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Cox et al.

[11] **3,891,429**

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[54] **METHOD FOR SELECTIVE DECARBURIZATION OF ALLOY STEELS**

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[52] **U.S. Cl.** **75/60**; 75/59

[51] **Int. Cl.** **C21c 5/34**

[58] **Field of Search** 75/60, 57, 51, 52

[56] **References Cited**

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3,330,645	7/1967	DeMoustier	75/60
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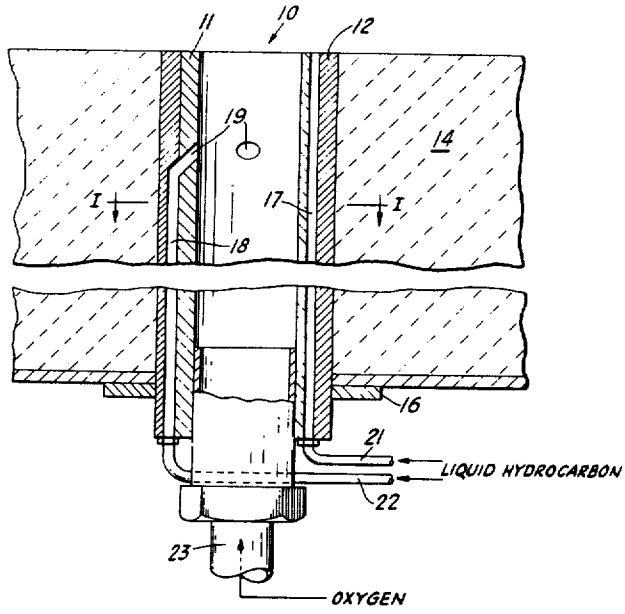
Attorney, Agent, or Firm—Robert D. Yeager

[57] **ABSTRACT**

A method for selective decarburization of crude, molten alloy steel by means of injecting into the bath, peripherally of a submerged tuyere, fuel oil which is maintained in the liquid state at least to the tuyere-bath interface and simultaneously injecting a mixture of oxygen and vaporized fuel oil axially through said tuyere into the bath until the carbon-alloy equilibrium is reached, and thereafter adjusting the mixture so as to be rich in vaporized fuel oil and continuing said fuel oil enriched injection until the desired carbon level is reached and thereupon discontinuing fuel oil and gaseous mixture injections and purging undesired hydrogen from said bath by injecting both axially and peripherally of said tuyere an inert gas.

4 Claims, 2 Drawing Figures



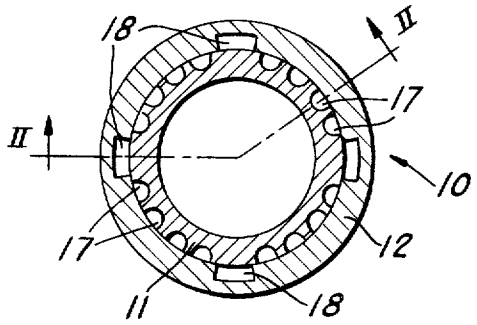

18
II
17
II
10
17
12
11
18

FIG. 1

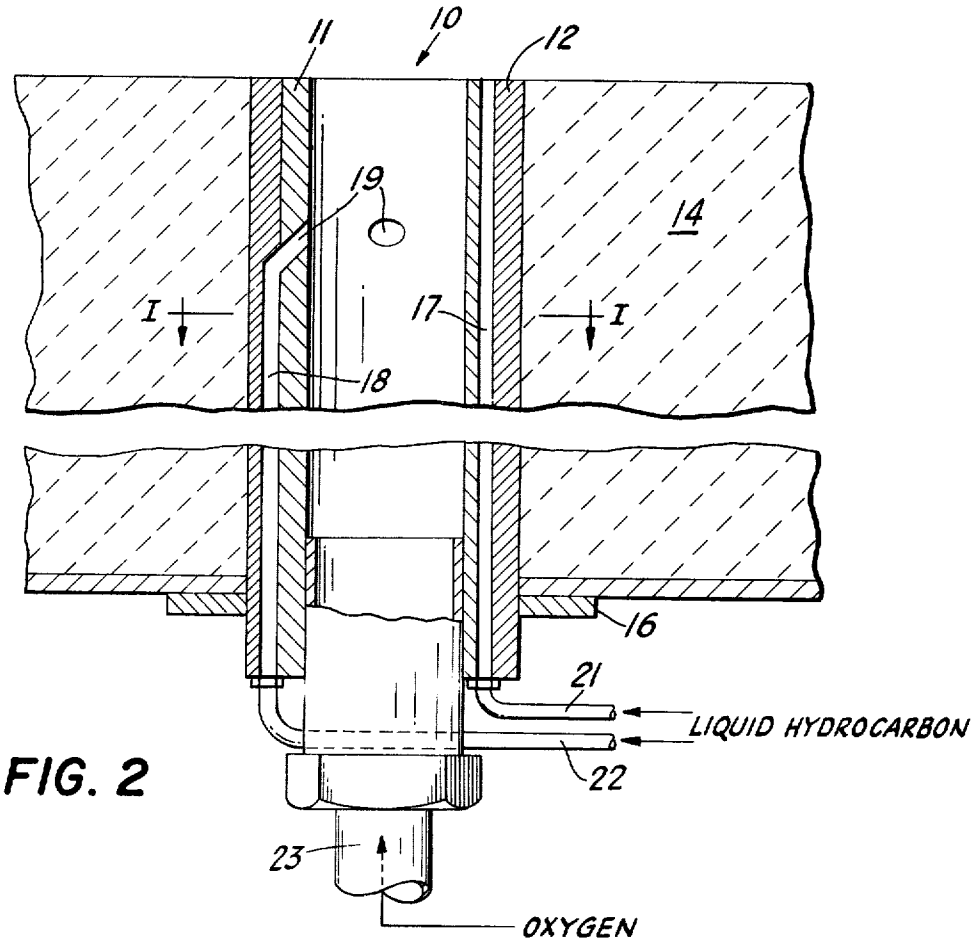

11
10
12
19
14
I
17
I
18
16
21
LIQUID HYDROCARBON
22
23
OXYGEN

FIG. 2

METHOD FOR SELECTIVE DECARBURIZATION OF ALLOY STEELS

FIELD OF THE INVENTION

The present invention relates to a method for the production of ferro-alloy steels and, in particular, to a method for the selective decarburization of high chromium steels and the like.

BACKGROUND OF THE INVENTION

In the refining of iron into steel, the desirability of utilizing oxygen to oxidize the impurities in the molten iron, particularly carbon, is well known. It has also become generally well known that substantially pure oxygen is useful in the decarburization of chromium steels. However, the amount of carbon that can be removed from a molten bath of chromium steel is limited by the equilibrium relationship between carbon, chromium and bath temperature. Attempts to remove carbon beyond the levels established by the equilibrium relationship result in the oxidation of chromium and other metal alloys and, thus, their consequential removal from the bath into the slag. Accordingly, a number of methods have been devised to obtain carbon levels below those established by the equilibrium relationship.

One of the most common methods is the utilization of ferro-alloy additives containing silicon. The addition of the additives to the melt after decarburization reduces the chromium and other metal oxides existing in the slag and returns them to the melt. While this method is very effective, it is also extremely expensive. Alternatively, decarburization has been carried out at higher temperatures to effectuate a shift in the equilibrium point resulting in a lower carbon level but these higher temperatures have also caused a substantial increase in refractory wear. Another method typically used to decarburize the melt is to reduce the partial pressure of the melt system by means of vacuum degassing.

The most significant improvement has been methods for preferentially oxidizing carbon during decarburization by utilization of an oxygen/argon mixture. Illustrative of these processes are U.S. Pat. Nos. 3,046,107 and 3,252,790. These processes generally utilize an electric arc furnace as a scrap and alloy melter to prepare a crude high-carbon, high-chromium hot metal which is thereafter converted in a refining vessel to the desired stainless steel. The decarburization of the crude melt follows the well known equilibrium relationship that exists between carbon, chromium and temperature. These processes are able to shift the equilibrium relationship by adding an inert gas to the reactant oxygen whereby the carbon monoxide formed by oxidation of carbon has a lower partial pressure than it has when oxygen alone is used. Thus, by reducing the partial pressure of the formed carbon monoxide, a lower carbon content can be obtained for a given chromium content and temperature level. The equilibrium condition of the melt: $C + MO \rightleftarrows M + CO$, where M is the metal in the melt, O is the oxygen in the melt and C is the carbon, it is shifted to the right.

This operation has gained general acceptance because of the high homogeneity of the steel produced as well as its quality. Notwithstanding the advantages of this method, certain disadvantages exist. The utilization of argon as an oxygen diluent is expensive even where

nitrogen is used during a portion of the blow. Moreover, extremely rapid wear is experienced by the tuyeres and the refractory bottoms adjacent the tuyeres caused by the high heat and/or ferric oxide generated by blowing pure oxygen. The tuyere and refractory wear is similar to the wear experienced by Thomas and Bessemer converters blowing substantially pure oxygen.

Early efforts with Thomas and Bessemer producers to cure the problem of rapid deterioration of the bottom by cooling the tuyeres during the oxygen blow produced no commercially practical results. Examples of these efforts include Lellep U.S. Pat. No. 2,333,654 wherein the tuyeres were cooled by circulating water in an annular duct around the oxygen supply pipe. Copper tubes were used to form tuyeres in converter bottoms rather than employing conventional tuyeres formed directly in the converter bottom, see Kosmider et al. U.S. Pat. No. 2,829,879. In this arrangement, the high heat conductivity of the copper was used to cool the tuyeres. Variations of the Kosmider et al. concept were attempted by Savard et al. U.S. Pat. No. 2,855,293 and Compagnie des Ateliers et Forges de la Loire French Pat. No. 1,503,756. Recent attempts to overcome erosion of the tuyere zones in a converter bottom blown with oxygen involve the use of a double tuyere, generally comprising concentric pipes located in the converter bottom. Gases such as steam or carbon dioxide were blown through the outer annulus to "shield" the oxygen jet blown through the axial pipe, see Westfalenhutte French Pat. No. 1,058,181; and Luxemburg Pat. No. 3,397,878. Hydrocarbon gases have also been used to shield the oxygen jet, French Pat. No. 1,450,718. A different approach has been taken effectively to increase tuyere and/or refractory life, Offenlegunsschift No. 2,033,975, but it has not been demonstrated to be applicable to the production of high chromium alloy steels. Other methods which sought to protect the refractory wear as well as the tuyeres such as in U.S. Pat. Nos. 3,330,645 and 3,490,755, in which porous refractory sheaths were utilized to percolate gas at the interface of the molten metal did not result in commercially adopted processes.

Accordingly, it is an object of the present invention to provide a method in which high chromium alloy steels can be made by utilizing submerged oxygen blowing without the deleterious effects commonly associated therewith. It is thus an object of the present invention to provide a method for oxygen decarburization of alloy steels without the use of expensive argon as a diluent and without high tuyere and refractory wear generally associated with oxygen decarburization.

SUMMARY OF THE INVENTION

The present invention provides a method for cooling a submerged tuyere in a refining vessel and for reducing the partial pressure of carbon monoxide in the melt to obtain low carbon levels. The method of the present invention provides a selective decarburization of a crude chromium alloy steel melt preferably prepared in an electric arc furnace.

Generally, the method comprises injecting a mixture of oxygen and vaporized fuel oil through the axial portion of a concentric tuyere for that period which is sufficient to achieve the theoretical carbon-chromium-temperature equilibrium of the melt. Simultaneously with the axial injection, fuel oil, maintained in the liq-

uid state at least to the tuyere-bath interface, is injected into the refining vessel peripherally of the axial portion of the tuyere. When the theoretical carbon-chromium-temperature equilibrium is reached, the volumetric ratio of vaporized fuel oil to oxygen in the gaseous mixture is increased to at least between 2:1 and 6:1 until the melt is decarburized to the desired carbon level. The peripheral fuel oil injection and gas mixture injection are stopped when the desired end point is reached, and an inert gas, such as carbon dioxide, argon and the like, is injected for a short time into the melt to purge the melt of any residual hydrogen.

More specifically, the present invention provides a process in which a high-carbon, high-chromium crude melt is prepared and deslagged in an electric arc furnace. Decarburization is carried out in a refining vessel having tuyeres submerged below the bath level and located, preferably, in the bottom thereof. The tuyeres are of a double or concentric tube configuration in which a liquid hydrocarbon, preferably fuel oil, is injected into the molten bath through a space between the peripheral and axial tubes, and a mixture of oxygen and vaporized liquid hydrocarbon is injected through the central or axial tube.

The liquid hydrocarbon injected through the peripheral tube is maintained in the liquid state at least to the tuyere-bath interface. By maintaining the hydrocarbon in the liquid state, that is preventing vaporization within the tuyere, the heat of vaporization as well as the endothermic heat of hydrocarbon cracking is available to cool the tuyere tip. The cracking may, under optimum conditions, provide preferential carbon donating residuum to the melt adjacent the tuyere. The carbon residuum is believed to act as a protective film or insulator between the melt and the refractory, but whether or not any carbon residuum is deposited the cracking will preferentially donate carbon to and effect reduction of the ferric oxide which is known to have the greatest corrosive effect upon the lining. Accordingly, by preventing vaporization of the liquid hydrocarbon within the tuyere it is possible to both protect the tuyere tip and the adjacent refractory material, thus substantially reducing the rapid wear experienced when blowing pure oxygen into the molten bath.

Generally, the decarburization is carried out in three stages. In the first stage, preferably oxygen alone, or a mixture of oxygen and vaporized liquid hydrocarbon is injected into the bath through the axial tuyere. Where a gaseous mixture is used, the liquid hydrocarbon is vaporized upon addition to the oxygen to provide an oxygen to hydrocarbon vapor volumetric ratio of at least 3:1 or 4:1. The second stage injection is commenced when the theoretical carbon-chromium-temperature equilibrium is reached as calculated upon the basis of the amount of oxygen injected in the first stage and an analysis of the melt. During the second stage the volume of vaporized hydrocarbon to oxygen is preferably about 3 to 4:1. Other ratios that can be employed for second stage blowing, range from 2:1 to about 6:1; but at the lower ratios, a higher percentage of chromium is oxidized than is generally preferred, and at the higher ratios the refining time is increased although very low carbon levels are achieved. The second stage is continued until the desired carbon content in the melt is reached. At the desired end point, the flow of both the oxygen-hydrocarbon mixture and the peripheral hydrocarbon cooling liquid is discontinued. An inert gas, preferably carbon dioxide or argon, is injected through the axial and peripheral circuits of the tuyere. The third stage injection of inert gas is continued for a period of from about 1 to 3 minutes to reduce any dissolved hydrogen in the melt as well as to deoxidize the melt.

While the process is well suited to stepwise operation, it is clear that the process can be practiced on the basis of a continual ratio adjustment without utilizing separate and discrete steps. In such a case, the desired volumetric ratios are applicable at the analogous times during refining.

The liquid hydrocarbon in the oxygen stream acts as a diluent for the carbon monoxide formed during decarburization of the crude melt. It is believed that the molecules of the liquid hydrocarbon, fuel oil, upon vaporization in the oxygen stream within the tuyere, are activated by the high temperatures prevailing at the interface between the tuyere and molten bath. The hydrocarbon and oxygen combine to form peroxides which decompose to water and aldehyde. This combination and decomposition is in extremely rapid transformation and is believed to occur almost simultaneously. The aldehyde very rapidly thereafter is converted to carbon dioxide and water, the latter of which dissociates into hydrogen and oxygen. The carbon dioxide and the hydrogen from the dissociated water vapor act as diluents for the carbon monoxide formed in the melt during decarburization.

In the first stage of the process, the amount of hydrocarbon required is substantially less than the amount of oxygen required even though the partial pressure of carbon monoxide does increase with increasing oxygen availability. The amount of oxygen supplied is substantially the same as that heretofore required to equilibrate the carbon-chromium-temperature equilibrium relationship. Since a reduction in the carbon below equilibrium requires a shift in the equilibrium point by a reduction in the partial pressure of the carbon monoxide in the bath, the second stage involves a substantial increase in the volumetric ratios of vaporized liquid hydrocarbon to oxygen, for example, up to 6:1. It is preferred, however, that in the second stage the volumetric ratio of the vaporized liquid hydrocarbon to oxygen is 3:1.

Utilizing a liquid hydrocarbon both for oxygen dilution as well as a cooling agent for the submerged tuyere, increases the availability of hydrogen for dissolution into the bath. Generally, a large portion of the available hydrogen becomes dissolved within the melt which if permitted to remain would render the heat unusable. To remove the dissolved hydrogen to levels of less than 12 PPM for 300 series stainless steel, for example, a third stage injection of an inert gas is used to flush the melt. This flushing also has the advantage of lowering the amount of oxygen dissolved therein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional plan view of a tuyere for use with the present invention; and

FIG. 2 is a sectional elevation taken along lines II—II of FIG. 1 of said tuyere.

PRESENTLY PREFERRED EMBODIMENT

The method of selective decarburization of alloy steel is preferably carried out as a duplexing operation. The process is particularly well adapted for the production of steels having chromium content in excess of 5%

and, preferably, from 15 to 25%, with the carbon and silicon each present in amounts less than 1%. By practicing the methods of the present invention, the carbon content can be reduced to around 0.2% without any substantial oxidation and loss of chromium or other alloys.

Preferably, an electric arc furnace is used to melt down scrap and alloy under dead melt conditions and to bring the melt temperature up to between 1600° and 1700°C. The molten metal is then tapped into a ladle, sampled and deslagged. The deslagged crude hot metal is then transferred into a reaction or refining vessel. The refining vessel can be a conventionally shaped Bessemer type converter adapted for rotation to facilitate charging, sampling and tapping. The converter is rotatable about a pair of trunnions which are designed to permit the passage of oxygen and fuel oil conduits therethrough. The bottom of the converter is fitted with a number of concentric tuyeres, for example, a 100 ton steel alloy converter would be provided with about five tuyeres.

Referring to FIGS. **1** and **2**, tuyere **10** is representative of the type of tuyere preferred for use in the present invention and includes an axial tube **11** and a concentrically aligned outer tube **12**. Tuyere **10** is adapted to be mounted through refractory bottom **14** of the converter by mounting means **16**. Axial tube **11** has a plurality of fluted passages **17** machined along the length of its outer surface. Passages **17** are designed to register with the inner surface of outer tube **12** to form a plurality of peripheral passages about the periphery of the axial tube for the peripheral injection of liquid hydrocarbon.

Outer tube **12** is provided with a number of grooves **18** machined along a portion of the inner surface and designed to register with the outer surface of inner tube **11**, but not with the fluted passages **17**. Grooves **18** extend from the base of tube **12** to a position near the tip of tuyere **10**, for example, within about one inch of the tuyere-bath interface. The tip ends of grooves **18** are positioned to register with openings **19** which are angularly formed through axial tube **11** and provide for introduction of fuel oil from the grooves **18** into the oxygen stream in axial tube **11**.

The inner diameter of axial tube **11** is preferably between 0.25 to 0.30 inches and is made of a high thermally conductive material such as copper or copper alloys. Outer concentric tube **12**, on the other hand, can be fabricated from any suitable material such as stainless or plain carbon steel. The inner diameter of outer tube **12** and the outer diameter of inner tube **11** are essentially the same so that a tight nesting relationship therebetween is established to provide the appropriate sealing between passages **17** and grooves **18**. Passages **17** are connected to a source of fuel oil by means of line **21**. Elongated grooves **18** are connected at the base of tuyere **10** to line **22** that is connected to an independently regulatable source of fuel oil. Axial tube **11** is connected to line **23** that is connected to a source of high pressure oxygen.

During the operation of the present invention, fuel oil is injected through line **21** and passages **17** peripherally of the axial oxygen tuyere. Pressure and/or flow rate in lines **21** and passages **17** is maintained to prevent the fuel oil from vaporizing before it reaches the tuyere-bath interface. Premature vaporization can be detected by fluctuations in the flow meters on lines **21**. Fuel oil in line **22**, on the other hand, is maintained at a pressure and flow rate which provides both proper fuel oil-oxygen vapor mixture ratio and preferably for vaporization of the fuel oil at the end of elongated grooves **18**.

By maintaining the fuel oil in a liquid state at least to the tuyere-bath interface, the tuyeres as well as the adjacent refractory lining **14** are protected from the rapid erosion of the bath. It is believed that both the heat of vaporization as well as the phenomena similar to cracking is used to absorb bath heat and to thereby cool the tuyere. Moreover, the cracked hydrocarbon fuel oil provides a carbonaceous layer or film in the area of the tuyere which either acts as a physical shield against the bath or preferably donates carbon to the ferric oxide. The fuel oil is preferably maintained at a pressure of between 125 and 160 psi.

Oxygen supplied by line **23** and vaporized fuel oil from elongated groove **18** in tuyere **10** are injected into the bath through the axial tubes **11** of tuyere **10**. In a 100-ton heat of a 300 series alloy steel for example, the total oxygen flow rate would, preferably, be about 1000 cubic feet of oxygen per hour per ton with 350 to 400 cubic feet of fuel oil per hour per ton of steel in the first stage. Since the first stage blow lasts until the theoretical carbon-chromium equilibrium point is reached, it is possible to blow in the first stage without the utilization of any fuel oil. The second stage preferably utilizes approximately 1000 to 1200 cubic feet of fuel oil per hour per ton of steel and about **300** to **400** cubic feet of oxygen. Number **2** fuel oil, for example, injected into tuyere **10** at 100 psi will provide approximately 10 to 11 cubic feet per gallon. The second stage blow is ended when the desired carbon level has been reached. The third stage blow of carbon dioxide or argon is utilized to stir the bath and remove any undesired hydrogen. The third stage blow is from about 1 to 10 minutes and preferably about 3 minutes in duration, depending upon the amount of hydrogen dissolved in the bath.

While presently preferred embodiments of the invention have been shown and described in particularity, it may otherwise be embodied within the scope of the appended claims.

What is claimed is:

1. A method of selective decarburization of a chromium-alloy steel melt, said decarburization being carried out in a refining vessel having at least one double tuyere submerged below the surface of the melt, said method comprising: injecting into said melt through a central tube of said tuyere a gas selected from the group consisting of oxygen and a mixture of oxygen and fuel oil for a period of time sufficient to reach the carbon-chromium-temperature equilibrium, while injecting, during the entire said period, fuel oil maintained in the liquid state to the tuyere-melt interface into said melt through said tuyere and peripherally of said central tube; injecting through said central tube into said melt a mixture of fuel oil and oxygen in a volumetric gas ratio of from about 2:1 to 6:1, until said melt is decarburized, while continuing said peripheral flow of fuel oil into said melt; and thereafter discontinuing the injection of fuel oil and said mixture of fuel oil and oxygen, and injecting into said melt an inert gas to purge the melt of hydrogen.

2. A method as set forth in claim **1** wherein oxygen is injected into said melt through said central tube for a period of time sufficient to reach the carbon-chromium-temperature equilibrium.

3. A method as set forth in claim **1** wherein said ratio of fuel oil to oxygen after equilibrium is 3:1.

4. A method as set forth in claim **1** wherein said inert gas is carbon dioxide.

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