

A. E. GREENE.  
PROCESS OF REFINING METALS AND ALLOYS.  
APPLICATION FILED APR. 7, 1909.

1,034,787.

Patented Aug. 6, 1912.  
2 SHEETS—SHEET 1.

Fig. 1.

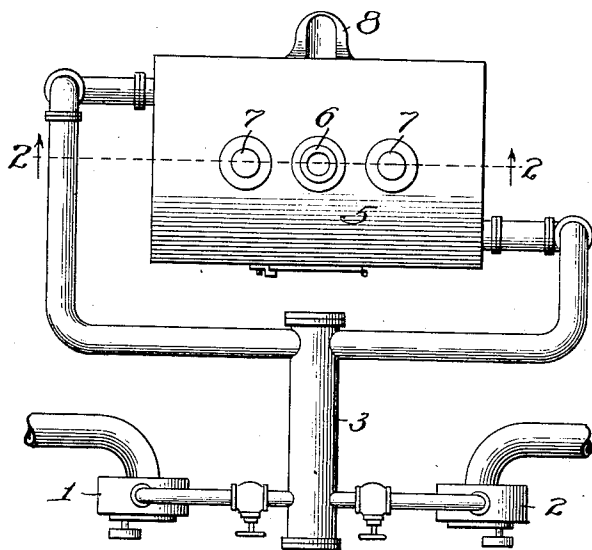


Fig. 2.

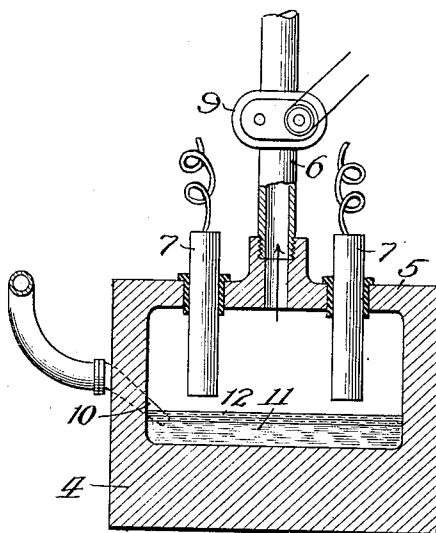


Fig. 3.

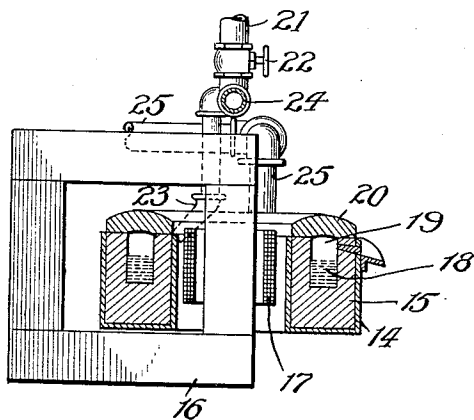
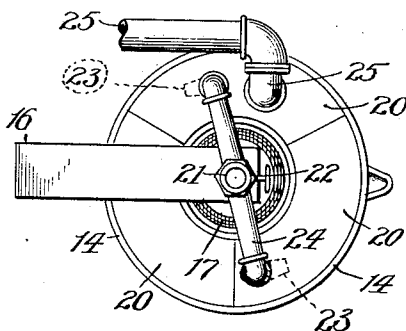


Fig. 4.



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2 SHEETS—SHEET 2.

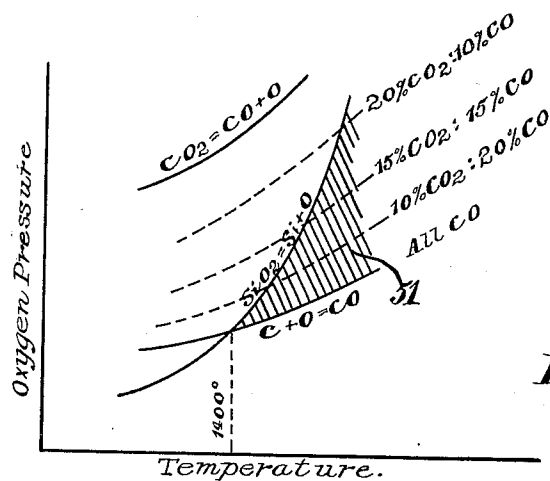


Fig. 5.

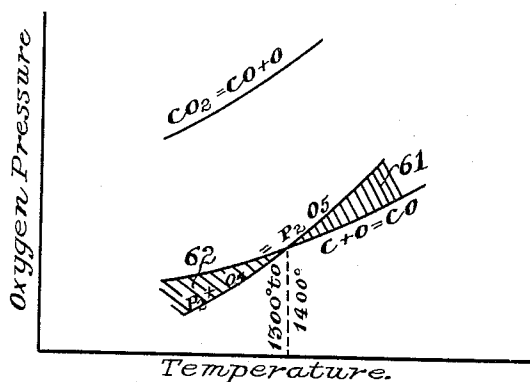


Fig. 6.

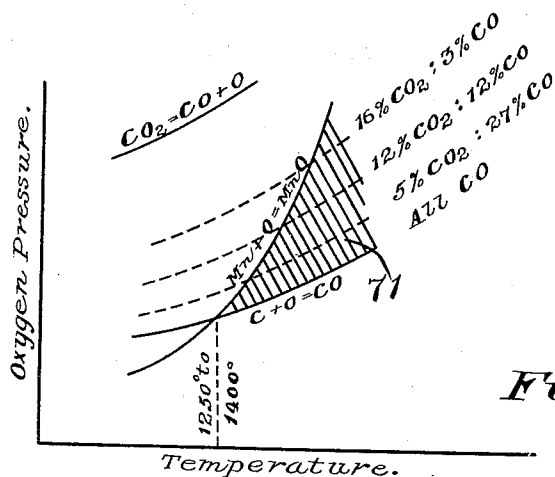


Fig. 7.

Witnesses.

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# UNITED STATES PATENT OFFICE.

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PROCESS OF REFINING METALS AND ALLOYS.

1,034,787.

Specification of Letters Patent.

Patented Aug. 6, 1912.

Application filed April 7, 1909. Serial No. 488,360.

*To all whom it may concern:*

Be it known that I, ALBERT E. GREENE, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a certain new and useful Improvement in Processes of Refining Metals and Alloys, of which the following is a full, clear, concise, and exact description.

My invention relates to a process of refining or otherwise treating metals or alloys of metals. In its more specific application it relates to a process by which one or more elements may be eliminated or separated from a mixture of elements, thereby leaving the remaining constituent or constituents of the mixture in a refined condition.

In metal refining processes based upon the oxidation of the impurity to be eliminated, the refining of the metal is usually accompanied by a greater or less oxidation of the metal itself. Such undesired oxidation of the metal results in a partial loss of the metal and is also an actual hindrance to the practice of the process, since the presence of the metallic oxid in the slag interferes with the removal of certain impurities, such as sulfur, which would otherwise be taken up by the slag. In the Heroult steel process designed to overcome those objections the removal of phosphorus from the bath is likewise accompanied by the presence of iron oxid in the slag, but such iron oxid may be deoxidized by means of calcium carbide formed from the lime slag employed. After the elimination of phosphorus and the deoxidation of the iron oxid the sulfur in the bath may be removed by a separate washing process with a lime slag.

My invention contemplates the formation of a compound of the elements to be eliminated from the material under treatment, without any attendant formation of undesired compounds of the elements to be retained.

My invention contemplates, in the more specific application of the process, the oxidation and the resultant removal of an impurity from a metallic mixture without the usual detrimental oxidation of the desired metal itself or other elements which it is desired to retain.

In certain cases my invention contemplates dispensing with the usual slag-forming flux, as, for example, where the oxidized impurity passes off in the form of gas, or where the temperature of the bath is such that the oxidized impurity is not susceptible to subsequent reduction by the metal of the bath.

In certain other cases my invention contemplates the use of a slag-forming flux for removing the oxidized impurity and also for simultaneously or subsequently removing other impurities, as for example sulfur, from the bath.

My invention consists broadly in the use of gaseous treating agents of such composition that, at the temperature maintained in the furnace, the equilibrium conditions of the gas and between the gas and the charge are so controlled as to prevent the oxidation of the desired metal (or even to reduce its compounds) and simultaneously eliminate the undesired element.

In one specific application of the process, my invention consists in the use of a gaseous reagent containing an oxidizing component and a reducing component and in so controlling the relative proportions of these components and the temperature of the material treated that the gaseous reagent is in equilibrium with the reduced metal, and therefore, prevents its oxidation, while at the same time the equilibrium of said gaseous reagent is displaced with respect to the undesired element and thereby oxidizes the undesired element.

Another feature of my invention consists in the control of the temperature of the material to be refined by means other than combustion in the furnace chamber and meanwhile treating the material with a gas of such composition as to reduce the metal desired and oxidize the impurity.

Another feature of my invention consists in the further regulation of the temperature of the material under treatment so that the element which it is desired to eliminate has a greater affinity for oxygen than the metal to be retained.

Still another feature of my invention applicable to the particular conditions consists in the regulation of the total gaseous pressure within the furnace chamber, there-

by giving a further control of equilibrium condition in the gas and between said gas and the material.

These and other features will hereinafter be more fully set forth.

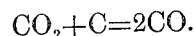
The affinity of oxygen for a given oxidizable element at different temperatures may be measured by the inverse of the oxygen-pressure of the oxid of the element, that is, by the tendency of the oxid to dissociate. Through the range of smelting furnace temperatures some elements always have less affinity for oxygen than others at any given temperature, but in other cases the affinities of different elements for oxygen vary relatively to each other at different temperatures to such an extent that they may even be reversed.

The dissociation pressure of oxids, or in other words their oxygen pressures, normally increase with the temperature. In some cases the curves representing the dissociation pressures at different temperatures for two compounds, always lie one below the other through the whole range of furnace temperature, but in other cases, these curves cross each other.

The fact that the oxygen pressures of the oxids of two elements are different for a given elevated temperature is taken advantage of in the process of my invention by the use of a gaseous mixture which can oxidize the more easily oxidizable element, but not the other. This is accomplished by using a reducing gas or component in the gas mixture together with an oxidizing component. The reducing gas acts in the nature of a protecting blanket to the metal, that is, the reducing gas has a greater affinity for any oxygen there is present than has the metal, but not so great an affinity for it as the other impurity has. For every temperature there is a limiting relation between the oxidizing and reducing components of the gas beyond which an increase of the oxidizing component would cause oxidation of the metal. This composition of gas is such as would produce the gaseous equilibrium which would result if the metal oxid were reduced by the reducing component at the given temperature.

In molten pig iron the carbon has a greater affinity for oxygen than has the iron. A reducing gas such as carbon monoxid (CO) will prevent iron from oxidizing or will reduce iron oxid. If carbon dioxid (CO<sub>2</sub>) were mixed with carbon monoxid, the resultant gas would still reduce iron oxid provided the amount of CO<sub>2</sub> were less than a certain definite amount, depending on the temperature and pressure. This gaseous mixture, which contains the reducing gas CO and the oxidizing gas CO<sub>2</sub> in suitable proportions, can and will oxidize carbon at the temperatures of molten iron without

oxidizing iron. In other words, at the temperature of molten iron, a gas containing CO and CO<sub>2</sub> may be in equilibrium with molten iron and yet oxidize carbon. The CO<sub>2</sub> would react with C as follows:



The proportions of reducing and oxidizing parts necessary to oxidize one element and not oxidize the metal, depend on the temperature at which the material is treated and on the elements to be retained and to be eliminated, respectively. This and the method of ascertaining the right composition of gas to use will be more fully explained hereinafter.

This process must not be confounded with the open-hearth process in which CO gas or some other reducing gas is burned in the furnace chamber with oxygen of the air. In such processes, in order to get the necessary temperature, the reducing gas must be completely burned, preferably with a slight excess of air. The oxidizing power of the burned gas is sufficient to oxidize the valuable metals, like iron and manganese, in the bath, and the reducing gas is not present in sufficient amount to prevent this oxidation. I am aware of the fact that the reducing gas is brought into an open hearth steel furnace underneath the air so that the oxidation of the metal may be minimized, but it is not possible under open hearth conditions to eliminate the impurities and still keep the metal from oxidation as my process does.

An important feature of my invention is, broadly, therefore, the control of the temperature of the material being refined by means other than combustion in the furnace chamber. The specific means described in this application is the electric furnace. Also any heat due to combustion in the furnace chamber, so long as the reducing component remains in excess, will increase the efficiency of the process without hindering its operation.

Another feature of the process relates to specific temperature control so that, for those elements whose oxygen pressure curves cross, the proper element may be selected. For example, for the two elements silicon and carbon there is a critical temperature above which carbon is oxidized in preference to silicon and below which the opposite is true. In such cases it is necessary to regulate the temperature so that the element to be eliminated has the greater affinity for oxygen. With the temperature so regulated, the process is similar to that described above for separation of carbon from iron. That is, the composition of the gas is controlled so that it keeps the metal desired reduced while the other element is oxidized.

The series of points representing the pressures of dissociation expressed in terms of

the pressure of oxygen of a given oxid or oxygen-compound at different temperatures form a curve which may be considered as the characteristic curve of the element which is united with oxygen to form the compound. These curves differ for different elements, and, within the working range of furnace temperature, the curves for two different elements may even cross each other. At the point of intersection of the two curves the relative affinities of the two elements for oxygen are reversed. The temperature at which two curves, each representing the pressure of dissociation of the oxid of a given element, intersect I designate as the critical temperature of one of said elements with respect to the other. At said point each of said elements has an equal affinity for oxygen, and their oxygen compounds have equal pressures of dissociation; on opposite sides of said points each of said elements has a different affinity for oxygen, and the oxid of the element having the greater oxygen-affinity has the lower pressure of dissociation, and, hence, a lower oxygen pressure.

I have discovered that, if at a given temperature a molten mixture containing two oxidizable elements be subjected to an oxygen-compound having itself a pressure of dissociation of oxygen intermediate the values corresponding to the pressures of dissociation of oxygen compounds of said oxidizable elements, such agent will act as a carrier of oxygen to the element whose oxygen-compound has the lower pressure of dissociation, and it will not oxidize the element whose oxygen-compound has the higher pressure of dissociation, but on the contrary may even tend to act as a reducing agent with respect to the oxids of such element. Hence by suitably regulating the temperature of a charge of material containing two elements having the above-described characteristics, and by subjecting the material to the action of a gaseous oxidizing agent having a suitable oxygen pressure, I can thereby selectively oxidize either element of the material under treatment without danger of "overblowing" the mixture, that is without risk of oxidation of the other element by a too long continuance of the treatment.

As it is rather impractical to select suitable gaseous mixtures by calculation of the oxygen pressure that a given mixture should have, and as the actual values of the dissociation pressures of the various oxids, etc., may not be familiar to those operating this process, a simple method of determining the composition of gas required will be described. The method is to try a gaseous mixture containing, say, about equal proportions of CO and CO<sub>2</sub>, for instance, and blow this into the metal maintained at a given temperature. If it is found that oxidation

of both metal and impurity result, the proportions of CO should be increased. On the other hand, if the gas is found not to oxidize the metal, then the CO<sub>2</sub> may be increased as long as the metal is not oxidized appreciably. Other reducing gases and other oxidizing gases may be used provided the reducing component prevents oxidation of the desired metal.

In the elimination of carbon from pig iron, the temperature may be maintained high enough to keep the metal suitably molten, say, not over 1500° C. and at this temperature a gas containing only 2 or 3% of CO and as much as 15% of CO<sub>2</sub> by volume will eliminate the carbon with almost no oxidation of the iron or manganese.

Blast furnace gas which might contain 22% CO, 12% CO<sub>2</sub> and 1% O may be mixed with air so that some of the CO is burned to CO<sub>2</sub> and then blown into the metal, or it may be mixed with ordinary stack gas consisting largely of CO<sub>2</sub> and nitrogen and blown into the furnace. The relative volumes of the different gases of the above mentioned gaseous mixtures are for gases at ordinary temperatures. Of course, when heated, the gas would come to equilibrium and there would be slightly less carbon dioxide and a little more free oxygen.

The higher the temperature of the metal the less carbon monoxid in the gas mixture will be required to prevent oxidation of the metal. Where it is desired to oxidize the carbon without oxidizing the silicon the temperature is preferably kept above 1400° C. and the gas preferably contains 4% to 5% CO and 15% CO<sub>2</sub>.

In mixing gases to produce a gas having suitable oxygen pressure, the mixing is preferably done by blowing each gas of known composition from a separate engine or compressor into a common receiver or pipe and regulating the speed of each unit to furnish the desired amount of each gaseous constituent of the mixture.

In practising the process of this invention, it is preferable to employ an electric furnace in order that the temperature can be satisfactorily controlled. Any of the well-known types of such furnaces may be employed. In the accompanying drawings two types of such furnaces are shown equipped for practising the process.

Referring to said drawings: Figure 1 is a plan view of a furnace somewhat similar to the Heroult tilting furnace; Fig. 2 is a section on the line 2—2 of Fig. 1; Fig. 3 is a vertical section of an induction furnace; Fig. 4 is a plan view of the furnace shown in Fig. 3; and Figs. 5, 6 and 7 are diagrams illustrating by curves the oxygen pressures for different substances at different temperatures.

Referring to Figs. 1 and 2, the apparatus

for regulating the gaseous mixture is shown as consisting of blowers 1, 2 communicating with a common receiver 3. The furnace consists of a crucible 4 closed by a roof 5 provided with a chimney 6. The electrodes 7 may consist of the usual carbon electrodes. A spout 8 serves for running off the metal on tilting the furnace. The furnace is provided above the base of the crucible with openings for receiving twyers 10, which communicate in the usual way with the pipe 3. The twyers preferably dip down through the slag 12 into the molten bath 11.

Any suitable source of electric current may be employed, the connections of the electrodes in the circuit being made in a manner well understood by those skilled in the art.

In order to control the total pressure of the gas within the furnace chamber, in cases where such control is advantageous, a suction fan 9 may be employed for removing the exhaust gases through the chimney or escape vent 6 at such rate as may be desired, thus controlling the pressure of the gas on the surface of the bath within the furnace chamber.

Figs. 3 and 4 show a well known type of induction furnace. The steel casing 14 thereof may be supported in any suitable manner. The walls 15 inclosed in said casing are annular in shape and surround one leg of the transformer core 16. Said core is wound with one or more coils 17, which serve as the primary of the transformer, the secondary thereof consisting of the metallic bath 18 contained in the furnace chamber 19. The chamber 19 is provided with a cover, which is preferably made in a plurality of sections 20. Gas is admitted from the gas main 21 and the flow thereof is controlled by the valve 22. The twyers 23 which are connected by means of pipe 24 with the gas main extend through the cover 20. The exhaust gas passes out through exhaust gas pipe 25.

Figs. 5, 6 and 7 are curves showing the approximate critical temperatures and also the nature of gaseous agents which can be used for selective oxidation of carbon with respect to silicon, phosphorus and manganese, respectively, from iron containing these elements. The only practical way of drawing these curves to scale of pressure is by use of logarithmic curves. As the interpretation of such curves requires mathematical calculations, it is more appropriate to show the relative position of certain oxygen-pressure curves for various gaseous mixtures, thereby indicating directly what the furnace operator must know, namely, what proper gas composition to use. The curves shown in these figures are for modified producer or blast furnace gas mixtures. Referring to these figures, the areas marked

51, 61 and 71 indicate gaseous compositions and temperatures suitable for selective oxidation of the carbon. It should be remembered in considering these curves that the element represented by the lower curve for a given temperature is the easier to oxidize. Referring more particularly to Fig. 6, the area 62 indicates conditions for selective oxidation of phosphorus in the presence of lime, but the curves shown here lie very close to each other over a considerable range of temperatures, so that the critical temperature is not closely defined and it may happen that both phosphorus and carbon oxidize simultaneously over a considerable part of this range of temperature.

Referring to Fig. 7, the area marked 72 indicates conditions for the selective oxidation of carbon from iron high in manganese. It is desirable, in this case, to work at low temperatures near  $1450^{\circ}\text{C}$ . in order to minimize volatilization of manganese. It may be noted here that the temperature for selective oxidation of carbon from ferro-manganese may be lower than for high manganese pig iron.

It is understood that the curves shown herein are relative; furthermore, that the oxygen pressure of a given oxid of a metal is in general different from the oxygen pressure of another oxid of the same metal, and the conditions for removal of a given element may be materially modified by using a fluxing agent which has a strong affinity for the oxid of said element, thereby tending to lessen its oxygen pressure. This method of further controlling oxygen pressure by use of fluxing agents, for example in oxidizing such elements as phosphorus and silicon, forms the subject matter of my co-pending application Serial No. 444,740, filed July 22nd, 1908.

While the process of my invention is applicable to the refining metals or alloys in general, said invention and the principles underlying the same may be more fully understood by reference to particular applications thereof.

In applying the process to the production of steel, a charge of the molten material, which may be either crude pig iron or metal previously partially refined, is introduced into an electric furnace and the temperature of the molten bath is regulated to a point at which the elements to be retained have a relatively low affinity for oxygen. While the temperature is thus regulated, the bath is blown with a gas, such as hereinbefore described, having a pressure of dissociation suitable for selectively oxidizing the particular element or elements of the bath which it is desired to eliminate by oxidation. In this manner carbon, for example, may be oxidized and removed without elimination of silicon, or silicon may be wholly or partly

removed while the carbon is retained, or both elements may be removed successively or at one operation, as may be deemed desirable. In the same way other elements, as for example phosphorus, may be selectively oxidized.

In case it is desired to remove two or more oxidizable elements successively, the mixture under treatment is heated to progressively varying temperatures by varying the supply of electric energy thereto, each different temperature corresponding to that at which the element to be eliminated has a higher affinity for oxygen than has the elements to be retained, and said heated material is then subjected to the action of a gas having a pressure of dissociation suitable for oxidizing said former elements but unsuitable for oxidizing said latter elements.

In practice I have found that a gaseous mixture consisting of fifteen per cent. of carbon dioxid ( $\text{CO}_2$ ), twenty per cent. of carbon monoxid ( $\text{CO}$ ) and one per cent. of oxygen, by volume, and the remainder of the mixture of some inert gas, with the gas at an actual pressure of five pounds above atmosphere pressure will, when the bath is maintained at a temperature of approximately  $1812^\circ \text{C}$ ., eliminate carbon to a trace without danger of overblowing iron. The oxidizing action is continued until a test sample of the material under treatment shows that the metal has been sufficiently refined.

The process is also applicable to the production of alloy-steels in which the alloying metal or metals consists of any one or more of the following, namely, manganese, titanium, silicon, nickel, cobalt, molybdenum, tungsten, chromium, and the like. Such specific application of the process is disclosed in and forms the subject matter claimed in my co-pending application, Serial No. 470,921, filed January 6, 1909. In case of the more easily reducible of the above mentioned alloying metals, low-carbon alloy-steel can, by this process, be readily produced directly from the ore or from the product of the blast furnace. For example, low-carbon manganese-steel can be thus produced, and, so far as I know, such direct production thereof has not heretofore been attained. In such direct production of alloy-steel, I preferably start with the blast furnace output containing the metals which enter into the alloy, which material ordinarily contains such impurities as carbon, silicon, sulfur and phosphorus, and remove any or all of the impurities to the desired degree, while retaining in the bath the metal which is desired to alloy with the iron to produce the alloy-steel.

In case the alloying metal is volatile at high temperatures I work at a temperature as low as it is practicable to maintain the

required relation between the elements to be retained and the elements to be eliminated. To remove the oxidizable impurities, which it is sought to eliminate, the molten bath is then blown with the gas having at said temperature a pressure of dissociation which renders it an oxidizing agent with respect to the impurity or impurities which it is desired to eliminate by oxidation but which gas is a non-oxidizing or even a reducing agent with respect to the elements which it is desired to retain in the bath. At these comparatively low temperatures a gas containing 14% of  $\text{CO}_2$  and 18% of  $\text{CO}$  by volume will eliminate the carbon to .05% without oxidation of the metals of the bath. For further diminution of carbon, I may in some cases operate the exhaust pump hereinbefore described in order to reduce the pressure in the furnace chamber, thus aiding in the removal of carbon as a compound of oxygen. This method of expediting the action by reducing the pressure on the bath of the gases escaping therefrom is more particularly applicable to cases in which the metal or metals to be reduced are volatile only at a high temperature as is the case, for example, with titanium. In working with very volatile metals such as manganese, on the contrary, I preferably increase the actual pressure of the gas and vary the constituents of the mixture so as to produce a suitable pressure of dissociation.

In some cases it is desirable to employ a flux to form a slag with the oxidized impurity, as for example, to remove phosphoric oxid ( $\text{P}_2\text{O}_5$ ) formed by the oxidation of the phosphorus. In case sulfur is present in the bath and it is desired to remove the same simultaneously with the oxidized impurity or subsequently thereto, a flux is also desirable. For these purposes a lime or other alkaline earth flux, such as one containing lime or fluorspar or a mixture thereof is melted on the top of the bath. Since the gas causes no oxidation of the iron, the absence of iron oxid in the slag permits of the slag serving to eliminate the sulfur.

The process of this invention may be employed for further treating the product of the Bessemer converter. In a Bessemer converter it is customary where the metal is blown to a high temperature to add scrap iron to bring the bath down to a pouring temperature. In my process, as practiced on the product of the Bessemer converter, the excessive heat from such high temperature is used in heating a flux which is added on the top of the bath. The bath is then transferred to the electric furnace, and, while electrically maintained at the proper temperature, is blown with a gas suitable for producing the desired reactions.

With a charge consisting of Bessemer

steel and a lime flux, maintained at a temperature of approximately 1700° C., a gas composed of 14% of CO<sub>2</sub> and 21% of CO and the remainder of some inert gas will satisfactorily eliminate the phosphorus and sulfur without danger of overblowing the iron. Under these conditions I have simultaneously reduced phosphorus in Bessemer steel from .096% to .019% and sulfur from .041% to .013% without oxidizing the iron.

In the production of low-carbon steel from pig iron, the basic pig iron is poured into the electric furnace, lime is added to the bath to form a flux and the bath is then blown with the gas having a pressure of dissociation suitable for eliminating the carbon without oxidizing the iron. The oxygen yielding constituent of the gas may consist of from 12 to 15 per cent. by volume of CO<sub>2</sub>, and the amount of CO may vary from 10 to 25%, if the gas be obtained from the blast furnace. The temperature of the bath is preferably maintained high, in order to hasten the elimination of the carbon. At 1800° C. such elimination is very rapid. When the temperature is lowered the content of CO must be increased relatively to the CO<sub>2</sub>, thereby lowering the percentage of available oxygen at low temperatures. At the same time a lime flux is being melted on top of the bath and any oxides of the metal under treatment are being acted on by the CO formed by the reaction of the CO<sub>2</sub> with carbon, and also by any other reducing gas which may be present in the gaseous mixture. The action of the reducing gas is continued until the lime itself is more or less reduced thereby, thus causing the free calcium to unite with sulfur and phosphorus to form a slag.

To still further illustrate my invention I will now describe its specific application to the production of low carbon manganese-steel.

A charge consisting of molten spiegeleisen or other form of manganese-containing metal, containing such proportion of manganese as will give the desired percentage of that metal in the resulting steel is introduced into the crucible of an electric furnace, preferably an induction furnace such as is shown in Figs. 3 and 4 of the drawings. Close temperature regulation is desirable in order to avoid volatilization of the manganese by excessive heat. I have found that a temperature of approximately 1400 to 1600° C. may be maintained without excessive volatilization of manganese; and that by selecting suitable gaseous mixtures the several reactions necessary to refine the material may be brought about at said temperatures. A flux consisting of burnt lime, calcium fluoride, or other alkaline earth composition, is added in sufficient quantities to slag off the sulfur and phosphorus. The bath main-

tained within the temperature limits above stated is blown with a gas having a pressure of dissociation suitable for oxidizing the carbon without oxidizing the iron or the manganese. For example, blast furnace gas containing approximately 15% of carbon dioxide, 12% of carbon monoxide, and the remainder of nitrogen and hydrogen, will give a satisfactory removal of carbon, silicon, sulfur and phosphorus at a temperature of 1500° C. without appreciably lessening the content of iron and manganese.

In case acid elements are desired in the steel they may be retained in the molten metal by increasing the reducing conditions and making the slag more acid.

In producing refined silicon-steel from high carbon iron containing silicon, a molten bath of the material is maintained at a temperature at which the oxygen-affinity of carbon is greater than that of silicon, and the bath is meanwhile blown with a gaseous mixture, such as that hereinbefore described, suitable for eliminating the carbon without oxidizing the silicon.

In accordance with this invention the two requirements for decarbonizing a metal or alloy are, first, a temperature at which carbon has the greater oxygen affinity; and second, a gas having sufficient reducing action to keep the desired metal reduced while oxidizing the carbon. In general, in the treatment of the ferro-alloys, such as iron-chromium, iron-manganese, iron-tungsten alloys (where the tungsten is present in relatively small amounts) a temperature of over 1600° C. will permit preferential oxidation of carbon. Usually, however, the temperature may be as low as 1450° C., as in the case of a spiegel iron. If the alloy has a high melting point, as for example an alloy containing much tungsten, a higher temperature is required in order to keep the metal molten.

For practically all the iron alloys containing low percentages of the alloy, that is below 20%, such as spiegel, armor plate metal, tool steel and the like, a temperature of 1600° C. will insure the selective oxidation of carbon, but the temperature should be kept as much lower than this as will permit of the selective action. Thus the temperature for a 12% manganese iron alloy may be as low as 1450° C. The determination of this lower temperature may be made after a few runs by trying lower temperatures until one is found at which best mechanical operation and lowest vaporization loss can be had.

The second requirement, namely gas composition, may be determined for any particular alloy by trial. In general, a gas having, for example, an equilibrium corresponding to that of a mixture containing 12% CO and 12% CO<sub>2</sub> and the remainder nitrogen will prevent the oxidation of the



metal. From such data the most efficient gas may be determined by trial, and one skilled in the art will have no difficulty in selecting a suitable gaseous mixture. It is of course preferable, in order to shorten the duration of the treatment, to make the gas carry as much oxidizing agent as possible and still maintain the gaseous mixture reducing with respect to the elements it is desired to retain unoxidized.

It is to be understood that I do not limit my invention merely to the selective oxidation of carbon, but such selective oxidation is given as illustrating one of the applications of the process.

In the case of separating an undesired element from a given metal, such as the separation of silicon from manganese-steel alloy, it is preferable, and in fact usually necessary, to assist the selective oxidizing action of the gas by a fluxing agent. Thus by using a basic flux like lime, it is possible to separate the acid element silicon very readily from the basic metal manganese.

In actual practice, I have found that by regulation of the composition of the gaseous oxidizing agent and the temperature of the material under treatment, the metal will not be oxidized even if the blow be continued after the oxidizable impurities have been eliminated.

With reference to the practice of my process in general it is to be understood that it is not limited to any particular method of regulating the temperature of the substance under treatment, or of subjecting the same to a suitable treating agent. Nor is it limited to any particular method of producing the desired composition of the gaseous mixture employed. While regulation of temperature is essential, no particular temperature is requisite other than that it be at a point at which undesirable oxidizable elements have a greater oxygen-affinity than the desired elements. The regulation forming a feature of my invention consists of a combined control of temperature of the material under treatment and of the equilibrium conditions of the treating gas, as hereinbefore set forth.

By practising the process as thus described, the metal can not be "overblown" if the proper conditions are maintained. In some cases, however, it may be desirable from a commercial standpoint to lessen the time required for practising the process at the expense of a slight loss of the metal or metals being refined. In such case it may even be desirable, after regulating the temperature in the manner hereinbefore described, first to subject the heated material to the action of a gas having relatively high oxidizing properties in order to quickly remove a portion of the undesired impurity or impurities, discontinuing such treatment

before there is injurious oxidation of the elements which it is desired to retain, and then to continue the refining process by blowing the mixture with a gas, such as hereinbefore described, having a pressure of dissociation suitable for oxidizing only the element or elements which it is desired to eliminate. It suffices if the conditions are such that no detrimental oxidation takes place. If the oxidation of the metal or metals being refined is so small as not to impair the product or to seriously interfere with the removal of the impurities, such practice of the process is within the scope of this invention.

It will be noted that by regulating the pressure of dissociation of the gaseous oxid forming the source of oxygen of the gaseous mixture, the oxygen available for oxidizing purposes is used up in oxidizing the element eliminated from the bath. Hence the resultant gas coming from the reaction constitutes a non-oxidizing or even a reducing atmosphere in the refining chamber, the  $\text{CO}_2$  gas being reduced by the reaction to  $\text{CO}$  gas. This non-oxidizing or reducing atmosphere in the furnace chamber is effective in protecting the molten metal from oxidation, and, in case carbon electrodes are employed for conducting the electric current to the bath, such atmosphere protects said electrodes from otherwise rapid oxidation.

The terms "high-carbon" and "low-carbon" as used herein are relative terms and are not intended to specify any particular percentage of carbon.

While I have disclosed herein the application of the process of my invention to the elimination of sulfur and phosphorus from metallic mixtures and have also set forth the application of the process to the production of alloy-steels, such, for example, as manganese-steel, since such modifications are broadly within the scope of the present invention, these modifications form the subject-matter, respectively, of my co-pending applications, Serial Number 444,740, filed July 22, 1908 and Serial Number 470,921, filed January 6, 1909.

What I claim herein, is:

1. The process of refining metals which consists in controlling the temperature of the material under treatment by means other than combustion in the furnace chamber and in the meanwhile treating the material with a gaseous reagent suitable, at the temperature maintained, for reducing compounds of the metal and for simultaneously combining with the impurity of the metal, and thereby eliminating such impurity.

2. The process of refining metallic substances which consists in controlling the temperature independently of combustion in the furnace chamber and maintaining the

material at a predetermined elevated temperature, and forcing into contact with the heated metal a gaseous mixture containing an oxidizing gas and a reducing gas which, at the predetermined elevated temperature, so displaces its equilibrium as to reduce the compounds of the metal and simultaneously oxidize the impurity.

3. The process of refining metals and eliminating impurities therefrom which consists in maintaining the material to be refined at an elevated temperature, blowing the heated material with a gaseous reagent containing an oxidizing component and a reducing component in such proportions that, at the temperature maintained, the gas will oxidize the impurity and prevent oxidation of the metal.

4. The process of refining metals containing undesired elements associated therewith, which consists in treating the impure material, at an elevated temperature in a suitable furnace, with a gas containing an oxidizing agent mixed with carbon monoxid (CO), the latter being in such proportions that, at the temperature maintained, the equilibrium conditions in the gas are such as to prevent the oxidation of the metal desired, but also in such proportions that the equilibrium is so displaced with respect to the undesired associated element as to oxidize the latter.

5. The process of refining metals which consists in treating the same at an elevated temperature with a gaseous mixture of carbon monoxid (CO) and carbon dioxid (CO<sub>2</sub>), the carbon monoxid being in such proportion as to prevent, at the temperature maintained, the oxidation of the metal from which the impurity is to be oxidized, and controlling the temperature by means other than combustion in the furnace chamber.

6. The process of refining metals and alloys which consists in subjecting the material under treatment to a mixture of an oxidizing gas and carbon monoxid in such proportions that carbon monoxid will constantly be present in the gaseous mixture to which the material is subjected, and in the meanwhile maintaining the material under treatment at a temperature at which the oxygen affinity of carbon monoxid is less than the oxygen affinity of the element which it is desired to eliminate and greater than the oxygen affinity of the element which it is desired to retain.

7. The process of refining metals and alloys which consists in subjecting the material under treatment to a mixture of carbon dioxid and carbon monoxid, and in the meanwhile maintaining the material under treatment at a temperature at which the oxygen affinity of carbon monoxid is less than the oxygen affinity of the element

which it is desired to eliminate and greater than the oxygen affinity of the element which it is desired to retain.

8. The process of removing one element from a mixture of elements by the action of a suitable gaseous treating agent, which consists in introducing into a suitable furnace a mixture containing the desired metal and the undesired impurity, maintaining said mixture as a molten bath at a temperature at which the pressure of dissociation of any compound capable of being produced by the action of the treating gas on the desired element is greater at that temperature than the pressure of dissociation of any compound capable of being produced by the action of said treating gas on the element to be eliminated, and in the meantime subjecting said molten bath to the gaseous treating agent having itself a pressure of dissociation at the working temperature exceeding the latter but not exceeding the former pressure of dissociation.

9. The process of removing one element from a mixture of oxidizable elements, which consists in maintaining the mixture, in a suitable furnace, at a temperature at which the oxygen pressure of the oxid of such element as it is desired to eliminate from the mixture is lower than the oxygen pressure of the oxid of the element or elements to be retained, and in subjecting the heated mixture to an oxidizing agent having an oxygen pressure intermediate the oxygen pressure of the oxid of the element to be eliminated and that of the element or elements to be retained.

10. The process of refining metals and alloys which consists in maintaining a molten bath of different oxidizable elements at an elevated temperature in a refining chamber, and subjecting said bath to the action of oxygen having an oxygen pressure suitable for the oxidation of an element which it is desired to eliminate from the bath, but unsuitable for the oxidation of the element or elements which it is desired to retain.

11. The process of refining metals and alloys which consists in maintaining a molten bath of different oxidizable elements at an elevated temperature in a refining chamber, and subjecting said bath to the action of an oxid having an oxygen pressure suitable for the oxidation of an element which it is desired to eliminate from the bath, but unsuitable for the oxidation of the element or elements which it is desired to retain.

12. The process of refining metals and alloys which consists in maintaining a molten bath of different elements at an elevated temperature in a refining chamber, mixing two or more gases in proportions to produce a gaseous reagent having a pressure of dissociation suitable, at the temperature at

which the bath is maintained, for the action of the gaseous reagent on the element of the bath which it is desired to eliminate, but unsuitable for the oxidation of the element or elements which it is desired to retain, and subjecting said bath to said gaseous reagent.

13. The process of eliminating an undesired element from a compound from which such element is susceptible to dissociation into a volatile form, which consists in heating the material under treatment in a closed furnace, and in regulating the dissociation pressure of the element to be eliminated by the combined regulation of the temperature of the furnace and of the pressure of the vapors liberated within the furnace chamber.

14. The process of separating two or more elements one of which is adapted to be formed into a compound susceptible to volatilization at elevated temperatures, which consists in heating the material under treatment in a closed furnace, and in regulating the dissociation pressure of the compound to be formed by the combined regulation of the temperature of the furnace and of the gaseous pressure of the gases liberated within the furnace chamber, and subjecting the heated material to an agent suitable for the formation of the volatilizable compound and having a pressure of dissociation suitable for selective action upon the element which it is desired to eliminate.

15. The process of refining metals and alloys which consists in heating in an electric furnace the material under treatment, subjecting said heated material to the action of an oxidizing gas having an oxygen pressure suitable, at a selected working temperature, for the oxidation of an element which it is desired to eliminate, but unsuitable for the oxidation of the element or elements which it is desired to retain, and maintaining said material at the required temperature during such selective oxidizing action by regulating the electric heating current.

16. The process of refining iron and alloys of iron containing undesired elements which consists in maintaining the metal molten in a suitable furnace and blowing the molten bath with a gaseous mixture containing an oxidizing gas and carbon monoxid (CO), the carbon monoxid being in such proportion as to prevent oxidation of the metal, but not sufficient to prevent the oxidation of the undesired element by the oxidizing gas.

17. The process of decarbonizing metals and alloys which consists in maintaining the metal molten by means other than combustion, and treating the molten metal with a gaseous agent containing an oxidizing component and a reducing component in such relative proportions that, at the temperature

of the molten metal, the carbon is oxidized approximately without oxidation of the metal.

18. The process of decarburizing metals or alloys which consists in treating the material with a gas containing a reducing and an oxidizing component in such proportion that between certain temperature limits the gas will oxidize the carbon with practically no oxidation of metal, maintaining the temperature between said limits, and discontinuing the treatment when sufficient decarburization has taken place.

19. The process of oxidizing impurities from metals, which consists in maintaining the metal at a temperature, suitable for refining, at which the affinity of the impurity for oxygen is greater than the affinity of the metal for oxygen, and meanwhile blowing the metal with an oxygen-containing gas which is in equilibrium with said metal but which is oxidizing with respect to said impurities.

20. The process of producing steel from a mixture containing iron, which consists in maintaining such mixture in a molten condition and in subjecting the molten bath to a gaseous oxidizing agent having an oxygen pressure, at the temperature at which the bath is maintained, which renders said gaseous agent a reducing agent with respect to oxid of iron and at the same time an oxidizing agent with respect to an element or elements which it is desired to eliminate from the bath.

21. The process of producing steel which consists in maintaining a mixture of iron and associated impurities in the form of a molten bath having a predetermined temperature, regulating the gaseous mixture emanating from the stack of a blast furnace to produce an oxygen pressure therein which is adapted at said predetermined temperature to act as a reducing agent with respect to iron oxid, and at the same time as an oxidizing agent with respect to the impurity or impurities which it is desired to eliminate from the bath, and in subjecting the bath to the action of said regulated mixture.

22. The process of producing refined metals and alloys, which consists in maintaining a molten bath of the metal or metals to be refined and the associated impurities at a predetermined temperature, and in subjecting the molten bath to a gaseous agent, containing oxygen having an oxygen pressure, at the temperature at which the bath is maintained, which renders said gaseous agent a reducing agent with respect to the oxid or oxids of such metal or metals as it is desired to retain in the bath, and at the same time an oxidizing agent with respect to the impurity or impurities which it is desired to eliminate.

23. The process of refining metals and alloys containing an undesirable oxidizable element or elements, which consists in heating the material under treatment to a temperature at which the oxygen-affinity of the element or elements which it is desired to eliminate is greater than that of the element or elements to be retained, and in subjecting the heated material to the action of a gas containing an oxygen-compound mixed with one or more of the products of dissociation of said oxygen-compound in proportions to produce a gaseous mixture having a pressure of dissociation suitable, at a temperature of the heated material, for oxidizing the element or elements which it is desired to eliminate but unsuitable for like action upon the element or elements which it is desired to retain unoxidized.

24. The process of producing refined metals and alloys from material containing such metal or alloys associated with an undesirable oxidizable element or elements, which consists in heating the material under treatment to a temperature at which the oxygen-affinity of the element or elements which it is desired to eliminate is greater than that of the element or elements to be retained, and in subjecting the heated material to the action of a gas containing an oxygen containing component mixed with a reducing component, said component gases being mixed in proportions suitable, at the temperature of the heated material, for oxidizing the element or elements which it is desired to eliminate but unsuitable for like action upon the element or elements which is desired reduced.

25. The process of refining metals and alloys containing an undesirable oxidizable element or elements, which consists in heating the material under treatment, to a temperature at which the oxygen-affinity of the element or elements which it is desired to eliminate is greater than that of the element or elements to be retained, and in subjecting the heated material to the action of a gas containing carbon dioxid mixed with carbon monoxid in proportions suitable for

oxidizing the element or elements which it is desired to eliminate but unsuitable for a like action upon the element or elements which it is desired to retain unoxidized.

26. The process of refining metals and alloys containing an undesirable element or elements, which consists in heating the material under treatment to a temperature at which the oxygen-affinity of the element or elements which it is desired to eliminate is greater than that of the element or elements to be retained, and in subjecting the heated material to the action of a gaseous oxygen-compound the oxygen-affinity of which, at the temperature of the bath, is greater than that of the element or elements to be retained but less than that of the element or elements to be eliminated.

27. The process of producing refined silicon steel from high carbon iron containing silicon, consisting in providing a molten bath of said iron, electrically heating said bath to a temperature at which selective oxidation of carbon in preference to silicon takes place, and passing therethrough a gas containing carbon dioxid in quantities suitable for the selective oxidizing action on carbon at the temperature at which the bath is maintained, but unsuitable for a like action upon silicon.

28. The process of producing low-carbon steel, which consists in subjecting high-carbon iron, maintained in a molten condition at a temperature such that the affinity of oxygen for the contained carbon is greater than its affinity for the elements to be retained, to the action of a gaseous mixture containing carbon dioxid and carbon monoxid in regulated proportions suitable for selective oxidation of carbon at said temperature, but unsuitable for a like action upon the element or elements which it is desired to retain unoxidized.

In witness whereof, I, hereunto subscribe my name this 5th day of April A. D., 1909.

ALBERT E. GREENE.

Witnesses:

ALFRED H. MOORE,  
GEORGE E. FOLK.