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[54] **METHOD FOR REFINING PIG IRON INTO STEEL**

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[51] **Int. Cl.** **C21c 5/28**

[58] **Field of Search** 75/51–60, 129, 75/130.5

[56] **References Cited**

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[57] **ABSTRACT**

A method for refining pig iron containing usual amounts of impurities and elements in a metallurgical vessel into which at least one stream of oxygen is introduced into the body of the pig iron to form at least one reaction zone, and introducing at least one oxide of an element contained in the pig iron in an amount sufficient to saturate the reaction zone with said oxide and thereby promote the oxidation of all other elements contained in the pig iron to the exclusion of the element whose oxide is introduced.

29 Claims, No Drawings

METHOD FOR REFINING PIG IRON INTO STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for refining molten metal and more particularly, it pertains to the refining of pig iron into steel.

2. Description of the Prior Art

In the past several methods have been used for refining molten metal such as steel by the introduction or blowing of air and/or oxygen into the body of molten metal. These methods rely on oxidation reactions with elements and impurities in the molten metal to reduce or eliminate them. Moreover, other compounds such as steam and/or hydrocarbons have been added to the air or oxygen for various reasons including increasing the life of the tuyere by which the air or oxygen is introduced.

The primary disadvantages of the introduction of compounds containing hydrogen into the reaction zone of the metal being refined such as steel is that the resulting steel has an undesirably high content of hydrogen. Moreover, the use of hydrocarbons also introduces additional carbon into the reaction zone which must ultimately be oxidized by the oxygen to eliminate carbon from the system. In addition, the use of hydrocarbons containing sulfur, introduces more sulfur into the reaction zone which must ultimately be removed by additional fluxing that requires more refining time.

In addition to the foregoing where gases or liquids of hydrocarbons are used to provide a casing of gases or liquids around an oxygen stream to protect the tuyere from early destruction, an intricate tuyere construction is necessary to provide an annular space around the oxygen conduit. Associated with the foregoing is the hazard of explosions where failure of tuyeres of oxygen tube permits intermixing of oxygen and hydrocarbons before reaching the reaction zone. Carbonaceous material build up occurs at the mouth of the tuyere which creates safety hazards or curtails the efficiency of the process.

Furthermore, excessive amounts of hydrocarbons must be used to preserve tuyere life in submerged blowing and the conservation of hydrocarbons is most needed in view of national shortage of capacity to supply the general need for this class of materials.

Associated with the foregoing has been the conventional practice of oxidizing all of the oxidizable elements contained in the charge materials. Some of these elements, such as manganese and chromium, are desirable and valuable. When these valuable metals are oxidized in the current oxygen processes, they are lost in the slag and/or the waste gases.

SUMMARY OF THE INVENTION

A method for refining molten metal containing minor amounts of oxidizable elements in a metallurgical vessel comprising the steps of introducing at least one stream of oxygen through at least one injector into the body of molten metal to form at least one reaction zone, introducing at least one oxide of the oxidizable elements present in the molten metal to at least one of the reaction zones in amounts sufficient to provide high concentration of the oxide or oxides to inhibit or eliminate oxidation of the elements in the molten metal bath that correspond to said oxide or oxides, and continuing to introduce oxygen and oxides until oxidation of the

element in the molten metal of the oxide introduced is reduced or prevented by the law of mass action.

The advantage of the method of this invention is that it not only accelerates the process of refining the molten metal, but, in addition, such elements as silicon, manganese, and chromium are conserved and are retained in the resulting refined metal. Ferroalloy additions may be omitted in most cases. As a result the cost of producing steel is lowered significantly.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process for refining molten metal of this invention is applicable to the refining of any metal that is ordinarily refined by oxygen. However, the process is particularly adaptable to the refining of steel either from pig iron or from some intermediate stage of refinement to the ultimate desired steel analysis. Pig iron contains small amounts of various elements depending upon varying factors such as the composition of the original ore and such elements usually include from about 3 to about 4.5% carbon, from about 0.15 to about 2.5% manganese, from about 0.5 to about 4.0% silicon, from about 0.8 to about 2.0% phosphorus, and from about 0.4 to about 1.0% sulfur. Other elements may also be included such as chromium, titanium, molybdenum, nickel, etc.

Moreover, although the method of this invention is particularly applicable to those processes where oxygen is introduced into a body or on the surface of the molten-iron-base metal, such as in various forms of the so-called basic oxygen process (BOP), the method may also be used for refining steel in an electric furnace, or open hearth furnace, by the injection of oxides through roof lances or submerged tuyeres.

Generally, the method of this invention is preferably employed for the refining of pig iron into various types of steel, such as steels containing various amounts of carbon, manganese, silicon, phosphorus, sulfur, chromium, titanium, molybdenum, nickel, vanadium, boron, columbium, copper, and mixtures thereof.

An example of the method of this invention involves pouring of a desired amount of molten steel into a basic oxygen converter, commencing to blow at least one stream of oxygen into the body of the molten metal, introducing the necessary amounts of slag-forming materials, such as burnt lime, fluorspar (CaF_2) or other slag conditioners, introducing with the steam oxygen particles of the oxide of one or more oxidizable elements present in the molten steel in amounts sufficient to reduce or eliminate oxidation of the element corresponding to the oxide being reduced, whereby the oxygen input then preferentially oxidizes the other elements in the metal such as phosphorus, sulfur, and carbon.

All forms of oxides of the oxidizable elements present in the molten metal are suitable for the purposes of this invention. When the oxides are transported by the oxygen stream, the oxides are physically sized to conform to the physical factors required for such transport. Ordinarily, where a regular carbon steel is to be produced, iron oxide is preferably introduced with the oxygen stream in order to minimize oxidation of iron during the refining process. The source of iron oxide to be used is dust of precipitators and collectors of dust resulting from the refining of steel in such furnaces as the open hearth, and the basic oxygen converter either top blown or bottom blown. Dusts of iron oxide and manganese oxide from collection systems are essential materials for introduction with oxygen in accordance with this invention. Characteristically these dusts have a particle size of about one micron. Sized iron ore or roll scale are further sources of iron oxide. This invention affords the metal industry the opportunity to utilize useless waste products of their refining processes to conserve vital raw materials, such as iron, manganese, chromium, nickel, by lowering the total amount oxidized from the materials charged and further drastically reduces the production of these waste products.

For example, when an oxygen stream containing particles of iron oxide and manganese oxide forms a reaction zone in a molten pig iron bath, the presence of said particles in the reaction zone absorbs heat in their conversion to the molten state and provides high concentrations of molten oxides of iron and manganese in the reaction zone. This diverts the oxidation reaction between the oxygen stream and the molten pig iron to elements other than iron and manganese. If particles of silicon oxide and manganese oxide were used, the oxidation of silicon and manganese would be reduced or precluded.

Further, if prior to introduction of the oxygen stream the molten bath contains an excess of an element, such as manganese, in comparison to the desired analysis of the steel to be produced, the introduction of the oxide of manganese is delayed until the excess quantity of manganese in the molten bath has been oxidized and given up to the slag.

Metallic oxides have high heat capacities and absorb heat from reaction zones in their conversion to the molten state. The effective temperature in the reaction zone is lowered below the vaporization temperatures of iron and manganese. Consequently, the emission of vaporized iron and manganese from the bath is reduced or eliminated by controlling the amounts of particulate oxide introduced with the oxygen stream.

In addition, by providing high iron oxide and manganese oxide concentrations in the reaction zone the oxidation of other oxidizable elements, such as carbon, is induced and conserves the original amounts of iron and manganese in the molten metal. It is noted in passing that the conservation of manganese is vitally important because of its ever increasing scarcity.

When elements other than manganese are to be retained in the molten bath, the oxides of such elements may be introduced into the oxygen stream either with or without iron oxide. Thus, oxides of such elements as silicon, phosphorus, sulfur may be added in particulate form, whereby the elements are retained through the refining process and in the resulting refined steel.

In accordance with this invention, the reaction zone of the molten metal receive particulates of the oxides of the elements that are to be retained in the refined metal and the oxygen in the oxygen stream oxidizes the other elements. The particulate of the oxides are introduced into the reaction zone or zones in quantities ranging from concentrations sufficient to inhibit oxidation of the elements desired to be retained in some cases in quantities sufficient to create saturation or supersaturation of said zone(s). Those elements to be retained or eliminated comprise any and all of those oxidizable elements ordinarily contained in molten pig iron and any other intermediate grade of refined steel. The oxides introduced may consist of at least one of the elements including iron, carbon, manganese, silicon, phosphorus, sulfur, chromium, titanium, molybdenum, nickel, vanadium, boron, columbium, copper, and the like. For example, where chromium exists in the metal to be refined, chromium oxide is introduced into the oxygen stream to prevent oxidation of the chromium in the molten metal.

The following example is illustrative of the present invention:

EXAMPLE

A charge of metal consisting of 79 tons of plain carbon steel scrap and of 184 tons of hot metal is charged into a basic oxygen furnace. The hot metal has a typical composition of 3.4% carbon, 1.0% manganese, 0.8% silicon, 1.2% phosphorus, 0.55% sulfur, and the balance is iron. A lance is introduced into the top of the converter and an oxygen stream at about 180 p.s.i. is directed into the top of the molten charge. Oxide particles of silicon and manganese having a size of from ½ to 30 microns (preferably 1 micron) are included with the oxygen stream. It is desired to retain about 0.35% silicon and about 0.40% manganese in the refined metal. To achieve this, after 6 minutes of blowing time 200 lbs./minute of silica is introduced and transported to the reaction zone to suppress oxidation of silicon in the molten charge. After 8 minutes in addition to the silica input to the oxygen stream, 200 lbs./minute of manganese oxide is added to the oxygen stream, or 1.1 pounds/minute/ton of pig iron charged. The blow continues transporting with the oxygen steam, the indicated amounts of oxides of silicon and manganese to the reaction zone until the end of the refining period, or about 20 minutes from the start of the initial blow. The composition of the resulting steel is about 0.1% carbon, 0.40% manganese, 0.35% silicon, 0.022% sulfur, and 0.18% phosphorus.

The cited example indicates a conservation of one ton of manganese and of 0.9 ton of silicon. That is, it was unnecessary to replace silicon or manganese that would otherwise have been removed from the bath by oxidation in conventional basic oxygen converter practice. Moreover, the emission of fine particulate matter from the converter is reduced by 38%, because the reaction zone temperature is lowered by the oxide introduction.

Further reduction in particulate emission may be realized by introduction of iron oxide, which would commence after the tenth minute of the blow. A useful range of input is from 10 to 2,000 lbs. per minute of iron oxide (or 0.06 to 11 lbs./minute/ton of pig iron charged) with a preferred range of from about 75 to about 300 lbs. per minute (or 0.9 to 1.63 lbs./minute/-ton). The broad ranges cited reflect the cumulative effect of more than one specific oxide being introduced both from a chemical and temperature standpoint. However, iron oxide may be introduced at earlier stages of the oxygen blow either with or without oxides to achieve desired final analysis.

In the foregoing example, the useful range of from about 10 to about 600 lbs./minute (0.06 to 3.26 lbs./minute/ton of pig iron charged) and a preferred range of from about 100 to about 500 lbs./minute of silicon dioxide (0.6 to 2.72 lbs./minute/ton) may be added. Likewise, the useful range of manganese oxide is from about 20 to about 1000 lbs./minute (or 0.11 to 5.4 lbs./minute/ton) with a preferred range of from about 175 to about 800 lbs./minute (0.95 to 4.35

lbs./minute/ton). The ranges for additions of oxides of silica and manganese are dependent upon such factors as the starting and ending analyses of silicon and manganese, the temperature of operation, the number and distribution of lances or other types of oxygen inlets such as tuyeres.

From the foregoing example, it is recognized that for a corresponding charge of scrap and hot metal a heat of stainless steel instead of plain carbon steel may be produced. For that purpose the original charge including scrap would contain higher precentages of nickel and chromium. Thereafter, during the oxygen blow, oxides of chromium, nickel, and/or other elements are added in particulate form with the oxygen stream.

Although the preferred procedure for introducing oxides of the elements set forth above is to introduce those oxides as particulates or powders through a lance with the oxygen stream, the oxides may be introduced into the reaction zone between the oxygen stream and the molten bath separately through other conduits or methods. Moreover, where a number of lances or streams of oxygen and oxides are introduced, the oxygen may be introduced axially or centrally of the oxides with the oxides peripherally of the oxygen. On the other hand, the oxides may be centrally or axially disposed with respect to the oxygen.

It is understood that the transport of particulate oxides to the reaction zone may be accomplished in diverse methods. Use of relatively inert gases such as steam, carbon dioxide, compressed air, argon, for transport of the oxide particulate and relatively inert gases plus controlled amounts of oxygen in a peripheral disposition in relation to a central oxygen stream represent the optimum concept for said introduction, but provision of the desired oxide particulate in the reaction zone can be achieved in a variety of ways or combinations. Moreover, the oxides may be introduced in a carrier stream of oxygen with or without inert gases. Further, the oxygen stream may be introduced by impinging on the molten bath from the top of the vertical axis, from the side of the vertical axis, or from the bottom of the vertical axis (submerged).

Accordingly, the method for refining molten metal and preferably steel of this invention provides for the elimination of extraneous sources of hydrogen into the molten metal, avoid unintentional introduction of sulfur and prevents the pollution of the atmosphere with SO_3 where iron oxide and/or manganese oxide is introduced, increases the yield of iron from pig iron from 1.0 to 1.5% by saturating the reaction zone with oxide particles, increases the yield of metallic manganese, avoids the use of critical energy producing hydrocarbons, and reduces oxygen consumption because excessive oxidation of iron is prevented and desirable elements are oxidized only to a desired degree.

What is claimed is:

1. A method of refining molten metal containing oxidizable elements in a metallurgical vessel comprising:

a. blowing an oxygen stream into the molten steel bath of create an oxygen-rich zone therein,

b. then introducing into the oxygen-rich zone a sufficient amount of an oxide of at least one of the oxidizable elements present in the molten bath in amounts sufficient to provide high concentration of the oxide in the oxygen-rich zone and thereby to maintain the oxidizable element at the desired analysis, and

c. continuing to blow oxygen and to introduce said oxide until the analyses of other oxidizable elements have reached desired analyses.

2. The method of claim **1** further comprising in step a) blowing oxygen into the molten metal bath until the content of at least one of the oxidizable elements has reached the desired analysis.

3. The method of claim **2** wherein the oxide are introduced in the oxygen stream.

4. The method of claim **1** wherein the oxide are introduced in a separate lance.

5. The method of claim **1** wherein the oxide introduced is selected from the group consisting of at least one of the elements including iron, carbon, manganese, silicon, phosphorus, sulfur, chromium, titanium, molybdenum, nickel, vanadium, boron, columbium, copper, and mixtures thereof.

6. The method of claim **1** wherein the oxide are introduced as particulates in a carrier stream of oxygen.

7. The method of claim **1** wherein the oxide are introduced as particulates in a carrier stream of a relatively inert gas.

8. The method of claim **1** wherein the oxide are introduced as particulates in a carrier stream of a relatively inert gas and oxygen.

9. The method of claim **8** in which one of the oxygen stream and the oxide carrier stream is introduced in an axially disposed stream and the other of the oxygen stream and the oxide carrier stream is introduced in a peripherally disposed stream.

10. The method of claim **9** wherein the particulate oxide is introduced in a carrier stream of relatively inert gas peripherally disposed to an oxygen stream.

11. The method of claim **10** wherein oxygen is introduced with the relatively inert gas and oxides.

12. The method of claim **11** wherein the oxides are introduced in a peripheral carrier stream of oxygen and the axial stream is oxygen.

13. The method of claim **9** wherein the axial stream is a relatively inert gas with oxides and the peripheral stream is oxygen.

14. The method of claim **13** wherein the axial stream also includes oxygen.

15. The method of claim **1** wherein the molten metal body consists essentially of pig iron into which silicon dioxide particles are introduced at a rate of from about 0.06 to about 3.26 lbs./minute/ton of pig iron charged.

16. The method of claim **15** wherein the silicon dioxide particles are introduced about 6 minutes after the start of the oxygen blow.

17. The method of claim **15** wherein the silicon dioxide particles are introduced at a rate of from about 0.6 to about 2.72 lbs./minute/ton.

18. A method of claim **15** wherein the silicon dioxide particles are introduced at a rate of about 1.1 lbs./minute/ton.

19. The method of claim **15** wherein manganese oxide particles are introduced at a rate of from about 20 to about 5.4 lbs./minute/ton with the silicon oxide.

20. The method of claim **19** wherein the manganese oxide is introduced about eight minutes after the start of the oxygen blow.

21. The method of claim **19** wherein manganese oxide is introduced at a rate of from about 0.95 lbs. to about 4.35 lbs./minute/ton.

22. The method of claim **19** wherein manganese oxide is introduced at a rate of about 1.1 lbs./minute/-ton.

23. The method of claim **1** wherein the oxide introduced is iron oxide.

24. The method of claim **23** wherein iron oxide is introduced at a rate of from about 0.06 to about 11 lbs./minute/ton

25. The method of claim **24** wherein iron oxide is introduced at a rate of from about 0.90 to about 1.63 lbs./minute/ton.

26. The method of claim **20** wherein iron oxide is introduced at a rate of from 0.06 to about 11 lbs./minute/ton about eight minutes after the start of the oxygen blow.

27. A method of refining molten metal containing oxidizable elements in a metallurgical vessel comprising:

a. introducing at least one stream of oxygen through at least one injector into a molten metal bath to form at least one oxygen-rich zone, and

b. introducing at least one oxide of the oxidizable elements present in the molten metal to at least one of the reaction, zones in amounts sufficient to provide high concentration of the oxide and thereby to maintain the desired analysis of said element or elements present in the molten metal that correspond to the oxides introduced and the time of said introduction being controlled by the amount of weight percent of said element of elements present in the initial molten metal bath in relation to the weight percent of said element or elements desired present in the end refined product.

28. The method of claim **6** in which one of the oxygen stream and the oxide carrier stream is introduced in an axially disposed stream and the other of the oxygen stream and the oxide carrier stream is introduced in a peripherally disposed stream.

29. The method of claim **7** in which one of the oxygen stream and the oxide carrier stream is introduced in an axially disposed stream and the other of the oxygen stream and the oxide carrier stream is introduced in a peripherally disposed stream.

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