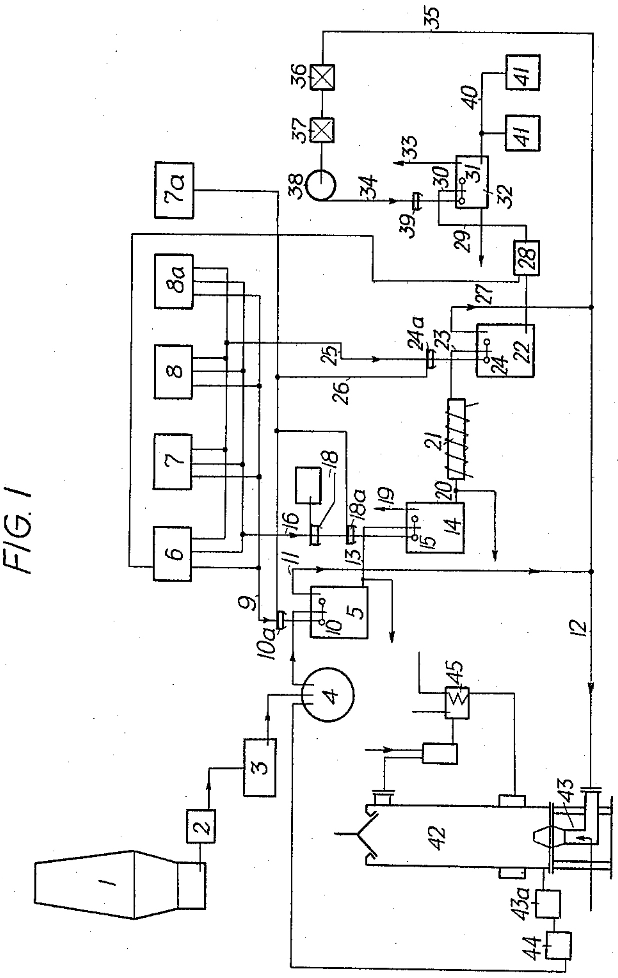
Feb. 22, 1966 A. MITTERMAYR 3,236,637

PROCESS OF CONTINUOUSLY CONVERTING MOLTEN CRUDE IRON INTO STEEL

Filed June 25, 1962 2 Sheets-Sheet 1

FIG. 1



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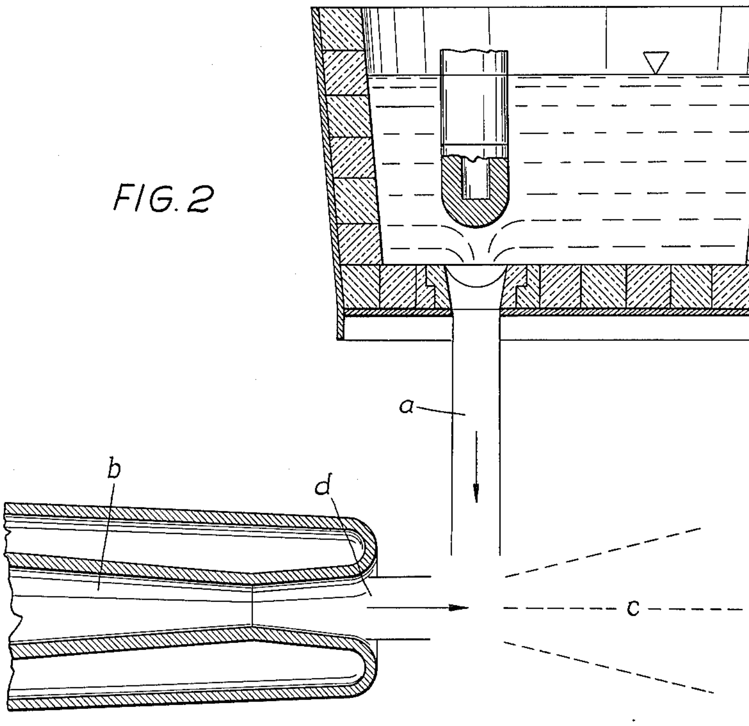
2 Sheets-Sheet 2

FIG. 2



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PROCESS OF CONTINUOUSLY CONVERTING MOLTEN CRUDE IRON INTO STEEL

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7 Claims. (Cl. 75—60)

The invention relates to a process of continuously converting molten crude iron into steel by refining with a refining agent containing gaseous oxygen in free or combined form.

Continuous refining processes are known, in which the reactants crude iron, refining agent and slag-forming substances are continuously introduced into a reaction vessel and the steel produced is continuously withdrawn. A known proposal of this kind calls for passing the molten crude iron in contact with the refining agent through a horizontal drum-type converter, which is divided by baffles into a plurality of cylindrical sections. It was an object of this proposal to divide the process into stages, in which different reactions (desiliconizing, decarburizing, dephosphorizing) take place.

According to another proposal of this kind the refining process is carried out in a plurality of separate reaction zones, including one or more prerefining reaction zones and a decarburizing zone, in which zones different temperatures are maintained and into each of which zones oxygen is blown with lances.

The known processes described have not been developed to a production scale, as far as is known, because they lack an essential requirement of continuous processing, namely, a high rate of reaction within a small space. In fact, the measures proposed, including the blowing of the refining agent by means of lances into relatively voluminous converters and the maintenance of liquid metal baths in the converters are based on the intermittent processes and are only suitable for processes carried out in successive heats.

It is an object of the present invention to eliminate the disadvantages and difficulties described. The invention provides a continuous process for converting liquid crude iron into steel, in which process the desired high rate of reaction in small reaction chambers is actually achieved.

The process according to the invention is carried out in a plurality of separate reaction zones, including at least one prerefining reaction zone and one decarburizing reaction zone, in which zones different temperatures are maintained, and is characterized in that the crude iron is atomized at its entrance into at least one of the reaction zones by means of the refining agent. The fact that the reaction is carried out according to the invention in a finely divided, e.g., atomized state, ensures the large contact surface required, which enables a maximum rate of reaction and, consequently, a minimum refining time in each zone, while optimum conditions regarding temperature and oxygen supply are maintained. As a result, small reaction chambers are sufficient and there is no need for extensive conveying and auxiliary installations.

In the process according to the invention, the reaction zones are completely separated, i.e., closed reaction chambers are used, which do not communicate with each other. As a result, different conditions regarding temperature and pressure can be maintained in the diverse chambers; any mutual influence is avoided, a formation

of smoke and dust is prevented and combustible waste gases from one chamber can be rendered utilizable. The reaction zones or chambers are suitably arranged one behind the other in cascade so that the crude iron can be transferred by gravity.

As has been mentioned hereinbefore, it is an object of the invention to divide the refining process into individual stages and to provide large reaction surfaces to achieve a maximum reaction. Regarding affinity to oxygen, the elements accompanying the crude iron do not have a uniform behavior. The consideration of the equilibrium relations of the oxidation reactions of each of the elements which accompany crude iron, particularly Si, Mn, P, Al, C, shows that in the temperature range in which steel is made the behavior of carbon differs basically from that of the other elements because the affinity of carbon to oxygen increases whereas the affinity of all other elements decreases with an increase in temperature. In the temperature range of the liquid iron manganese has the highest affinity to oxygen; this is followed by silicon and aluminium.

In the process according to the invention, these relations are taken into account by the maintenance of specific temperatures in the individual zones and/or by the maintenance of the optimum oxygen supply. If the accompanying elements contained in the crude iron—besides carbon—comprise only manganese and silicon, which can be removed without addition of slag-forming substances, a single prerefining reaction zone is sufficient. When phosphorus is also present, an additional prerefining reaction zone is provided; in this case silicon and/or manganese will be removed in the first reaction zone without addition of slag-forming substances and phosphorus will be removed in the second reaction zone, to which lime, particularly lime dust, is added. The prerefining and the dephosphorizing reaction zones are preferably held at a temperature of 1250–1350° C. whereas the decarburizing zone is held at a higher temperature, of 1550–1800° C. In the prerefining reaction zone or zones a refining agent having a relatively small oxygen content, such as air or a mixture of oxygen and CO_2 or H_2O is suitably employed. In the decarburizing zone, best results are obtained with oxygen-enriched air or technically pure oxygen. Solid oxides, particularly oxides of iron, may be added to the gaseous refining agent, as will be described more fully hereinafter. The individual reaction zones are suitably held at the predetermined temperature by a heating which is independent of the refining process.

In view of the above-mentioned principles of the process according to the invention, a preferred embodiment for the conversion of crude iron which contains phosphorus in addition to silicon and manganese comprises the following stages:

I. Oxidation of silicon and manganese at a low temperature and removal of the oxidation products of iron formed.

II. Oxidation of phosphorus and sulfur in the presence of slag-forming substances at a low temperature, separation of the slag from the iron.

III. Heating up to the carbon reaction temperature and steel melting temperature.

IV. Oxidation of carbon at a high temperature.

V. Deoxidation of steel with gaseous and/or solid reducing agents.

VI. Killing and alloying.

In the heating-up zone, the crude iron is heated to the temperature of the decarburizing zone. As distinguished from the known refining processes the heat of combustion of silicon, manganese, phosphorus and iron, which are highly expensive heating means, is not required for this purpose, the heating being accomplished with an inexpensive heating means, such as gas or electric heat. The oxidation of the crude iron-accompanying elements in the prerefining reaction zones should not result in a substantial temperature rise because this would lower the reaction rate in the prerefining zones. As has been mentioned hereinbefore, prerefining is preferably effected with a slightly oxidizing gas, such as CO_2, H_2O or air or mixtures thereof. In particular, the refining agent may be selected from the group consisting of air, a mixture of oxygen and CO_2, H_2O, and a mixture of oxygen and H_2O. Alternatively, a mixture of solid and gaseous reactants may be employed. The most economical operation will be obtained when a mixture of gaseous and solid oxidizers is used for refining because in this case the iron ore (solid oxidizer) is reduced to iron in a direct steelmaking process by the elements silicon, manganese, phosphorus, and carbon. In this phase, the refining process constitutes a combined smelting and refining process.

The process according to the invention and the plant for carrying it out will now be explained more in detail with reference to the drawing. FIG. 1 is a flow sheet, FIG. 2 is a diagrammatic showing of a preferred method of atomizing the metal.

In FIG. 1, **1** is a blast furnace, which can be operated with a minimum coke requirement (stahleisen). The crude iron passes over a slag separator, which is shown as a forehearth **2**, to the desulfurizing unit **3**, in which the crude iron is to be desulfurized to a high degree because a special desulfurizing step is not provided for in the succeeding refining process.

A mixer **4** precedes the cascade refining plant according to the invention. This mixer serves as a crude iron storage and equalizing container. The mixer is not essential because the crude iron may be supplied directly from the blast furnace if the same supplies crude iron continuously.

The cascade refining process comprises the previously listed stages I to VI; the oxidizing and refining stages are carried out in the closed oxidizing chambers **5**, **14** and **22** lined with refractory material.

Stage I is carried out in reaction chamber **5**. Gaseous refining agent is blown through the nozzle **10** onto the crude iron entering in a vertical jet and the crude iron is atomized. CO_2, O_2, H_2O steam, air from storage containers **6**, **7**, **8** and **8***a* or mixtures thereof may be used as refining agents, and iron ore from the storage container **7***a* may be added. The refining agent is conducted through the conduit **9** to the nozzle **10**. In the preceding mixing nozzle **10***a* the gaseous and solid refining agents are mixed.

Before the refining begins, the reaction chamber **5** is heated to the desired temperature of about 1250° C. Electric heating is preferable to gas heating because the former will not produce waste gases which contaminate the reaction product and will not increase the volume of gas in the reaction space. It is sufficient if iron having low silicon and manganese contents is obtained in stage I. The oxidation of silicon and manganese in stage I is about 70% so that about 0.1–0.3% silicon and manganese remain where steelmaking iron is used as a starting material. A complete oxidation in stage I is not desired because the iron should be protected from oxidation in the following stages. Slag and metal flow through an outlet out of chamber **5**. The slag is separated from the metal outside of the reaction chamber, e.g., in a device as is used at the crude iron tap of the blast furnace.

The CO liberated when $2CO_2$ are decomposed into $2CO$ and O_2 is conducted through the waste gas conduit **11** to the manifold **12**. The same applies to some H_2 formed by a decomposition of H_2O.

In stage I, carbon, phosphorus and sulfur are hardly changed and correspond approximately to the values they have in the crude iron. In conduit **13** the metal is conducted into the reaction chamber **14**, which is at 1250° C., and in which stage II is carried out. In this stage, oxygen from container **7** and ore from container **7***a* are supplied through the mixing nozzle **18***a* and the conduit **16**. The metal flowing in through the conduit **13** is atomized by means of the nozzle **15**. To pass the resulting phosphoric acid into slag, lime dust is used, which is supplied through the mixing nozzle **18** in a mixture with the oxygen. The share of ore must be increased if the reaction temperature is too high when pure oxygen is used.

The P_2O_5-containing slag is separated from the iron as in the first chamber. The iron flowing out of stage II is almost free of manganese, silicon, phosphorus and sulfur.

In furnace **21**, the high-carbon iron is heated from about 1300° C. to 1650° C. (stage III). Heating is effected by an electric or flame heating system. When discharged from the furnace, the iron is at steel melting temperature, which enables also the carbon oxidizing reaction.

Carbon is oxidized in chamber **22** (stage IV) of the refining cascade. The metal enters through nozzle **23** and is atomized by the refining agent supplied through nozzle **24**. The oxidizing effect may be controlled by mixing O_2, Fe_2O_3, H_2O steam, CO_2 and air. This control of the oxygen supply serves to prevent a combustion of iron. The carbon reaction chamber **22** is preheated to 1650° C. to 1800° C. The CO formed during the reaction is conducted through conduit **27** into the manifold **12**. Any existing slag is separated from the iron outside chamber **22**, as in connection with stages I and II.

The iron is caused to flow through the several stages I to IV of the cascade as a result of the head. If this is prevented by the structural arrangement, i.e., when the required head is not available for all zones, the metal may be raised between zones with an elevator. This possibility is indicated in the diagrammatic showing of FIG. 1 after zone IV. Behind the carbon reaction stage, the iron flows into a pressure chamber **28**, which serves to raise the iron to a level which corresponds to the structural arrangement. In this case the iron is raised with the aid of CO_2; this may be effected with a mammoth pump.

Iron passes through conduit **29** and nozzle **30** into the reaction chamber **32**, in which the deoxidizing stage V is carried out. The deoxidation is carried out in accordance with the same principle as the oxidizing processes described, i.e., with the metal in atomized condition so that a maximum reaction surface is obtained and the residence time in the deoxidizing chamber corresponds to the residence time in the oxidizing chambers.

By the deoxidation, the oxygen content of the iron should be reduced and the resulting deoxidation product should be completed separated from the iron. A complete separation can be effected mostly reliably when the deoxidation product is gaseous. A gaseous deoxidation product will be obtained where carbon is used as a deoxidizer. This deoxidizer, however, can be applied only in rare cases (only with high-carbon steels). In most cases, other deoxidizers must be used, such as magnesium, aluminium etc. These agents are blown in powdered form together with the atomizing gas. The atomizing gas is a non-oxidizing gas, such as CO. CO is removed through conduit **35** from the CO conduit **12** and is cooled in cooler **36** to purifying temperature, purified in the washer **37** and fed by the pump **38** through the conduit **34**. In a mixing nozzle **39** the atomizing gas is mixed with the solid deoxidizer. The metal is atomized with the aid of nozzles **30** and **31**. The deoxidizing stage is heated to 1650° C. The steel and the deoxidation slag flow together out of chamber **32** and are separated outside. The resulting waste gas is discharged through the pipe **33**.

A simpler deoxidation is enabled by a deoxidizing slag, which is held in a liquid state in the deoxidizing chamber and into which the steel to be deoxidized is introduced or blown. The device used for this purpose is virtually the same as before, but the slag-forming substances must be blown in together with the atomizing gas.

Alloying stage VI is carried out in chamber **41**, into which alloying elements are introduced in solid or liquid condition. Chambers **41** should be heatable for the production of high-alloy steels.

In the process according to the invention, scrap cannot be melted in the various stages. Scrap can be melted, however, with the aid of the CO from stages I and IV so that the process according to the invention is not inferior to other methods also in this respect.

The shaft furnace **42** is provided for melting the scrap.

Because the cascade refining process according to the invention is carried out in gastight chambers, there are no or only small gas losses. For this reason the waste gases which contain combustible components may be collected and used for heating purposes so that heat is available for melting the scrap.

The shaft furnace is a combined gas and solid fuel furnace. The CO from stages I and IV is blown in unpurified condition into conduit **12**. The bottom nozzle **43** of the shaft furnace **42** consists of a burner, in which the unpurified CO is burned. The coke layer in the shaft furnace reduces any Fe_2O_3-containing dust which may be blown in with the CO so that a separate cleaning of the gas is not required.

The process of the shaft furnace is not a pure melting process but lies between that of a blast furnace and that of a foundry shaft furnace. The iron from the shaft furnace passes over the forehearth **43***a* and the soda desulfurizer **44** to the hot metal mixer **4** and from there into the cascade refining plant. Depending on its composition, the waste gas from the cupola is either passed into the hot blast stove **45** or supplied to a different use.

As has been mentioned, the heating up in stage III to steel-melting temperature may be electrically effected by means of a flow furnace **21**. This heating step can be omitted if the heating up to steel-melting temperature and decarburization are simultaneously effected in stage IV. Stage IV must be held at 1650–1750° C. and the atomization must be effected with the strongly oxidizing heating flame. Owing to the large metal surface available due to the atomization, the radiation effects a quick transfer of heat so that stage III can be eliminated.

A preferred structure of an atomizing nozzle is diagrammatically shown in FIG. 2. The atomizing nozzle has an outlet piece *a* for forming a dropping metal jet and blowing nozzles *b* which extend at right angles or at an oblique angle thereto and have an orifice member *d*. The pressurized gaseous refining agent is blown in through the blowing nozzles. *c* is the turbulence-producing edge. The relative position of *a* and *d* influences the atomizing effect.

Example

Crude iron was refined in a cascade refining plant according to the invention. In separate chambers, a prerefining reaction zone and a decarburizing reaction zone with an intervening heating-up zone were provided. The prerefining chamber was held at a temperature of 1250° C. Air under a pressure of 8 kg./sq.cm. gauge was used as a refining agent in the prerefining zone. The atomizing nozzle was 12 mm. in diameter. The outlet member for forming the dropping crude iron jet was 14 mm. in diameter. Complete atomization was achieved under these conditions.

The decarburizing chamber was held at a temperature of 1550° C. Pure oxygen was used as a refining agent. The atomizing conditions were the same as in the prerefining zone (nozzle diameter 12 mm., diameter of iron jet 14 mm., pressure 8 kg./sq.cm. gauge).

The following test results were obtained:

EXPERIMENT NO. 1

Sampling after seconds	First Oxidizing Stage (Air)						Second Oxidizing Stage (O_2)		
	C, percent	Si, percent	Mn, percent	C, percent	Si, percent	Mn, percent	C, percent	Si, percent	Mn, percent
	Before oxidation			After oxidation			After the oxidation		
30	4.10	0.63	1.74	3.70	0.12	0.36	0.92	0.10	0.26
45	------	------	------	3.71	0.13	0.35	0.98	0.08	0.26
60	------	------	------	3.72	0.11	0.34	0.95	0.12	0.25
75	------	------	------	3.68	0.12	0.35	0.95	0.12	0.25
90	------	------	------	3.71	0.13	0.35	0.96	0.11	0.25

EXPERIMENT NO. 2

30	4.30	0.95	1.50	4.10	0.24	0.38	0.86	0.12	0.21
45	------	------	------	4.00	0.23	0.34	0.84	0.10	0.21
60	------	------	------	3.90	0.24	0.31	0.83	0.10	0.20
75	------	------	------	4.10	0.20	0.31	0.85	0.11	0.22
90	------	------	------	4.00	0.18	0.31	0.85	0.10	0.21

EXPERIMENT NO. 3

30	4.00	0.80	1.00	3.93	0.21	0.33	0.83	0.08	0.26
45	------	------	------	3.98	0.21	0.33	0.80	0.10	0.26
60	------	------	------	3.97	0.18	0.31	0.81	0.11	0.24
75	------	------	------	4.00	0.14	0.35	0.80	0.06	0.25
90	------	------	------	3.98	0.16	0.33	0.82	0.10	0.25

Whereas in the preferred embodiment of the invention the crude iron is reacted in atomized or sprayed condition in each reaction zone, i.e., in the prerefining reaction zone or zones and in the decarburizing reaction zone, the inversion in an atomized or sprayed state is not effected in vention in an atomized or sprayed state is not effected in all stages but only in part thereof.

What I claim is:

1. A process of continuously converting molten crude iron containing more than 0.1% silicon and more than 0.3% manganese and also containing phosphorus, sulfur, and carbon into steel, comprising the steps of placing the iron in a first zone, maintaining the iron in the first zone at a temperature of about 1250° C. to about 1350° C., forming a dropping jet of molten iron in the first zone, blowing a slightly-oxidizing gas into the jet in the first zone to atomize the iron in the first zone and simultaneously facilitate oxidation of at least a part of the silicon and manganese to form oxidation products and reduce the silicon content of the iron to about 0.1% and the manganese content of the iron to about 0.3%, removing the oxidation products, placing the iron in a second zone separate from the first zone, maintaining the iron in the second zone at a temperature of about 1250° C. to about 1350° C., forming a dropping jet of molten iron in the second zone, blowing oxygen and a slag-forming substance into the jet in the second zone to atomize the iron in the second zone and simultaneously facilitate oxidation of at least a part of the phosphorus and sulfur to form slag and render the iron substantially free of phosphorus and sulfur, removing the slag, placing the iron in a third zone separate from the first and second zones, bringing the iron in the third zone to a temperature of about 1300° C. to about 1650° C., placing the iron in a fourth zone separate from the first through third zones, maintaining the iron in the fourth zone at a temperature of about 1550° C. to about 1800° C., forming a dropping jet of molten iron in the fourth zone, blowing an iron-combustion-preventing mixture into the jet in the fourth zone to atomize the iron in the fourth zone and simultaneously facilitate oxidation of at least a part of the carbon to form decarburized iron and reaction products, removing the reaction products, placing the iron in a fifth zone separate from the first through fourth zones, maintaining the iron in the fifth zone at a temperature of about 1600° C. to about 1700°

C., forming a dropping jet of molten iron in the fifth zone, blowing a deoxidizing slag suspended in an inert gas into the jet in the fifth zone to atomize the iron and simultaneously facilitate deoxidation of the iron to form deoxidized iron and deoxidation products, removing the deoxidation products, placing the iron in a sixth zone separate from the first through fifth zones, and forming an alloy in the sixth zone, the alloy comprising the deoxidized iron.

2. A process of continuously converting crude iron into steel comprising the steps of

(a) heating said crude iron to bring it to a molten state,

(b) effecting introduction of said molten crude iron into a prerefining reaction zone in which a given reaction involving separation from said molten crude iron of at least one element selected from the group consisting of silicon and manganese is adapted to take place,

(c) concurrently with said introduction of said molten crude iron into said prerefining reaction zone, maintaining said prerefining reaction zone at a temperature of 1250° C. to 1350° C.,

(d) also concurrently with said introduction of said molten crude iron into said prerefining reaction zone, effecting introduction into said prerefining reaction zone of a first gaseous refining agent having a given oxygen content in such a manner as to atomize said molten crude iron,

(e) effecting withdrawal of said molten crude iron from said prerefining reaction zone,

(f) effecting introduction of said molten crude iron into a decarburizing zone separate from said prerefining reaction zone,

(g) concurrently with said introduction of said molten crude iron into said decarburizing zone, maintaining said decarburizing zone at a temperature of 1550° C. to 1800° C., and

(h) also concurrently with said introduction of said molten crude iron into said decarburizing zone, effecting introduction into said decarburizing zone of a second gaseous refining agent having an oxygen content higher than that of said first gaseous refining agent.

3. In the process of claim **2**, the step of

(i) selecting said first gaseous refining agent from the group consisting of air, a mixture of oxygen and carbon dioxide, steam, and a mixture of oxygen and steam.

4. In the process of claim **2**, the steps of

(i) selecting oxygen as said second gaseous refining agent and

(j) effecting introduction of said oxygen into said decarburizing zone in such a manner as to atomize said molten crude iron.

5. In the process of claim **4**, the step of

(k) passing said molten crude iron through a heating zone separate from said prerefining reaction zone and said decarburizing zone subsequently to said withdrawal of said molten crude iron from said prerefining reaction zone and prior to said introduction of said molten crude iron into said decarburizing zone.

6. In the process of claim **2**, the steps of

(i) selecting air as said first gaseous refining agent,

(j) selecting oxygen as said second gaseous refining agent,

(k) effecting introduction of said oxygen into said decarburizing zone in such a manner as to atomize said molten crude iron,

(l) passing said molten crude iron through a heating zone separate from said prerefining reaction zone and said decarburizing zone subsequently to said withdrawal of said molten crude iron from said prerefining reaction zone and prior to said introduction of said molten crude iron into said decarburizing zone,

(m) effecting introduction of said molten crude iron into a deoxidizing zone separate from said prerefining reaction zone, said decarburizing zone, and said heating zone subsequently to said withdrawal of said molten crude iron from said decarburizing zone,

(n) concurrently with said introduction of said molten crude iron into said deoxidizing zone, maintaining said deoxidizing zone at a temperature of 1600° C. to 1700° C., and

(o) also concurrently with said introduction of said molten crude iron into said deoxidizing zone, effecting introduction into said deoxidizing zone of an inert gas containing an oxidizable metal suspended therein in such a manner as to atomize said molten crude iron.

7. In the process of claim **2**, the steps of

(i) selecting air as said first gaseous refining agent,

(j) selecting oxygen as said second gaseous refining agent,

(k) effecting introduction of said oxygen into said decarburizing zone in such a manner as to atomize said molten crude iron,

(l) effecting introduction of said molten crude iron into a dephosphorizing zone separate from said prerefining reaction zone and said decarburizing zone subsequently to said withdrawal of said molten crude iron from said prerefining reaction zone and prior to said introduction of said molten crude iron into said decarburizing zone,

(m) concurrently with said introduction of said molten crude iron into said dephosphorizing zone, maintaining said dephosphorizing zone at a temperature of 1250° C. to 1350° C.,

(n) also concurrently with said introduction of said molten crude iron into said dephosphorizing zone, effecting introduction into said dephosphorizing zone of oxygen having lime dust suspended therein in such a manner as to atomize said molten crude iron,

(o) effecting withdrawal of said molten crude iron from said dephosphorizing zone, and

(p) passing said molten crude iron through a heating zone separate from said prerefining reaction zone, said decarburizing zone, and said dephosphorizing zone subsequently to said withdrawal of said molten crude iron from said dephosphorizing zone and prior to said introduction of said molten crude iron into said decarburizing zone.

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