

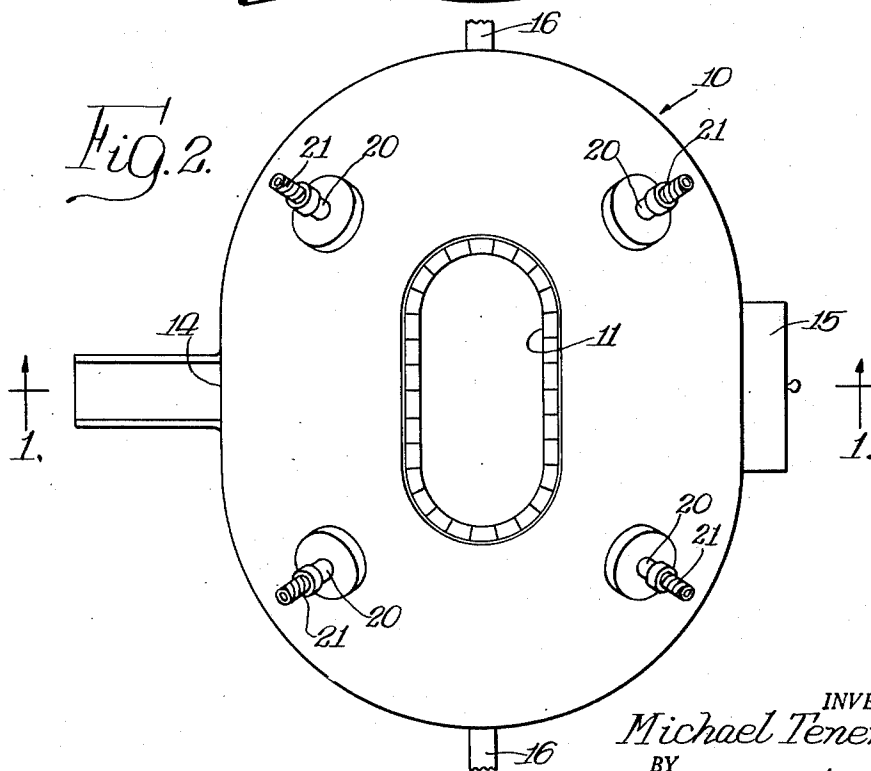
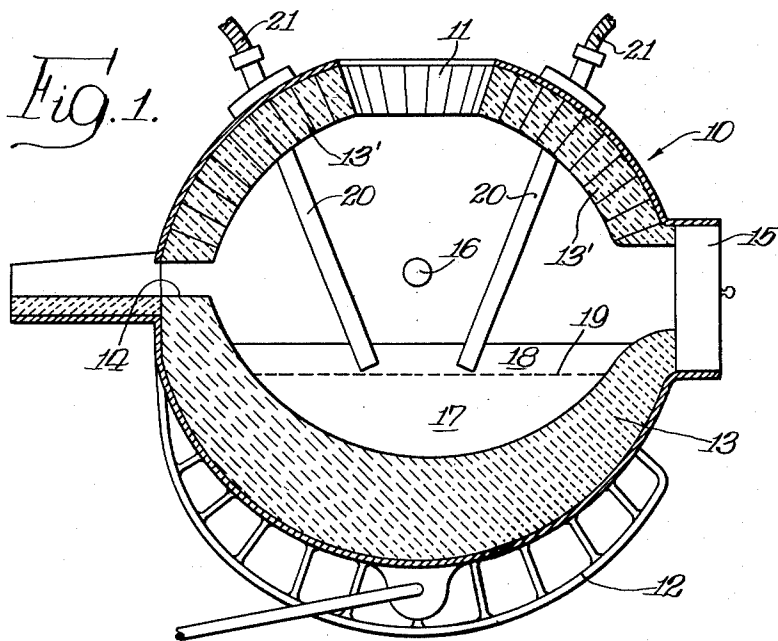
Feb. 9, 1954

M. TENENBAUM
STEELMAKING PROCESS

2,668,759

Filed May 22, 1952

2 Sheets-Sheet 1



INVENTOR.
Michael Tenenbaum,
BY
Davis, Luchey, Hibben & Noyes
Attys

Feb. 9, 1954

M. TENENBAUM
STEELMAKING PROCESS

2,668,759

Filed May 22, 1952

2 Sheets-Sheet 2

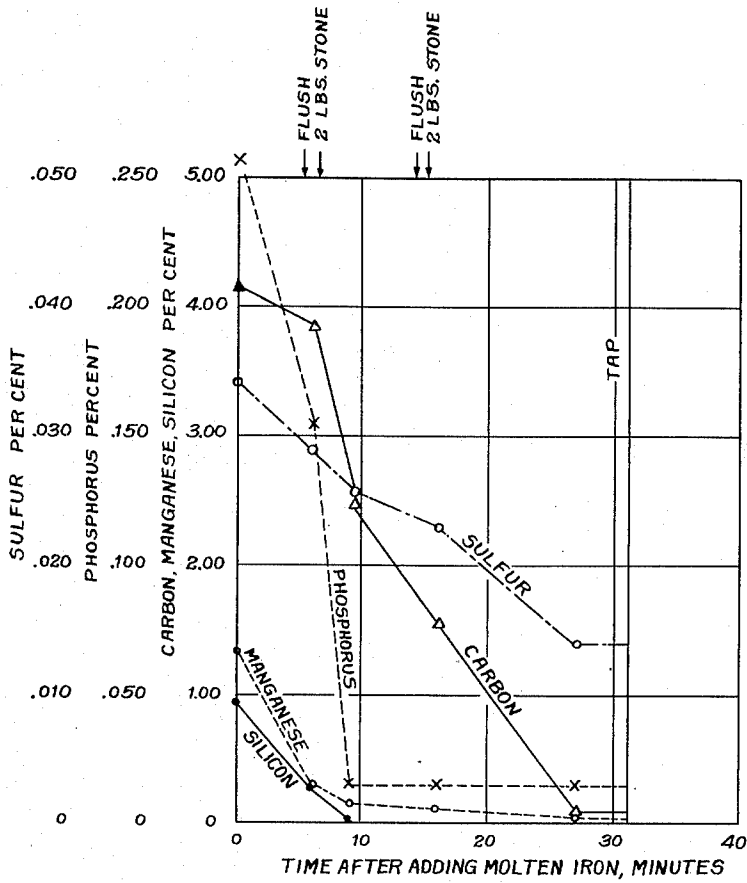


Fig. 3.

INVENTOR,
Michael Tenenbaum
BY
Davis, Lueckey, Hibben & Noyes
Attys.

UNITED STATES PATENT OFFICE

2,668,759

STEELMAKING PROCESS

Michael Tenenbaum, Flossmoor, Ill., assignor to
Inland Steel Company, Chicago, Ill., a corpora-
tion of Delaware

Application May 22, 1952, Serial No. 289,353

6 Claims. (Cl. 75-52)

1

This application is a continuation-in-part of my copending application Serial No. 109,475, filed August 10, 1949, now abandoned.

This invention relates broadly to a process for the manufacture of steel and more particularly to improvements in the refining stages of such a process.

Although various steelmaking processes differ with respect to equipment, raw materials, and end products, the general objectives of the several processes are quite similar. In general, steelmaking processes are intended (1) to obtain and maintain the entire metallic charge in a molten state and (2) to refine the liquid metal by the removal of impurities therefrom and to make additions thereto, if necessary, in order to meet a desired chemical analysis. The distinguishing features of the various processes relate primarily to the methods employed to obtain and maintain a completely molten charge and the extent to which the primary refining reactions can be accomplished.

The source of heat for a steelmaking process may vary dependent largely upon the nature of the raw materials charged to the process. For example, if the initial charge is largely composed of molten iron, it is possible to utilize the internal heat evolved during the refining reactions in order to maintain the necessary temperature level. If, however, a substantial part or all of the initial metallic charge is cold, an external source of heat must usually be employed to obtain and maintain the desired molten condition. In the latter case, the required heat input may be obtained electrically or by combustion of a suitable fuel in or prior to reaching the refining zone.

Except for the production of premium grades of steel and other special purposes, the use of electric sources of heat in steelmaking processes has not been warranted economically. The use of various liquid and gaseous fuels as a source of heat necessitates the provision of large and expensive combustion equipment to conserve heat and to attain the desired temperatures. Furthermore, such fuels usually contain detrimental amounts of sulfur some of which may be introduced into the steel during the refining operation.

The prior art steelmaking processes which have relied on the exothermic heat of reaction of the refining reactions to supply the heat requirements of the process usually involve passing or blowing air through a bath of molten iron to effect oxidation of the impurities, e. g. the Bessemer process. Generally, such processes have

2

been severely limited by the fact that the removal of phosphorus to low levels is difficult or impossible and low phosphorus content steels cannot readily be produced. In addition, the passage of air through the metal bath results in the introduction of nitrogen into the steel product in amounts which are excessive for most uses of steel.

The refining of molten iron has as its objective the removal, in the form of gases or slag-forming compounds, of such impurities as carbon, phosphorus, sulfur, silicon, and manganese. The critical elements are carbon, phosphorus, and sulfur, and the adaptability or attractiveness of a steelmaking process is largely determined by the degree to which the removal of these three critical elements can be controlled. Carbon is eliminated by combination with oxygen to form oxides of carbon which are removed from the refining zone as gases. Phosphorus elimination is accomplished by combination with oxygen followed by reaction of the resultant oxide with lime or similar basic oxide, such as magnesia or manganese oxide, in the slag. Sulfur is eliminated largely by reaction with lime or a similar basic oxide in the slag. Manganese and silicon are also eliminated by oxidation and subsequent incorporation of the resultant compounds in the slag. Thus, it will be seen that the primary refining actions involve oxidation and slag-formation, and under proper conditions sufficient heat may be evolved as a result of such reactions to supply the heat requirements of the refining process.

In addition to the aforementioned impurities, mention must also be made of nitrogen and hydrogen since under certain conditions that may exist during the manufacture of steel, these elements may be introduced into the steel in excessive or detrimental amounts. It is now recognized that the control of nitrogen and hydrogen in the finished steel product is an important factor determining the selection of a steelmaking process and the permissible uses of the finished steel.

The elimination of phosphorus can be accomplished only under basic oxidizing conditions. Thus, the major steelmaking processes in use today that are capable of removing phosphorus are the basic electric, the basic Bessemer, and the basic open hearth. However, each of these processes is characterized by certain limitations.

The basic electric furnace is expensive to operate, has a relatively low production rate, and usually results in a product containing relatively

3

large amounts of nitrogen because of the action of the electric arc.

In the conventional basic Bessemer process the iron charge must contain more than about 1.5% phosphorus in order to provide sufficient heat for the process. Furthermore, in the basic Bessemer process phosphorus cannot be effectively removed until substantially all of the carbon has been eliminated. Accordingly, the production of low phosphorus-high carbon steels by the conventional basic Bessemer process is not practical. Moreover, consistent elimination of sulfur to low levels cannot generally be accomplished in the conventional basic Bessemer process, and the air-blowing technique results in undesirably high nitrogen content of the final product, as hereinbefore mentioned.

Although the basic open hearth process accounts for the major tonnage of steel produced in the United States, this process too has serious limitations. In this process, the controlling reaction rates are determined in part by diffusion mechanisms in a heterogeneous system and consequently the rate of refining and the production rate are relatively slow. The conventional basic open hearth process requires an elaborate external heating and regenerating system in order to melt the charge, carry out the necessary refining reactions, and attain a satisfactory tapping temperature. Although phosphorus elimination is under control in the basic open hearth process, in most instances the iron charged must have a phosphorus content not greater than about 0.4% in order to make all types of steel. In addition, only moderate amounts of sulfur can usually be eliminated in the basic open hearth process, and sulfur removal is further complicated by the fact mentioned above that many of the fuels employed in the external heating system contain considerable sulfur which seriously diminishes the net extent of sulfur removal from the metal.

Accordingly, a primary object of my invention is to provide a novel steelmaking process which overcomes the aforementioned difficulties of the known processes and which is adapted for use in the production of steel of both high and low carbon content from molten iron of wide analysis range.

A further object of the invention is to provide a novel steelmaking process capable of producing a steel having generally the character of an open hearth steel but at a lower cost of production.

Another object of my invention is to provide a steelmaking process capable of refining a relatively high phosphorus content iron to produce a steel of low phosphorus content while at the same time avoiding the introduction of excessive nitrogen into the steel.

Another object of the invention is to provide a steelmaking process capable of producing a low phosphorus-high carbon steel from molten iron of high or low phosphorus content.

A further object of the invention is to provide a novel steelmaking process in which substantially the total heat requirements of the process are supplied by the exothermic heat of reaction during the refining steps while at the same time avoiding introduction of nitrogen into the steel.

A still further object of the invention is to provide a novel steelmaking process characterized by the rapid development of a basic highly oxidized slag at a relatively early stage of the refining period.

An additional object of the invention is to pro-

4

vide a steelmaking process in which sulfur is removed more effectively and to a lower level than in the known basic oxidizing processes.

Still another object of the invention is to provide a steelmaking process in which no external source of heat is required to effect refining of the metal, the requisite heat being supplied by the exothermic refining reactions, and in which one or more slags may be removed.

Other objects and advantages of the invention will become evident from the subsequent detailed description of the invention and the accompanying drawings in which:

Fig. 1 is a diagrammatic sectional view taken along the lines 1—1 of Fig. 2 and showing the general characteristics of one type of apparatus suitable for use in practicing my invention;

Fig. 2 is a plan view of the apparatus shown in Fig. 1; and

Fig. 3 is a graphical presentation of certain experimental data illustrating the rate and extent of removal of impurities in my process.

Referring now to the drawings, the process of my invention may be conducted in a reaction or refining zone defined by a generally elliptical vessel 10 having a roof opening 11 at the upper portion thereof and mounted for tilting or rocking movement on a pair of curved supports or rockers 12 adapted to coact with rollers or the like. The vessel 10, which may be of steel construction, is provided at its bottom with a monolithic basic refractory lining 13 such as burnt dolomite, magnesite, or the like. The upper portions of the vessel 10 are lined with refractory brick, indicated at 13', which may be either basic or acidic in character. A suitable tap hole or port 14 is provided at one side of the vessel 10 for the withdrawal of slag during the course of the steelmaking process, and a charging door 15 is disposed at the opposite side of the vessel. Although only one slag-removal opening is shown in the drawings, it will be understood that a plurality of such outlets may be provided, if desired. A supplementary external heat source, such as a pair of burners 16, may be provided for maintaining the refractory temperature between successive heats and for making refractory repairs.

In Fig. 1 the refining vessel 10 is illustrated as containing a charge or bath of molten metal 17 and a supernatant layer of slag 18, the interface between the molten metal and the slag being indicated diagrammatically by a broken line, as at 19. It will be apparent from the subsequent detailed discussion of the operation of my process that under actual operating conditions the metal bath may be in a turbulent or agitated state such that there is no distinct separation of the metal and slag phases into layers. For purposes hereinafter described, the upper portion of the refining vessel 10 is provided with a plurality of adjustable injection conduits or lances 20 extending through the walls of the vessel into the refining zone. The outer end of each of the lances 20 is connected by a suitable coupling or other connecting device to a flexible hose 21 which communicates with a source of oxygen under pressure. Each of the lances is arranged to permit adjustment of its position and the extent to which it projects into the vessel 10 dependent upon the liquid level therein.

It will be understood that Figs. 1 and 2 of the drawings comprise merely a diagrammatic or schematic illustration showing the general characteristics of the equipment suitable for carrying out the steelmaking process of my invention. In

other words, the drawing is intended merely to facilitate a better understanding of the process steps and principles involved and it is not intended to imply that the specific vessel structure and arrangement shown would constitute the only appropriate engineering design. As will be seen from the subsequent detailed description of the process, a suitable apparatus for carrying out my process would necessarily include the general features shown in the drawings or their equivalent. For example, the reaction or refining vessel for practicing my process must have a basic refractory lining, an opening for the removal of fumes and gases, means for introducing oxygen into the liquid bath, suitable outlet means for the discharge of slag and finished metal, and, preferably, means for tilting the vessel to facilitate such discharge.

In carrying out my process, molten pig iron may be introduced into the vessel 10 through the door 15 along with a basic slag-forming material, such as limestone, and an iron oxide-bearing material such as iron ore, sinter, or mill scale. The limestone and iron oxide-bearing material may be charged simultaneously with or immediately following the liquid metal, but I prefer to introduce the solid limestone and iron oxide-bearing material to the refining zone first and then pour the molten iron over the solid raw materials in order to facilitate mixing and distribution of the reactants whereby to hasten the refining reactions. Although limestone is the preferred basic slag-forming material, other basic oxides or substances capable of yielding basic oxides may also be used, e. g. magnesia, manganese oxide, or prepared slag mixtures. In order to avoid excessive cooling of the molten iron charged, it is desirable that the refractory lining 13 be preheated to an elevated temperature by means of the burners 16 or that the vessel be charged while still hot from a previous heat.

Immediately following the charging of the molten metal to the vessel 10, an oxidizing gas containing a relatively high concentration of free oxygen is introduced through the lances 20. The positions of the lances 20 are adjusted, within any possible limitations of operation and design factors, to inject the oxidizing gas substantially at the metal surface whereby to effect direct contact of free oxygen with the molten metal and thereby obtain rapid transfer of oxygen to the metal. In most instances I prefer that the outlet ends of the lances extend below the surface of the slag in the refining zone in order to inject free oxygen substantially at or adjacent to the surface of the metal layer. However, it is also contemplated that the outlet ends of the lances 23 can be positioned slightly above the slag surface in the refining zone, the distance of the lances above the surface being such that the flow of oxidizing gas through the lances will blow aside or displace the supernatant slag layer so that free oxygen is directly contacted with the molten metal.

Although I prefer to employ commercial grade undiluted free oxygen, it is also within the scope of the invention to utilize oxygen diluted with other gases such as air or inert gases. In such cases, it is preferred that the oxidizing gas stream contain a relatively high concentration of free oxygen, and by the term "high oxygen content gas" as used hereinafter I mean a gas having an oxygen content in excess of the normal oxygen content of air, i. e. greater than about 21% by volume.

An important feature of my invention is the

fact that the heat requirements of the process are supplied substantially entirely by the exothermic heat of reaction evolved during the refining of the molten iron. Inasmuch as the process does not contemplate or require an external source of heat during the refining steps, it is important that the introduction of oxygen to the refining zone be started as soon as possible after the vessel has been charged in order to maintain the necessary temperature level.

As the molten iron is thus contacted with free oxygen, or with oxygen in the iron oxide charged initially as a raw material, a large part of the silicon, manganese, and phosphorus in the iron is rapidly oxidized to form the corresponding oxides together with simultaneous oxidation of a small but definite portion of the carbon. The oxides of silicon, manganese, phosphorus, and iron together with lime obtained from the charged limestone are then incorporated in an oxidized slag containing most of the phosphorus and substantially all of the silicon and manganese. If desired, most of the slag may be withdrawn at this point, preferably by tilting the vessel 10 to discharge the slag through the tap hole 14.

One of the important novel aspects of my process resides in the formation of the slag. In the conventional basic open hearth process, the initial slag formed during the melting-down period has a high iron oxide content and consequently may be quite corrosive to the burnt dolomite or magnesia in the banks and bottom of the furnace with the result that calcium oxide and magnesium oxide may be dissolved from the furnace refractories. In the usual open hearth practice, no significant amount of limestone rises into the slag layer until most of the charged solid scrap is melted and the lime boil period is well under way. Obviously, therefore, the solution of lime in the slag formed after the hot metal addition is seriously delayed by the period of time required to effect complete melting-down of the scrap charge. In addition, it has been found that in the conventional basic open hearth process individual lumps of partly calcined limestone that rise into the early slag tend to become coated with a hard protective shell composed predominantly of dicalcium silicate. This refractory shell or coating acts to retard solution of the limestone in the slag and also prevents rapid penetration of fluxing slag constituents into the limestone lumps. As a result, the rate at which lime dissolves in and becomes an active constituent of early open hearth slags is relatively slow. In general, substantial solution of lime is not accomplished until furnace additions of fluorspar and ore have been made. Such additions appear to have a general softening or dissolving effect on the limestone lumps whereby the lumps finally lose their identity in a heavy mushy moderately basic slag.

In the process of the present invention a large proportion of the charged limestone rises almost immediately to the surface of the molten metal. At first, the limestone is largely uncalcined and unpenetrated by slag constituents, and the oxides of silicon, manganese, and phosphorus formed as described above, together with iron oxide and lime form the early slag. However, turbulent intermixing of the slag, iron oxide, and metal phases is obtained promptly and localized high temperatures and a highly oxidizing atmosphere are developed upon the introduction of gaseous oxygen to the bath with the result that rapid

calcination of the limestone and rapid solution of the resultant lime in the slag are realized. The amount of lime that is dissolved in the early stage of the process may be regulated merely by charging controlled amounts of limestone. In this way the fluidity of the early slag as well as its phosphorus content can also be regulated.

In the steelmaking art the customary method of expressing the basicity of the fluid body of slag is by some form of the ratio (often referred to as V-ratio or V-value) of lime to silica. When this ratio is above a certain more or less critical level, usually around 2, elimination of sulfur occurs, phosphorus removal becomes more complete, and the possibility of phosphorus reversion from the slag to the metal is reduced. Accordingly, an important characteristic of the present process is the fact that the process permits the early development of a slag having a ratio of weight per cent lime to weight per cent silica of at least about 1.5, and preferably at least about 2.0. In the conventional basic open hearth process the development of a slag of this degree of basicity is not ordinarily possible before a substantial degree of carbon elimination has taken place, for example, not before the carbon content of the metal has been reduced below about 1.25%. In the present process, on the other hand, I am able to effect rapid and substantial entry of phosphorus into the slag and at the same time I am able to obtain a slag having a sufficient degree of basicity before the carbon content of the metal is reduced to a low level, e. g. at least before carbon falls below about 1%, and in most instances before carbon falls below about 2%, to retain practically all of the eliminated phosphorus throughout the balance of the refining period. In this manner reversion of phosphorus from the slag to the metal is minimized. In general, by means of the process of the present invention, a slag may be readily obtained having a weight per cent lime to silica ratio of at least about 1.5 while the carbon content of the metal bath is substantially above about 1.0%, and preferably I obtain a weight per cent lime to silica ratio of at least about 2.0 while the carbon content of the metal is substantially above about 2.0%.

It will be understood that in order to obtain rapid formation of a highly basic slag as specified above it is necessary to charge limestone or other slag-forming reactant to the process in a predetermined amount sufficient to yield the specified high V-ratio when the lime content thereof has been dissolved in the slag phase. Obviously, the particular quantity of slag-forming reactant to be charged in any given instance will depend on a number of factors such as the lime content of the slag-forming reactant, the silicon content of the iron, the slag removal practice to be followed, and the nature of the furnace lining. However, one skilled in the steelmaking art, having knowledge of the sequence of operations to be employed, the composition of the raw materials, and the type of furnace, will have no difficulty in determining how much slag-forming reactant must be charged in any given heat in order to obtain the desired V-ratio in the slag.

Thus, it will be seen that my process is characterized by the rapid development of a highly basic highly oxidized slag at a very early stage in the refining period while carbon is still at a relatively high level. The rapid formation of such a slag is attributable (1) to the greater availability of the limestone to the slag phase as a result of the physical mixing effect and turbulence created in

the bath, and (2) to the more rapid rate of solution of lime in the slag phase as a result of the localized high temperatures and highly oxidizing atmosphere which are developed upon direct contacting of free oxygen with the metal in the manner described. In addition, the combined effects of turbulence in the bath and the local high temperature conditions tend to minimize the formation of and to otherwise overcome the detrimental effects of the aforementioned dicalcium silicate shell formation around the individual lumps of limestone, thereby further facilitating the rapid solution of lime in the slag phase.

The desired turbulent intermixing of the slag, iron oxide, and metal phases in my process is obtained as the result of two interrelated effects. First of all, the injection of oxygen-containing gas downwardly below the surface of the bath causes a certain degree of local agitation due to the mechanical effect of the gas injection. However, the injection of oxygen in this manner also induces prompt carbon-oxygen reactions in the bath with the resultant evolution of gaseous oxidation products in abundant amounts. It is characteristic of the carbon-oxygen reaction that carbon oxide gas forms at the sides and at the bottom of the bath and the gases escape upwardly throughout the bath so that there is widespread turbulence and intermixing thereby greatly enhancing the immediate mechanical turbulence and agitation which is a direct result of the mode of oxygen injection. In other words, the highly turbulent condition of the bath which is characteristic of my process is due (1) to the direct, and primarily local, effect of oxygen injection per se, and (2) to the evolution of gaseous oxides of carbon which produces widespread turbulence throughout the entire bath. As a result of the high degree of turbulence, the lime charged to the process becomes rapidly available for solution in the slag phase and the desired rapid solution is further promoted by the localized high reaction temperatures and by the highly oxidizing atmosphere which prevail in the regions of oxygen injection.

The high degree of bath turbulence which is essential to my process requires early elimination of a certain proportion of carbon from the metal simultaneously with the rapid removal of phosphorus to the maximum amount usually given in common steel specifications so as to realize the combined benefits of mechanical agitation due to the mode of oxygen injection and the violent mixing effect produced by the evolution of gaseous oxides of carbon. For example, my process accomplishes early elimination of phosphorus from the metal to not more than about .04% and simultaneous elimination of at least about .4% carbon but leaving at least about 1% carbon in the metal which is above the usually desired final carbon content. The resultant high degree of bath turbulence facilitates the desired rapid solution of lime in the slag, as hereinbefore described, so that my process does not depend on relatively slow diffusion mechanisms. On the contrary, the refining reaction rates in my process are fast and the refining period is relatively short, e. g. from about ½ to about 3 hours as compared with the much longer period of time required to produce a comparable product by the conventional open hearth process. Moreover, as a result of the injection of oxygen and the highly turbulent condition of the bath in my process, an operating temperature of not less

than about 2500° F. is quickly developed so that the process takes advantage of the benefits of high temperature in promoting rapid solution of lime in the slag and in insuring rapid phosphorus removal. As hereinbefore described, the rapidity of phosphorus removal and basic slag formation in my process may be defined more specifically by the fact that obtainment of a weight per cent ratio of lime to silica in the slag of at least about 1.5 and elimination of phosphorus to substantially the extent required in the final product are both accomplished while the carbon content of the metal is not less than about 1%. In the preferred operation, a lime:silica ratio of at least about 2.0 and the required degree of phosphorus elimination are both accomplished while the carbon content of the metal is not less than about 2%.

Several very important results follow as a consequence of the very rapid formation of a highly basic highly oxidized slag. In the first place, the rapid development of a highly oxidized basic slag is responsible for the elimination and retention of substantially all the phosphorus while the carbon content of the metal is still at a relatively high level. For example, as will be seen hereinafter in connection with the specific example, effective phosphorus removal to a very low level may be accomplished while the carbon content of the metal is substantially greater than 2%. In the conventional basic open hearth process the development of a slag of sufficient basicity to retain the eliminated phosphorus requires a substantially greater period of time because of the much slower rate of solution of lime in the slag. As a result it is tedious and sometimes difficult to produce a high carbon-low phosphorus steel by basic open hearth techniques. Another important result of the rapid development of a basic slag in my process resides in the unusually effective degree of sulfur elimination as compared with the conventional basic open hearth process. A further advantage obtained as a result of the rapid development of a basic slag in the present process is found in the greatly reduced corrosive action on the refractory lining of the refining vessel. Following the addition of molten iron in the conventional basic open hearth process an early slag is formed which is high in silica content and is therefore corrosive to the basic lining. Consequently, there is a substantial period of time in the conventional basic open hearth process during which an early acid slag is in contact with the refractory lining of the vessel. In my process the rapid development of the basic slag substantially eliminates this source of corrosive action on the refractory lining.

The elimination of most of the phosphorus, substantially all of the silicon and manganese, and a part of the carbon having been completed during the development of the aforementioned basic slag, the introduction of oxygen through the lances is then continued until the carbon content of the metal is reduced to the desired final extent. The gaseous oxides which are formed during carbon oxidation are discharged through the roof opening 11. Additional limestone may be charged to the vessel at an intermediate stage of the process, if desired, in order to facilitate the removal of sulfur and some residual phosphorus. Because of the rapid solution of lime in the presence of oxygen, as described above, a relatively rapid reaction of sulfur with lime occurs. Elimination of sulfur in this manner is also favored by the absence of sulfur in the refining zone atmosphere.

When a desired final carbon content has been reached, the refining reactions involving the removal of silicon, phosphorus, sulfur, and carbon have been completed to the desired extent and a suitable tapping temperature obtained. The molten steel may then be removed by tapping through a discharge outlet, such as the tap hole 14. Before such removal the metal composition may be adjusted, if desired, by additions according to techniques well known in the art.

In most instances, a single phosphorus-containing slag will be withdrawn at an intermediate stage of the refining process. Of course, at the conclusion of the refining operation a tapping slag will usually be removed at the time the finished steel is discharged from the vessel. However, it is a further important feature of my invention that in the event that the phosphorus content of the raw materials is higher than usual, one or more additional phosphorus-containing slags may be removed in order to insure the elimination of phosphorus to a low level. In this connection, it will often be desirable to charge additional limestone to the vessel when it is desired to remove more than one slag during the course of the process.

Under certain conditions some scrap steel may be charged before the molten iron. Once the refining operation is under way, further scrap steel additions may be made in controlled amounts dependent upon the temperature of the liquid metal. In other words, scrap steel may be added whenever the temperature of the bath is sufficiently high to accommodate the chilling effect of the scrap addition. Further control over the permissible scrap addition may be exercised by regulating the proportion of oxygen in the oxygen-containing gas introduced into the refining zone. An additional advantage of my process with respect to the raw materials which may be employed is the fact that widely varying proportions of iron ore or other iron oxide-bearing material can be utilized thereby permitting direct reduction of the ore and direct recovery of metallic iron as a usable steel product.

Other important advantages of my process, as described above, reside in the ability of the process to eliminate effectively large amounts of phosphorus and sulfur. As previously mentioned, the conventional basic open hearth process is limited in the amount of phosphorus that can be removed under optimum operating conditions with the result that in order to make all types of steel in the open hearth process the phosphorus content of the pig iron must be below about 0.4%. The basic Bessemer process, while capable of eliminating considerable phosphorus, requires a high phosphorus charge and does not usually result in the removal of phosphorus to low levels (e. g. under .020%) because under basic Bessemer operating conditions appreciable phosphorus removal does not take place while the carbon content of the metal bath is high, e. g. over .15%. Under the conditions necessary for acceptable phosphorus elimination, considerable nitrogen is also picked up during blowing of the metal. By means of the present invention, pig iron of widely varying phosphorus content can be refined to obtain a product having much lower phosphorus and nitrogen content than is usually obtained by the basic Bessemer process and which is usually superior to the type of product obtained in the conventional basic open hearth process.

A further advantage of my process lies in the fact that the oxidizing gas introduced into the

refining zone can be essentially free of moisture or any other substances which may contribute hydrogen to the molten metal. Thus, the value of my process may be further enhanced by a relatively low hydrogen content in the product.

A completely unexpected advantage of my invention is the ability of the process to remove sulfur to a much lower level than has been possible heretofore in conventional basic oxidizing processes. For example, sulfur is eliminated to some extent in the basic open hearth and basic-Bessemer processes, but the sulfur content of the final product is rarely lower than .025%. In the process of the present invention, however, I am able to obtain steel of consistently low sulfur content, e. g. of the order of .02% and less.

I attribute this superior degree of sulfur removal to several factors. In the first place, the absence of an external heating system for supplying the heat requirements of the refining process by the combustion of a sulfur-containing fuel avoids the introduction of sulfur into the steel from this source. Furthermore, by effecting direct contact of the metal bath with high oxygen concentration gases I greatly increase the opportunity for direct oxidation of sulfur contained in the metal to form gaseous oxides of sulfur which may be removed through the roof opening of the refining vessel. Since the partial pressure of sulfur or sulfur-bearing gases in the atmosphere over the refining zone is very low or negligible, the tendency toward direct oxidation of sulfur is further facilitated. Perhaps the most significant factor responsible for the excellent degree of sulfur removal in my process is the fact, hereinbefore discussed, that there is a rapid development of a basic slag in the refining zone.

Another significant feature of my process is the provision for the removal of more than one slag, where desired, during the refining stage. As illustrated in the drawing, the refining vessel for my process is preferably mounted for tilting movement in order to facilitate removal of slag. Because of the ease with which slag may be removed, it is not necessary to rely on the vigorous apparent "boiling" action in the bath to flush-out the initial slag from the refining zone. When the phosphorus content of the initial iron charge is low, it will be possible to obtain a satisfactory product without removing any intermediate slag. With moderate phosphorus content in the initial iron, the removal of a single slag at an intermediate stage in the refining operation will usually suffice to obtain a low phosphorus product. However, high phosphorus iron charges may also be readily processed and two or more phosphorus-containing slags may be withdrawn in such cases to insure the desired degree of phosphorus removal. In addition, the formation and removal of more than one basic slag will enhance the elimination of sulfur from the liquid metal.

The temperature in my process is controlled primarily by regulating the rate of oxygen addition and also by adjusting the oxygen content of the gases introduced through the lances or other injection devices. The oxygen thus supplied must be sufficient to oxidize the various impurities in order to obtain the desired extent of impurity elimination and must also be sufficient to supply the heat requirements during the refining stage. An auxiliary means of temperature control is by the addition of scrap, as hereinbefore described, and also by addition of iron

ore. The addition of limestone from time to time will, of course, have some effect on temperature but such additions are made for purposes other than temperature control.

Because the oxidizing gas is introduced at or near the surface of the metal bath, the possibility of introducing excessive amounts of nitrogen into the steel is minimized, even when oxygen diluted with air is used, because of the decreased opportunity for absorption of the nitrogen by the steel. My process thereby provides a distinct advantage over the conventional Bessemer techniques. In addition the turbulence produced throughout the metal bath promotes rapid reaction rates thereby greatly increasing the production rate for the process as contrasted with the conventional open hearth process wherein both the reaction rate and the production rate are relatively slow because of the time required for the transfer of heat and reacting substances in the heterogeneous slag-metal-gas system existing in the refining zone.

If desired, it is also within the scope of my invention to introduce powdered iron ore and/or limestone as a suspension in the oxygen gas supplied to the lances. This manner of introducing iron ore or limestone permits rapid and intimate mixing of the added materials to the molten metal thereby further increasing the refining reaction rates. In the conventional open hearth process, it has sometimes been found necessary to subject iron ore or iron ore concentrates which are often available in finely divided form to an agglomeration step, usually by sintering, before charging the ore to the open hearth furnace. However, by supplying iron ore in powdered or comminuted form in suspension in the oxygen gas, I am able to eliminate the agglomeration or sintering steps thereby realizing a substantial economic advantage. Thus, this feature of my process permits direct conversion of the iron in a finely divided iron ore or other iron-bearing material to a usable steel product. By introducing limestone to the bath in suspension in the oxygen gas supplied thereto, the rate of solution of lime in the slag phase is further accelerated thereby further contributing to the rapid development of a basic highly oxidized slag at an early stage of the process. In addition, the introduction of powdered iron ore or limestone in the aforementioned manner provides a convenient and effective additional method for controlling the temperature of the bath.

As an illustration of the results obtainable by the process hereinbefore described, the following experimental data are presented, it being understood, however, that such data are included merely for purposes of illustration and not by way of limitation:

A 100 lb. magnesia crucible was employed, the crucible having the following chemical analysis: MgO 88.1%, SiO₂ 5.0%, R₂O₃ 3.8%, CaO 3.1%.

After preheating, the crucible was charged with 2 lbs. of one inch pieces of limestone preheated to 900° F. The limestone was covered with 3 lbs. of sintered iron ore preheated to 1700° F. and the ore layer was covered with 3 lbs. of plate scrap preheated to 1700° F. Fifty lbs. of molten pig iron was then poured into the furnace at a temperature of about 2600° F.

Immediately upon addition of the molten iron, introduction of undiluted oxygen beneath the surface of the metal bath was started using a lance comprising a 1/2 inch pipe and oxygen ad-

dition was continued substantially continuously throughout the heat except for brief interruptions during sampling, slag removal, and for replace of the oxygen lance. The oxygen pressure at the source was 20 lbs. per square inch gauge and the flow rate was approximately 5 cubic feet per minute. The total time of the heat was approximately thirty-one minutes and the total oxygen supplied was about 100 cubic feet. At two different times during the first half of the heat a flush slag was removed and 2 lbs. of limestone added shortly thereafter on each occasion. In addition, samples of the metal bath were removed for analysis at the start of the heat and also at approximately equal intervals of time throughout the heat.

Reference is now made to Fig. 3 of the drawings wherein the chemical changes which took place in the metal are illustrated graphically. It will be seen from these curves that phosphorus was removed rapidly from the molten metal, the phosphorus content of the bath being reduced to .015% while the carbon content was still well over 2.0%. Likewise the manganese and silicon were eliminated to very low values early in the heat. The elimination of carbon to an exceptionally low level was also accomplished within the relatively short duration of the heat.

A highly unexpected and extremely important result is found in the unusually large percentage of sulfur which was eliminated during the heat. From an initial content of .034% in the original metal the sulfur was reduced to .014% in the final bath.

In addition, the final steel product had a nitrogen content of about .002% which is an exceptionally low value even for a conventional open hearth steel.

The curves of Fig. 3 clearly demonstrate that by means of the process of my invention phosphorus can be reduced to a low value while the carbon content of the metal is still very high. These curves also illustrate the outstanding superiority of the process, as compared with the conventional open hearth process, in the rapid elimination of sulfur. As hereinbefore explained, such rapid and effective sulfur elimination is believed to be attributable to the extremely rapid solution of lime in the slag phase, to the maintenance of a substantially sulfur-free atmosphere, and also to the maintenance of conditions conducive to direct oxidation of sulfur by free oxygen.

A careful analysis of the heat relationships during the run showed that beyond question the use of oxygen provided a definite excess over the heat requirements of the process. The metal temperature was raised from 2600° F. to a tapping temperature of about 2950° F. for the final steel. As a consequence, the process is readily adapted for the utilization of substantial amounts of scrap or iron ore. In addition, further temperature control can be realized by dilution and control of the oxygen gas stream.

Examination of the crucible at the completion of the heat showed it to be substantially unattacked.

I claim:

1. A process for making low phosphorus low nitrogen steel from pig irons of widely varying phosphorus content, said process comprising introducing into a basic lined refining zone the iron in molten state, an iron-oxide bearing material, and a lime-containing basic slag-forming reactant in a predetermined amount sufficient

to obtain a basic slag having a weight per cent ratio of lime to silica of at least about 1.5, injecting an oxidizing gas having an oxygen content in excess of about 21% by volume substantially at the metal surface and thereby turbulently intermixing the slag, iron oxide, and metal phases with consequent early elimination from the metal of phosphorus to not more than about .04% and simultaneous elimination of at least about .4% carbon but leaving at least about 1% carbon in the metal, said turbulent intermixing being substantially enhanced by the gases evolved during said simultaneous elimination of carbon and an operating temperature of not less about 2500° F. being developed whereby obtainment of said ratio of lime to silica in the slag and elimination of phosphorus to substantially the extent required in the final product are both accomplished while the carbon content of the metal is not less than about 1%, and continuing the injection of said gas into the molten metal until the carbon content is reduced to the desired final extent by oxidation thereof, the heat evolved during the exothermic refining and slag-forming reactions being the sole source of heat during the process.

2. A process for making low phosphorus low nitrogen steel from pig irons of widely varying phosphorus content, said process comprising introducing into a basic lined refining zone the iron in molten state, an iron-oxide bearing material, and a lime-containing basic slag-forming reactant in a predetermined amount sufficient to obtain a basic slag having a weight per cent ratio of lime to silica of at least about 2.0, injecting an oxidizing gas having an oxygen content in excess of about 21% by volume substantially at the metal surface and thereby turbulently intermixing the slag, iron oxide, and metal phases with consequent early elimination from the metal of phosphorus to not more than about .04% and simultaneous elimination of at least about .4% carbon but leaving at least about 1% carbon in the metal, said turbulent intermixing being substantially enhanced by the gases evolved during said simultaneous elimination of carbon and an operating temperature of not less than about 2500° F. being developed whereby obtainment of said ratio of lime to silica in the slag and elimination of phosphorus to substantially the extent required in the final product are both accomplished while the carbon content of the metal is not less than about 2%, and continuing the injection of said gas into the molten metal until the carbon content is reduced to the desired final extent by oxidation thereof, the heat evolved during the exothermic refining and slag-forming reactions being the sole source of heat during the process.

3. A process for making low phosphorus low nitrogen steel from pig irons of widely varying phosphorus content, said process comprising introducing the iron in molten state, an iron oxide-bearing material, and a lime-containing basic slag-forming reactant into a basic lined refining zone, injecting an oxidizing gas having an oxygen content in excess of about 21% by volume substantially at the metal surface and thereby turbulently intermixing the slag, iron oxide, and metal phases with consequent early elimination from the metal of silicon and manganese, early elimination of phosphorus to not more than about .04%, and simultaneous elimination of at least about .4% carbon but leaving at least about 1% carbon in the metal, withdrawing a flush slag from said

zone at an intermediate stage of the process, providing said slag-forming reactant in a sufficient amount so that a basic finishing slag having a weight per cent ratio of lime to silica of at least about 1.5 is formed thereafter whereby to retain substantially all the eliminated phosphorus throughout the remainder of the process, said turbulent intermixing being substantially enhanced by the gases evolved during said simultaneous elimination of carbon and an operating temperature of not less than about 2500° F. being developed whereby obtainment of said ratio of lime to silica in the finishing slag and elimination of phosphorus to substantially the extent required in the final product are both accomplished while the carbon content of the metal is not less than about 1%, and continuing the injection of said gas into the molten metal until the carbon content is reduced to the desired final extent by oxidation thereof, the heat evolved during the exothermic refining and slag-forming reactions being the sole source of heat during the process.

4. The process of claim 1 further characterized in that said oxidizing gas consists essentially of free oxygen.

5. The process of claim 2 further characterized in that said oxidizing gas consists essentially of free oxygen.

6. The process of claim 3 further characterized

in that said oxidizing gas consists essentially of free oxygen.

MICHAEL TENENBAUM.

5 References Cited in the file of this patent

UNITED STATES PATENTS

| Number | Name | Date |
|-----------|----------|----------------|
| 1,032,655 | Brassert | July 16, 1912 |
| 1,352,580 | Chinille | Sept. 14, 1920 |

FOREIGN PATENTS

| Number | Country | Date |
|--------|---------------|---------|
| 11,854 | Great Britain | of 1885 |

OTHER REFERENCES

15 Basic Open Hearth Steel Making. By the Committee on Physical Chemistry of Steel Making, Iron and Steel Div., A. I. M. E., pages 511, 512, and 513. Published in 1944 by the American Institute of Mining and Metallurgical Engineers, New York.

20 Physical Chemistry of Steel Making, Control of Iron Oxide in the Basic Open-Hearth Process, Co-operative Bulletin 68, pages 33 and 34. Published in 1934 by the Mining and Metallurgical Boards, Pittsburgh, Pa.

25 Metallurgia, August 1948, pages 193 and 194. Published by the Kennedy Press, Manchester, England.