A METHOD OF REFINING LOW-PHOSPHORUS PIG-IRON IN STEEL

The following statement is a full description of this invention, including the best method of performing it known to us:

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This invention relates to a method of refining low-phosphorus crude iron melts in a converter, in which oxygen is blown into the melt through the inner nozzle of at least one pair of coaxially arranged nozzles which project through the refractory lining of the converter below the surface of the melt, a liquid or gaseous protective medium being blown through the outer nozzle so that the protective medium jackets the oxygen jet as it enters the melt. Low-phosphorus crude iron melts are to be understood as iron melts having a phosphorus content of from 0.02 to 0.5%, a manganese content from 0.1 to 3%, and a silicon content from 0.1 to 2%.

The refining of crude iron melts using pure oxygen introduced below the melt surface, preferably through the bottom of the converter, leads to phenomena when refining low-phosphorus crude irons which are not obtained with the oxygen top blowing process. With phosphorus-rich crude irons, for which the bottom blowing process was originally developed, it is a particular advantage that the behaviour of the melts during blowing is appreciably better than in the known Thomas process and the oxygen top blowing process. It is therefore all the more surprising that with low-phosphorus crude irons, even those with a low silicon content which in a phosphorus-rich crude iron ensures a splash-free refining, pronounced splashing occurs even after a short period of refining. Until now, it was only possible to reduce the splashing by reducing considerably the quantity of oxygen blown in per unit time, generally to less than one half of the usual quantity, and this substantially reduces the yield. This phenomenon is so pronounced with low-phosphorus pig iron, that the efficient refining of low-phosphorus pig iron using
pure oxygen blown through the bottom of the converter is extraordinarily difficult.

It has already been proposed, for the purpose of improving the behaviour of the melt during blowing in a bottom-blown converter operating with pure oxygen, that lime should be introduced in finely divided form onto the melt. This does indeed lead to an improvement in blowing behaviour, but a splash-free refining with short refining times cannot be achieved by this method.

It has also been proposed that phosphorus-rich pig iron should be refined in a bottom-blown converter with finely divided lime being introduced into and carried by the oxygen stream, in order to advance the dephosphorisation, as has already been achieved in an oxygen top blowing process of refining phosphorus-rich pig iron. The improvement of melt behaviour during blowing is not however the primary objective behind this proposal since with phosphorus-rich crude irons a relatively quiet blowing behaviour is achieved without the addition of lime dust.

It has now been found that in the refining of low-phosphorus crude irons by a method of the kind described, the addition to the melt of powdered or finely granulated lime with the oxygen is surprisingly effective, resulting in a completely quiet and splash-free refining together with short refining times.
According to the invention therefore, there is provided a method of refining a low-phosphorus crude iron melt in a converter having a plurality of nozzles which project through the refractory lining of the converter below the surface of the melt, each nozzle consisting of a pair of co-axially arranged pipes, whereby finely divided lime is blown with an oxygen jet into the melt through the inner of said pair of pipes and a liquid or gaseous hydrocarbon or alcohol protective medium is blown through the outer pipe so that the protective medium jackets the lime carrying oxygen jet as it enters the melt, the amount of protective medium being blown into the melt being up to 10% by volume of the oxygen blown into the melt.

The improvement in the refining
process provided by the invention is so substantial that the refining time can be reduced to less than one half of the time which can be achieved without the addition of lime, appreciable splashing also occurring in this longer period while not even slight splashing occurs in the improved process. The improvement is particularly pronounced if the lime is not introduced uniformly throughout the whole refining period, but is added at a variable rate to the oxygen so that, for example, the major portion of the total lime blown into the melt is added during a first part of the total blowing period, and then the smaller balance of lime is blown in during a second period. This form of operation is therefore particularly preferred.

Preferably the measures in accordance with the invention which lead to an appreciable improvement in melt behaviour during blowing are combined with other measures, which produce particular metallurgical advantages or lead to an especially economic process. For example, it has been demonstrated that the durability of the refractory lining of converters is considerably increased, the desulphurisation substantially improved and the refining carried out completely free from splashing if during the silicon burn-up stage of the refining a quantity of lime is blown in which amounts to two to four times by weight the quantity of silicon removed by the refining. The loading of the jet oxygen with the lime dust under these circumstances is between 2.3 and 4.6 Kg/Nm$^3$ oxygen. For an optimum desulphurisation without adversely influencing the blowing behaviour, it is advantageous in this case to blow in
quickly the whole quantity of lime required for silicon removal. Thus, instead of a uniform charging of the oxygen jet during desiliconisation with a mean lime dust quantity of, for example, 2.5 Kg/Nm³, it is more advantageous to add a lime dust quantity of 5 Kg/Nm³ oxygen during the first half of the desiliconisation stage. For this method of operation, it is necessary to design the lime feed apparatus to be able to cope with an appreciably higher output rate, than would be necessary for uniform supply. Depending upon the silicon content of the melt, from 30 to 60% of the finely divided lime blown into the melt is preferably blown during the silicon burn-up stage.

The same effect upon the blowing behaviour is obtained if a portion of finely divided lime is blown into the melt together with an inert gas, e.g. nitrogen, or even an oxygen-nitrogen mixture, before the refining with the oxygen jet. With this method of operation, effective desulphurisation of the pig iron melt is obtained at the same time. In this case, approximately 20% of the total lime blown into the melt is generally blown in during a period which is about 10% of the refining period.

Although nitrogen will normally be used as the inert gas for the desulphurisation, this is preferably replaced by another inert gas, e.g. argon, if a steel having a low nitrogen content is to be made. It has incidently proved advantageous that, while the inert gas charged with lime powder is being blown through the inner nozzle, the protective medium should also be blown through the outer nozzle. This promotes the desulphurisation of the melt.

If a high charge of lime is blown in during a first part
of the refining process, the refining may be continued with only a low lime charge, amounting to up to 10% of that added during the first phase, or even with no lime added at all. If however, with this method of operation, some splashing occurs, it can be subdued completely within some 10 to 20 seconds by the addition, for a short period of time, of lime dust at a high rate approximately equal to that at the commencement of the refining process. In a similar operation, the refining period has first and second phases and the major part of the slag formed in the first refining phase is separated from the melt before the second phase, the oxygen jet in the second phase carrying into the melt up to 20% of the amount of finely divided lime added in the first phase.

In order to produce an optimum influence upon the blowing behaviour with a minimum quantity of lime, intermittent addition of the lime is especially effective, each charge exceeding 2 Kg of lime pore Nm$^3$ of oxygen blowing it. For example, in each minute, a lime charge of about 5 Kg/Nm$^3$ of oxygen is added in a period of approximately 10 seconds.

It is sometimes also necessary, for metallurgical reasons, to operate with a very high lime load for a brief period of about 1 to 3 minutes within a total refining time of about 10 minutes, to achieve effective dephosphorisation almost independently of the magnitude of the carbon content of the melt. The duration of this period of high lime charge is determined by the initial phosphorus content of the crude iron and the desired final phosphorus content. For an initial phosphorus content in the crude iron of 0.25%, it is satisfactory, for example, to refine the melt with an oxygen feed of 3 Nm$^3$/minute per metric ton of steel and with a lime
charge of 4.5 Kg lime/Nm$^3$ oxygen for a period of 2 minutes, or with a lime charge of 3 Kg lime/Nm$^3$ of oxygen for 3.5 minutes. With a higher lime charge, a better dephosphorisation is achieved. It is also found that the pressure at which the oxygen jet is blown exerts an influence upon the metallurgical reactions. The most favourable results are achieved with an oxygen pressure of at least 10 atm. In general, this method of operation is important for steels which are manufactured as so-called tapping charges, in which the carbon content does not have to be refined down to a low level.

For metals which do have to be refined to a low carbon content, and which are therefore not produced as so-called tapping charges, a relatively small quantity of lime is required for the removal of the phosphorus. In these cases it is sufficient to add a total lime quantity which results in a CaO-SiO$_2$- ratio of about 2.5:1 in the slag, in order to arrive at low final phosphorus contents in melt of approximately 0.01%. In this case it may be favourable to introduce the remaining quantity of lime in a high charge, e.g. at least 3 Kg/Nm$^3$ of oxygen, near the end of the blowing period, that is during about the last 20% or even 10% of the total refining period. It has surprisingly been found that with this measure, the slag pumice which sometimes occurs at the end of the refining process and which in general is difficult to deal with, is completely avoided.

The method in accordance with the invention makes it possible, using a converter with a relatively small specific volume of about 0.5 to 0.9 m$^3$/metric ton of steel, to refine low phosphorus pig iron in an extremely short overall period of about 10 minutes, without any splashing. All previous methods resulted in only limited improvements, whereas the
The present invention makes it possible to achieve a previously unobtainable quiet blowing behaviour in economically extremely advantageous conditions. It has also been found that the rapid refining which is achieved by the splash-free method of operation, combined with the low specific converter volume, leads to intense circulation in the melt which makes possible a rapid dissolving of scrap metal introduced to the melt.

When carrying out the method according to the invention it was observed that coarse dust with a grain size of approximately 0.1 to 1 mm was discharged from the converter. The composition of this coarse dust was approximately 40% lime, 30 to 40% iron and iron oxide, 10 to 20% silica, and a residue of impurities such as MnO. Normal dust extraction plants can usually deal with this coarse dust without difficulty, but it may however be advantageous to take measures to prevent this dust arising. The following measure has proved particularly effective: as a cooling agent, iron ore is added instead of a portion of the scrap metal charged to the melt. The measure is most effective when the addition of ore commences after about 10% of the total refining time has elapsed and continues for about 50% of the total blowing time. The ore may be added either in batches or continuously, and it is sufficient for about one third of the normal scrap metal charge to be replaced by ore. It has been found that an ore having a fairly high silicate content of about 5%, which is normally not suitable for use in a converter, is particularly favourable for this purpose. The ore may be added in the form of pellets or in fine granular form; it may also be added in the form of dust, optionally mixed with the lime dust which is blown into the melt.
The use of ore instead of scrap favours a higher charging of the converter with hot metal per ton of steel produced. It has been found that the same effect can be achieved without the addition of the ore, by blowing into the melt with the lime, fluxing agents such as flourite, bauxite or felspar. If these fluxing agents are added in lump form, their effect is only slight. When, however, they are added as a powder the effect is marked. For example, it was possible to suppress almost completely the formation of coarse dust by adding 20% bauxite to the lime blown in at the commencement of the refining period.

The action of the method in accordance with the invention is improved by using nozzles which direct the gas jets at an angle of about 10° to the longitudinal axis of the converter and in a direction which causes rotation of the melt.

The method in accordance with the invention not only makes it possible to refine in an economic manner low-phosphorus pig iron with compositions for which the oxygen top blowing method is normally used, but also affords the advantage that within wide limits there is no dependence of the metallurgical behaviour of the melt upon the composition of the pig iron. The method therefore makes it possible for the production of the pig iron for refinement to be carried out largely in accordance with economic considerations without substantial limitations with regard to quality. It has also been found that, in following the invention, FeO-contents in the slag of about 15% can be achieved, leading to an appreciable increase in the yield compared with the known oxygen top blowing process, and ensuring easy handling due to the fluid consistency.
Particularly smooth refining with very little splashing is obtained when the following conditions are used. The oxygen pressure in the nozzles is between 3 and 20 atmospheres. The oxygen carries 1 to 2 Kg of powdered lime/Nm\(^3\) of oxygen on average throughout the entire blowing time. The inner nozzle or nozzles used has or have an internal diameter which is about 1/25 of the depth of the melt in the converter. The oxygen containing the powdered lime is blown in at a rate which is about 30% lower than that used for oxygen containing no lime. For example, if pure oxygen is blown in at a pressure of 8 atm, this corresponds to 300 Nm\(^3\) oxygen per hour and per cm\(^2\) of nozzle cross-section (=300 Nm\(^3\)/hour x cm\(^2\)). For a converter with a capacity of 30 metric tons and a melt depth of 0.6 to 0.7 m, 50 Nm\(^3\) of oxygen were consumed per metric ton of steel. The maximum blowing period necessary was 12 minutes. The oxygen flow rate was therefore 7,500 Nm\(^3\) per hour. On this basis, the necessary total cross-sectional area of the nozzles can be calculated as about 7,500/200 = 38 cm\(^2\). For a melt bath depth of 0.6 to 0.7 m, the most favourable nozzle diameter is 2.5 cm, and therefore the number of nozzles required is 38/(1.25\(^2\) x 3.14), which equals 8. In a further example, for a converter having a capacity of 200 metric tons, the oxygen consumption is about 10,000 Nm\(^3\) per charge. The oxygen pressure is about 10 atm. The total blowing time, in general between 8 and 12 minutes, is about 10 minutes for the charge stated. The oxygen flow is thus about 60,000 Nm\(^3\) per hour. The total nozzle cross-section or oxygen blowing area can thus be calculated as about 60,000 Nm\(^3\)/hour + 250 Nm\(^3\)/(hour x cm\(^2\)) = 240 cm\(^2\). For a bath depth in the range 1 to 1.5 m (e.g. 1.2m) the internal diameter of the
oxygen nozzles will be 48 mm, based on a ratio of internal diameter of oxygen nozzles to bath depth of 1 : 25. A diameter of 48 mm corresponds to a cross-sectional area of about 18 cm². For blowing charges of this order of magnitude, 13 nozzles should therefore be provided, the oxygen feed pipe having an internal diameter of 48 mm.

These calculations give the internal diameter for the oxygen pipe for optimum blowing conditions of the melt. The calculation is based upon the assumption that the nozzles are at an angle of 10° to the longitudinal axis of the converter. Similar blowing behaviour is obtained if the internal diameter for the oxygen pipe or pipes varies from the value calculated above within ±25%.

A lower oxygen pressure makes possible a larger internal diameter for the oxygen pipe. For an oxygen pressure of 3 atm, for example, the internal diameter of the oxygen pipe can be increased by about 30%. On the other hand, an increase of oxygen pressure to about 20 atm requires a reduction in the internal diameter of the oxygen pipe of about 15%.

The suspension of the reaction constituents (e.g. oxygen and finely divided lime) may be fed into the converter through a pot of small diameter located below the converter bottom, the mixture entering the pot through a tangential inlet pipe and leaving the pot through feed pipes each of which leads to a nozzle. The feed pipes may depart radially from the pot, their connections at the pot being spaced sufficiently from the entrance of the inlet pipe. Very uniform distribution of the lime powder can be achieved over a number of feed pipes arranged in this manner. In one example the inlet pipe enters near the head of a conical pot and a number of regularly spaced feed
pipes for the nozzles leave the lower part of the pot. Alternatively, the converter may possess a cylindrical distributor pot arranged below the converter bottom and subdivided into two compartments by a horizontal, gas-permeable partition. The suspension of, for example, oxygen and lime powder is introduced into the upper part of the distributor pot through an inlet line, while pure oxygen is introduced into the lower part of the distributor pot through an oxygen inlet line. At least one nozzle feed pipe departs radially from upper part of the distributor pot above the inlet line, and preferably, the suspension of the reaction constituents (i.e. oxygen and lime powder) is fed to the converter nozzles through a number of distributor pipes which depart radially at regular intervals from the upper part of the distributor pot above the inlet opening to the upper part. The refining gas used in the method in accordance with the invention is pure oxygen, and the protective medium is preferably a pure hydrocarbon or a gaseous or liquid medium consisting essentially of a hydrocarbon such as propane, butane, natural gas, methane, coke oven gas, light fuel oil, kerosene, benzene, alcohol or a dispersion of one or more liquid hydrocarbons in water. Alcohol may also be used as the protective medium.

Hydrocarbons have proved particularly successful as the protective medium surrounding the oxygen jet, and are therefore preferred. Such protective fluids have a cooling effect in the vicinity of the nozzles and therefore protect them and also the ceramic material surrounding them from too-rapid deterioration. Particularly favourable results are obtained, if the protective medium contains hydrocarbons in a quantity up to 10% of the oxygen. This is the average value taken over the total
The lime dust can be blown in, according to requirements, through every inner nozzle of the converter, although the process can be carried out with pure oxygen without any lime, being blown through some of the nozzles, the protective medium still being blown from every outer nozzle.

A particularly effective utilisation of the slag-forming substances, that is principally the lime, is achieved by blowing it with the oxygen through every nozzle, the lime being uniformly distributed among the nozzles. Preferably 90% of the finely divided lime blown into the melt has a particle size below 0.1 mm.

Three examples of the method in accordance with the invention will now be described:—

Example 1

60 tons of crude iron containing 4.2% carbon, 0.9% silicon, 0.8% manganese, 0.25% phosphorous, and 0.050% sulphur, 13 tons of scrap, and 4.5 tons of ore were used to charge a 70-ton converter. A total lime quantity of 4.2 tons was blown through a plurality of nozzles extending into the melt each nozzle consisting of a pair of coaxially arranged pipes. The lime was blown in through the inner pipe of each nozzle. The lime consumption was 60 Kg/ton of raw steel. After the scrap and crude iron had been charged into the converter, 600 Kg of powdered lime together with nitrogen was blown in for about 1 minute and the sulphur content was thereby reduced from 0.050% to 0.012%. Then for two minutes, 250 Nm$^3$/oxygen/minute, together with a total of 1.5 tons of the lime dust, were blown in, followed by 7 minutes of further refining with a mean lime charge of 0.7 Kg/Nm$^3$/oxygen and an oxygen flow of 300 Nm$^3$/minute. Towards the end of refining, 0.6 tons of powdered lime with an oxygen flow of 250 Nm$^3$/minute was introduced during 1 minute.
analysis of the melt at tapping gave 0.02% carbon, 0.15% manganese, 0.008% phosphorus and 0.015% sulphur. It is particularly noticeable that by the method of operation carried out in accordance with the invention, the nitrogen content was appreciably lowered, amounting to 0.0010%. The ore was added after the second, fourth and fifth minutes in equal batches. During the entire refining period, propane was blown as the protective medium through the outer nozzles. It was possible to vary the volume ratio of propane to oxygen with good results between 0.5:100 and 7:100. On average, it was substantially 3:100. The propane pressure was from 4 to 6 atm.

Example 2

Using the same crude iron compositions as in Example 1, a steel containing approximately 0.5% carbon was refined. The raw iron quantity used was 63 tons, the scrap 13 tons. Ore was not added. During the first 2 minutes of blowing, a quantity of 1.2 tons of lime dust was added. After a total of 8 minutes blowing with an oxygen rate of 350 Nm$^3$/minute and an intermittent line charge of 4 Kg/Nm$^3$ oxygen added over a period of 10 seconds in each minute, a remaining 2.3 tons of lime was blown in over 3 minutes. The essential difference compared with Example 1 is that the high residual quantity of lime was added when the carbon content was about 0.8%. An analysis of the finished steel yielded 0.50% carbon, 0.45% manganese, 0.015% phosphorus, 0.017% sulphur. This analysis shows that the method in accordance with the invention makes it possible to protect an appreciable proportion of the manganese from becoming slagged. Natural gas having the following composition was used as the protective medium: about 90% methane, about 8% other constituents having the general formula C$_m$H$_n$, and
The natural gas was blown into the melt in the same manner as in Example 1, about 2% nitrogen. The volume ratio of natural gas to oxygen varied between 2:100 and 18:100 and was preferably 7:100. The natural gas pressure was from 5 to 10 atm.

Example 3

A crude iron of the same composition as in Example 1 was used for a charge consisting of 58 tons of crude iron and 20 tons of scrap. 3 tons of lime was added in the form of usual lump lime, and during the first 2 minutes 1 ton lime dust was blown in together with the oxygen. During the succeeding 7 minutes the refining was carried on with an oxygen flow of 300 Nm$^3$/minute without lime addition. During the last minute, 900 Kg of finely divided lime was added with an oxygen flow of 250 Nm$^3$/minute. The final analysis of the steel produced gave 0.02% carbon, 0.17% manganese, 0.012% phosphorus, 0.014% sulphur and 0.0013% nitrogen. In this example, light fuel oil having a specific gravity of about 0.9 was used as the protective medium. The oil feed varied from 4 to 35 litres per minute, the preferred rate being 20 litres per minute. The oil pressure was from 5 to 10 atm when each nozzle had its own feed line, and from 20 to 25 atm when a distributor apparatus was installed near the nozzles with only a single feed line.
The claims defining the invention are as follows:

1. A method of refining a low-phosphorus crude iron melt in a converter having a plurality of nozzles which project through the refractory lining of the converter below the surface of the melt, each nozzle consisting of a pair of co-axially arranged pipes, whereby finely divided lime is blown with an oxygen jet into the melt through the inner of said pair of pipes and a liquid or gaseous hydrocarbon or alcohol protective medium is blown through the outer pipe so that the protective medium jackets the lime carrying oxygen jet as it enters the melt, the amount of protective medium being blown into the melt being up to 10% by volume of the oxygen blown in to the melt.

2. A method according to Claim 1, in which an inert gas is blown into the melt through the inner pipe of each nozzle before the refining with the oxygen jet, and some finely divided lime is blown into the melt with the inert gas jet.

3. A method according to Claim 1 or Claim 2, in which the rate at which the lime is added to the melt is varied during the refining period.

4. A method according to Claim 3, in which from 30 to 60% by weight of the finely divided lime added to the melt is blown in during the desiliconisation stage of the refining period.

5. A method according to Claim 3 or Claim 4, in which the refining period has first and second phases, in the second of which the oxygen jet carries into the melt from 0 to 10% of the amount of finely divided lime added in
the first phase.

6. A method according to Claim 3 or Claim 4, in which the refining period has first and second phases and the major part of the slag formed in the first refining phase is separated from the melt before the second phase, the oxygen jet in the second phase carrying into the melt up to 20% of the amount of finely divided lime added in the first phase.

7. A method according to any one of Claims 3 to 6, in which at least three Kg. of finely divided lime/Nm$^3$ of oxygen is blown into the melt during the last 10 to 20% of the refining period.

8. A method according to any one of Claims 1 to 7, in which the finely divided lime is blown into the melt intermittently, each charge exceeding 2 Kg of lime/Nm$^3$ of the oxygen blowing it.

9. A method according to any one of the preceding claims, in which finely divided ore is introduced into the melt with the oxygen.

10. A method according to any one of the preceding claims, in which 90% of the finely divided lime blown into the melt has a particle size below 0.1 mm.

11. A method according to any one of the preceding claims, in which the total quantity of lime used in the refining of the melt is introduced into the melt in the form of the finely divided lime which is blown into the melt below the melt surface.

12. A method according to any one of the preceding claims wherein said liquid or gaseous protective medium is a hydrocarbon or mixture of hydrocarbons.
13. A method according to any preceding claim wherein oxygen without any lime is blown into the melt through the inner pipe of at least one nozzle with the mixture of oxygen and lime being blown through the inner pipe of the remainder of the nozzles.

14. A method according to Claim 1, substantially as described in any one of the Examples 1 to 3.

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