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METHOD OF METÁL PURIFICATION Marvin William Sage and Eugene R. du Fresne, Chicago, Ill., assignors to General Dynamics Corporation, New York, N.Y., a corporation of Delaware No Drawing. Filed Dec. 12, 1962, Ser. No. 244,024 2 Claims. (Cl. 75–60)

This invention relates to the purification of metals, and more particularly to the decarburization of molten metals 10 in the steel making process.

Normally a conventional blast-furnace process produces molten pig iron containing about 4% carbon which must be largely removed in the conversion into steel. The molten metal is removed from the blast furnace and 15 is decarburized in the steel making process by selective oxidation of the carbon. The types of general processes in which this change is carried out can be grouped into the following classifications, the pneumatic or Bessemer process, the open hearth process and the electric process. 20

Previously air or oxygen has been employed in these processes to reduce or to aid in the reduction of the carbon content of the molten metal (commonly known as blowing of iron). However, it is necessary to closely control the amount of air or oxygen used so as to prevent the oxidation of the iron itself, an undesirable reaction which is termed overblowing.

In the pneumatic or Bessemer process, for example, it is important that the progress of the blowing is closely observed in order to stop the operation at the proper end 30 point. If the blow is continued after all the carbon is consumed, i.e., overblown, rapid oxidation of the metal itself ensues. The color and luminosity of the flame emitted from the mouth of the reaction vessel is commonly used to accomplish this end point control. Because of 35 the relative shortness of the blowing time, about 15 minutes, success of the process is in main part dependent upon the personal skill of the blower, since an analysis of the sample of melt cannot be taken in this short time.

If the melt is overblown and the air forms undesirable ⁴⁰ oxides with the iron, the quality of the steel is impaired. Castings from a melt which has been overblown contain large pores as a result of the subsequent reaction of residual carbon with the iron oxides unless deoxidizers are added to prevent this reaction.

Furthermore, it has become well known to shorten the time necessary for the removal of the carbon by enriching the air with oxygen or by substituting gaseous oxygen for air in the blow. However, when oxygen is used in conjunction with, or in substitution of, air, control of the end point becomes even more critical because of the high oxidation potential of gaseous oxygen in comparison with a like volume of air.

It is an object of the present invention to provide an improved process for the treatment of molten metal in a steel making operation. Another object of the present invention is to provide an improved process that eliminates the necessity for close control to prevent overblowing. A further object of the invention is to provide an improved process which will substantially increase the rate at which the carbon in the molten metal is eliminated. A still further object of the invention is to provide a process for the production of high quality steel without the addition of deoxidizers. These and other objects of the invention are more particularly set forth in the following detailed description.

Generally in accordance with the present invention, pure carbon dioxide or substantially pure carbon dioxide is used as an oxidizing agent in the steel making process to reduce the carbon content of the molten metal. Carbon dioxide accomplishes decarburization of the melt 2

without the inherent disadvantages that accompany the use of air or oxygen for the same purpose. For the purposes of this application, the term "substantially pure carbon dioxide" is intended to refer to a gas which includes at least 95% carbon dioxide, and preferably an even higher percent with the remainder being as free of N_2 , H_2O , O_2 and hydrocarbons as it is possible under practical conditions.

In one embodiment of the present invention, a melt in a Bessemer converter is treated by employing a stream of substantially pure carbon dioxide for the blow, instead of either air or oxygen. The carbon dioxide eliminates carbon from the melt in accordance with the following general formula: $Fe_3C+CO_2 \rightarrow 3$ Fe+2 CO. Although the carbon dioxide removes the carbon from the iron oxide in the melt as carbon monoxide, it does not significantly oxidize the iron in the melt. Therefore, even if the blow with carbon dioxide is continued after the removal of the carbon, no significant oxidation of the iron occurs, as it does when air or gaseous oxygens are used. Because continuation of the blow of carbon dioxide for a short period of time after the removal of all the carbon does not produce the previously mentioned undesirable effects, the criticality of end point control disappears. Therefore, the process of the invention has a potentially semi-automatic characteristic that is clearly not a part of the normal blow with oxygen or air.

Use of substantially pure carbon dioxide also has other advantages over the use of air. The use of air for the blow necessarily introduces a large amount of nitrogen into the melt, for air includes over 75% nitrogen, by volume. The passing of a gas through the melt having such a high partial pressure of nitrogen results in the absorption of nitrogen in the melt. The absorbed nitrogen, if not quickly removed, forms unstable iron nitrides. These unstable nitrides subsequently give up nitrogen as the melt is allowed to solidify, with a resultant porosity in the ingots that is undesirable. Furthermore, the use of air for the blow usually introduces some water vapor into the melt, for the air will not likely be completely dry. Any water vapor present in the air is likewise undesirable for it reacts with the melt to form hydrogen which also produces a porous ingot. The substitution of substantially pure carbon dioxide for air avoids both of these difficulties attendant to the use of air and, accordingly, results in a steel of higher quality.

Preferably, for economic reasons, the entire blow is not made with carbon dioxide, but instead the blow is begun in a normal manner with air and then switch to gaseous carbon dioxide after about 50 to 80% of the carbon has been eliminated from the melt. Because this split process still uses carbon dioxide to complete the decarburization, it likewise has the desirable feature of the elimination of need for close control of the end point of the process. The passage of the carbon dioxide through the melt after the completion of the air blow also serves as a purge flow. Both the carbon dioxide and the carbon monoxide formed in the decarburization during this second period purge the melt of nitrogen and hydrogen which may have been absorbed during the initial period.

Carbon dioxide of the required purity can be obtained readily and economically by bulk supply from railroad or truck tank cars. Preferably, the carbon dioxide supplied is pre-heated before it is blown into the Bessemer converter to avoid undesirably lowering the temperature of the melt. Pre-heating may be accomplished in any suitable manner by utilizing any of the various heat sources which would otherwise be lost from associated installations in a steel making plant.

In a second embodiment, the carbon dioxide is employed as a refining agent in an open hearth process, by introducing the carbon dioxide in the same manner as oxygen has been previously introduced into the open hearth furnace. In this connection, the carbon dioxide is introduced either by blowing carbon dioxide onto the surface of the melt or into the molten metal. The carbon 5 dioxide may be introduced through a lance, i.e., a steel tube that is slowly consumed, or through a water-cooled gun positioned slightly above the surface of the molten metal. The chemical reaction which takes place in this application to open-hearth steel making is similar to the 10 reaction which was previously described with regard to the pneumatic process. Thus, by employing a stream of substantially pure carbon dioxide as a refining agent in the open-hearth melt, at least near the end of the decarburization process, the concern for formation of iron 15 oxides is alleviated for the reasons set forth above. Accordingly, the need for close control of the decarburization end point is eliminated and the quality of steel produced is increased.

In a third embodiment, the carbon dioxide is employed 20 as a refining agent in the making of steel by the electric furnace process. The carbon dioxide is introduced into the melt in a manner similar to that described with respect to the open hearth process, preferably by lancing. Because steels of generally higher quality are produced by 25the electric furnace process, the present invention is particularly advantageous here. In the production of high grade steel, it is especially important to eliminate formations of iron oxides during the decarburization operation. Inasmuch as this elimination is one of the primary features of the present invention, use of carbon dioxide lancing to reach the decarburization end point has proved especially satisfactory. Steels of consistently high quality are produced in this manner.

In its elimination of the formation of iron oxides, the ³⁵ present invention achieves another important advantage. The iron oxide fumes in the exhaust gases from steel making furnaces have long proved a problem to the industry. By eliminating the formation of iron oxides, the present invention eliminates this operational problem. 40

It has also been found that the use of a carbon dioxide blow increases the rate of carbon removal and therefore reduces the overall steel making time. It is well known that one of the reasons for the use of oxygen in the steel making process is the acceleration of the refining process by increasing the rate of carbon removal. Carbon dioxide is superior to oxygen in this aspect of the refining process. In this connection, when oxygen is introduced into the melt so that it bubbles upwardly therethrough, 50 each bubble of oxygen is quickly surrounded by a layer of molten oxide. This surrounding coating of the bubbles restricts the access of the gas within the bubble to the iron carbide in the melt and thus delays the reaction. This coating effect is not a substantial problem with bubbles 55 of carbon dioxide, probably because of the lower oxidation potential of carbon dioxide in comparison with pure oxygen. Therefore, the carbon dioxide is more quickly brought into contact with the carbon in the melt. The elimination of the carbon in the melt by the formation 60 of carbon monoxide accordingly proceeds at a more rapid rate.

Thus, the present invention provides a process for the production of steel of consistently high quality by the elimination of the need for relying upon the judgment of a skilled worker to closely control the end point of the decarburization process. Accordingly, the invention allows steel of higher quality to be produced by workers of lesser skill. At the same time, the process provides for the acceleration of the decarburization step thereby reducing the overall operational time of the steel making process.

While the invention has been disclosed with respect to several preferred embodiments, it will be apparent to those skilled in the art that various modifications may be made within the spirit and scope of the invention.

Various of the features of the invention are set forth in the following claims.

What is claimed is:

1. In the manufacture of steel in which molten carbon-containing iron is treated at a refining temperature in a steel-making furnace using a blow of oxidizing gas, a process for controlling the carbon removal end point of the steel which process comprises halting the blow of oxidizing gas into the molten iron after at least between about 50 to 80 percent of the carbon has been removed and then passing a stream of substantially pure carbon dioxide into the molten iron until the carbon removal end point is reached whereby the carbon content of the iron is lowered by the elimination of carbon as carbon monoxide without significant oxidation of iron so that close

³⁰ control of blowing relative to said carbon removal end point is not necessary to prevent iron oxide formation.
2. In the manufacture of steel in which molten carbon-

containing iron is treated at a refining temperature in a steel-making furnace using a blow of oxidizing gas, a process for controlling the carbon removal end point of the steel which process comprises halting the blow of oxidizing gas into the molten iron after at least between about 50 to 80 percent of the carbon has been removed and then passing a stream of substantially pure carbon dioxide into the molten iron until the carbon removal end point is reached and for a substantial period of time

45 blowing relative to said carbon removal end point is

not necessary to prevent iron oxide formation.

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