to 0.007 percent by melting in a beryllia crucible, but similar melts in magnesia and alumina retained respectively 0.010 and 0.016 percent of silicon. These figures were further reduced by holding the metal quietly molten for long periods of time, but the silicon was never eliminated completely in any of these simple melts, even in beryllia crucibles. The removal of silicon (or silica) apparently was accomplished through the formation of an iron silicate slag that was absorbed by the crucible. There was little if any evidence of slag on the upper surface of the melt, but the inner walls of the crucible were noticeably discolored. If the silicon content of the sponge iron could be reduced 50 percent or more by slagging in the presence of a small amount of oxygen or FeO, it appeared probable that further reduction of the silicon content could be obtained if more slag, that is, more FeO, were present. Accordingly, mixtures of sponge iron and purified iron oxide were briquetted, melted in beryllia crucibles, and held quietly molten for 30 minutes. A melt without added oxide contained 0.004 percent of silicon; addition of 0.5 and 1.0 g of iron oxide to 100 g of sponge iron decreased the silicon content progressively, and a minimum silicon content of about 0.001 percent was obtained with an addition of 2 percent by weight of iron oxide. Larger amounts of iron oxide, up to 8 percent by weight of the sponge iron, showed no further improvement, and incorporation of 2 percent of iron oxide in the briquettes was therefore adopted as regular practice in melting the sponge iron.

Considerable difficulty was encountered in melting the briquetted sponge iron in vacuo in a high-frequency induction furnace, because of the poor conductivity of the briquettes and their high shrinkage during melting. The usual result was that the lower portions of the charge melted, but the upper portions only softened enough to adhere to the crucible, and remained suspended above and not in contact with the pool of the molten metal. Melting of the bridged material required the application of so much power that the pool of molten metal was heated to a high temperature, and there was danger of failure of the crucible and loss of the melt. These difficulties were not encountered when the sponge iron was melted in a resistance furnace of the Arsem type, heated by a graphite spiral resistor. In this furnace a crucible full of briquettes melted smoothly and completely, without overheating any portion of the charge. The atmosphere in this furnace was chiefly carbon monoxide, at a pressure of 3 or 4 mm of mercury. There was a possibility, therefore, of contaminating the iron by absorption of carbon or CO; but this possibility appeared to be slight, particularly in view of the high oxygen contents of the briquettes and of the molten iron.

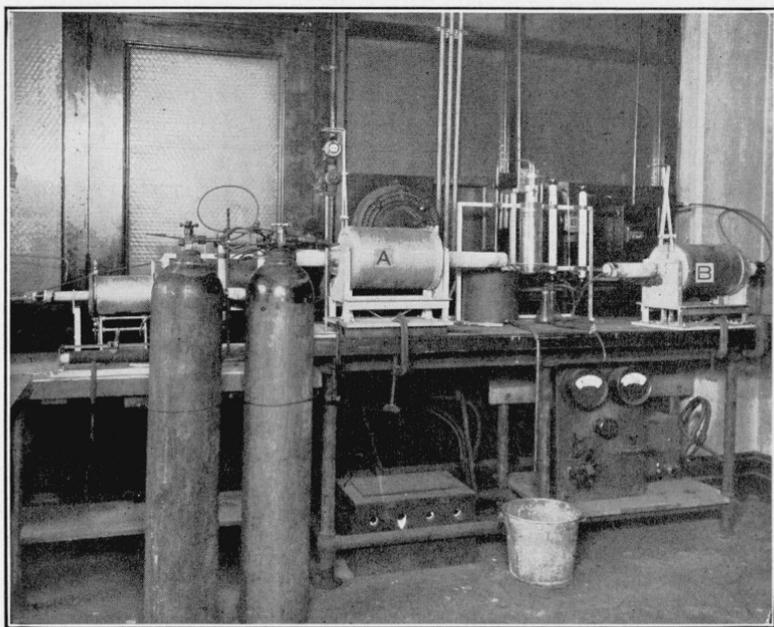


FIGURE 1.—Apparatus for the reduction of iron oxide to sponge iron.

Hydrogen from the cylinders is passed successively through a purification train, over iron oxide in furnace A, through a water trap and drying train, and over a second portion of iron oxide in furnace B.

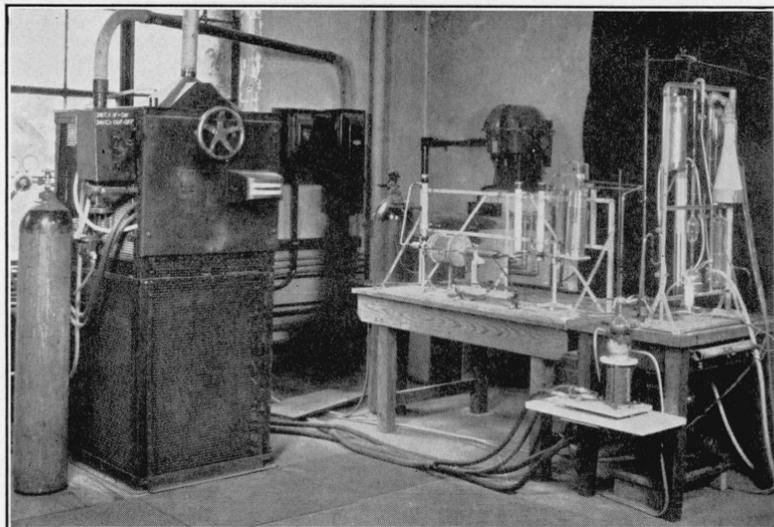


FIGURE 2.—Apparatus for melting oxygen-rich ingots under hydrogen and in vacuo.

The furnace is heated by a high-frequency induction coil and is connected with a source of purified hydrogen or with vacuum pumps.

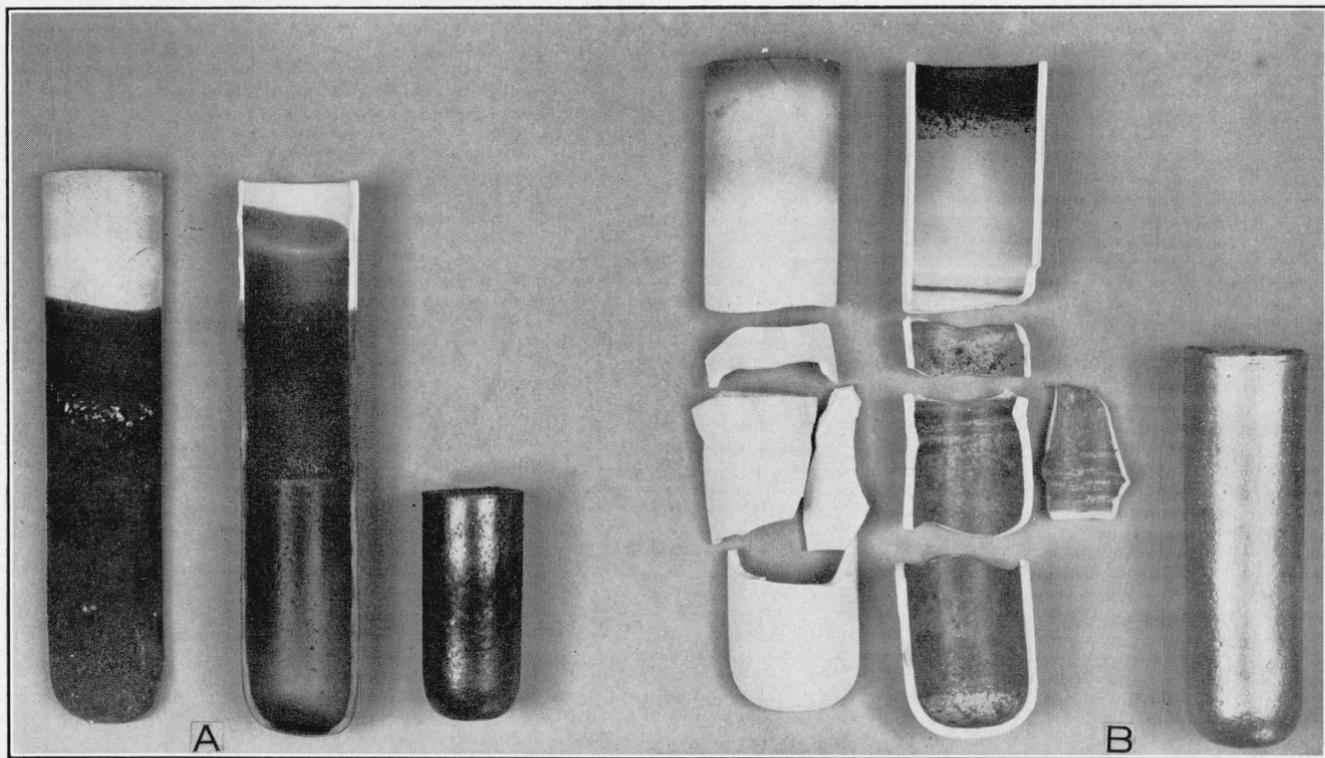


FIGURE 3.—Steps in the conversion of sponge iron to high-purity solid iron.

A, ingot prepared by melting a crucible full of briquetted sponge iron with added iron oxide to facilitate removal of silica by slagging; *B*, ingot prepared by remelting, under hydrogen and in vacuo, two ingots from operation *A*.

The melts of briquetted sponge iron, with 2 percent of iron oxide to assist in removal of silica, therefore were made in the Arsem furnace. Beryllia crucibles approximately 3 cm in inside diameter by 18 cm long were used. The crucible, supported in a graphite shell, was filled with approximately 350 g of briquetted sponge iron. The briquettes were melted slowly and maintained molten for 30 minutes. The power was then shut off and the ingot allowed to cool in the furnace. Ingots so prepared contained about 0.2 percent of oxygen. The appearance of the ingot, the shrinkage of the sponge iron on melting as indicated by the relative volumes of ingot and crucible, and the discoloration of the slip-cast crucible by absorption of iron oxide and silica, are illustrated at the left of figure 3.

V. REMOVAL OF OXYGEN FROM MELTED SPONGE IRON

The logical procedure to deoxidize the oxygen-rich ingots was to hold the iron molten under hydrogen for a sufficient length of time, with subsequent evacuation of the molten metal to remove dissolved hydrogen. Heating by induction was desirable for these operations because the deoxidation and subsequent evacuation would be expedited by stirring the molten metal, and further, because the crucible remains colder than the metal, which decreases the possibility of contamination of the melt by the refractory.

In contrast to the sponge-iron briquettes, the oxygen-rich ingots were readily melted in an induction furnace, particularly in an evacuated furnace. Melting under hydrogen required more power and was more susceptible of bridging of the charge, because of cooling of the exposed top of the ingot. If the cold ingot fits too snugly in the crucible, the latter may be cracked by thermal expansion of the ingot before it melts, but this difficulty was avoided by using a slightly larger crucible, with an internal diameter about 3 mm greater than that of the ingot.

The apparatus used for the final deoxidation of the oxygen-rich ingots is shown in figure 2. The hydrogen purification train, mounted on the table at the left of the furnace, was similar to the one used in the reduction of iron oxide to sponge iron. It contained a tube of Ascarite, to remove hydrogen sulfide and carbon dioxide, a platinized silica catalyst maintained at 750° C, a tube of anhydrous magnesium perchlorate to remove water, and a trap cooled with a mixture of solid carbon dioxide, chloroform, and acetone, to remove the last of the water vapor. The furnace chamber was a silica tube, 40 cm long and 6 cm in inside diameter, mounted vertically in an induction coil that was 7.5 cm in diameter. The upper end of the furnace tube was sealed with Picene wax to a Pyrex dome equipped with an inlet connection to the hydrogen purification train and with outlet connections to a vent and to the vacuum pumps. A small silica tube was attached to the inlet tube, inside the glass dome, to conduct the incoming stream of hydrogen directly onto the surface of the melt. The apparatus for evacuating the furnace, shown in figure 2 behind and to the right of the induction furnace, consisted of a rotary oil pump, mercury diffusion pump, McLeod gage, and a trap to prevent back diffusion of mercury vapor.

The procedure of melting, deoxidation, and evacuation was as follows: Two oxygen-rich ingots, weighing about 300 g each, were placed in a beryllia crucible, the second ingot being inverted on the

first, so that the flat tops of the two ingots were in contact and the rounded bottom of the second ingot was uppermost and free from contact with the crucible walls. This arrangement materially reduced the danger of bridging. The crucible was packed for about three-fourths of its length in granular beryllia in a slip-cast shell that fitted loosely in the silica furnace tube. The glass dome was sealed in place, the furnace was evacuated, and power was applied to the induction coil slowly, to minimize the thermal shock to the crucible. The initial 3 kva of power was increased by 1 kva each 5 minutes until the first signs of melting were noted, usually at about 10 kva. At this point the power was increased to about 20 kva to hasten the melting and to avoid bridging. As soon as melting was completed, the power was reduced to about 6 kva, just sufficient to keep the iron molten.

In the meantime the flow of hydrogen through the purification train and out the vent had been adjusted to 2.5 liters per minute. When the iron was completely molten, the furnace was disconnected from the vacuum pumps and hydrogen was introduced slowly into the evacuated furnace. When the pressure in the furnace reached 1 atmosphere, indicated by the escape of hydrogen through a safety trap, the exit connection of the furnace was turned to permit release of the hydrogen to the vent, and the inlet connection was opened to divert the full stream of hydrogen into the furnace. The power input was adjusted until the temperature of the metal was slightly higher than the melting point, just enough to render the metal fluid and inductively stirred, to facilitate the reduction. Overheating of the metal was avoided because of the attendant possibility of reduction of the refractory at high temperatures and consequent contamination of the melt. About 12 kva was required to maintain 600 g of iron molten under hydrogen, in contrast to the 6 kva that kept the same metal molten in vacuo.

The iron was maintained in the molten condition under hydrogen for periods that varied from 45 minutes for a 600-g melt to 60 minutes for an 800-g melt. Most of the oxygen was removed from the iron rapidly, as was indicated by the formation of drops of water on the cooler portions of the furnace tube and in the outlet tube. These drops disappeared within a few minutes and thereafter there was no more condensation. Preliminary experiments had indicated that 30 minutes' exposure to hydrogen under these conditions reduced the oxygen content of a 600-g melt from about 0.2 percent to 0.001 or 0.002 percent, which values were not improved by longer treatments. Treatment for 45 minutes therefore should insure complete deoxidation with a reasonable margin of safety.

At the expiration of the allotted time for the deoxidation, the hydrogen inlet to the furnace was closed and the furnace outlet was connected to the vacuum pumps. During evacuation of the furnace the temperature of the molten metal was maintained approximately constant by gradually decreasing the power input, to 5 or 6 kva. When the pressure in the furnace was reduced to 0.02 mm or less, the power was cut off and the metal was allowed to solidify and cool to room temperature in the evacuated furnace.

Ingots prepared in the manner just described had clean, bright surfaces in contrast to the dark-colored, oxidized surfaces of the oxygen-rich ingots. As is shown in figure 3, the final ingots required practi-

cally no cleaning or grinding after removal from the crucible. The inner surface of the slip-cast beryllia crucible was slightly discolored by iron oxide, presumably absorbed during the first melting of the oxygen-rich ingots. The black band at the top of the crucible was a metallic deposit, apparently of vaporized iron.

VI. HIGH-PURITY IRON

Nineteen ingots, with an average weight of about 1 lb each, were prepared. The top surface of each ingot was flat and solid, but the interior contained a concealed pipe that frequently extended for half the length of the ingot as is shown in figure 4. The structures were coarsely crystalline, and some evidence of porosity was noted, particularly in the vicinity of the lower portions of the pipes. Better structures would have been obtained from chill-cast ingots, but equipment for melting and casting in vacuo was not available at this time.

In preparing the specimens shown in figure 4, the ingots were sawed in two and one-half was ground flat and smooth on a surface grinder. The parallel striations running lengthwise of each ingot are evidence that the surface grinding work-hardened the metal to an appreciable depth. The striations persisted through several repolishings and etchings.

The data from analyses of the ingots are summarized in table 2. Copper, silicon, beryllium, and aluminum were determined by spectrochemical methods; carbon, sulfur, and phosphorus by chemical methods; and oxygen, nitrogen, and hydrogen by vacuum-fusion methods. Because many of these determinations approach the limits of uncertainty of available analytical methods, brief descriptions of the procedures by means of which these numerical values were obtained are given in an appendix to this report.

The data of table 2 show that the elimination of metallic impurities has been quite successful, except for copper. This element was practically unaffected by the purification process to which the material was subjected, and the copper contents of the final ingots are essentially the same as those of the iron oxide and sponge iron. A trace of copper is present in all of the ingots, but in seven of them copper is the only metallic impurity whose presence could be detected. The calibration of the spectrochemical procedure did not permit a more precise statement of the copper contents than that they are all less than 0.002 percent. Direct determinations of the copper content of each ingot, by chemical methods, has not been practicable because of the amount of sample material consumed in the multiple determinations necessary to establish with precision copper contents of this magnitude. Four direct determinations of copper have been made, two on samples of the sponge iron from which the ingots were made and two on composite samples of the ingots themselves. The results of these four determinations range from 0.0018 to 0.0006 percent of copper, which indicates that the figure 0.002 percent is an adequate and in some cases perhaps a liberal estimate of the amount of copper.

TABLE 2.—Composition of ingots of high-purity iron

Element	Ingot number ¹																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Cu ² -----	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Si ² -----	.001	.001	.003	.001	.003	.001	.001	.001	nil	nil	nil	.002	nil	.002	nil	nil	<.001	nil	nil
Be ² -----	<.001	<.001	<.001	nil	nil	<.001	nil												
Al ² -----	nil	nil	nil	nil	<.001	nil	<.001	nil	nil	nil	nil								
C-----	<.001	.001	.001	.001	.001	<.001	<.001	nil	nil	nil	nil	<.001	<.001	.001	.001	nil	nil	.001	<.001
S-----	.002 ₂	.002 ₂	.002 ₂	.001 ₀	.001 ₀	.001 ₂	.002 ₁	.001 ₀	.002 ₂	.002 ₂	.001 ₂	.001 ₂	.002 ₄	.001 ₁	.001 ₂	.004 ₁	.002 ₂	.001 ₁	.002 ₂
P-----		<.0005															<.0005		
O ₂ -----	.001 ₃	.000 ₂	.000 ₂	.003 ₂	.004 ₀	.004 ₂	.002 ₀	.003 ₂	.003 ₂	.001 ₀	.004 ₂	.001 ₄	.004 ₀	.002 ₀	.001 ₀	.001 ₂	.003 ₀	.003 ₄	.004 ₂
N ₂ -----	.000 ₁	.000 ₂	.000 ₄	.000 ₄	.000 ₂	.000 ₂	.000 ₁	.000 ₀	.000 ₀	.000 ₁	.000 ₂	.000 ₂	.000 ₂	.000 ₂	.000 ₀	.000 ₁	.000 ₃	.000 ₁	.000 ₂
H ₂ -----	.000 ₁	.000 ₂	.000 ₁	.000 ₂	.000 ₁	.000 ₁	.000 ₁	.000 ₂	.000 ₁	.000 ₁	.000 ₂	.000 ₁	.000 ₂	.000 ₂	.000 ₂				
Total of identified impurities	<.009 ₂	<.008 ₂	<.011 ₁	<.009 ₂	<.012 ₀	<.011 ₇	<.008 ₀	<.008 ₀	<.009 ₂	<.008 ₄	<.009 ₂	<.008 ₂	<.010 ₂	<.008 ₀	<.008 ₂	<.009 ₀	<.010 ₂	<.008 ₄	<.010 ₂

¹ Ingots 1 to 6, inclusive, were made from sponge iron from oxide A; ingots 7 to 12, inclusive, from oxide B; ingots 13 to 15 from oxide C; and ingots 16 to 19 from oxide D.

² The arc spectrum of each ingot was examined for the presence of sensitive lines of 49 elements. Determinations of Cu, Si, Be, and Al are recorded above, the expression "nil" meaning that the amount of the impurity if present at all, was less than the sensitivity of the analytical method. None of the following 45 elements could be identified in any of the ingots: Ag, As, Au, B, Ba, Bi, Ca, Cb, Cd, Ce, Co, Cr, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Se, Sn, Sr, Ta, Th, Ti Tl, U, V, W, Y, Zn, and Zr.

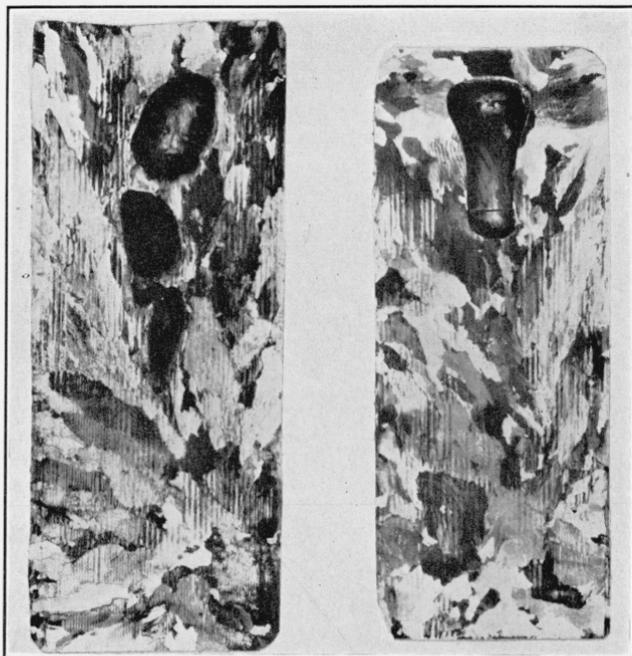


FIGURE 4.—*Macrosections of two ingots of high-purity iron, showing the concealed pipes and the coarsely crystalline structure.*

Etched with 1-percent nital.

Silicon was the chief impurity in each of the lots of purified iron oxide (see table 1) and sponge iron, but the silicon contents of the ingots are, in general, satisfactorily low. As much as 0.024 percent of silicon was present in some of the sponge iron, but the maximum silicon content in any of the ingots is only 0.003 percent, and in 8 of the ingots silicon could not be detected. The silicon contents of ingots 1 to 6, inclusive, that were prepared from the high-silicon sponge iron *A* are perhaps a trifle higher than those of other groups; but, in general, the uniformity of the silicon contents of the ingots, irrespective of the silicon contents of the sponge iron from which they were made, attests the effectiveness of the removal of silicon by slagging. The slagging operation likewise was efficient in removing the "dust elements," calcium and magnesium, that were present in or on the purified oxides.

Traces of beryllium in four of the ingots undoubtedly represent contamination from the beryllia crucibles. The trace of aluminum that was detected in two ingots probably also originated in the refractory. It has not been possible to determine whether these traces of beryllium and aluminum represent random inclusions or material in solution in the iron. Inclusions of BeO or Al_2O_3 have not been identified in the course of microscopic examinations.

Nonmetallic elements, particularly oxygen and sulfur, constitute the bulk of the impurities in most of the ingots. The oxygen contents range from 0.0003 to 0.0045 percent. The lower values are close approximations of the irreducible minimum content of oxygen in iron, as determined by the vacuum-fusion method. The higher values presumably represent incomplete deoxidation in the final stages because, in attempting to avoid overheating of the molten metal with attendant danger of contamination from the refractories, the temperature may have dropped enough to cause the molten metal to become viscous, and thereby to retard the progress of the deoxidation. The oxygen contents presumably represent FeO ; oxide inclusions have not been identified in microscopic studies, and there is no correlation between the oxygen and silicon contents.

Sulfur contents ranging from 0.001 to 0.0041 percent cause this impurity to rank second to oxygen. The presence of sulfur could not be detected in the purified oxide; its presence in the final ingots represents contamination during melting, probably from refractories, although the beryllia was precalcined and washed with acid to remove sulfur compounds. The presence of 0.001 percent or less of carbon in 11 of the ingots likewise is ascribed to contamination from the crucibles, which were fired in an Arsem furnace. Because the carbon determinations consumed large quantities of material, and further, because a uniform carbon content was indicated in 11 determinations, the carbon contents of the other eight ingots were not determined.

The remaining impurities—nitrogen, hydrogen, and phosphorus, whose presence was determined in some or all of the ingots—are present only in amounts that approach the limits of uncertainty of the analytical methods. The nitrogen contents range from undetectable amounts to a maximum of 0.0006 percent; hydrogen in all cases is either 0.0001 or 0.0002 percent; phosphorus was not expected to be a serious contaminant in the iron, and analyses of two ingots showed that only a faint trace of phosphorus was present. Additional deter-

minations of phosphorus were not made because of the quantity of sample material required.

The totals of identified impurities, out of the 55 elements that were sought, as listed in table 2, include the maximum values for all determinations that were reported as "less than" a maximum value. It was further assumed that the carbon and phosphorus contents of each ingot were, respectively, 0.001 and 0.0005 percent. These totals of identified impurities range from 0.0083 percent for ingot 18 to 0.0129 percent for ingot 5, with 13 of the 19 ingots having contents of less than 0.010 percent of total impurities. Such figures are comparable with the best available analyses of other pure irons [15, 19], and the compositions given in table 2 are noteworthy in the limited number of impurities whose presence could be detected. This is particularly true of metallic impurities; in seven of the ingots, only one metallic impurity, copper, could be identified.

The material remaining after analysis of the ingots will be used for determinations of the properties of high-purity iron and to observe the effect on these properties of the variations in composition of the different ingots.

VII. REFERENCES

- [1] H. E. Cleaves and J. G. Thompson, *The Metal—Iron* (McGraw-Hill Book Co., Inc., New York, N. Y., 1935).
- [2] J. G. Thompson and H. E. Cleaves, *J. Research NBS* **16**, 105 (1936), RP860.
- [3] H. E. Cleaves and J. G. Thompson, *J. Research NBS* **18**, 595 (1937), RP996.
- [4] F. M. Perkin and L. Pratt, *Trans. Faraday Soc.* **3**, 179 (1908).
- [5] H. Goldschmidt, *Z. Elektrochem.* **4**, 494 (1898).
- [6] J. A. Poumarede, *Compt. rend.* **29**, 518 (1849).
- [7] A. Hiorth, *Norwegian Patent* 18,750 (1908).
- [8] C. J. Smithells, *Gases and Metals* (John Wiley & Sons, Inc., New York, N. Y., 1937).
- [9] L. Luckemeyer-Hasse and H. Schenck, *Tech. Mitt. Krupp* **1**, 121 (1933); *Arch. Eisenhüttenw.* **6**, 209 (1932-33).
- [10] G. Tammann and N. Nikitin, *Z. anorg. allgem. Chem.* **135**, 201 (1924).
- [11] H. Kamura, *J. Iron Steel Inst.* **112**, 278 (1925).
- [12] K. Hoffmann, *Z. angew. Chem.* **38**, 715 (1925).
- [13] G. P. Baxter and C. R. Hoover, *J. Am. Chem. Soc.* **34**, 1657 (1912).
- [14] A. Smits and G. Wallagh, *Rec. trav. chim.* **44**, 130 (1925).
- [15] F. Adcock and C. H. Bristow, *Proc. Roy. Soc. (London)* **153**, 172 (1935-36)
- [16] W. H. Swanger and F. R. Caldwell, *BS J. Research* **6**, 1131 (1931), RP327.
- [17] D. Turner, *Trans. Ceram. Soc.* **33**, 33 (1933-34).
- [18] J. H. Partridge and J. R. Lait, *J. Soc. Glass Tech.* **20**, 200 (1936).
- [19] C. Wells, R. A. Ackley, and R. F. Mehl, *Trans. Am. Soc. Metals* **24**, 46 (1936).

VIII. APPENDIX. ANALYTICAL METHODS EMPLOYED IN THE ANALYSIS OF HIGH-PURITY IRON

1. Spectrochemical Analysis

By Bourdon F. Scribner

The samples of high-purity iron consisted of rods approximately $\frac{1}{4}$ in. in diameter and 1 in. long, sawed from the ingots and rounded by filing. Tests showed that a few of the rods were contaminated on the surface, probably by handling, and, to avoid errors, all samples were cleaned in dilute acid. The rods were used directly as electrodes for spectrochemical analysis in which the spectra were excited by a direct current arc of 6 amperes. The spectra were photographed in the region 2450 to 5000 Å, using a Bausch & Lomb large Littrow spectrograph and a stigmatic concave grating spectrograph built in this laboratory. The dispersion obtained in the spectrograms was 5 Å (or less) per millimeter, so that the complex iron spectrum was sufficiently well resolved for the identification of impurities.

The photographed spectra were examined on a micrometer comparator for the sensitive lines of the following elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cb, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Se, Si, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. The sensitivity of the test is indicated by data, for several elements, obtained chiefly from National Bureau of Standards Standard Samples of iron and steel. Concentrations, in percentage by weight, which have been detected with certainty are as follows:

Al	0.0005	Ge	0.0002	Si	0.001
Co	0.001	Mn	0.0005	Sn	0.0003
Cr	0.0001	Mo	0.001	Ti	0.0005
Cu	0.0001	Ni	0.001	V	0.0005

Although the sensitivity of the test is known to be well below 0.001 percent for a number of elements, the quantitative interpretation of spectrochemical data for concentrations of the order of 0.001 percent frequently is uncertain because of a lack of reference standards. Estimations of the concentration of aluminum, copper, and silicon in the iron samples were made by comparison with the spectra of available standards.

2. Determinations of Carbon, Sulfur, Phosphorus, and Copper

By Harry A. Bright

The carbon content of high-purity iron was determined by direct combustion in oxygen. The porcelain combustion tube ($\frac{3}{8}$ -in. internal diameter) was maintained at 1,050° to 1,100° C. The oxygen was passed through a preheater and through a tower containing Ascarite (asbestos impregnated with sodium hydroxide) and Anhydron (anhydrous magnesium perchlorate) before entering the combustion tube. The purification train at the exit end of the combustion tube consisted of a U-tube filled with platinized silica-gel maintained at 450° C., and a tube containing ironized asbestos and Anhydron. The absorbing tubes were glass-stoppered 4-in. U-tubes, containing 20- to 30-mesh Ascarite and a layer of Anhydron, about $\frac{1}{2}$ in. deep, at the exit end. A platinum boat approximately 4 in. by $\frac{3}{4}$ in. by $\frac{1}{2}$ in., and a well-burned cover of nickel were used. The bedding material was R. R. Alundum, specially prepared for carbon determinations. The boat and contents were heated in oxygen at 1,050° to 1,100° C. until the blank correction for a 10-minute run, including removal and reinsertion of the boat in the furnace, was uniform and less than 0.2 mg of carbon dioxide.

Three grams of iron was placed on the bedding material so that the particles were in intimate contact. The covered boat was placed in the hot combustion tube and preheated for $1\frac{1}{2}$ to 2 minutes. Oxygen was admitted at a rate sufficient to maintain a flow of 300 to 350 ml per minute through the exit end of the tube during the combustion period. When combustion was complete, the flow of oxygen was reduced to about 150 ml per minute and maintained at this rate for about 10 minutes. The absorption tube filled with oxygen was disconnected, placed in the balance, and weighed, using the same procedure and time intervals as in the blank determination.

The percentage of carbon was calculated from the increase in weight of the absorbing tube minus the weight of carbon dioxide obtained in the "blank" run. Before burning another sample of iron, the sequence of preburning the boat, cover, and alundum, to obtain a small and uniform "blank," was repeated.

Sulfur in high-purity iron was determined by the evolution method. A 5-g sample was placed in a 500-ml Florence flask which had a ground-glass stopper with an inlet thistle tube and an outlet tube to the absorption vessel. The latter was a 25- by 200-mm test tube containing 50 ml of water and 20 ml of an ammoniacal solution of cadmium chloride.² 100 ml of diluted hydrochloric acid (1+1) was added to the sample in the Florence flask, and a slow stream of hydrogen was passed through the inlet tube and through the solution. The flask was heated gently until the sample dissolved, after which the solution was boiled for 3 to 4 minutes. The delivery tube was disconnected, and the ammoniacal cadmium chloride solution was filtered through a small, close-textured paper without

² Ammoniacal cadmium chloride: Dissolve 10 g in 400 ml of water and add 600 ml of ammonium hydroxide (sp gr 0.90).

washing. The paper was transferred to a beaker containing 150 ml of water, 2 to 3 ml of starch solution,³ and 25 ml of diluted hydrochloric acid (1+1) were added, and the solution was titrated immediately, with 0.03 N iodate solution,⁴ to a permanent blue color. The receiver (test tube) was washed with the titrated solution. If the color was bleached, it was restored by a further addition of iodate solution. The percentage of sulfur was calculated after deducting the volume of iodate solution used in a "blank" determination.

The phosphorus content of high-purity iron was determined in 3- to 4-g samples by the conventional alkali-molybdate method.

For the determination of copper, a 25-g sample was placed in an 800-ml beaker, 300 ml of diluted sulfuric acid (1+5) was added, and the mixture was heated gently until the action ceased. The solution was diluted to 500 to 600 ml with water, heated to boiling, and a stream of hydrogen sulfide was passed in for 1½ to 2 hours. After it stood for about 30 minutes, the solution was filtered through a close-textured paper, which was washed with diluted sulfuric acid (1+99) that had been saturated with hydrogen sulfide.

The residue and paper were transferred to a 25-ml tall-form porcelain crucible, ignited at a temperature below 550° C, and fused with 2 g of alkali pyrosulfate. The cooled fusion was dissolved in 15 ml of diluted sulfuric acid (1+2), and the solution was diluted with water to a volume of 70 to 75 ml.⁵ 2 ml of nitric acid (sp gr 1.42) was added, and the copper was determined by electrolysis, with small (1 to 1.25 g) platinum electrodes made from 50 to 60 mesh gauze. Electrolysis, in a beaker covered with split watch glasses, was continued for 15 to 17 hours (overnight), with a current of about 0.1 ampere at 2 to 2.2 volts. When the deposition was completed and with current still flowing through the solution, the cathode was quickly removed and washed with a stream of water to remove electrolyte. The cathode was then dipped in alcohol, the excess alcohol was shaken off, and the cathode was dried for 1 minute at 100° C. After being cooled in a desiccator, it was weighed,⁶ preferably on a microbalance.

The results of some of the electrolytic determinations of copper in high-purity irons were confirmed by colorimetric determinations⁷ made on 30 to 50-g samples, using a solution of 0.1 g of copper per liter for the comparison. The electrolytic method was preferred, however, because of susceptibility of the colorimetric determination to interference by minute amounts of iron.

3. Determination of Oxygen, Nitrogen, and Hydrogen

By Vernon C. F. Holm

Oxygen, nitrogen, and hydrogen in samples of high-purity iron were determined by the vacuum-fusion method. The procedure was essentially as described by Vacher and Jordan,⁸ although some modifications in the apparatus have been made. Mullite radiation screens have been replaced by slotted graphite screens, as described by Chipman and Fontana.⁹ To facilitate removal of the gases from the furnace, the outlet connections have been increased in diameter and decreased in length, and a three-stage high-capacity diffusion pump has been installed. Determinations were made by observing the pressure in a closed system before and after absorption of one of the components of the gaseous mixture.

³ Starch solution: Suspend 5 g of soluble starch in 25 ml of water, add to 500 ml of boiling water, cool, add a cool solution of 5 g of sodium hydroxide in 50 ml of water, then add 5 g of potassium iodide and mix thoroughly.

⁴ Iodate solution: Dissolve 1.12 g of potassium iodate and 12 g of potassium iodide in 1,000 ml of water. Standardize by means of sodium oxalate through potassium permanganate and sodium thiosulphate. (See Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, John Wiley & Sons, Inc., New York, N. Y., p. 242, (1931).)

⁵ If a small residue of siliceous material remained, the solution was filtered.

⁶ Traces of silver, if present in the sample, will accompany the copper. Likewise, if molybdenum and tin are present, a small proportion of these elements may be deposited. None of these three elements was detected in the samples of high-purity iron.

⁷ Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, John Wiley & Sons, Inc., New York, N. Y., p. 274 (1931).

⁸ BS J. Research 7, 375 (1931) RP346.

⁹ Ind. Eng. Chem., Anal. Ed., 7, 391 (1935).

Samples usually weighed about 12 g, although samples as small as 9 g and as large as 18 g were used. The samples were prepared for analysis by lightly grinding the entire surface, rinsing with ether, and drying in the air until the ether had evaporated. The samples were then placed in the sample holder and evacuation of the apparatus was begun. Redeterminations of the gas content of completely outgassed residues from previous vacuum-fusion determinations have shown that oxygen and nitrogen equivalent, respectively, to about 0.0009 and 0.0002 percent by weight, are present in a surface film on samples thus prepared for vacuum-fusion analyses. Consequently, these corrections for surface gases, in addition to the customary blank correction for the apparatus, were applied to determinations of the gas content of high-purity irons.

The determinations of oxygen and nitrogen in these samples are believed to be accurate to within ± 0.001 percent. The maximum amount of hydrogen determined in any of the samples of high-purity iron was 0.0002 percent.

WASHINGTON, March 28, 1939.