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PROCESS FOR BLOWING PIG-IRON

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This invention relates to an improved process for refining pig-iron which contains less than 0.5% silicon and more particularly to the removal of phosphorous from such pig-iron to produce steel containing less than 0.050% phosphorous.

This is a continuation-in-part of my application Serial No. 427,659, filed May 4, 1954, now abandoned.

Processes in which the oxygen is blown against the surface of the molten impure iron in a converter for refining the iron are already known. In these top blowing processes, the reaction develops in such a manner that, after ignition and formation of a restricted, highly-heated center of reaction on the surface of the melt during the first period of blowing, the silicon and the major part of the manganese are burnt away. This results in a considerable excess of heat, a rise in temperature of the melt, and a partial liquefaction of the slagging agents floating on the surface of the melt. Combustion of the carbon commences simultaneously with the reaction of the silicon, proceeding steadily and regularly while any carbon remains present in the bath, and causing, by the development of gaseous reaction products such as carbon monoxide, a lively agitation of the bath. This agitation of the bath is essential for the desired orderly development of the refining reaction, since over-refining phenomena and an excess of oxygen in the bath are prevented by the continuous convection between the refined and the as yet unrefined portions.

While the above-mentioned reactions are in their metallurgical development easily understood and apparently relatively easy to control, the slagging of the phosphorous actually is attended with appreciable difficulties. The steelmaker has to effect the dephosphorizing as rapidly as possible, and substantially complete it during the period of decarburization, because with completion of the combustion of the carbon, the turbulent motion of the bath also ceases. While phosphorous can be eliminated after the carbon has been removed by continuing blowing, this socalled "after-blow" period produces other serious difficulties, especially as regards the quality of the steel produced. In particular, too much iron is thereby oxidized, simultaneously with removal of the phosphorous, and the slag becomes too rich in iron oxide. Owing to equilibrium reactions between slag and melt, excessive quantities of ferrous oxide dissolve in the bath. The result is redshortness, embrittlement, and a far higher sensitivity to corrosion of the steel. Melts in which it has not been possible to remove the major portion of the phosphorous during decarburization cannot be used for any heavy-duty purposes. Frequently they have in fact to be scrapped.

It has already been proposed to overcome such difficulties by adding oxidic ores to the bath together with or immediately following on the limestone charge. The introduction of ferrous oxide enables the formation of a ferritic calcareous slag which is of a basic character and capable of reaction, and which promotes rapid elimination of the phosphorous. However, this known procedure implies the availability of a considerable excess of heat, since the reactions in question are endothermal. A calcoferritic slag is only capable of absorbing phosphorous when it is heated to a high temperature, and is correspondingly liquid. If these conditions cannot be satisfied,

e.g., when the pig-iron used contains insufficient heat-producing constituents such as silicon and manganese, the addition of oxidic ores does not lead to the desired result. On the contrary, the cooling effect of the added ore causes a considerable increase in the viscosity of the liquid slag, and hence, not only reduces its ability to dephosphorize the iron, but also generally disturbs all of the metallurgical reactions.

The present invention relates to the refining of pig-iron having a low silicon content, by blowing the pig-iron from above with oxygen or oxygen-enriched air so that the blast passes through a slag cover on the pig-iron and penetrates into the molten pig-iron without material agitation of the bath by the impact of the gas stream, and conducting the refining operation in the presence of a single slag of a character suitable for reducing the phosphorous content thereof to less than .05% and preferably less than .02%.

The process of the invention is based on the surprising realization that dephosphorizing can be accomplished by means of a single thinly-liquid lime-silcate slag of a specific degree of basicity which does not require a surplus amount of heat to maintain its fluidity. In accordance with the invention, a suitable slag is formed by the addition of a silicon compound and limestone to the bath. Limestone is usually added to the bath before blowing of the bath is begun and also periodically during blowing of the bath. Silicon compounds can be added before or after the blowing begins and also periodically during blowing to maintain the required proportion of silica in the slag to maintain the slag liquid at the temperatures prevailing in the converter. While the melting point of pure CaO is 2600° C. and of pure SiO_2 about 1800° C., the mixture of these substances with other slag-forming constituents produces a melt which is thinly liquid at 1400–1500° C.

The best results with regard to reactivity are obtained when the slag has a SiO_2 content of about 10–18%, both the degree of basicity necessary for slagging of the phosphorous and sufficient fluidity of the slag being then assured. Inasmuch as in the refining of pig-iron containing not more than 0.5% Si in the charge, oxidation produces not more than 8% SiO_2 content in the slag (e.g., with addition of 5% lime), the invention provides for addition to the bath of silicon compounds in such quantity as to attain a silica content of 10–18% in the slag. Such silicon carriers can be, for instance quartz, sand, ores containing SiO_2, and so forth. It is, however, also possible to add silicon to the bath in the form of ferrosilicon, in which case the latter turns immediately to FeO and SiO_2 with liberation of heat which causes a rise in the temperature of the bath. It is consequently possible by adding ferrosilicon to treat pig-iron charges for the production of low-phosphorous steel which have hitherto been altogether useless for refining by a blowing process due to their insufficiently high chemical heat content.

The following specific example is presented for the purpose of illustrating the blowing process of the invention. It must, however, be understood, that this invention is not to be limited to conditions, operations or manipulations used in the example.

Example

14,000 kg. of molten pig-iron with a content of 4.20% C, 0.34% Si, 2.10% Mn, 0.135% P and 0.038% S was charged into a converter of pear-like shape and 2300 kg. of scrap consisting of 0.20% C, 0.50% Mn, 0.050% P, 0.04% S, traces of Si and the rest of iron was added to the molten mass. In the upper part of the converter, centrally above the surface of the bath, there was provided a nozzle connected with an oxygen-source with a purity of at least 98% O_2. The distance between the nozzle and

the metal-surface was about 50 cm., the pressure in the oxygen line 8 atm. Using these conditions, the gas blast delivered from the nozzle contacts the surface of the molten iron under a pressure of 0.5 atm., forming thereon a highly-heated reaction center at about the center of the surface of the bath, the size of which is about 1/25 of the whole surface area of the bath.

After the introduction of 750 kg. CaO necessary for slagging into the bath, oxygen was blown against the surface of the molten metal causing by the development of CO a uniform circulation of the bath. After two minutes of blowing, 80 kg. SiO_2 in the form of sand was added to the charge, whereby a thinly liquid reactive slag capable of removing the phosphorous from the bath was formed. From the 11th to the 14th minute an amount of 200 kg. $CaCO_3$ in portions was added to the bath.

Then, after a few more minutes, the development of gaseous reaction products decreased, being a signal, that the carbon contained in the bath had burned away. Blowing was then terminated.

Analysis of steel in the blown charge showed the steel had a composition of 0.05% C, 0.035% Mn, 0.020% P, 0.022% S, traces of Si and rest of iron. It is seen therefore, that the phosphorous contained originally in the charge had been removed by the slag during the period of decarburization.

Inasmuch as only a single slag was used, the losses in time, heat, and steel which result from multiple slagging operations were avoided and greater efficiency and economy are achieved.

Similar results are obtained when SiO_2 is added to the converter with the initial charge of CaO prior to the beginning of the blow. Additional SiO_2 can be introduced at intervals during the blow, also, so that between about 10 and 18% of SiO_2 is present in the slag, thereby keeping it liquid, even at the low temperatures encountered with impure irons having low concentrations of heat producing impurities.

The compositions of the slag and of the metal refined were tested in many runs in which the amounts and the nature of the silicon-carriers were varied. A relationship was found between the content of SiO_2 and of Fe in the slag and of the content of the phosphorous in the metal. The following table shows the pertinent data.

Composition of the slag		P content in the metal, percent
Fe-content, percent	SiO_2-content, percent	
17	14	0.015
16	14	0.020
15.8	15	0.022
15	15	0.025
14	16	0.035
13	17	0.045

It is seen from this data that a slag containing 14–17% SiO_2 and 13–17% Fe is capable of a far-reaching dephosphorizing. This result is quite suprising, because if the dephosphorizing is effected by means of a calco-ferritic slag, as known, the content of Fe is always higher than 18%.

Using ferrosilicon instead of SiO_2 as silicon-carrier the blowing process runs off in a quite similar manner. Inasmuch however, as ferrosilicon is a exothermic reactant, the slag is more rapidly liquefied.

Further the process according to the invention can also be modified in the manner that known fluxing media, reducing the melting point, such as fluorspar or bauxite, are used as slagging agents, by which the range of application of the invention is correspondingly extended.

I claim:

1. In a process for refining molten impure pig iron containing less than 0.50% silicon in the presence of a single basic slag in a vessel having a refractory lining which comprises forming a basic calco-ferritic-silica slag on a bath of molten impure pig iron, blowing said bath with a stream of a gas selected from the group consisting of oxygen and oxygen-enriched air directed substantially vertically downwardly through the slag layer onto and below the surface of a bath of said pig iron at substantially the central portion thereof, to an extent to avoid material agitation of the bath by the gas stream, the contact of the gas with the bath resulting in reaction of the oxygen with a portion of the iron and with the oxidizable impurities of the bath in a localized reaction zone spaced a substantial distance from the refractory lining, the improvement for reducing the phosphorous content of said iron to an amount less than 0.05 percent comprising the step of retaining said slag on said bath during substantially the entire duration of blowing said gas and maintaining a silica content of from about 10 to 18 percent in the slag during substantially the entire blowing time.

2. A process according to claim 1 wherein the phosphorous content of said iron is reduced to an amount less than 0.02 percent.

3. A process according to claim 1 wherein the iron content of said slag is less than 18 percent.

4. In a process for refining molten impure pig iron containing less than 0.50% silicon in the presence of a single basic slag in a vessel having a refractory lining which comprises forming a basic calco-ferritic-silica slag on a bath of molten impure pig iron, blowing said bath with a stream of a gas selected from the group consisting of oxygen and oxygen-enriched air directed substantially vertically downwardly through the slag layer onto and below the surface of a bath of said pig iron at substantially the central portion thereof, to an extent to avoid material agitation of the bath by the gas stream, the contact of the gas with the bath resulting in reaction of the oxygen with a portion of the iron and with the oxidizable impurities of the bath in a localized reaction zone spaced a substantial distance from the refractory lining, the improvement for reducing the phosphorous content of said iron to an amount less than 0.05 percent comprising retaining said calco-ferritic-silica slag on said bath during substantially the entire time of blowing with said gas maintaining the silica content of the slag between about 10% and 18% during the entire time of said discharge of gas, and the iron content of said slag below 18 percent.

5. A process according to claim 4 wherein the phosphorous content of said iron is reduced to an amount less than 0.02 percent.

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