United States Patent Office 2,826,488 Patented Mar. 11, 1958

2,826,488

PROCESS OF MAKING STEEL FROM PIG IRON

James J. Bowden, Cortland, Ohio

No Drawing. Application June 24, 1955
Serial No. 517,939

4 Claims. (Cl. 75—52)

This invention relates broadly to the manufacture of low phosphorus, low nitrogen steel wherein the major component by weight of the charge is molten pig iron, and wherein oxygen gas of high purity is blown on to the surface of the molten metal. This invention does not relate to steel manufacture by either the open hearth, Bessemer or the electric furnace methods as they are commonly understood in the industry, nor to the use of air.

The Bessemer process comprises substantially the steps of introducing molten pig iron into a converter and supplying atmospheric air or oxygenated air through tuyeres in the bottom of the converter. During its passage through the metal bath the oxygen of the gas will first oxidize those components of the pig iron which have a greater affinity to oxygen than iron, such as silicon, manganese, carbon and in the basic process (Thomas process) also phosphorus.

There is another and more recent process in the manufacture of steel which is characterized by injecting the oxidizing gas at the surface of the molten metal. One of the drawbacks of this latter method is due to the fact that the slag covering the molten metal, which slag results from the action of the oxygen on the molten metal and the added flux (lime, mill scale and fluorspar), is of such a consistency that the high purity oxygen only with difficulty is able to contact the molten metal that is to be refined. And this condition necessitates the use of excess oxygen pressure, greater consumption of oxygen and additional time for the reaction to go to completion, because of the difficulty resulting from the highly viscous slag. This has been recognized, being reported in the Hauttman Patent No. 2,644,746, patented July 7, 1953. In fact, this patentee asserted that "even when the oxygen jet was directed obliquely, it proved impossible to free the surface of the steel, since with an obliquely directed jet the motion of the slag is such that it is continuously drawn to and over the point of contact." And further in this same patent it is pointed out that when attempting to overcome this difficulty of penetration of oxygen into the molten metal by increasing the pressure, this obviously increases the cost of using oxygen to a not inconsiderable extent. Hauttman proposed to solve this problem of securing direct contact between the oxygen and the molten metal by rotating the stream of oxygen about its axis to cause rotation of the slag at the point of impact.

A primary object of the present invention is to increase the extent of contact between the oxygen gas and molten metal, more particularly pig iron, in the manufacture of steel, by increasing the fluidity of the overlying slag. This results in a decreased resistance of the slag to the penetration by the oxygen gas to the molten metal surface.

Another object of the invention is to make possible the utilization of the oxidizing gas at a lower pressure than would otherwise be the case in securing contact of the molten metal with the oxygen gas in the manufacture of steel.

Still another object of the invention is to provide a novel steel-making process characterized by a more rapid development of a basic, highly oxidized slag at a relatively early stage of the refining period than has been hitherto known. This will be explained in more detail subsequently herein.

A more specific object of the present invention is to decarbonize molten pig iron in the manufacture of steel using high purity oxygen in an improvement upon the Linz and Donawitz process, which process is described in an article appearing in the magazine "Journal of Metals," issue of April 1955. In the process described there, the flux normally consists of lime, limestone, fluorspar, dolomite, and mill scale. In this Linz and Donawitz process high purity oxygen is blown on top of the molten pig iron. The products of oxidation in any manufacture of steel are silica (SiO_2), iron oxides, oxides of manganese, magnesium, and phosphorus. The flux mentioned in this paragraph is used in order to remove these products of oxidation.

In the M. Tenenbaum Patent No. 2,668,759, issued February 9, 1954, on steelmaking, which is a variation of the Linz and Donawitz process, a lime-containing, basic slag-forming reactant and an iron oxide-bearing material, such as iron ore, sinter or mill scale is used. Other basic oxides or substances capable of yielding basic oxides, may also be used, e. g., magnesia, manganese oxide.

In the manufacture of steel by the Linz and Donawitz process the important thing is to have the slag fluid and reactive early in the process when the metal charge has as much of the initial chemical and physical qualities as it is possible to have; this kind of condition will give the slag and metal ample time to do their work. In that manner the slag should be so conditioned that it will be possible to have the slag act as a cleanser, and remove the undesirable elements and compounds from the molten metal underlying the slag. This means then that when a slag is fluid for as long as possible during the steel-making process that it has more time to do its work; or to put it otherwise, the sooner the slag becomes fluid the easier it will be to do the desired refining, and the more efficiently the oxygen will be brought into contact with the molten metal for the oxidation of the elements that will eventually be found in the slag. In short, a good slag is a fluid slag, and it is difficult to make a basic slag fluid in the ordinary approach, using only lime, mill scale and fluorspar (which tendency will be to make the slag thin in order to get fluidity and thinness is detrimental quality in a slag and sometimes gets out of control due to this excessive thinning).

In accordance with the present invention in making steel from molten pig iron, with or without steel scrap, using a basic lined converter there is employed as a basic, slag-forming material a flux of lime, iron oxide and alumina, which components are present within certain percentage ranges and are either simply premixed, premixed and briquetted, or premixed and fused, or premixed as in a slurry, such as in making concrete. The preferred type flux is premixed and briquetted under pressure, with the next preference premixed as a slurry; the premixed and fused would be better than the merely premixed materials. The choice is one mainly of economy. Instead of lime, calcium hydrate, limestone or a mixture of limestone with lime can be used. The source of iron oxide is preferably mill scale, although the source could be iron ore or sinter.

The source of alumina, which I prefer to use, is a cement, preferably a high alumina cement, known in the trade as "Lumnite."[1] Nevertheless, other source of alumina may be used advantageously, such as a low-alumina Portland cement, corundum, feldspar, gibbsite, cryolite, diaspore, bauxite, aluminum dross and skimmings, and red mud (a waste product of the aluminum industry). Alumina, as contained in combined form (kaolinite), is not satisfactory, because it increases the silica content in the slag formed, making it necessary to add additional

[1] A trademark of the Universal Atlas Cement Company for composition of about 41% Al_2O_3: 38% CaO and 12% Fe_2O_3 with minor amounts of silica, etc.

lime to combine with the silica thus added, resulting in a more viscous slag because the dicalcium silicate formed has a high melting point.

The oxygen which is employed should be not less than 95% O_2, preferably pure.

The temperature of the molten iron in the charge should preferably not be less than 2500° F.

The metallic charge which is employed, and which also is representative of that in the Linz and Danowitz process referred to above, consists of 20–35% unmelted steel scrap, with the balance, 65–80%, of molten pig iron, each by weight. However, as much as 100% of molten pig iron could be charged, or 60—almost 100% of molten pig iron, with the remaining percentage being unmelted steel scrap.

In the refining of molten pig iron by contact with free oxygen, the carbon, which usually amounts to about 4%, is eliminated as a gas; the silicon is oxidized to silica (SiO_2); that part of the iron which is oxidized initially appears in the slag as ferrous oxide and ferric oxide; the manganese which initially appears in the slag occurs as manganese oxide. The iron oxide and manganese oxide which are present from oxidation, as explained, combine in the presence of silica to form a silicate of iron and manganese believed to be ($FeOMnOSiO_2$). Calcium oxide which has been added, in excess, combines with silica to form dicalcium silicate. And at this step the iron and manganese oxides in the silicate of iron and manganese are replaced by calcium oxide which forms dicalcium silicate. Alumina combines with excess lime, and with iron oxide, to form tetracalcium alumino ferrite. Alumina also combines with lime to form calcium aluminate. Both these types of aluminum oxide compounds tend to lower the M. P. of the entire slag system.

The type of mineral-containing slag in either the Tenenbaum process or the Linz and Donawitz process referred to above is difficult to make fluid under normal operating conditions due to its high M. P. and viscosity. In order to overcome this shortcoming of high viscosity in such a slag, I propose to add an excess of lime and a certain percentage of alumina. Because of the affinity of lime for alumina and also the affinity of calcium ferrites for alumina, and also because of the law of eutectics, the dicalcium silicate is fluxed. The M. P. of the entire slag system is lowered. This results in the thinning of the slag at the conventional operating temperatures, making it fluid and basic; and it lowers the resistance of penetration of this slag to such an extent that the gaseous oxygen more easily penetrates this resulting slag to reach the surface of the molten metal. The removal of the impurities depends upon preferential oxidation.

As has been pointed out in the oxygen steel-making process developed at Linz and Donawitz (Journal of Metals, issue of April 1955), the flux consists of lime, limestone, mill scale, fluorspar and dolomite. The fluidity of the slag, however, leaves much to be desired. By eliminating the fluorspar and dolomite and substituting for the fluorspar the proper amount of alumina in a premixed flux, the desired fluidity of the slag can be achieved. And in so doing there results conditions favorable to a more intimate contact between the high purity oxygen and the molten metal to be refined. As a consequence the process of steel making is speeded up; there is a more economical use of the charged materials with increased yield of saleable steel; the quality of the finished steel is improved because of the close control of the process.

It has been mentioned previously that the basic flux which is added in making steel from pig iron according to the present invention is characterized by pre-mixed lime, iron oxide and alumina, each of which is present within certain percentage ranges. The percentage composition of the components thereof in the total flux mixture calculated at 100% should be within limits herewith

set out, the percentages being based upon representations in terms of calcium oxide (lime), ferric oxide and alumina:

	Percent by weight inclusive
CaO	50–90
Fe_2O_3	5–35
Al_2O_3	0.5–15

The total weight of this flux mixture will vary from approximately 2% to 10%, inclusive, of the weight of the metallic charge (steel) or pig iron.

If this flux composition is simply pre-mixed and given no other physical treatment, this may be done by mixing the components, such as lime, mill scale and a high alumina cement, in a cement mixer, or a ball or rod mill or a muller, etc., prior to its addition to the molten pig iron.

If the flux composition is pre-mixed and briquetted with the addition of cement, a convenient way is to form a slurry or paste from the components within the percentage ranges supra using a high alumina cement as a binder, then cast, crush after hardening, and screen. It is then added to the molten pig iron in the furnace. However, instead of using cement, the components can be mixed in the proportions given above, and then briquetted under pressure. Or the components can be mixed with or without the cement and briquetted.

By the fourth mode, the components of the flux composition are mixed, then the composite melted or fused, thereupon cast, and after cooling crushed and screened. The maximum diameter of these screened pieces should be about one inch. This choice of size is that which would be chosen also as to second, third and fourth modes discussed.

The preferred composition of the pre-mixed flux is, on the basis of percentage by weight:

	Percent
CaO	83
Fe_2O_3	14
Al_2O_3	3.5
Total	100.5

The amount of the flux composition is based upon the weight and composition of the metal charge in the furnace, particularly on the silicon content of the iron in the charge. The approximate ingot yield of steel is 90% of the charge metal weight. In a representative run by the process of the present invention, for 93,000 pounds of metallic weight charged in the basic lined furnace, consisting of 27,000 pounds of scrap iron and 66,000 of pig iron, the components by weight in the pre-mixed flux composition were 5,400 pounds of CaO, 900 pounds of Fe_3O_4 and 210 pounds of Al_2O_3. These are calculated as equivalent in terms of calcium oxide, ferrosoferric oxide, i. e., iron oxide (ous, ic) and alumina, rather than existence in this form. To reiterate, the CaO could be present in whole or in part as calcium carbonate. The total based on pounds is 6,510 pounds of the flux calculated in the terms mentioned: 93,000 pounds of the metallic charge. Based upon the charge metal weight, this typical flux composition would compute percentagewise:

Component	Weight in lbs.	Percent of metal charge weight, approx.	The flux in terms of percent
CaO	4,600	5	59.5
Limestone	2,000	2.1	26.0
Fe_3O_4*	900	1	11.7
Al_2O_3	210	0.25	2.6
Total	7,710	8.35	99.8

*1 Fe_2O_3=0.69 Fe_2O_3.

The basic slag-forming material characterized by alu-

minum oxide, calcium oxide and ferric oxide in certain percentages by weight of its total weight facilitates the fusion of the slag upon the molten pig iron, wherein the molten iron is contacted with free oxygen at the metal surface. The presence of alumina in the basic slag-forming material is believed to be new. The addition of the alumina-containing, basic slag-forming material of my invention may be charged simultaneously with or immediately following the charging of the liquid metal, or to introduce the pre-mixed alumina-containing slag-forming material to the refining zone and then pour the molten iron over this additive in order to facilitate mixing and distribution of the reactants which hastens the refining of reactions.

The pre-mixed, basic slag-forming material of the present invention facilitates the formation of a very desirable melting point mineral. And being of lower melting point than that of dicalcium silicate, which melts at 2130° C., and lime, which melts at an even higher temperature, namely, 2572° C., my pre-mixed, basic slag-forming additive greatly assists the fluxing or solubilizing of these higher melting point materials in the slag. Because of the alumina being present in the basic, slag-forming additive and by virtue of the law of eutectics, these two compounds derived from alumina, namely, tricalcium aluminate and tetracalcium alumino ferrite, as well as others of its compounds definitely assist in lowering the fluxing temperature of the lime, slag or mixture to a point that it is believed to be lower than that of either of these two alumina-bearing compounds. It is also true that any other alumina-bearing compound except its silicates will assist in the same manner by combining with the lime and lowering its fluxing point. The practical aspect is that the alumina assists in putting the lime and dicalcium silicate present in the slag in solution much below the temperature at which either of the two latter components dissolve. By lowering the melting point of the flux, time will be saved in reaching the temperature necessary to make the flux active in a role to remove impurities from the molten pig iron, i. e., in reaching the M. P. of the predesigned flux.

The premixed basic slag-forming compound will be calculated to result in a composition which, when added to the molten metal, will promptly become fluid. This means that the pre-mixed flux will have a very desirable melting point, and as further additions of it are made, the part that is already melted will act as a receiver for the newly added pre-mixed mineral with a consequent increased percentage rate of low melting point mineral being added to the system. Hence, the greater the amount of melted mineral there is in the system the quicker will the additions which follow be liquefied and made useful in the proper assimilation of the undesirable products of oxidation resulting from the action of the oxygen on the contained silicon.

For a better understanding of this invention a specific embodiment of the process is herewith presented, setting out the mode of operation and the principle of the invention.

EXAMPLE

A metallic charge of 93,000 lbs., which is made up of 27,000 lbs. of steel scrap and 66,000 lbs. of molten pig iron, whose temperature is not less than 2,500° F. is introduced into the refining vessel in that order of addition. The analysis of the pig iron is:

4.0 to 4.5% carbon
.80 to 1.20% silicon
.70 to 1.80% manganese
.200 to .500% phosphorus
Iron by difference

The metal charge above is followed directly by the addition of a pre-mixed slag-forming material made up as follows:

4,600 lbs. of burned lime (CaO)
2,000 lbs. of limestone
900 lbs. of mill scale
210 lbs. of aluminum oxide (as dress, cement, etc.)

Immediately afterward, the high purity (99%) oxygen under pressure is introduced through a lance substantially at the surface of the molten mixture. This blowing of high purity oxygen at this point of time, if such is to be successful, must have conditions in the vessel that make it possible for the oxygen to easily and readily reach the surface of the molten metal, where the oxidation takes place. The basic, slag forming material which has been added is intermixed with the molten metal phase. There is an exothermic reaction when oxygen is blown on the metal surface which results from the rapid oxidation of carbon, silicon, iron, manganese and other elements in the charge. The injection of oxygen at the metal surface is continued until the carbon is reduced to the desired final extent by oxidation. The resistance to penetration of the slag has been lowered to such an extent by the addition of my flux, which is high in alumina and also contains an excess of lime, that the oxygen gas has been able to readily reach the surface of the molten metal.

It should be pointed out that it is not necessary to use limestone as such for a flux; it is only necessary to get the CaO that is needed in the slag, regardless of where it comes from. In fact, a principal source of lime that I intend to use is the residue that comes from the manufacture of acetylene and the residue that comes from the manufacture of caustic soda, chlorine and soda ash or from other suitable waste products that contain the right type of lime availability.

Composition of a typical pre-mixed flux charge for the manufacture of a single heat wherein the metallic charge is 93,000 lbs. (scrap and molten metal) and the yield is about 90% as ingots

Flux making constituent	With relation to the premixed flux itself		With relation to the metallic charge only, weight 93,000 lbs., percent
Constituent	Weight, lbs.	Percent	
CaO (burned lime)	4,600	59.7	4.9
$CaCO_3$ (limestone)	2,000	25.9	2.2
Fe_3O_4 (mill scale)	900	[1] 11.5	.97
Al_2O_3 (aluminum dross cement, etc.)	210	2.7	.23
Total	7,710	99.8	8.30

[1] =7.9% Fe_2O_3.

Same as above but calculating limestone as CaO or using any other addition containing CaO as CaO with relation to a slag mix and a metallic charge of 93,000 lbs.

	Pounds	Percent	Percent
CaO (equivalent)	5,600	83.5	6.0
Fe_3O_4 (mill scale)	900	[1] 13.4	.97
Al_2O_3 (dross, cement, etc.)	210	3.1	.23
Total	6,710	100.0	7.20

[1] =9.2% Fe_2O_3.

Numerous other modifications and alternatives may be made within the scope of the present invention which is not to be limited to the specific example or the compositions or theories of operation except insofar as covered by the following claims.

I claim:

1. A process of making low phosphorus, low nitrogen steel from pig irons, which process comprises introducing into a basic lined refining zone the pig iron in molten state, a pre-mixed, basic, slag-forming composition which is an iron-oxide bearing material, an aluminum oxide bear-

ing material, and a lime-containing material, in which CaO represents 50–90%, Fe_2O_3 5–35%, and Al_2O_3 0.5–15%, each by weight in a predetermined amount of 2–10% inclusive of the weight of the metal charge the major component of which is molten pig iron, injecting an oxidizing gas having a free oxygen content of at least 95% by volume substantially at the metal surface, and intermixing the slag and metal phases and continuing the injection of said gas substantially at the metal surface until the carbon is reduced to the desired final extent by oxidation thereof.

2. A process of making low phosphorus, low nitrogen steel from pig irons, which process comprises introducing into a basic lined refining zone the pig iron in molten state, a pre-mixed briquetted and sized basic, slag-forming composition which is an iron-oxide bearing material, an aluminum oxide bearing material, and a lime-containing material, in which CaO represents 50–90%, Fe_2O_3 5–35%, and Al_2O_3 0.5–15%, each by weight in a predetermined amount of 2–10% inclusive of the weight of the metal charge the major component of which is molten pig iron, injecting an oxidizing gas having a free oxygen content of at least 95% by volume substantially at the metal surface, and intermixing the slag and metal phases and continuing the injection of said gas substantially at the metal surface until the carbon is reduced to the desired final extent by oxidation thereof.

3. A process of making low phosphorus, low nitrogen steel from pig irons, which process comprises introducing into a basic lined refining zone a metallic iron charge consisting of 20–35% by weight unmelted steel scrap and from 65–80% by weight molten pig iron in molten state, a pre-mixed basic, slag-forming composition which is an iron-oxide bearing material, an aluminum oxide bearing

material, and a lime-containing material, in which CaO represents 50–90%, Fe_2O_3 5–35%, and Al_2O_3 0.5–15%, each by weight in a predetermined amount of 2–10% inclusive of the weight of the metal charge, injecting an oxidizing gas having a free oxygen content of at least 95% by volume substantially at the metal surface, and intermixing the slag and metal phases and continuing the injection of said gas substantially at the metal surface until the carbon is reduced to the desired final extent by oxidation thereof.

4. A process of making low phosphorus, low nitrogen steel from pig irons, which process comprises introducing into a basic lined refining zone steel scrap and molten pig iron in the ratio 60—approximately 100% molten pig iron, the remaining percentage of the metal charge being unmelted steel scrap, a pre-mixed basic, slag-forming composition which is an iron-oxide bearing material, an aluminum oxide bearing material, and a lime-containing material, in which CaO represents 50–90%, Fe_2O_3 5–35%, and Al_2O_3 0.5–15%, each by weight in a predetermined amount of 2–10% inclusive of the weight of the metal charge, injecting an oxidizing gas having a free oxygen content of at least 95% by volume substantially at the metal surface, and intermixing the slag and metal phases and continuing the injection of said gas substantially at the metal surface until the carbon is reduced to the desired final extent by oxidation thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

1,890,485	Amsler	Dec. 13, 1932
2,416,179	Kemmer	Feb. 18, 1947
2,668,759	Tenenbaum	Feb. 9, 1954