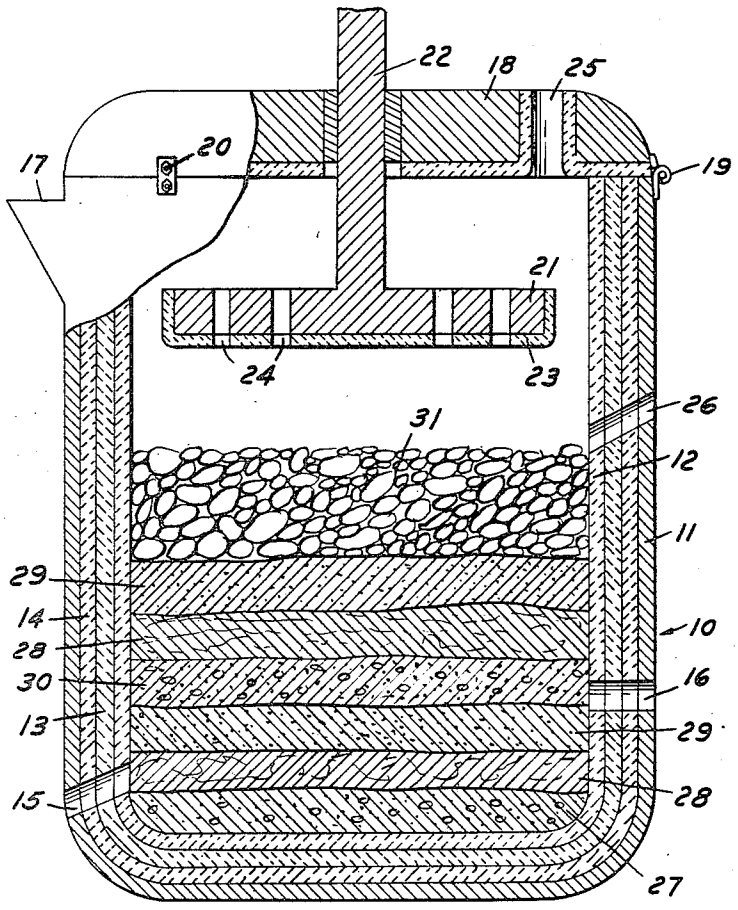
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METALLURGICAL PROCESS

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METALLURGICAL PROCESS

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My invention relates to a method of creating very high temperatures in a vessel by means of the exothermic heat of formation of two or more materials. In my method, a substantial part of the amount of heat liberated is utilized for supplying the heat quantity necessary to raise the temperature of the charge to a very high degree, and for carrying on chemical reactions between two or more substances that react to a substantial degree only at very high temperatures and where the reaction is endothermic. The use of the heat of exothermic reaction for supplying the needed amount of heat for carrying on the endothermic reaction also serves for controlling the temperature.

Some of the heat absorbing reactions and preheating of the materials are performed separately, as far as it is practical to perform them, in other vessels before the reacting and other materials are brought together for final reaction, so that as much heat credit is added to the materials as is practical and desirable.

A suitable apparatus for carrying out my new process is illustrated in the drawings. The numeral 10 designates a ladle or crucible-like apparatus having a steel shell or casing 11 which is lined on the inside with carbon blocks or a solid dense carbon wall 12. A lining of refractory material is provided between the casing 11 and carbon lining 12, the type and construction of said refractory lining depending upon the process to be carried out within the ladle and the materials available. Anyone familiar with handling molten metals can easily determine what type of lining is best in each case; however, as specifically illustrated, the refractory consists of a layer of high temperature material 13 next to the carbon 12 and a layer of refractory material of low thermal conductivity 14 next to the steel casing. An iron tap hole 15 and a slag tap hole 16 are provided near the bottom of the ladle, however both the iron and slag may be withdrawn through the same hole if desired. Also, with the type of construction illustrated, the molten materials may be poured out through a spout 17, however any other suitable construction of ladle and lining may be used without departing from my invention.

A refractory lined door or cover 18 is fastened to the top of the ladle by a suitable hinge 19, and one or more suitable clamps 20 are provided for holding the cover closed. The door may be solid as shown or may be formed as a lattice work or some other construction.

A plunger 21 is located within the ladle and

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is provided with an operating rod or stem 22 which extends upward through an aperture in the cover. The plunger is preferably constructed of perforated metal protected by means of a refractory layer 23 which is provided with suitable apertures 24 permitting escape of gases.

If a solid door or cover is used, a suitable refractory lined opening 25 is provided therein to permit pouring of molten metal or other material into the ladle without opening the door. In some cases, where the ladle does not have to be covered, a ring frame for holding the plunger may be substituted for the door. The plunger 21 may be of any construction best suited for the particular operation to be carried out as will hereinafter be described. Any suitable means (not shown) may be operably connected to the stem 22 for operating the plunger.

One or more openings 26 are provided in the side of the ladle as a means of introducing liquids or gases into the ladle, however in some cases such liquids or gases may be introduced through either of the tap holes 15 and 16 or through the opening 25 in the cover.

Into the ladle are put alternate layers of preheated hot sand or lumps containing mostly alumina, some silica and whatever other metallic oxides there are in it, and of hot lime. These layers are separated by layers of carbon between them. Either into the lime or into the alumina sand or at any suitable place there are lumps or briquettes or grainy metallic oxide or oxides mixed with carbon preferably in a hot state.

As illustrated, the bottom layer 27 consists of carbonaceous material, which may be in the form of coke, crushed charcoal or other type of carbon. On top of the carbon is a layer of hot lime 28 which may have some carbon mixed therewith if desired, and which is covered by a thin layer of carbon on top. Next comes a layer of hot alumina sand 29 which may contain any desired amount of silica along with other metallic oxide impurities. This layer may have some carbon intermixed if desired, and is also covered by a thin top layer of carbon. Also, other metallic oxides and carbon may be added to this layer in the form of pellets or briquettes. Over the layer 29 is a layer of charcoal 30 similar to bottom layer 27, and the layers are repeated in the above described order to fill the ladle to any desired height. A fill of charcoal 31 on top of the last layer completes the charging of the ladle.

It will be understood that the above constitutes but one method of charging the materials into the ladle, and that the composition of the ma-

terials such as ores, fluxes and fuels may vary a great deal depending upon the particular operations being carried out in each instance. Some of the greatest economic and operating advantages of my invention are due to the fact that lower grade ores, fuels and other materials may be used in my process in the same condition in which they are mined than can economically and practically be used in other processes. The products produced by my process will meet the widely varying requirements of analysis, quality and other special characteristics demanded in industry.

The required quantities of oxides and carbon in the mixtures, as well as the relative amounts of sand, lime and other materials, will depend upon the specific analysis of materials to be used and results to be achieved in each particular instance and for each particular purpose. In each specified case, any person versed in the art of melting or of metallurgy will be able to calculate and determine the requirements according to the methods of calculation to be hereinafter described.

After the ladle is properly filled and the door or cover is closed, hot molten metal, such as molten iron, for instance, is poured into the ladle. In contact with the carbon layers, the hot molten metal starts absorbing part of the carbon. Also, some agitation is soon developed which, in addition to the absorbing of some of the carbon, brings the hot lime or other basic oxides together with the hot acid oxides. The acid oxides may consist partly of silica, but preferably the greater part will be present as alumina. Slag begins to form quickly. The heat of slag formation is so high that it raises the temperature of the slag and other materials in the ladle to an exceedingly high degree. For instance, the formation of calcium silicate slag ($CaOSiO_2$), releases about 372 B. t. u. per lb. of slag or 770 B. t. u. per lb. of lime reacted. The specific heat of this slag is about 0.23 B. t. u. per degree F° per lb., which would be sufficient to raise the temperature of the slag alone by about 1,620° F.

The reaction between lime an dalumina, however, in forming slag releases approximately 1,460 B. t. u. per lb. of slag consisting of

$$2CaO{\cdot}Al_2O_3$$

or 2,800 B. t. u. per lb. of lime, which would be enough heat to raise the temperature of this slag alone by more than 6,000° F. This great heat creates more boiling and agitation bringing together more and more basic and acid oxides (lime and alumina, for instance) from the different layers, the hot molten foamy slag working upward and in all directions so that the slag formation is quickly completed. During this time the plunger is holding down the charcoal, if so desired, to carburize the molten iron, to cause the reducing reactions to proceed in presence of carbon and to prevent the violently boiling slag splashing out of the ladle.

It should be noted that excessively high temperatures do not actually develop in practice. This is possibly because the oxides and other compounds reach the temperature where they dissociate or will not associate until the excess heat is used, thereby checking the temperature rise, and partly because the reactions such as reducing the oxides with carbon as described above will check the rise of heat and maintain certain heat balances.

In general, with my invention, the generation of heat, the temperatures developed, the reduction of specific amounts of specified oxides, the degree of carburization, the production of products and by-products such as slag for making alumina or cement and other features are under control, and the operations are performed under control.

The figures given above are only approximate, but are adequate for performing the needed calculations and to describe and illustrate the working of my invention.

A substantial part of this heat of exothermic slag formation is available for supplying the needed balance of heat for the carbonaceous reduction of metallic or other oxides, while the endothermic reducing reactions occur in presence of carbon. The carbonaceous reduction of silica (SiO_2) to Si will illustrate the method of calculation and method of operation.

In forming calcium aluminate slag as shown above, approximately 1,460 B. t. u. per lb. of slag is liberated. Let us assume that the materials originally mixed in the ladle have been brought to 2,500° F. It is well known that in presence of carbon silica reduces to silicon very rapidly in the temperature range of 3200° F.—3500° F. Assuming that the slag temperature remains at about 3500° F. raising all materials to this temperature absorbs about 300 B. t. u. per lb. of slag and there is a heat loss of about 100 B. t. u./lb. of slag, leaving 1,060 B. t. u., or in round figures 1,000 B. t. u. per lb. of slag for supplying the heat for endothermic reductions. The reduction of silica therefore will proceed as long as there is silica and carbon present and the slag is not cooled below a stage where silica no longer will reduce. An example will make this clearer.

Assuming a total of 100 lbs. of lime-alumina slag, approximately 100,000 B. t. u. of useful heat for reducing SiO_2 is liberated by the slag formation. In round figures 7,000 B. t. u. net is absorbed by reducing one lb. of silicon with carbon from SiO_2. Therefore with 100 lbs. of slag, approximately 14 lbs. to 15 lbs. of silicon is reduced. If there is more silicon in the slag it will stay combined in the slag as SiO_2 unless more lime is added, or lime and alumina as may be required by the acidity of the slag, because the reduction of silica cools the slag to a temperature where the silica will not reduce rapidly enough. It is evident that the reduction of silica comes to a balance or heat equilibrium and also controls or balances the temperatures of the slag and of the molten metal and carbon. Care should be taken that the slag is of such acid composition that it releases the silicon at the particular temperature of operation. The heats of reaction of slag formation of any particular slag analysis are easily calculated.

In a manner similar to the reduction of silica, practically all other metallic oxides may be reduced with carbon, the heat of formation of slag supplying the needed amount of heat. The temperatures at which the various oxides reduce in presence of carbon and their heats of reaction are known to any metallurgist or melting operator versed in the art, and also may be found in technical books. In order to facilitate the description and clarification of my invention, approximate heats of reaction and practical approximate temperatures of reaction of some of the most common lower and higher oxides will be given here.

Iron: FeO to Fe at 1900° F. 2,060 B. t. u./lb. Fe.
Manganese: MnO to Mn at 2900° F. 3,800 B. t. u.;
MnO_2 to Mn—7,600 B. t. u.

Silicon: SiO_2 to Si at 3200° F. 12,900 B. t. u.
Vanadium: V_2O_3 to V at 3100° F. 5,800 B. t. u.
Molybdenum: MoO_3 to Mo at approx. 3000° F. 3,300 B. t. u.

Copper oxide at very low temperature, 1080 B. t. u.; titanium from titanium oxide at 3500° F. 7100 B. t. u.; chromium from its oxide at 4500° F. 4720 B. t. u. These values are per pound metal. Temperatures of reduction and negative heat of reaction vary somewhat, according to what speed of reaction is desired or assumed. From these heat values, approximately 3270 B. t. u. should be deducted for each pound of oxygen liberated from the oxide and combined with carbon to form CO. In each particular instance the oxygen combined with a lb. of metal is calculated from the atomic weights.

A simple example will suffice to illustrate the case. The atomic weight of iron is 56 and of oxygen is 16; therefore 16/56 lbs. or 2/7 lb. of oxygen is combined with every pound of iron when oxidized to FeO. When this oxide is reduced with carbon this amount of oxygen therefore will combine with the carbon and release approximately 935 B. t. u. This subtracted from 2,060 B. t. u. gives 1125 B. t. u. which must be supplied. This, of course, assumes that only CO will form which is actually the case in such high temperature reduction. In each instance the heat generated by the oxygen combining with the carbon will vary somewhat and can be easily calculated by the analysis of the gas evolved.

By a further example I will show the specific method of calculating the heat needed to reduce silicon from the lime-silica-aluminate slag. Assume roughly that the aluminate slag is in the form of $CaOAl_2O_3$, which gives 100 B. t. u. per pound of slag or 2840 B. t. u. per lb. of lime. Also assume that the silica slag is in the form of $CaOSiO_2$, which gives 372 B. t. u. per lb. of slag or 768 B. t. u. per lb. of lime. Therefore the difference of heat generated by the slag forming reaction with a lb. of lime under the above conditions is 2840—768=2072 B. t. u. From the atomic weights it is calculated that every 28 lbs. of silicon reduced will set free 56 lbs. of lime, or 2 lbs. of lime per lb. of silicon. This lime, when recombining with alumina generates 5680 B. t. u. heat and therefore gives $2\times2072=4,144$ B. t. u. heat credit. Similarly, with 28 lbs. of silicon, 32 lbs. of oxygen is combined, or 1.17 lbs. of oxygen per lb. silicon, which from the previous figures, when combining with carbon gives $3270\times1.17=3820$ B. t. u. per lb. of silica. This with the heat credit obtained from the slag adjustment gives approximately 7964 B. t. u. heat credit, or 8,000 B. t. u. in round figures. The heat of formation of SiO_2 is 13,000 B. t. u. from which by subtracting the 8,000 B. t. u. heat credit 5,000 B. t. u. per lb. of silicon theoretical heat requirement is obtained. Now, while the heat losses in the process of reducing silica by my method is comparatively very small, 1000 B. t. u. loss per lb. of silicon may be assumed. This added to the theoretical heat requirement makes the total net heat requirement 6,000 B. t. u. per lb. silicon.

It should always be borne in mind that even under the same conditions with approximately the same kind and analysis of materials the slag and temperature conditions will always vary. This is characteristic of all similar reducing, melting and smelting operations. There is much more variance, however, when materials of highly differing analysis and temperatures are charged in the various instances. In such operations calculations are only a guide to help determine the approximate values and requirements. The essential characteristics of my new invention are that by following my method of operation the required or desired materials will be obtained with great savings in both labor and materials, and different and higher qualities, along with many other advantages, will be attained. In every instance and to each operator versed in the art of melting, smelting and similar operations, these calculations and descriptions will give an adequate guide to determine his operations so that by following my method of operation and by using my equipment he will obtain savings and other benefits.

In every instance, heretofore or hereinafter described, it should be borne in mind that there is no specific temperature to which the lime or other materials are to be heated in order to follow my method. However, any heat added to the materials will be so much more heat available for the reactions at higher temperatures. For instance, the specific heat of lime is 0.23 B. t. u./F°. Therefore it requires the addition of 460 B. t. u. to heat a pound of cold lime to 2,000° F. Therefore, if the lime is charged cold about 460 B. t. u. is to be subtracted from the balance of the heat of slag formation that may be applied for accomplishing other reactions as previously shown. The average specific heat of sand is approximately 0.25 and that of the iron oxide approximately 0.36. From these and similar available data any required or needed heat calculations may be made.

These examples give the method of calculation for each specific case. Since the different alumina sands and different metallic oxides contain varying amounts of iron oxides, manganese oxide, titanium oxide and other oxides, it is possible only by analysis or approximation of all the reacting materials to calculate how much carbon is to be mixed in and how much metal will be reduced from its oxide, or sulphide or other chemical combination.

The oxides will reduce in the order of their places as determined by the electro-potential series of metals. For instance, practically all iron oxide will be reduced first, then will follow manganese and then silicon reduction. The reduction proceeds as long as there is enough carbon present, and there is oxide to be reduced and there is enough heat to supply the heat needed at any particular temperature for the continuance of any particular endothermic reaction. Whenever there is no carbon or no heat available, the oxide that could otherwise have been reduced will remain as part of the slag. When there is no oxide available that could be reduced at a particular temperature the available heat will raise the temperature of the slag and the carbon that is submerged into it and will heat some of the iron until all come to a temperature equilibrium.

My invention of a method for treating oxides is also a new method of preparing calcium aluminate from various grades of bauxite. The bauxite ore is heated to drive out the moisture and the combined water. The iron oxide usually present is partially or fully reduced, or if so desired, no reduction of the iron oxide is performed. The hot dehydrated bauxite ore is then charged into the ladle or crucible together with alternate layers of carbon, lime, carbon and ore,

in any suitable sequence as previously described, and the top is covered with charcoal or other form of lumpy carbon. The reaction is started either by pouring molten slag or molten metal into the crucible, or by blowing hot air into it through the tap hole. The air burns with the charcoal creating intense heat and also bringing the acids and basic slag forming materials together. When the reaction has a good enough start to progress by itself, the indication of which will be the formation of molten slag, the tap hole is plugged in any known manner. The slag will be forming, creating intense heat and raising the temperature of the slag and of anything in contact with it. Charging hot charcoal instead of cold charcoal speeds up the slag formation and enhances the progress of reactions. The hot slag boils and rises, thus further speeding the reaction. When the temperature is high enough, around 2000° F. for instance, the iron oxide contained in the mixture quickly reduces wherever it is in contact with carbon. The unreduced iron oxide forms a part of the slag and is reduced from the slag by coming in contact with carbon. The reduction of each pound of iron reduced from FeO to Fe absorbs roughly 1,000 B. t. u. net.

When all the iron oxide is reduced the temperature rises further to a range where any manganese oxide which may be present is reduced. The temperature will then rise to a range over 3000° F. where the reduction of silica to silicon progresses rapidly. The molten iron, manganese and silicon flow down to the bottom forming a metal bath, and if desired all or any part of it may be removed at the different stages of operation to obtain the desired combination of metals. The hot charcoal is pushed down into the slag, or even into the metal bath and the reduction of the silica to silicon proceeds as long as there is silica available and there is heat available from the heat of slag formation to supply the needed heat to carry on the endothermic reaction of reducing silica to silicon. When there is no more silica to reduce, the temperature rises to a degree determined by the available remaining heat. If there are other higher oxides in the mixture, when the slag temperature reaches their range of reduction with carbon the reduction of the higher oxide proceeds, checking the rise of temperature. If the original silica content is so high that there is not enough heat produced by the slag formation to reduce all of the silica, the reduction stops at whatever temperature is reached, and the remaining silica stays as a combined part of the slag. If all or most of the silica content has been reduced and heat is still available, more silica or other desired suitable oxide or oxides may be added to utilize the excess available heat for the reduction of these oxides.

As shown before, the reduction of each pound of silica requires roughly 7,000 B. t. u. The exact theoretical amount, of course, corresponds to the heat of formation of the oxide, minus the heat of the formation of the evolved carbon monoxide and of a small amount of carbon dioxide and the available heat provided by the liberated lime due to reduction of silica to combine with the lime-aluminate. The radiated and conducted heat losses are, of course, losses from the net heat created by the slag formation.

Some more silica may be reduced from the molten bath if necessary by blowing very hot carbon monoxide or hydrogen into the slag through the openings **25** or **26**, or through the tap holes **15** and **16**. This, however, cools the slag quickly and no more reduction can be done without added heat.

When the desired reactions are completed, the molten metal and slag are tapped off through tap holes **15** and **16**. The remaining unabsorbed hot carbon that was on top will descend to the bottom and will serve as the bottom layer of carbon in the new pile as described above, or part of it may be removed.

After all or most of the iron oxide, silica and other contents that are considered as impurities, are reduced out of the mixture, the slag remaining will be concentrated molten calcium aluminate ($CaOAl_2O_3$) which forms the material from which the substantially pure alumina is separated to be used for the manufacture of aluminum and for other uses. The lime is recovered to be used over again in forming new alumina slag.

My invention also includes a process for making substantially pure alumina for the manufacture of aluminum and is described and carried out as follows:

As previously described, the bauxite ore or other suitable high alumina content ore together with the included impurities are preheated to a high predetermined temperature and charged into the ladle with a proper amount of preheated lime and carbon, preferably charcoal, and smelted as heretofore illustrated.

The degree of preheating of the charged materials and the amount of lime charged depend in each instance upon the amount and nature of the impurities contained in the charge, as previously explained.

In the smelting process the metallic oxides are reduced and separated and recovered as valuable metals and the remaining slag becomes substantially pure calcium aluminate.

This calcium aluminate slag is then treated with sodium carbonate (Na_2CO_3) solution in water whereupon the lime (CaO) is regenerated into calcium carbonate ($CaCO_3$) and precipitated out and will be recalcined and used again to form new slag with additional heated bauxite.

The remaining solution consists of sodium hydroxide (NaOH) and water, and alumina. Into this solution carbon dioxide (CO_2) which is obtained from the recalcining of the recovered calcium carbonate or obtained otherwise is introduced into the above solution, thereby precipitating the alumina. The sodium carbonate solution is recovered and used over again in the cycle of treating more calcium aluminate. The commercially pure alumina is dehydrated by the application of heat in a known manner, and is a valuable product in the manufacture of aluminum by electrolysis or by other suitable processes.

My invention has great industrial and economic advantage over all other known processes including those where sodium hydroxide and sodium carbonate are employed to precipitate the calcium carbonate and manufacture aluminum mainly because the impurities such as iron and other oxides and especially silica are separated and extracted in the smelting as valuable metals, also, the formed calcium aluminate slag is of substantially high purity as compared to calcium aluminate slag produced by other processes, which slag contains a rather objectionable amount of silica.

Obtaining calcium aluminate in a substantially pure form especially without objectionable silica content results among other advantages in the

following great economic and technological advantages:

The sodium hydroxide and sodium carbonate solutions are greatly concentrated as compared to the concentration of solutions used by other processes where approximately only two or three pounds of alumina, for instance, can be practically dissolved in a ton of solvent without dissolving too much silica with the alumina and thereby excessively contaminating the solution with silica.

Using my process, it is practical to dissolve ten times as much or even more alumina in the same amount of solution, as can be successfully accomplished in other processes. This can be carried practically to the limit of solubility of alumina. In contrast, the other processes will either dissolve an objectionable amount of silica while trying to dissolve more alumina, or, in order to reduce the silica content before the alumina is separated, a separate and expensive treatment is necessary. In my process no such separate silica treatment is required.

Furthermore, in other processes, eliminating even part of the silica from the slag wastes a great deal of time, alumina, and solvent, resulting in appreciable and serious material and economic losses.

My process also has the great advantage that it can use unconcentrated bauxite or alumina sand having a much greater content of silica and other impurities than it is practical to use with present processes. While at present there are only a few and meager amounts of commercially usable bauxite deposits throughout the world, there are vast deposits of less concentrated bauxite practically in all parts of the world that are practical to be used with my process and are not practical to be used with other processes without previous expensive concentration. Also my process extracts the silica in form of valuable silicon from these so-called low grade unusable bauxite sands, while with the other processes the silica is an expensive loss and a most objectionable impurity.

In general, the overall economy of my process in producing metals, iron and alloys and commercially pure alumina, and ultimately substantially pure aluminum from various bauxite ores is much greater than all other known processes.

The sequence of reactions is summarized as follows:

$$CaO.Al_2O_3 + Na_2CO_3 + H_2O \longrightarrow CaCO_3 + Al_2O_3 + 2NaOH + H_2O$$

$$Al_2O_3.2NaOH + H_2O + CO_2 \longrightarrow Na_2CO_3 + H_2O + Al_2O_3$$

$$CaCO_3 + \text{heat} \longrightarrow CaO + CO_2$$

It is evident that when my method is used in the above described manner, it is a new process for making ferro-silicon from the iron oxide and silica of the bauxite ores and preparing commercially pure or usable molten calcium aluminate ready for making aluminum.

Without departing from my invention, the hot lime and hot alumina ore with its iron, or iron oxide and silica content which may be poured or passed in two separate streams in proper proportions is also added. When the crucible is filled to the desired level with oxides, charcoal is added to the top, if desired, as previously described, and held down by the door or pushed down by the plunger 18. The molten slag flows down into the hot carbon at the bottom and the iron and silica or the other reducible oxides react with the charcoal as previously described. It is also practical, if so desired, to pour molten slag into the charge together with the two streams of hot lime and hot sand.

The slag reaction in any desired case may be expedited by pouring back into the crucible some of the molten metal or molten slag produced and previously tapped out, instead of pouring new iron into the ladle. In this manner a higher alloy content ferro alloy is produced. The iron content is controlled by analysis and selecting the proper bauxite or if desired, adding more iron.

In order to expedite the carbon distribution in the hot aluminum ore and hot lime, after they are heated, if so desired, hot cracked natural gas or other hydrocarbon gas containing carbon black is passed through them filling the pores of the mass with carbon black. Partly cracked methane or other hydrocarbon can be used to crack in the hot alumina ore, and also in the hot lime, depositing the carbon black in the pores. The cracked gas is at a very high temperature, possibly at about 2,500° F. It will reduce most of the iron oxide and will also supply the heat for the endothermic reaction of cracking the hydrocarbon. Also, the solid alumina and lime are hot and will give up some of the heat to the cracking gas. One ton of lime will supply about 140,000 B. t. u. and one ton of alumina 180,000 B. t. u. when cooled 300° F. Five thousand cu. ft. of gas cooled from 2,500° F. to 2,000° F. together with the heat in the contained free carbon and of its 20% methane, for instance, supplies about 65,000 B. t. u. This makes a total of roughly 210,000 to 220,000 B. t. u. which is enough to crack over 2,000 cu. ft. of methane, therefore more than enough to crack the methane content of the hot gas. In this manner over 100 lbs. of carbon black is deposited in a ton of alumina and about the same amount in a ton of lime, making about 200 lbs. carbon in two tons of slag material. This carbon deposit alone is enough to reduce 500 lbs. of silica to form 200 lbs. of silicon, provided the needed heat is supplied by the slag formation.

The carbon to be supplied is easily calculated in the following way: When the alumina sand contains 10%, that is, 200 lbs. of silica per ton of sand, and the lime to be used contains about 100 lbs. silica per ton lime, there is 300 lbs. silica to be reduced. This contains 140 lbs. silicon, requiring 120 lbs. carbon which is 3% by weight of 4,000 lbs. of reacting materials. When the deposited carbon is not sufficient, the charcoal sunk in the molten slag supplies the needed balance of carbon.

When 4,000 lbs. of alumina and lime are brought together in proper proportion, as shown previously, roughly 4,000,000 B. t. u. useful heat will be liberated. This is enough to reduce 572 lbs. of silicon from over 1,230 lbs. of silica which means about 30%–31% silica content of the combined weight of 4,000 lbs. slag. This clearly illustrates how important my new process is for making ferro alloys and high grade molten calcium aluminate not only from currently used grade of bauxite but also from very low grade and present non-commercial bauxite.

It is practical with my invention to apply the above shown 4,000,000 B. t. u. of useful heat for the manufacture of iron and other metals from their oxides on a commercial scale at a great economic advantage over the other known processes.

The iron ore is preheated and preferably prereduced to the extent where the reduction with reducing gas is fast, easy and efficient. In some

cases this stage of reduction in general, is desirable only to a stage where all the iron oxide is reduced to FeO, but in most of the cases it is easy and efficient to reduce the ore to a point where approximately one-half of the iron oxide is metallized and the remainder is in the form of FeO.

This partially reduced hot iron ore is charged into the ladle or crucible with the proper amount of carbon, hot lime and proper amount of alumina content slag forming acid as previously illustrated. As it is known, the addition of approximately 1,000 B. t. u. of heat is needed for reducing one lb. of iron from FeO. Therefore, the 4,000,000 B.t.u. of useful heat mentioned above supplies the heat for the carbonaceous reduction of 4,000 lbs. of iron from FeO. Since with every pound of FeO one pound of metallized iron is also present, it is readily seen that the 4,000,000 B.t.u. are sufficient to supply the heat for the manufacture of 8,000 pounds or more of metallic iron where combined with the separate partial reduction of iron ore. At the same time the formed slag will be useful for the manufacture of cement and, in some instances, of high grade alumina for the aluminum industry or for other purposes. The extent of partial reduction of iron ore and the amount of alloys reduced and manufactured in my process is easily determined in each particular instance by following the illustration and information given at several places in this specification.

Similarly, the process is used for preparing high alumina content cement by way of molten slag. The ratios of alumina, silica and lime are varied and controlled at will. The following description illustrates the method.

A desired and controlled amount of hot lime and hot high alumina sand are brought together in the ladle in presence of carbon by either of the methods described above. As slag forms, heat develops and the iron contained in the slag reduces and collects at the bottom, and also if desired, all or part of the silica is reduced. The slag when cooled is ground to make cement in the usual manner. By selecting the proper silica and alumina content sand, or making the proper mixture of sand, and considering the composition of the lime, practically any desired analysis of slag is formed to make any commercial grade cement.

Thus it is readily seen that my invention is also a usable and very economical method for the combined manufacture of iron and other metals and cement.

If desired, all or part of the iron oxide contained in the hot sand and hot lime is reduced by passing hot reducing gas through it preferably in the pulsating manner, described in my U. S. Patent No. 2,243,110. While reducing the iron oxide entirely or partially, or after it is reduced, a desired amount of carbon is also deposited in the sand or lime or both. Also, as previously described, carbon can be mixed in while charging the sand, silica and lime, or may be added separately. The sand and lime for the purpose of making cement or for any of the purposes coming within the scope of my invention, are so selected or are so mixed that the ultimate analysis of the slag satisfies the requirements for which it is intended, whether it is for cement, calcium-aluminate for making aluminum or refining slag for iron, steel or other metals.

If the sand, bauxite and lime as naturally found, does not give the required composition of slag or develop the required heat for the purposes intended, instead of adding the required lime or sand or bauxite to the original mixture the balance of hot sand, hot alumina or hot lime or all of them may be added to the hot molten slag in determined amounts. This method also comes within the scope of my invention.

In forming Portland cement a great deal of silica content is required. This silica with lime gives only approximately 372 B. t. u. per lb. of slag, which, however, is enough to raise the temperature of both by over 1,600° F. while the contained calcium aluminate slag adds about 1,400 B. t. u. per pound of slag. When high silica slag is to be formed it is rather important that most of the iron oxide content of the sand should be fully or partially reduced as may be desired, since there is not much surplus heat for iron oxide reduction when preheating the sand as described previously.

Furthermore, my method of utilizing the generated heat of slag formation for useful purposes, such as melting or reducing lower or high oxides into their metals or both, is also used for melting hot sponge iron with a considerable amount of gangue content, refining and carburizing the iron and reducing it into its alloys like manganese or silicon. The method is the following:

Hot carbon is charged into the bottom of the crucible or ladle, or hot residual carbon is left in it: The carbon is covered with hot lime, then with a block or quantity of hot sponge iron which has a definite amount of gangue of definite analysis, requiring a rather predetermined amount of lime for fluxing. Lime can also be charged around the sponge iron between it and the wall of the crucible. In some cases hot alumina or carbon or both is also added to the lime or on top of the lime or below it for the purpose shown below. Lime and carbon may be added to the charge in the ladle in any other suitable manner without departing from my invention.

In cases where the hot sponge iron does not form a more or less solid block but is broken up into lumps or is loose, like gravel or sand or powder, while charging into the crucible, the lime and also some carbon, preferably charcoal, if desired, is mixed in with it. In many cases it is also desirable to deposit a predetermined amount of hot carbon in the hot sponge iron as previously described.

In order to start the slag forming reaction, hot air or oxygen enriched hot air is blown through either tap hole to burn with the carbon. After the hot alumina slag starts forming, it will liberate heat and the slag formation proceeds by itself. The hot slag rises taking lime with it that further slags with the gangue of the iron, liberating heat and melting the iron. The reaction of slag formation and melting then proceeds rapidly and automatically, provided the proper amount of lime is present to form the proper hot fluid slag. Any person versed in melting or smelting iron or any trained metallurgist is able to calculate and determine easily the proper proportions of various acids, such as silica and alumina and bases such as lime, magnesia, etc. to obtain the proper slag and evolve the proper desired amount of heat. Some briquettes or pellets of a mixture of fine alumina and lime may be put in, if desired, right under the sponge iron or at any other suitable place to start the

hot slag formation and thereby liberate heat. Any other heat forming mixture, for instance, such as magnesium and other oxide, known as thermit, is satisfactory and is added if desired to start the slag forming reaction. In such a case, care should be taken that the heat of formation is not too violent, does not lift or blow the charge and does not affect the vessel or the personnel. It is also practical in order to start and promote the slag formation to pour molten slag over the top of the sponge iron or into the lime at the side.

When the desired proportions of silica and alumina are not present in the iron ore and consequently in the sponge iron to supply the heat for melting by the heat of slag formation, a predetermined amount of high alumina sand is added to the ore. Alternatively, hot high alumina sand may be added in the ladle or to the sponge iron while preparing the charge in the ladle. Of course, enough hot lime is also added to form the proper slag with the alumina sand or lumps. The alumina sand usually contains some silica.

Melting a ton of hot iron which contains carbon from sponge iron, which is at 1800° F., and raising its temperature to about 2,700° F. requires approximately 400,000 B. t. u. This amount of heat is supplied by forming approximately 350 lbs. of calcium aluminate slag. Usually, however, there is more than enough gangue of proper composition in the ore to supply the required heat of melting the hot sponge iron and slagging of the gangue by adding the proper amount of lime to form the desired slag.

As an example of operation a typical washed East Texas ore illustrates the case. The approximate analysis of the ore is 47% Fe, 11% Al_2O_3 and 10% SiO_2. After this ore is reduced to sponge iron at about 1,800° F., it requires approximately 400,000 B. t. u. to melt a ton of iron containing carbon and to raise it to 2,700° F. There are roughly 425 lbs. of silica and 475 lbs. of alumina with 2,000 lbs. iron. Adding about 900 to 1000 lbs. of lime forms 1,800 to 1,900 lbs. of slag. The 850 lbs. of calcium silicate slag has 200,000 B. t. u. heat of formation which is liberated and the 950 lbs. of calcium alminate slag 1,300,000 B. t. u. liberated, making a total of 1,500,000 B. t. u. liberated and available, as follows: Assume the case where the lime is charged at 2,400° F. It takes approximately 500,000 B. t. u. to raise the slag temperature by 1,000° F. leaving 1,000,000 B. t. u. About half of this heat is used by melting and raising the temperature of the iron, while the other half million B. t. u. is available for reducing silica to silicon. In presence of carbon this will supply enough heat if desired to reduce about 40 lbs. to 70 lbs. of silicon, which enters the iron bath, and which makes 2% to 3½% silicon iron. The high temperature thus reached also serves to carburize the iron to a high degree. If more heat is required, as mentioned above, more hot alumina is added and the required amount of lime or other suitable basic oxide with it. Similarly, manganese oxide is also reduced by the carbon. Heats of reaction of other slags of any definite composition may be easily determined as previously explained and illustrated.

Thus the melting, as well as the silicon, manganese and carbon content of the iron is controlled by the gangue content of the iron ore, by the amount of lime added and by the temperatures of the materials, which is the total heat in the materials.

My process is used also for melting and refining solid scrap or pig iron or steel or their mixtures. The solid iron or steel is preheated to any desired temperature, for instance to about 1500° F. At the bottom of the ladle is placed some carbon and some hot lime or hot alumina. The hot solid iron is charged into the ladle and a predetermined amount of hot alumina sand and hot lime is added. If the lime and alumina sand are not hot enough to start the reaction, some amount of hot molten iron is poured in which will start the slag formation that will proceed rapidly and come to completion generating large amounts of heat. The slag formation is started, if so preferred by blowing hot air through the tap hole.

To the solid mixture of preheated steel or iron or both and slag forming materials and carbon, it is practical to pour hot molten pig iron in any desired quantity into the ladle where, together with the iron and steel which had been added in solid form and become melted, the pig iron is refined. By regulating the temperature and carbon content and adding the desired alloying elements, it is practical and economical to manufacture almost any type and grade of steel known at present.

It is also practical with my invention to pour molten pig iron into the ladle without the addition of solid iron and to refine the pig iron and make steel out of it. In such a case in order to decarburize the molten iron, iron oxide is added. The usable generated heat of slag reaction supplies the heat for the endothermic reaction for reducing the added iron oxide with the carbon contained in the pig iron.

It is thus readily seen that my invention is a new and practical process for melting and refining iron and making steel out of it directly, whether the iron is in the form of solid iron and steel scrap alone or in form of molten scrap or molten pig iron or any of their combinations. Furthermore, this is done without addition of external heat after the initial preheating of some or all of the materials charged.

In the well known process of open hearth refining and melting the same results are possible only with the addition at high temperatures of large amounts of external heat, which is inefficient. In the open hearth it is also difficult and costly to make steel either from scrap or pig iron alone, and usually a mixture of the two is needed.

In the electric furnace, steel may be made from either or both separately but this again requires the addition of external heat in form of electrical energy which for this and other reasons is a costly operation.

My process is also easily used for partially refining or refining and making into steel iron which has been melted or partially prepared in other types of furnaces. If desirable, the material thus prepared by my process may be further treated in other types of furnaces.

In order to finish the melting of the red hot scrap or pig iron, about 350 B. t. u. is needed per lb. or 700,000 B. t. u. per ton. This amount of heat is furnished by the formation of about 700 lbs. of alumina slag, the formation of which also raises the temperature of the whole charge to about 3000° F.

The carbon in the ladle reduces the iron oxide formed on the surface of the heated iron. If some such iron oxide is left it will serve for combining with the phosphorous in the iron and with the slag in the well known manner. If not enough iron oxide is left it can be added to the molten charge as heavy lumps sinking into the iron bath, causing it to boil while melting and partially re-

ducing and combining with the phosphorous. Thus the hot slag forming acids and bases serve not only as source of heat for melting the iron but also for refining the iron and steel.

The amount of heat to be developed, the amount of lime and alumina sand, and their temperature as well as their composition, are easily calcualted by any technician versed in the art of melting and metallurgy, who can also easily determine the amount of carbon and iron oxide, which always depends upon the nature or analysis of the desired end-product of carbon or steel.

My invention is also a new method of carburizing the hot iron, and if desired, carburizing it to a higher degree than it has been heretofore practical or economical. It is also a new method for attaining different and highly desirable carbon structures, some of which will be different from any heretofore attained in any comparably economical process.

It is a scientific fact that iron, well above 3000° F. absorbs substantially more carbon than below this temperature and also that the structure of the carbon content is much finer, different and more desirable than the structure that can be obtained below these high temperatures. The different steel and iron castings made with this fine carbon structure have many desirable characteristics not obtainable or practical with the coarser carbon structure obtained from carburization at lower temperature. With the present processes such high temperatures are either not attainable or not practical, while with my process the obtaining of extreme high temperatures are not only possible but commercially feasible, practical and economical.

The degree of various high temperatures is controlled and regulated according to the need for a particular carbon structure and other specified requirements.

For this purpose, preferably charcoal is placed at the bottom of the ladle, and hot alumina sand and hot lime are poured or charged on top of the carbon. A layer of hot charcoal, coke or carbon in other form is charged as top layer. When the lid is closed, the molten metal to be carburized is poured in, starting slag formation. The very hot slag collects on top of the iron and penetrates the charcoal charge. Now the plunger is moved upward and the charcoal is lifted from the molten iron by the heavy, fluid iron and the hot slag surrounds the carbon, heating it considerably. This superheated charcoal is then pushed down into the iron which absorbs some of the hot carbon. Again the carbon is allowed to lift and is heated by the slag again and then is pushed down into the molten iron again, increasing its temperature and carbon content. By repeating the operation any desired number of times the desired degree or a very high degree of carburization is reached.

The carbon pile may not only be alternately submerged deep into the molten charge and allowed to lift, but may be oscillated up and down so that it constantly changes its level in the bath and thereby its contact with the particular layers of metal and slag.

It should be borne in mind that while I have shown a particular type of plunger for submerging the carbon pile, it is obvious that there are many other suitable ways and means of accomplishing the same purpose without departing from my invention. Similarly, any particular construction of top, or door or shape of vessel, or gas outlet or other details obviously are not essential to carry out the purposes and operation of my process, as different materials and different production will require somewhat different designs. Different designers, builders or users of equipment will construct the plant in somewhat different ways. In some instances the plunger, or even the door may be dispensed with since a lesser degree of carburization can be achieved by letting the carbon pile float in the molten metal or slag. The carbon pile may also be pushed down by other simpler means than by a plunger, for instance by a rod, weight or other device.

My method will also be useful for putting into the metals alloys lighter than the metals themselves. For instance, by my method magnesia can be added easily and economically to the iron for alloying the two metals. Lumps or bars or sheets of magnesia are placed on the bottom of the ladle and hot carbon lumps are placed over the solid magnesia and the carbon pile is held down as previously described. The molten iron melts the magnesia, absorbs it and becomes alloyed with it. In this way the oxidation of most of the magnesia is prevented, practically all the magnesia is absorbed and the amount is controlled, except for the amount which combines with the oxygen contained in the molten iron. The hot carbon maintains a reducing atmosphere so that there will not be much tendency for oxidizing the magnesium.

If absorption of carbon is not desired, some very dense carbon such as broken electrodes or possibly dense refractories may be utilized.

The magnesia may be added without removing the carbon pile. For instance, a hole may be made in the center of the pile whereby the magnesia block or lumps may be placed at the bottom and held down by a block or rod of electrode or of other type of solid carbon or refractory while the molten iron is poured down into the pile.

The solid magnesia can also be held down at the bottom of the ladle by a solid carbon rod, column or electrode which preferably has a hollow space at the bottom, while the molten metal is poured into the ladle. The magnesia will be prevented from floating to the top and therefore from becoming oxidized. The molten metal then will dissolve and absorb the magnesia, part of which will also act to deoxidize the molten metal.

Another method of submerging the reactive light alloy or carbon or their combination is as follows: The ingredients to be absorbed are placed into the hollow on the end of a rod and sealed by any suitable substance easily dissolved by the hot molten iron such as wax, pitch or a thick or thin layer of concrete. The rod may be carbon, refractory or simply steel. The deoxidizer, carburizer or nodulizer or other mixtures are pushed down into the bath and held down until absorbed. The part of the steel rod is dissolved by the hot metal but by that time the lightest metals and the carbon will be completely absorbed. At the end of the rod may also be placed a closed container of easily meltable metal of suitable composition. The lower end of the container may be sealed with easily solvable material so that the molten metal absorbs the contents of the container before it has a chance to float to the surface where it would become oxidized.

It should be kept in mind that, while for the sake of simplicity and brevity only magnesia as light metal has been mentioned, nevertheless all other deoxidizing light metals, such as calcium, barium, titanium, cesium, etc. may be used, or

even heavy metals or any combination thereof may be used without departing from my invention.

The above described method of submerging the deoxidizing, alloying and other elements into the molten metal bath is not limited in its application to the ladle illustrated, but may be used in any type of melting or refining furnace such as an electric furnace, gaseous melting furnace, mixing ladle or other device. The ladle or crucible construction may be such that the top or roof of an electric furnace will fit over it, in the manner of top charged electric furnaces. After the desired reactions and operations are accomplished in the crucible, the electrodes with the roof may be placed over it, or the crucible moved under the electrodes, and further operations practical in electric arc furnaces may be carried out. Thus the electric furnace may be practically combined with my process for performing the operations as taught by my invention.

Another but similar method of carburizing the metal and at the same time putting in the deoxidizing light metal or other alloys is as follows:

Finely divided or granular carbon and finely divided or granular metal or metals are mixed and made into briquettes, rods or any other suitable form. If desirable, a suitable binder or other materials such as lime, alumina, etc. may be also mixed in. This mixture may also be coated with suitable coating like tar or clay, or may be enclosed into metallic casing to prevent slow oxidization or even possible ignition. The briquettes may have any desired looseness and porosity, or the mixture may even be kept in a loose state when surrounded by a casing or coating. These briquettes will then be submerged into the ladle or furnace as described above. Since the molten iron has a great affinity for the magnesia and other similar elements mentioned above, it will absorb the magnesia, leaving the carbon very porous and thereby facilitating the absorption of carbon also.

The carbon and the alloys or deoxidizers or any of their combinations may be so proportioned in the briquettes or "pills" that they will leave the desired amount of carbon and the other metallic elements in a molten or solidified metal. For this reason several different mixtures may be made from a properly selected combination from which the desired ultimate results of analysis of alloyed metal may be obtained.

A combination of slag forming refractories such as alumina, silica and lime may also be so mixed with carbon that they react with each other in the molten iron and form slag. The carbon mixed with them is absorbed by the metal to provide the proper carburization or to add the balance of carbon desired. Preferably, mainly alumina and lime should be used as slag forming materials. At the same time the slag forming materials are reacting to form slag, they develop a large amount of heat helping not only the carburization but also, if desired, the temperature rise of the molten metal as well as the refining of the metal.

This, for instance, will be very important when making iron or steel with nodular structure, the so-called nodular iron. In the nodular iron the very low sulphur content is very important. The hot slag formation which will cause boiling and agitation of the molten metal will have great affinity for the sulphur, especially if so proportioned that it is strongly on the basic side. It is also partly due to the high temperature developed.

Another practical method of preventing reoxidation of the alloys and light metals in the ladle is so to construct the ladle that reducing atmosphere is maintained in the ladle while pouring the metal into it. The reducing atmosphere may be maintained for instance by covering the ladle and keeping it gas tight while blowing reducing gas or neutral gas into it through a pipe suitably placed into the cover or into the side while pouring molten metal through a hole or spout into the ladle in which the above mentioned materials have been previously placed, thus preventing them from reoxidization.

The same purpose may be accomplished by pouring the molten iron first into the ladle and keeping reducing atmosphere over the molten metal while adding the above named elements and while those elements are being absorbed by the molten bath.

This method is also used for raising the temperature of the molten iron to any desired practical degree. It is interesting to consider that the specific heat of slag is about 0.23, that of the carbon is roughly about 0.4 while that of the iron only about 0.15 B. t. u./lb. which shows how favorable the heat quantities are for increasing the temperature of the molten iron or of other metals by following my method of doing it.

Preheated air may also be blown into the carbon bed at any time during the operation. This should be done preferably after the pressure on the carbon is released and it is lifted out of the metal bath. The carbon will burn with the hot air at a very high temperature making the carbon very hot. When the carbon is forced down into the metal bath, part of the excess heat of the carbon will be transferred to the metal that again penetrates the pores of the carbon. Since the temperature increase enhances the absorption of carbon, the hotter metal will absorb more carbon when the carbon is very hot than it will when the carbon is cooler.

If even higher temperature of carbon is desired than it is practical to reach with preheated air the air may also be enriched with oxygen, or oxygen alone may be used instead of preheated air. The oxygen is blown in preferably near the contact of carbon pile with the molten iron, creating very intense localized heat near the metal surface but away from the refractory wall of the ladle (or of the furnace). This intensely heated carbon, when pushed down into the metal bath, will not only be absorbed more readily by the metal, but also will transfer its excess heat to the metal. Thus the carburization will be materially aided and intensified, partly by the increase of temperature of the metal and partly and to a greater degree by the much greater temperature of the incandescent carbon.

Since the specific heat of the carbon is almost three times as much as that of iron, the heat of the carbon over and above the heat of the iron at a lower temperature of the iron bath will add to a considerable amount to the temperature of iron in contact with the carbon, thereby further enhancing the absorption of the carbon.

A considerable but lesser amount of carburization is accomplished, of course, by blowing hot air or oxygen into the carbon more continuously over or near to the surface of iron, making the carbon intensely hot. As the carbon is absorbed by the iron more hot carbon is pushed down into the bath. For this type of carburization an up and down motion of the plunger and carbon may be required.

By alternately bringing the carbon to such an intense heat substantially above the temperature of the metal bath and by pushing down the hot carbon into the bath, not only is the absorption of carbon enhanced but the temperature of the iron is increased much faster and more efficiently than by the present method of firing with gas or oil over the metal surface, as in the case of the open hearth furnace, for instance. This will be illustrated by a numerical example.

Eighty pounds of pressed carbon occupies about 2 cu. ft. and has about 1 cu. ft. of void. When heated, for instance, to 600° F. above the temperature of the metal and pushed into the metal bath, the 80 lbs. of carbon will be penetrated by about 500 lbs. of iron when the temperature of iron and carbon has become equalized, thereby raising the temperature of the iron by about 200° F.. By repeating the operation, the temperature of the iron may be easily and quickly raised by 400–500° F., without excessive overheating of the refractories and without excessive heat loss.

In releasing the weight of force over the top of the carbon pile and allowing it to rise to the surface there will be some molten iron in the pores and on the surface of the carbon. By blowing hot air or oxygen into this part of the pile, the iron is oxidized with great speed, allowing the rapid heating of the pile. Of course the molten iron oxide again will reduce with the hot carbon, but the net result of temperature still will be the same as if the oxygen had burnt fully with carbon alone. This is due to the law of conservation of energy. However, the heating will be more intense and the absorption of the carbon by the reducing iron more complete.

When the desired amount and composition molten metal accumulates, it may be tapped out of the ladle together with the molten slag. The firing of the pile may also be done by a pulsating or intermittent repeated blow or stream of air or of oxygen. In this way only part of the iron lifted by the carbon pile will be oxidized. Part of the intense heat developed on the surface of the carbon pieces is transferred to the iron in the pores of the carbon. The hotter iron will absorb more carbon and become more fluid, and will drip down into the iron bath carrying with it more carbon.

By following the above described method some silica can also be reduced from the molten slag to silicon which will flow down into the iron bath and will alloy with the iron. Some silica lumps or sand may be charged with the charcoal in layers, or scattered in the charcoal which is preferably ground, near the vertical center line of the furnace or ladle. As the charcoal descends the very hot gases and hot carbon will reduce the silica to silicon. The silica may also be charged in a very hot plastic form or poured in over the top in a molten form. It may also be blown into the hot carbon bed through the air or gas inlet in a powdered form by the heated air, oxygen or some other gas. Oxygen especially will create very intense heat, which combined with the very hot carbon monoxide and very hot carbon will greatly enhance and intensify the reduction of silica. While any spot in the furnace or ladle would be overheated when fired with oxygen, the heat necessary for heating the silica and the heat absorbed by the endothermic reaction of reducing silica to silicon will cool the carbon bed to a temperature where it will not excessively damage the lining of the surface.

Also manganese and other oxides may be treated in a manner similar to silica. Any of these oxides may be powdered and mixed with carbon to which a binder may be added if so desired, and briquettes made from the mixture. These briquettes may be gradually charged so that in descending they reach the hottest part of the furnace. The ratio of the oxide and carbon preferably should be such that the amount of carbon will be greater than determined by the stoichiometric ratio for reducing the metallic oxide. The surplus residual carbon will protect the oxide from being affected by any slag formation and protect the reduced metal from reoxidization. It is thus readily seen that my process of repeatedly submerging hot carbon into the molten metal and into the slag above it and blowing hot air or oxygen into the carbon pile while it is floating above the surface of the metal or slag is used in a practical and economical way for recovering the desired metals from the metallic oxides in the molten slag.

My invention is also used as a new method for producing zinc from its oxides, sulphates or chlorides. The zinc oxide is charged between two layers of bases and acids consisting preferably of lime and high alumina sand. Molten iron is poured over the mixture. The oxygen of the zinc oxide is removed from the zinc by oxidizing the iron, whereupon the zinc is vaporized leaving the oxidized iron in the slag. The zinc vapor is condensed after leaving the crucible. For this purpose the top of the ladle or crucible is so constructed that the vapor leaves through a pipe without leaking into the atmosphere and is condensed. Such construction needs no illustration here as it can be designed and constructed by an average mechanic from the information and specification heretofore given.

The iron oxide is combined in the slag and is reduced from it by carbon in the manner previously shown.

Similarly, zinc sulphate will give up its sulphur to the iron, from which it is oxidized by blowing hot air into the hot slag and replacing the sulphur in the iron by oxygen. The iron oxide is then combined in the slag from which it is reduced out by carbon in a manner previously shown.

Reducing the iron oxide, manganese oxide and other oxides from the hot molten slag that is formed in the crucible as shown above is also accomplished when desired in the following way without departing from my invention.

My invention of utilizing the potential energy of cold or preheated basic and acid oxides for forming heat energy in a vessel for melting metals and their oxides and gangue materials and forming very hot slag and then reducing some of their metallic oxide content either from the slag or from the hot solids, is also combined with reducing the iron oxide, manganese oxide and silica from the hot slag by blowing hot reducing gas into the slag through the opening **26** in the side of the ladle. This reducing gas is either carbon monoxide, hydrogen or the combination of both. Preferably hot cracked gas is used as it comes from the thermal cracker, or hydrocarbon gas containing the carbon black that is carried out of the checker work of the gas cracker along with the hot cracked gas may be used. The reducing gas as well as the carbon black reacts with the oxide in the slag or in the sponge iron block. The reduction of iron oxide with hydrogen and carbon monoxide is exothermic at such temperatures, and adds heat to the slag to further raise its temperature. Some

of the heat produced, however, by the reducing reaction, is carried out by the reacting gas that becomes further heated in the ladle or crucible before leaving it.

The crucible or ladle may be so constructed that the lid or top is made gas tight, while the gas leaves the crucible through a pipe or stack preferably through the side of the ladle. The gas leaving the crucible is utilized for heating if desired, or the steam is condensed and the carbon dioxide is scrubbed out or reacted to form carbon monoxide which is preheated and passed back into the crucible as reducing gas.

The top of the slag is preferably covered with charcoal or other carbon that floats over the top of the slag or stays over the top of the solids. The reducing gas that is blown through gas hole **26** makes the slag foamy so that it splashes over the charcoal providing more surface contact for the reacting oxide and gas. The charcoal layer prevents the foamy slag or molten oxides splashing or being carried up by the gas.

Some of the oxidized gas reacts with the carbon that cracks the steam and CO_2, but this reaction is so cooling that soon the temperature of the carbon is lowered and the reaction is stopped. A temperature balance is established between the carbon and used gas in any operation.

In many instances some reducing gas is passed into the crucible with a sudden great velocity so that the slag is made more foamy and splashes over the charcoal covering the charge. The oxide to be reduced thus becomes more exposed to the action of the reducing gas. This jet of high speed gas is then followed by a more steady flow of reducing gas, alternating between a jet and steady flow, in a pulsating manner.

My process may also be used to great economic and operating advantages in connection with utilizing open hearth, electric furnace and blast furnace slags to form cement. The refining slag in an open hearth furnace contains too much iron oxide to be used for cement making directly, and in most cases also contains too much phosphorus. Such slag, however, may easily be turned into usable and high grade cement by following the teachings of my invention.

After the molten slag is poured off or tapped out of the open hearth it is transferred into my ladle for further treatment to extract from it the iron oxide and phosphorus and some other impurities to any desirable degree. The proper amount of lime or other bases are added to the slag for adjusting the composition to obtain the proper cement and to assure reaching the proper temperature for reducing the iron oxide and the phosphorous out of the slag. After this, hot reducing gas is blown or passed through the slag in any suitable manner. This reducing gas may be hydrogen, carbon monoxide or both, and if desired may contain carbon.

It may also be feasible, as previously described, to treat the slag with charcoal or other carbonaceous reducing material. Whenever the molten slag contains enough surplus sensible heat to maintain the reducing reaction with carbon, no addition of heat will be necessary. Otherwise heat may be added by first preheating the carbon before submerging it into the molten slag, or it will also be practical to produce heat by adding more lime and high alumina content slag forming acids. The reaction with reducing gas, especially with carbon monoxide, will be strongly exothermic, and in most cases will not require the addition of heat.

It will also be practical in most instances not to add any lime to the reducing slag whether it is from open hearth or from basic electric furnace, since these slags in most cases contain much lime, usually enough to form good cement. If desired, lime may also be added to the slag after the iron and some other oxides are reduced, in order to meet the desired specification.

Molten blast furnace slag may also be treated by my method by adding the required amounts of hot or cold acids or bases to produce the type of cement desired. Sulphur compounds may be burned out by means of hot air, and the various oxides present may then be reduced as previously described.

What I claim as my invention is:

1. A method of refining metal comprising introducing carbon, lime, alumina and silica into a molten metal bath and holding said materials submerged in said bath until said materials are absorbed by said bath.

2. A method of refining metal comprising introducing carbon, lime, alumina and silica into a molten iron bath and submerging said materials in said bath until said materials are absorbed by said bath.

3. A method of refining metal comprising adding carbon, lime, alumina and silica to a molten iron bath and maintaining a reducing atmosphere over the molten metal while said elements are being absorbed.

4. A method of refining iron comprising forming briquettes of a predetermined mixture of carbon, lime, alumina and silica, adding said briquettes to a molten iron bath and maintaining a reducing atmosphere over the molten iron while said mixture of carbon and slag is being absorbed.

5. A method of refining iron comprising forming briquettes of a predetermined mixture of carbon, lime, alumina and silica, adding said briquettes to a molten iron bath, and holding said briquettes submerged in said bath until the carbon is absorbed and the slag is formed.

6. A method according to claim 5 wherein a deoxidizing atmosphere is maintained over said molten iron bath.

7. A method according to claim 5 wherein additional alloying materials are included in the briquette.

8. A method of refining iron comprising charging carbon, lime, alumina and silica into a ladle, pouring molten iron over said materials, and maintaining a reducing atmosphere in the ladle while said charged materials are being absorbed by said molten metal.

9. A method of producing calcium aluminate slag comprising charging alternate layers of carbon, lime and alumina sand into a ladle, pouring molten metal over the charge to start the slag forming reaction and generate heat, and maintaining proper reducing conditions and temperature within the ladle to effect reduction of oxide impurities to their respective metals.

10. A method of producing calcium aluminate slag comprising charging carbon, lime and alumina sand into a ladle, pouring molten metal over the charge to start the slag forming reaction and generate heat thereby producing molten slag, and submerging the carbon in said molten slag to effect reduction of oxide impurities to their respective metals.

11. A method of producing calcium aluminate which is substantially free from silica comprising charging preheated carbon, lime and a mix-

ture of alumina and silica into a ladle, introducing oxidizing gas into the carbon to generate heat thereby, causing the lime to react with said alumina and silica to generate additional heat and produce molten slag, and then submerging the carbon in said molten slag while maintaining high temperature to effect reduction of said silica to silicon.

12. A method of producing calcium aluminate comprising charging preheated carbon, lime and a mixture of alumina and silica into a ladle, introducing oxidizing gas into the carbon to generate heat thereby causing the lime to react with said alumina and silica to generate additional heat and produce molten slag, heating carbon substantially above the temperature of molten slag to supply heat balance for reducing the silica to silicon, and then submerging heated carbon into the slag, permitting carbon to rise to the top of the slag, reheating the carbon and resubmerging and continuing the alternate heating and submerging of the carbon until iron oxide and silica are reduced.

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