PROCESS FOR PRODUCTION OF STAINLESS STEEL

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Abstract
A process is disclosed for the production of stainless steel wherein a chromium-containing melt suitable for producing stainless steel is blown with oxygen in an oxygen converter, and an inert gas is introduced through at least one tuyere in the bottom of the converter while the interior of the converter above the liquid level is maintained at subatmospheric pressure.

13 Claims, 3 Drawing Figures
1 PROCESS FOR PRODUCTION OF STAINLESS STEEL

BACKGROUND OF THE INVENTION

The well-known oxygen steel process is effected by blowing substantially pure oxygen through a lance onto or slightly below the surface of molten iron maintained in a basic oxygen converter. The process is an improvement over Bessemer converters because it produces a far superior product, and it is an improvement over open hearth converters because of high production rates per unit of capital and per unit of time that are obtainable by the basic oxygen process. The process may be employed for making plain carbon steel and for making stainless steel.

In the oxygen steel process, relatively pure oxygen is blown onto the liquid bath that is maintained at high temperature. Although a stream of pure oxygen simply impinges on the surface of the bath, the exhaust gases from the process contain substantially no oxygen. The high temperature molten metal bath is extremely active chemically, and there are many reactions competing for the oxygen. Among these, for producing stainless steel, are the reaction of iron with oxygen to produce iron oxide, the reaction of chromium with oxygen to produce chromium oxide, the reaction of carbon with oxygen to produce carbon oxides and the reaction of various other ingredients such as aluminum, silicon and manganese to produce their respective oxides which generally become part of a slag phase.

Of the various reactions mentioned above, the primary reason for the refining process is to effect the reaction between carbon and oxygen for the purpose of removing carbon from the liquid metal. The reaction between oxygen and iron is desirably avoided because it represents a loss of iron product. The reaction between oxygen and chromium also should be avoided because it results in a loss of chromium from the molten metal phase to the slag phase, and the presence of chromium oxide in the slag phase gives a viscous slag which interferes with the metal refining process. A viscous slag is undesirable because it shields the surface of the molten metal bath which retards the escape of carbon oxides and therefore interferes with the removal of carbon from the melt as will be described more fully hereinafter.

In the oxygen steel process apparently the oxygen introduced through the lance impinges on the liquid phase within the converter and reacts with carbon, chromium, iron and anything else capable of being oxidized. It is thought that the oxygen doesn't necessarily react directly with carbon but rather becomes part of an oxygen inventory within the converter. At the conditions prevailing during conversion there is vigorous stirring and oxygen is mobile. For example, oxygen impinging against the surface may react with iron to form an iron oxide which becomes part of the oxygen inventory within the converter, but the iron oxide may react with carbon to produce iron and carbon oxide so that the ultimate effect of the oxygen is to produce a carbon oxide. The thermodynamics of the system will determine, among other things, what compounds are formed. For example, carbon and oxygen may react to form either carbon dioxide, carbon monoxide or both.

The thermodynamics at the conditions within the converter are such that the equilibrium distribution between carbon monoxide and carbon dioxide is such that more than 90 percent of the carbon oxide formed will be carbon monoxide.

An entirely different effect is caused by the mass action principle. According to the mass action principle, the distribution between reactants and products is affected rather than the distribution between various products. For example, oxygen may react with carbon to form carbon oxide in the system. Thus, to promote a reversible reaction it is necessary, according to the mass action principle, to remove the reaction products and therefore drive the reaction toward making more of them. In the various reactions noted above which compete for the available oxygen, both the affinity of oxygen for the different ingredients in the melt and the concentration of the reaction products of the various reactions are involved in determining which of the ingredients of the converter will react with oxygen.

To promote the reaction of oxygen with carbon, many variations of the oxygen steel process have been attempted. Among these are introducing oxygen below the surface of the melt so that the bubbles of oxygen may be distributed throughout the melt and therefore oxygen is available to carbon throughout the melt, and the introduction of mixtures of oxygen and inert gas, e.g., argon, so that the bubbles of oxygen will not become too concentrated with carbon oxides as the reactions proceed. However, the intense heat of the oxidation generally causes oxygen or argon-oxygen mixtures, which are introduced beneath the surface of the melt, to burn or otherwise destroy the tuyeres or porous plugs through which the gas mixtures are introduced; and in order to reduce the concentration of carbon oxides significantly within the bubbles, extremely large volumes of argon are required, in the range of 500 scf/ton of steel refined. Also, oxides may form in the vicinity of the tuyeres which can flux the lining as they rise to the surface of the bath thereby decreasing lining life.

THE INVENTION

The process of this invention provides an economical and effective means to solve or greatly mitigate the abovementioned problems. The process of the present invention is a process for producing stainless steel by the oxygen steel process which includes providing a liquid charge suitable for producing chromium-containing stainless steels in an oxygen steel converter having a tuyere in its bottom, introducing oxygen into the converter through a lance so that it impinges against or is introduced beneath the surface of the liquid charge in the converter, introducing an inert or endothermic gas through the tuyere in the bottom of the converter, and maintaining a subatmospheric pressure within the converter. Although a liquid charge is referred to, the charge may be a mixture of liquid and solid material.

The term inert gas is intended to define a gas that does not participate to any significant extent in the reactions taking place in the converter. Typical inert gases are argon and nitrogen. The term endothermic gas is intended to define a gas that experiences an endothermic reaction in the bath but neither the gas nor its reaction products affect the metal product. Water (steam), which breaks down to hydrogen and oxygen at the conditions within the bath, and CO₂, which becomes oxygen and carbon monoxide, are two typical endothermic gases. Argon is the preferred gas where
low-nitrogen steels are to be made. In a preferred embodiment, one or more tuyeres in the bottom of the converter are located on or near the center line of the bottom that lies in the same plane as the axis of rotation of the converter so that the tuyere is above the liquid level in the converter when the converter is tilted one way or another for loading or discharging. It is also preferred to introduce argon or other inert gas at a relatively high pressure so that expansion of the gas at the tuyere will produce a local cooling effect which will prevent or at least diminish damage to the tuyere from the heat of the surrounding molten charge.

Also, reference to tuyere(s) in the "bottom section" of the converter as used in the specification and claims is intended to include the side walls of the converter at or near the actual lower most surface. Thus, the tuyeres may either be inserted through the lining horizontally or vertically. In the horizontal case, the lining life will probably be poorer than when the tuyeres are centrally located, but mixing may be more thorough.

The converter must be maintained at subatmospheric pressure during the conversion process of this invention. Subatmospheric pressure is maintained by employing a sealed hood and providing a forced exhaust system capable of removing gaseous reaction products and inert gas at a sufficient rate to maintain the desired subatmospheric pressure. Preferably, the pressure in the conversion vessel will be progressively decreased as the conversion proceeds. Pressures of at most 100 mm Hg must be maintained, but lower pressures will frequently be required depending on the final alloy chemistry desired. For example, when carbon contents of 0.02 percent or lower are desired, a vessel pressure lower than 20 mm Hg will usually be required.

As stated above, it is desirable to effect the reactions in an oxygen steel converter so that the oxygen reacts with carbon to the exclusion of reactions between oxygen and iron and oxygen and chromium. It is an objective of the present invention to promote the oxygen-carbon reaction, and the process of the present invention provides at least four means to promote that reaction and diminish the others. First, effecting the conversion under subatmospheric pressure favors removal of vapor phase materials from the converter. Since the reaction of oxygen and carbon produces mostly carbon monoxide and a small amount of carbon dioxide and since both of these products are gases, the operation of the converter under subatmospheric pressure causes oxygen to react with carbon to a greater extent than if the process were effected at atmospheric or superatmospheric pressures.

Second, even under vacuum the liquid-static head of the melt is considerable and the mass transfer of carbon oxides through the melt is time consuming. The introduction of an argon stream below the liquid creates bubbles of gas within the melt in which there is a very small partial pressure of carbon oxide. In effect, each bubble of argon is an in situ carbon oxide vacuum which causes the carbon oxide to leave the melt and enter the bubbles, thereby driving the oxygen inventory toward carbon oxide production even at the higher pressures below the surface of the melt.

Third, the bubbles of gas rising through the melt create violent agitation thereby exposing all portions of the molten material in the converter to the subatmospheric pressure at the surface thereby promoting the release of carbon oxides and the escape of them from the converter again, thereby driving the oxygen inventory toward the production of carbon oxides.

Fourth, by driving the oxygen inventory toward the reactions with carbon rather than other materials, the formation of chromium oxide is minimized, and as a result the slag phase is less viscous, facilitating exposure of the molten metal to the subatmospheric pressure to promote the escape of carbon oxides from the surface of the melt. It is also an objective of this invention to minimize erosion of refractory linings by promoting reactions within the bath at locations remote from the refractory linings.

DETAILED DESCRIPTION OF THE INVENTION

An embodiment of the invention will be described with reference to the accompanying drawings.

FIG. 1 is a sectional elevation view of a device suitable for carrying out the process of the present invention taken along the line 1-1 of FIG. 2.

FIG. 2 is a sectional plan view of the device illustrated in FIG. 1 taken along the line 2-2.

FIG. 3 is a sectional elevation view of the device illustrated in FIG. 1 in position where molten metal is being discharged from the converter.

The drawings illustrate a converter 10 which is formed of a steel shell 11 and a refractory lining 12. The converter is equipped with a supporting ring 13 upon which axles 15 are mounted for rotating the converter around a horizontal axis so that it may be tilted for loading and unloading. The converter is equipped with a lance 16 which extends through a hood 17 via a flanged fitting 18. The hood seals against the top of the converter by bearing against a sealing ring 20 through a gasket 21.

Through the bottom of the converter 10, two tuyeres 22 are illustrated which are connected via lines 23 to a header 25 which supplies lines 23, and accordingly tuyeres 22, with argon. A charge 26 that is at least partly liquid is maintained in the converter through which argon bubbles 27 pass.

The process of the present invention is initiated with the hood 17 and lance 16 withdrawn to a position well above the converter 10. The converter 10 is rotated on the axles 15 to a tilted position wherein it receives a charge suitable for the production of stainless steel. The charge includes molten iron, contains 0–30 percent chromium, 0–80 percent nickel, 0.1–7 percent carbon and the usual impurities and conventional slag forming materials. During charging, the tuyeres 22 are above the liquid level for the most part; however, to insure maintaining the tuyeres open, a constant flow of gas, preferably air or nitrogen because they are inexpensive, is maintained through the tuyeres to avoid any possibility of molten metal entering them.

When all of the charge is in the converter, it is rotated around axles 15 and returned to its upright position as illustrated in FIG. 1. The hood 17 is lowered to seal against the sealing ring 20 and the lance 16 is inserted through the flanged fitting 18 and lowered to a position immediately above the surface of the liquid charge as illustrated in FIG. 1. An exhaust device which is not shown is placed into operation to draw gases out of the hood 17 and the converter 10 to the extent that a subatmospheric pressure as previously described is maintained in the converter.

Conversion is effected by blowing oxygen through the lance onto the surface of the molten charge with
sufficient force to cause a dimple in the surface of the charge as illustrated at 28. A separate slag phase is not shown although one will exist in operation. During the oxygen blowing portion of the conversion, argon gas is passed through tuyeres 22, and ultimately through tuyeres 22, and bubbles violently through the molten metal maintained in converter 10. Preferably, the argon is introduced at a high pressure, at least 100 psi, so that it expands as it enters the molten metal bath to create a cooling effect immediately in the vicinity of the tuyeres thereby preserving the refractories in that area. Argon is introduced at a rate of from 5–100 scfm.

As explained hereinabove, the low partial pressure of carbon oxides in the bubbles 27, the violent agitation effected by the rising bubbles of argon which exposes all portions of the molten metal 26 to the surface of the converter 10 all tend to drive the reaction of oxygen with carbon rather than with iron or chromium and as a result there is very little formation of detrimental chromium oxides or wasteful iron oxides and a high production of carbon oxides per unit of oxygen introduced.

Upon completion of the conversion, it may be desirable to mix some natural gas with the argon passing through tuyeres 22 to deoxidize the melt, after which the lance 16 is withdrawn, the hood 17 is raised, and the converter tilted to a position shown in FIG. 3 to discharge molten metal through the pouring spout 30. During conversion, the pouring spout 30 is provided with a vacuum cap to prevent air from being drawn into the converter and to prevent the liquid charge from splashing out.

The product from the process may be a ferritic or austenitic stainless steel or nickel superalloy.

As a specific example of this invention, a process embodying the invention was employed to produce stainless steel containing a maximum of 0.025 percent carbon, from 1.5–1.9 percent manganese, from 0.3–0.6 percent silicon from 18–19 percent chromium, from 8.75–10 percent nickel, a maximum of 0.04 percent phosphorus and 0.015 percent sulfur.

The process was initiated by tilting the vessel and charging it with 153,000 pounds of molten metal containing 0.96 percent carbon, 0.94 percent manganese, 0.031 percent phosphorus, 0.015 percent sulfur, 0.38 percent silicon, 19.05 percent chromium, 9.25 percent nickel and the balance substantially iron. Although the entire charge in this case was molten metal, the process may be effected using a charge that is partly molten and partly solid. The solid portion of the charge may include stainless steel scrap, ferrochromium alloys or other solid metal-bearing materials.

While charging the vessel, argon gas was passed through the bottom tuyeres to prevent fouling of those tuyeres by molten metal. Argon gas was introduced at a rate of 15 scfm. Nitrogen, carbon dioxide or even air may be passed through the tuyeres at this point in the process to conserve expensive argon. At this point in the process, when the hood is not sealed to the vessel and the vessel is in a tilted position, it is convenient to measure the temperature of the bath. In the process described herein, the temperature of the bath after charging was 2,820°F.

When the charging of the vessel was complete, the vessel was rotated to vertical position and the hood was engaged with the top of the vessel to create a seal capable of holding a vacuum. The lance was lowered to a height of 40 inches above the surface of the bath, the vacuum system was started and oxygen was blown through the lance at a rate of 1,000 scfm. The vacuum system was operated to maintain an absolute pressure within the vessel of 180 mm Hg. A permissible variation of the process of this invention is to start the oxygen blow before a vacuum is provided in the vessel so that the initial carbon burn is effected at atmospheric pressure. It is also a permissible variation of the process to deslag the vessel after a short atmospheric oxygen blow after which a subatmospheric oxygen blow is effected.

The oxygen blow was effected at progressively decreasing oxygen rates and progressively lower absolute pressures. Oxygen was blown into the vessel at 1,000 scfm under a chamber pressure of 180 mm Hg for a period of 10 minutes after which the oxygen blow rate was reduced to 850 scfm and the chamber pressure was diminished to 150 mm Hg. After 17 minutes at that rate, the oxygen blow rate was diminished to 700 scfm and the chamber pressure diminished to 135 mm Hg, and 5 minutes later the chamber pressure was diminished to 50 mm Hg. After another 5 minutes, the oxygen blow rate was diminished to 450 scfm and the chamber pressure diminished to 35 mm Hg, and after another 9 minutes oxygen blowing was terminated, and the chamber pressure was diminished to 6 mm Hg.

In order to reduce the nitrogen content of the steel, theargon flow rate was then increased to 30 scfm and the chamber pressure progressively reduced to 0.6 mm Hg over a period of 16 minutes, after which the vacuum seal was broken and the vessel was rotated in order to take a test sample and to measure the bath temperature. The test sample was analyzed to determine what later additions would be required to adjust the chemistry, and the bath temperature was found to be 3,080°F. The sample was found to contain 0.009 percent carbon, 0.58 percent manganese, 0.03 percent phosphorus, 0.014 percent sulfur, 18.4 percent chromium, 9.38 percent nickel and 0.08 percent silicon.

While the vessel was in its rotated position, 1,500 lbs of 50 percent ferrosilicon, 3,000 lbs of burnt lime and 450 lbs of fluor spar were added as a slag reduction mix. The vessel was returned to vertical position, and the contents were stirred with argon bubbles. The ferrosilicon in the reduction mix reduced the chromium oxide in the slag and returned the chromium to the metal phase while the burnt lime and fluor spar maintained the slag fluid. After the slag has been thoroughly reduced, the vessel was tipped again and deslagged, the bath temperature was measured and another metal sample was taken. This metal sample was analyzed and found to contain 0.009 percent carbon, 0.75 percent manganese, 0.03 percent phosphorus, 0.012 percent sulfur, 18.7 percent chromium, 9.35 percent nickel and 0.54 percent silicon, and the temperature of the bath was 3,020°F.

A refining slag, consisting of 2,500 lbs of burnt lime, 300 lbs of fluor spar and 250 lbs of 50 percent ferrosilicon, was then added to the vessel; and the vessel was rotated to the vertical position and stirred with argon to fuse the slag. The refining slag was added to further reduce the sulfur content of the metal. After thoroughly exposing the metal to the refining slag, the vessel was again tilted and 1,380 lbs of electrolytic manganese was added to bring the metal within the specifications. The bath temperature was again measured and
found to be 2,930°F and the vessel was further stirred with argon to insure that the manganese addition was uniformly distributed. The vessel was then tilted again and deslagged, rotated to the vertical position, covered and evacuated to aid in decreasing the temperature of the bath and finally tapped into a teeming ladle. The final chemistry of the metal was found to be 0.007 percent carbon, 1.58 percent manganese, 0.03 percent phosphorus, 0.009 percent sulfur, 18.32 percent chromium, 9.28 percent nickel and 0.48 percent silicon.

Throughout the entire blow, the slag remained fluid and as is evident from the data herein, the loss of chromium to the slag phase was minimal.

What is claimed is:

1. A process for producing stainless steel comprising:
   A. providing a charge that is a least partly liquid and suitable for producing a chromium-containing stainless steel in an oxygen steel converter having a tuyere in its bottom section,
   B. introducing oxygen through a lance onto or beneath the surface of said charge,
   C. introducing an inert gas or an endothermic gas through said tuyere,
   D. maintaining a subatmospheric pressure in said converter, and
   E. recovering a stainless steel product.

2. The process of claim 1 wherein the inert gas comprises argon introduced at a rate of about 5–100 scfm.

3. The process of claim 1 wherein the inert gas is introduced at a pressure of at least 100 psi.

4. The process of claim 1 wherein the tuyere is substantially on the diameter of the converter bottom that lies in the same plane as the horizontal axis of rotation of the converter.

5. The process of claim 1 wherein the pressure maintained in said converter is at most 100 mm Hg absolute.

6. The process of claim 1 wherein the stainless steel product contains less than 0.02 percent w carbon, and the final pressure in said converter is at most 20 mm Hg absolute.

7. The process of claim 1 wherein, subsequent to the introduction of oxygen but prior to recovering a product, the contents of said converter are contacted with a reducing slag.

8. The process of claim 1 wherein oxygen is introduced through said lance at progressively diminishing rates.

9. The process of claim 1 wherein the pressure in said converter is progressively diminished.

10. The process of claim 1 wherein said inert gas is argon, and it is introduced through said tuyere after oxygen introduction is terminated and while a subatmospheric pressure is maintained in said converter, whereby the nitrogen content of the stainless steel is diminished.

11. The process of claim 1 wherein said endothermic gas is water vapor.

12. The process of claim 1 wherein said endothermic gas is carbon dioxide.

13. The process of claim 1 wherein said inert gas or endothermic gas is introduced through a plurality of tuyeres in the bottom section.