METHOD OF REFINING CRUDE IRON

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This invention relates to a method of refining crude iron containing more than 0.5% phosphorus by blowing pure oxygen or an oxygen-enriched gas onto the surface of molten crude iron and producing a limited reaction area of high temperature at the surface of the bath.

Processes of this kind, which have been developed in recent times, have been described as so-called surface blowing converter processes. They aim at utilizing the economical and technological advantages of converter processes without involving the disadvantages thereof.

The blowing of pure or oxygen gases with a high content of oxygen onto the surface of the bath of molten crude iron produces a high-grade steel which is free of nitrogen and which has properties comparable or even superior to those of steels produced in open-heARTHs. A typical surface blowing converter process is the so-called "LD Process" developed by the assignor of this invention and described more fully in "Stahl und Eisen," 1952, pp. 992 et seq., and in the book "Drei Jahre LD-Stahl" published by the assignor of this invention in 1956.

In the surface blowing converter processes the dephosphorization of a phosphorus-containing crude iron is effected with the aid of a lime-ferrite slag, which is capable of absorbing phosphorus. Sufficient amounts of iron oxide and lime are required for producing a reactive lime-ferrite slag, as well as a relatively high temperature—which should be attained at the beginning of the blowing process, if possible—in order to achieve a slag of high fluidity, which is essential for the absorption of phosphorus by the slag at a sufficiently high rate.

Two known methods have previously been available for the production of a lime-ferrite slag: After the necessary amount of lime or at least the major portion of said amount has been charged at the beginning of the process the necessary amount of iron oxides may be continually added, e.g., in one-minute intervals, during the refining process or the process may be carried out without adding iron oxide, the amount of iron oxide required for forming the lime-ferrite slag being produced from the crude iron charge itself by oxidizing a portion of the iron in the charge; this can be achieved by a slight blowing of the oxygen under lower pressure or by increasing the reaction area owing to a greater distance of the blowing nozzle from the surface of the bath or by other variations of the blowing technique. Whereas this second method is relatively expensive and causes appreciable losses of iron it is sometimes preferred to the first method involving an addition of iron oxide because the second method has the advantage that the reactive slag is formed more quickly and in a more highly fluid state because the oxidation of iron in the bath is an exothermic process. Where it is desired to make steel containing less than 0.030% P from crude iron having more than 0.5% P one or several deslagging operations are required in both of the known methods.

A consideration of the metallurgical reactions taking place during the refining of crude iron with oxygen under an iron-oxide containing slag reveals the following relations:

From the theoretical relations in the system iron-carbon-oxygen it is known that an equilibrium relation exists between the carbon content and the oxygen content of the melt. This relation may be represented in a simplified manner by curves coordinated to different temperatures. Such a representation is given in Fig. 1, which shows three curves indicating the carbon content of the bath in percent by weight as a function of the oxygen content of the bath in percent by weight at temperatures of 1500 deg. C., 1600 deg. C., and 1650 deg. C., respectively, in the state of equilibrium.

It is also known that the equilibrium relation which is characteristic for the decarburization of crude iron is influenced by the composition of the slag inasmuch as the FeO content of the slag tends also to establish an equilibrium with the oxygen content of the slag. The higher the FeO content of the slag the higher is the oxygen content of the bath where other conditions are equal. In other words, in an equilibrium condition a steel having a given carbon content and refined under a slag rich in iron oxide will contain more oxygen than a steel having the same carbon content and refined under a slag having a lower content of iron oxide.

Whereas this equilibrium can never be actually achieved in commercial refining operations, of course, because it would be established only after an infinitely long time, these relations involve an important requirement: At the end of the refining process, when the desired carbon content has been reached, the oxygen content should not be substantially above the equilibrium curve because a higher oxygen content will impart brittle properties to the steel produced and will preclude its use for special applications.

In the LD process this requirement is fulfilled in an almost ideal manner. The steels produced by the LD process are known to have a minimum oxygen content of 0.020 to 0.040% in conjunction with a carbon content of 0.20 to 0.05%. A comparison of the carbon-oxygen relation achieved during the LD process with the equilibrium curve, e.g., for the temperature of 1600 deg. C., shows that the values obtained in practice do not greatly differ from the curve. Fig. 2 shows the results achieved in practical experiments with LD charges in the form of the solid line A in the carbon-oxygen chart, the line G1 in Fig. 2 is the equilibrium curve for 1600 deg. C.

If the problem involved in the dephosphorization is reconsidered with all the general metallurgical aspects set forth hereinbefore being taken into account, it must be stated first that the known methods of dephosphorization mentioned hereinbefore do not fulfill the important requirement that the carbon and oxygen values at the end of the refining process should remain close to the equilibrium curve. It is true, however, that in this connection the metallurgist faces a dilemma which cannot be readily solved because on the one hand there must be an ample amount of iron oxide in the slag to ensure a reactive lime-ferrite slag for an effective dephosphorization, on the other hand the steel should have only a minimum oxygen content. This problem has not been solved before. Entering the carbon-oxygen values obtained by the known dephosphorizing method mentioned in the first place hereinbefore, in which iron oxide is added in one-minute intervals, into the chart of Fig. 2 will give a curve which corresponds to the dash-and-dot line C. The carbon-oxygen values obtained when iron oxide is formed by an oxidation of the charge, according to the second method, correspond also approximately to the dash-and-dot line of the chart, which is also designated with D. In both cases it is apparent that the oxygen contents achievable when refining according to line C, D are considerably
above or spaced from the equilibrium curve G1 and no steel can be produced which contains less than 0.050% O, which is inadmissibly high for high-grade steels, whereas the object of the invention is to make a steel containing less than 0.030% phosphorus and less than 0.050% oxygen from crude iron containing more than 0.5% phosphorus. According to the invention this object is achieved by adding an excessive amount of iron oxide as a single batch to the bath when a carbon content between 2.0% and 0.1% has been reached, which batch forms together with the other constituents of the slag a reactive slag, which absorbs the phosphorus and is then skimmed off, whereafter the process is continued in the same manner as an usual LD process and completed in known manner. If the carbon-oxygen values obtained with the process according to the invention are entered in a similar manner as those obtained with the known methods into the chart of Fig. 2 the solid line B will be obtained, which coincides with the line A of the LD process. Thus, the process according to the invention gives at the end of the refining process the same favorable oxygen values as the known LD process and the steel thus produced is suitable for the highest requirements.

The results achieved according to the invention may be explained with the fact that the establishment of the equilibrium between the FeO content of the slag and the oxygen content of the bath proceeds more slowly than the reaction between the CaO and FeO in the slag and the phosphorus content of the bath, by which reaction the phosphorus is extracted from the bath. Assuming that phosphorus is present as phosphide, the decisive reaction is the following.

\[ Fe_3P_2 + 5FeO = 3P_2O_5 + 8Fe \]
\[ P_2O_5 + CaO = Ca_3(PO_4)_2 \]

The reaction is dependent on temperature; the equilibrium will be displaced toward the right if a relatively cold slag covers a hot bath, and toward the left if a hot slag covers a relatively colder bath. It has been found that a very short time of contact is sufficient for a considerable dephosphorization and for a formation of considerable amounts of Ca₃(PO₄)₂. During this short time of contact the equilibrium of distribution between the FeO in the slag and the bath will not be established and the bath will not absorb oxygen. Any surplus FeO in the slag will react with the carbon of the bath and the values approach gradually the equilibrium curve.

The characteristic features of the process according to the invention compared to the known methods are apparent from Fig. 3, which shows the relations between the carbon content of the bath and the FeO content of the slag. Line G1 corresponds to the equilibrium curve; line A represents the known process of an LD process, using a slag of 6 to 8% by weight FeO and continuing the process until a carbon content of 0.3 to 0.2% C has been reached. Line C shows the known method of adding iron oxide in one-minute intervals and line D represents the known method of surface-blowing oxygen at low pressure to cause a formation of iron oxide. In both of the known methods the iron oxide content is above 20% FeO throughout the refining process; this involves high oxygen contents of the charges, as is apparent from the lines C and D of Fig. 3 corresponding to line C, D of Fig. 2.

As contrasted therewith the line B in Fig. 3 illustrates an advantageous process according to the invention. In this example the LD process is exactly followed until a carbon content of 1.1% has been reached, whereafter a single batch of iron oxide is added to the bath. As is shown by curve B of Fig. 3 there is a sudden strong increase in the iron oxide content of the slag, e.g., to values above 25% or even above 30%; having a high content of iron oxide this slag reacts suddenly with the phosphorus in the bath. This is followed by dephosphorizing, whereafter the process is continued according to the known LD refining curve (line A). During the short time of contact between the slag having a high content of iron oxide and the bath the equilibrium of distribution between the FeO content of the slag and the oxygen content of the bath cannot be established. Line B of Fig. 2 shows that the oxygen content of the bath does not or does not substantially increase during the dephosphorizing from the oxygen phase. However, the oxygen values are not available for this phase owing to the violent reaction, line B has been shown only as a broken line in that region in Fig. 2. In any case the oxygen values after dephosphorization and continuing of the blowing are not higher than before dephosphorizing.

The addition of a single batch of iron oxide according to the invention should preferably be effected when a carbon content between 1.5% and 1.0% has been reached, as has been mentioned hereinbefore. Whereas the addition may also be made at a somewhat lower carbon content the time available for finishing the charge is then relatively short and there may be a shortage of time if the iron oxide is added when the carbon content is less than 0.8%.

The amount of iron oxide added should be sufficient to effect a strong increase in the FeO content of the slag, at least of 30% and preferably of 200%. After approximately half a minute the iron oxide has completely dissolved and the dephosphorizing reaction begins; the high-iron-oxide slag may be skimmed after about one minute.

Additional CaO and, if desired, some FeO may be added after dephosphorizing. However, the slag added after dephosphorizing should not contain more iron oxide than an ordinary LD charge, i.e. less than approximately 15% FeO.

As has been mentioned hereinbefore the dephosphorizing reaction is dependent on temperature and its progress is optimum if the slag is colder than the bath. From this aspect too the addition of a larger amount of iron oxide as a single batch, as taught by the invention, is favorable because it has a cooling effect. For this reason the dephosphorization takes place within a very short time in the process according to the invention.

The slag skimmed off after the addition of iron oxide may contain 15% and more P₂O₅. It is very suitable as a fertilizer.

The process according to the invention will be explained more fully by the following examples:

**Example 1**

The following charge is introduced into a tiltable converter provided with a refractory lining: 30,210 kg. molten crude iron containing 3.96% C, 0.72% Si, 1.74% Mn, 1.14% P, 0.042% S, 4,330 kg. scrap, 2,700 kg. CaO, 150 kg. scarfing scale and 400 kg. CaFe₂ as are slagforming agents. Then an oxygen blowing tube having a nozzle 35 mm. in diameter is adjusted at a distance of 80 cm. above the bath surface and oxygen is blown vertically onto the surface at a pressure of 10 kg./sq. cm. gauge.

After a blowing time of 11.50 minutes the nozzle is removed and 200 kg. of scarifying scale and 200 kg. ore (containing 76% iron) are added. A violent reaction begins in the time between 11.45 minutes and 12.25 minutes after the beginning of the blowing time. The converter is slowly lowered; the slag is skimmed off after samples have been taken. The steel sample has the following analysis: 1.5% C, 0.91% Mn, 0.22% P, 0.014 S. The temperature measured with a Pt/Pt-Rh immersion pyrometer is 1565 deg. C.

The slag has the following analysis: 11% Fe, 5.85% Mn, 12.26% SiO₂, 5.38% Al₂O₃, 9% CaO, 4.79% MgO, 4.99% P. After raising the converter, 1800 kg. CaO, 100 kg. scarifying scale, 300 kg. bauxite, 300 kg. manganese ore and 350 kg. quartz sand are added 21.80 minutes after
the beginning of the blowing time. 22.80 minutes after
the beginning of the blowing time the oxygen nozzle
is again adjusted to a distance of 80 cm. from the bath
surface and the blowing of oxygen is continued at a
pressure of 8 kg/sq. cm. gauge. 30 minutes after the
beginning of the heat the nozzle is removed, the con-
verter is lowered and samples of steel and slag are
again taken. The sample has the following analysis:
0.07% C, 0.25% Mn, 0.020% P, 0.01% S. The tem-
perature is 1615 deg. C. The slag sample has the follow-
ing analysis: 15.95% Fe, 5.92% Mn, 8.34% SiO₂, 4.19% Al₂O₃, 51% CaO,
4.19% MgO, 1.73% P. The steel is poured into the ladle and 70 kg. ferro-
manganese (77% Mn) are added. The final analysis of the
steel is: 0.07% C, 0.0% Si, 0.31% Mn, 0.015%
P, 0.01% S.

Example 2

The blowing charge is introduced into a converter
similar to that of Example 1: 29,300 kg. molten crude
iron containing 3.80% C, 0.72% Si, 1.7% Mn, 2.03% P,
0.5% S; 3,500 kg. scrap.
2000 kg. CaO, 250 kg. bauxite, 150 kg. CaF₂ and 460
kg. molten LD slag from a previous charge are added
to the charge. The LD slag has the following composi-
tion: 15.4% Fe, 7.30% Mn, 10.74% SiO₂, 1.24%
Al₂O₃, 51.8% CaO, 4.22% MgO, 0.63% P.

The blowing tube equipped with a 35-mm. nozzle is
adjusted to a distance of 1 meter from the bath surface
and oxygen under a pressure of 10 kg/sq. cm. gauge
is blown vertically on the surface for a period of 11.20
minutes. 700 kg. CaCO₃ are added in increments in the
fifth to tenth blowing minutes. After a blowing time of
11.20 minutes a bath of 500 kg. scarping scale is added
to the bath. The dephosphorizing reaction begins, which
continues until the end of the twelfth minute. The
slag is skimmed off after samples of steel and slag have
been taken. In this stage the steel has the following analysis:
0.87% C, 0.34% Mn, 0.34% P, 0.032% S. The tempera-
ture measured with the Pt/Pt-Rh immersion
pyrometer is 1505 deg. C.
The slag has the following composition: 15.53% Fe,
7.1% Mn, 16% SiO₂, 1.06% Al₂O₃, 40% CaO, 6.14%
MgO, 7.85% P.
10 minutes are required for skimming off the slag
while the converter is tilted so that 22 minutes have
delayed after the beginning of the blowing time.
After the converter has been raised, 1053 kg. CaO,
100 kg. scarping scale, 100 kg. bauxite, 300 kg. manganese
ore and 250 kg. quartz sand are added. After the 23rd
minute the oxygen blowing tube is again adjusted to a
distance of 1 meter above the bath surface and the
blowing is continued for 7.7 minutes so that 30.7
minutes have elapsed after the beginning of the heat.
Then the nozzle is removed, the converter is lowered and
samples of steel and slag are taken.
The steel sample has the following analysis: 0.03% C,
0.27% Mn, 0.033% P, 0.024% S. The temperature is
1605 deg. C.
The slag sample has the following analysis: 17.30%
Fe, 5.22% Mn, 7.76% SiO₂, 4.25% Al₂O₃, 44.8% CaO,
4% MgO, 3.56% P.
The steel is carburized while being poured into the
ladle and 50 kg. ferromanganese are added. The final
analysis is: 0.11% C, 0.0% Si, 0.43% Mn, 0.02% P,
0.015% S.

What I claim is:

1. A method of refining molten crude iron containing
more than 0.5% phosphorus in a refractory-lined con-
verter, which comprises blowing oxygen onto the surface
of the molten crude iron to produce a reaction zone in
which the oxygen reacts with the carbon and other impuri-
ties accompanying the in the presence of a basic slag,
adding an iron oxide carrier to the bath when a
carbon content between 2.0% and 0.8% in the molten
charge has been reached to increase the iron oxide con-
tent of the slag at least 50% and form thereby a reactive
slag and allowing said slag to react with the bath for a
period not substantially in excess of one minute to ex-
trace at least the major portion of the phosphorus, skim-
ming off the slag and continuing the blowing until a
steel having the desired content of carbon and a content
of less than 0.030% phosphorus is produced.

2. A method of refining molten crude iron containing
carbon and other oxidizable impurities and more than
0.5% phosphorus in a refractory-lined converter which
comprises blowing oxygen against the surface of the
molten crude iron to produce a reaction zone in which
the oxygen reacts with the carbon and other impurities
accompanying the iron in the presence of a basic slag
containing iron oxide in an amount insufficient to extract
the phosphorus from the bath, adding a batch of an iron
oxide carrier to the bath when a carbon content between
2.0% and 0.8% in the molten charge has been reached in
an amount to increase the iron oxide content of the
slag by between about 50% and 200% to form thereby
with the other constituents of the slag a highly reactive
slag, allowing said slag to react with the bath for a period
not substantially in excess of one minute, skimming off
the reacted slag containing the major portion of the phos-
phorus of the bath and continuing the blowing until a
steel having the desired content of carbon and a content
of less than 0.030% phosphorus is produced.

3. A method as set forth in claim 2, in which said ex-
cessive amount of an iron oxide carrier is added, when a
carbon content between 1.5 and 0.0% has been reached.

4. A method of refining molten crude iron containing
more than 0.5% phosphorus in a refractory-lined con-
verter, which comprises blowing oxygen against the sur-
face of the molten crude iron in a sufficient amount to
produce a high temperature reaction zone in which a
rapid reaction between the oxygen and the carbon and
other impurities accompanying the iron takes place in
the presence of a basic slag containing burnt lime and
less than 15% by weight iron oxide, adding an iron oxide
carrier to the bath as a single batch to form a reactive
basic slag having an iron content of more than 25% by
weight, when a carbon content between 2.0% and 0.8% in
the molten charge has been reached, allowing said
slag enriched with iron oxide to react with the bath for a
period not substantially in excess of one minute, skimming
off the reacted slag containing at least the major
portion of the phosphorus contained in the crude iron
and continuing the blowing under a basic slag having an
iron oxide content of less than 15% by weight, when a
steel having the desired final content of carbon and a
content of less than 0.030% phosphorus is produced.

5. A method as set forth in claim 4, in which the blow-
ing after deslagging is continued under conditions caus-
ing a combustion of the carbon still contained in the
bath at a lower rate than before the batch-wise addition
of iron oxide.

6. A method as set forth in claim 5, in which the blow-
ing after deslagging is continued at a lower pressure of
oxygen than before the batch-wise addition of iron oxide.

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