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PROCESS FOR THE MANUFACTURE OF BASIC STEEL OF LOW PHOSPHORUS CONTENT

Marc Louis Allard, Valenciennes, France, assignor to Société Anonyme des Forges et Aciéries du Nord & de l'Est, Paris, France

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This invention relates to a process for the manufacture of basic steel of low phosphorus content.

It is known that in the process of manufacturing steel by the Thomas converter, the elimination of the phosphorus results from the formation, on the surface of the bath, of a slag constituted by the lime added to the bath and by the phosphorus pentoxide and other oxides, particularly oxides of iron, resulting from the blow.

For obtaining basic steel of low phosphorus content (about 0.025%), there will now be described a particular process of dephosphorisation in two stages, in each of which certain determined quantities of lime are added and a blow is carried out. In the first stage, the blow effects successively the combustion of the silicon, then the carbon, the phosphorus and a partial oxidation of the iron, and the temperature of the bath rises. The slag formed on contact with the lime is removed. In the second stage, a fresh quantity of lime is added in order to eliminate a fresh quantity of phosphorus and a fresh blow is carried out. The fresh addition of lime and of blast air introduced in order to effect the oxidations necessary for the formation of the second slag nevertheless involve a certain cooling; but particularly when it is desired to leave the metal to stand before tapping in order to decant the impurities, or when it is desired to tap slowly, it may be desirable to obtain a refined steel at a high temperature.

It is furthermore known to effect the dephosphorisation in the second stage with the aid of an oxidising fused basic slag, known as "second slag," and, in the presence of this slag, to proceed with a blow intended to effect intense mixing of the slag and the metal to be treated, leading practically to complete chemical equilibrium between the slag and the metal.

When, in one of these two-stage processes, it is desired to obtain hard steels of low phosphorus content quality, the use of ordinary recarburising cast irons must be abandoned, because they are always too high in phosphorus and it would not be possible to eliminate the phosphorus, whilst introducing them at the end of the second phase. If, besides, and in order to thus eliminate the phosphorus, said addition would be made at the end of the first stage, the carbon would be burnt during the blow in the second stage and the recarburising addition would consequently be ineffective.

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The present invention aims at providing an economic dephosphorising process enabling a high temperature to be attained at the end of the operation, if required, while obtaining a phosphorus content of at most 0.025% whether the steels concerned are soft or carbonised steels, particularly rail steels, the final steel exhibiting an extremely low degree of oxidation and possessing excellent qualities. This process embodies the following steps. A first dephosphorisation is effected in accordance with the customary Thomas process (the phosphorus content of the steel may only be reduced to between 0.2 and 0.06%, for example); the slag resulting from this first dephosphorisation is eliminated as completely as possible, and thereupon a convenient proportion—of very hot and liquid oxidised basic slag is poured on to the surface of the bath. Good superficial contact between said slag and the surface of the bath is ensured by light rocking of the converter, allowing just sufficient blast to prevent the stopping up of the holes, and taking precautions to ensure that no appreciable stirring up of the bath takes place. The slag is dried by a stream of lime, after having removed immediately a fraction thereof if there is too large a quantity of it, and finally the tapping is carried out with dams, making the usual additions.

The process of the invention differs from processes already known in that not only is no complete equilibrium attained between metal and slag, but, on the contrary, every endeavour is made to avoid intense stirring up which would be liable to lead to said equilibrium.

Experience has shown in fact that, by having recourse simply to very short contact as described above, providing that a sufficient quantity of a slag of suitable composition be employed, extensive dephosphorisation is obtained simultaneously with practical freedom from oxidation of the metal in the case of the dephosphorisation of soft steels, as well as the possibility of recarburising the steel in the converter and then of effecting the final dephosphorisation of this recarburised steel.

In fact, the experiments made show that by applying the present process, a partial reaction of dephosphorisation is effected which is sufficient for the majority of cases in practice, since a phosphorus content of below 0.025% is easily attained and that at the same time, the diffusion into the metallic bath of large quantities of oxygen is avoided, the effect of which would be a detrimental increase of the oxygen content, with all the inconveniences involved thereby, particularly extensive combustion of the carbon in the case of hard steels.

The chemical equilibrium between the slag and the metal is not obtained. However, one observes the unexpected fact that, while the dephosphorisation reaction has time, during the duration of the surface contact between the metal and the slag, to progress to a degree sufficient in practice, the diffusion of oxygen takes place only to a far smaller extent.

The amounts of slag to be employed, all other things being equal, must naturally be larger than for operations in which equilibrium is desired.

By virtue of the process of the present invention, it is possible, by selecting a basic cast iron sufficiently rich in thermogenous elements, to obtain in the first stage of the treatment a bath the temperature of which is relatively high and to effect, after removal of the first slag, a fresh dephosphorisation by the addition of the liquid slag without lowering the temperature of the bath. It is also possible to add to the bath, before adding the liquid slag, a recarburising cast iron, even one high in phosphorus, provided that the quantity of slag utilised is in proportion to the average phosphorus content of the mixture, and to effect the second dephosphorisation almost instantaneously without needing a vigorous stirring up—and hence without combustion of the recarburising carbon of the bath. By virtue of the process of the present invention, it is thus possible to obtain in the converter hard dephosphorised steels, the recarburisation being effected by means of a cast iron, even of a phosphorised nature.

In order to carry out the process of the invention, the procedure may be as follows:

The molten cast iron being in the converter, the procedure at first follows the usual lines, but at a temperature which may be higher than normal, and the operation is stopped (which is easy for a trained operator) at a phosphorus content sufficiently high to ensure that the bath is not highly oxidised. This content, depending on the tapping temperature, generally varies between 0.060% and 0.200% and the slag formed is quite fluid.

This first slag is evacuated the more carefully, the lower the final phosphorus content desired is to be.

At the same time, a liquid oxidised basic slag must be available, which may be prepared by one of the following modes of operation.

According to a first method of preparation, use is made of a neighbouring converter, which may be one of the service converters or a converter of very small dimensions reserved for this purpose, in which the oxidised basic slag is formed from a certain quantity of unrefined steel taken from the preceding tapping. In order to prepare this slag, when utilising a service converter, a quantity of steel will be charged into the apparatus (the latter being well cleaned from its phosphatised slag) and will be after-blown, burning iron and proceeding progressively to the addition of good

quality granulated lime necessary for obtaining finally a slag containing 40 to 45% of lime. In addition, this slag must normally have an iron content of 30 to 35%, in the form of oxides, the whole of the steel not being incorporated in the slag. These contents are not imperative, the essential condition being to have a quite fluid and very hot basic oxidised slag. The oxidising blow to which reference has been made above will be effected very rapidly, so that the duration of the contact of the oxidised iron and the lining will be as short as possible. When operating in a converter of very small dimensions, the quantity of steel utilised may be much more restricted and may more closely approximate to the quantity strictly necessary for obtaining the above-specified composition.

According to a second method of preparation, the slag is taken during an operation in a steel refining furnace, for example a Siemens-Martin or electric furnace. In this case, this slag could, if necessary, be corrected by additions of oxides of iron, of fluxes and/or of lime or like substances.

Finally, a special slag melting furnace may also be utilised, this latter method of preparation permitting greater adjustability in the composition of the slag to be prepared.

The quantity of slag to be utilised depends at once on the phosphorus content of the metal at the end of the first stage, on the greater or lesser perfection of the cleaning, on the initial content of P_2O_5 in the slag itself, on the temperature and also on the final phosphorus content to be attained. By way of indication, if the slag has been prepared in a converter and contains, for example, 2% of P_2O_5, and if the metal contains 0.06% of phosphorus, the quantity of slag to be introduced into the operation is of the order of 2.5%, after a cleaning carried out normally, without particular precautions, and at a temperature slightly above the usual temperature of basic steel at the end of the operation. For a phosphorus content of 0.200% in the metal to be dephosphorised, the other conditions remaining the same, the quantity of slag to be utilised is of the order of 8%. In these two cases, the final phosphorus content obtained is lower than 0.025%.

The percentages of slag can be reduced considerably if particularly careful cleaning be carried out, if the temperature is lower, and if the initial content of P_2O_5 is very low—which may be achieved particularly when preparing the slag in a special furnace.

It should, moreover, be noted that, conversely, if it is desired to effect appreciable desulphurisation of the bath at the same time as dephosphorisation, the proportion of slag to be added must be larger, all other things being equal.

Similarly, the addition of dephosphorising slag, and also its composition, can be varied in such a manner as to compensate for the retarding action of the raising of the temperature by means of an increase in the quantity of slag or by means of an increase in its basicity or its content of oxidised iron.

It should be observed that in accordance with the foregoing principles, the use of a furnace for the preparation of the second slag enables the composition desirable for each particular case to be obtained at will, and, in consequence, furnishes additional flexibility in the application of the process. In fact, the preparation of the slag in a Thomas converter leads to compositions

which are, moreover, very advantageous to the majority of practical cases, although they are necessarily restricted in a certain measure by the very nature of the operation carried out in the converter.

The high temperature slag formed by one of the foregoing methods of preparation is removed, while carefully avoiding the removal of steel at the same time, in a ladle of dimensions as suitable as possible and lined with a refricatory lining, for example having a high alumina content, and it is poured into the converter on to the bath of cleaned steel to be dephosphorised.

In order that good superficial contact may be established betwen metal and slag, the converter is gently rocked, providing just sufficient blast to prevent the stopping up of the base holes. On the other hand, it is important that no vigorous and prolonged stirring is effected, which, by emulsifying the slag into the steel, might leave large quantities of iron oxides in the latter. The activity of the slag and the contact over a large surface are sufficient to ensure that the dephosphorisation is effected very rapidly during the very short time necessary and sufficient to effect a single gentle rocking under the above-specified conditions. The decantation of the slag and the drying thereof by superficial projection of granulated lime may then be carried out immediately.

The great rapidity of the operation and the very early decline in activity of the slag due to its cooling on contact with a steel at a lower temperature, and above all to its almost immediate drying, have the result that, contrary to current opinion, the metal is only extremely slightly oxidised in practice through its contact with the added slag.

That is moreover the reason that recarburization is possible in the case of hard steel, by adding to the bath of soft skimmed steel, before the slag treatment, recarburising cast iron. The latter may be high in phosphorus, provided that the quantity of slag utilised is then in proper proportion to the mean phosphorus content of the mixture. The recarburising cast iron must nevertheless be almost completely free from silicon, in order to avoid any difficulty; that is why, when recarbonising with basic cast iron, it is preferable to take from a neighbouring converter cast iron in which the combustion of the silicon is completed and the decarburisation of which has not commenced.

Once the soft or carburised steel has been dephosphorised in the aforedescribed manner, it may be brought to the desired manganese content by the usual additions, either in the converter or in the ladle. An excellent yield, and hence a low consumption of added ferro-manganese, is observed.

The slightly phosphatised slag, containing an appreciable quantity of iron which it is desirable to recover, may, as will be seen later on, be incorporated in the succeeding charge. To this end, if there is a large amount thereof, the bulk of it may be removed very rapidly before drying, this removed fraction being introduced into the next tap, while the fraction remaining may be retained in the converter by careful damming. On the other hand, this skimming is useless in the majority of cases, the amount of slag being too small to be conveniently retained by the dam. During the next tapping, carried out with the slag remaining or re-introduced into the converter, the iron in said slag is regenerated by the cast-iron and thus recovered without any

appreciable cooling resulting therefrom, although such cooling could easily be compensated by suitable dosing of the scrap iron.

If the slag is prepared in a normal service converter, the steel, and possibly the excess slag, may be left in the apparatus and are recovered in the next tap carried out in that apparatus.

The process is particularly economical in the case of the preparation of slag by blowing, because it does not require any supply of heat from external sources and, despite special refining, needs no heating up of the steel. The recovery, on the one hand, of the slag remaining in the converter and, on the other hand, of the residue from the preparation of said slag, obviates any supplementary loss of iron and thus the process not only does not increase the loss, but cannot fail to reduce it.

In a general way, moreover, the final slag, if it is not re-incorporated in another Thomas operation, can be re-utilised (when skimmed and placed aside) in any metallurgical operation requiring originating materials of this composition.

In addition, with a dephosphorised steel, it is possible to obtain a higher bath temperature than normal and a steel which may be either soft or hard, owing to the possibiltiy of adding into the converter recarburising material not necessarily constituted by cast iron of a very low phosphorus content, since this phorphorus can be eliminated by the action of the liquid slag added, without any appreciable fresh blowing. Finally, the bath being safeguarded against any appreciable oxidation both during the first dephosphorisation (because the latter is incomplete) and during the second, as indicated in the foregoing, the total consumption of manganese can be considerably reduced. In fact, not only is the yield of the final addition of manganese improved but, all other things being equal, it is possible to treat by this process, without inconvenience, cast irons having lower manganese contents than normal, the importance of the protective role of this element being reduced by reason of the smaller final oxidation of the bath.

I claim:

1. A process for obtaining in the Thomas converter steel of low phosphorus and oxygen contents and possessing a high temperature, comprising blowing molten cast iron in the converter to reduce the phosphorus content, skimming off the slag formed, adding to the skimmed metal a fused basic oxidizing slag, slightly raising the converter and strictly maintaining the blast necessary for preventing the stopping up of the blow holes of the converter whereby superficial contact of short duration is insured between the second slag and the molten iron, and avoiding any appreciable stirring in order to prevent the attainment of equilibrium between the molten iron and slag.

2. A process according to claim 1, in which, for the manufacture of hard steel, recarburizing material is added before the addition of the second slag.

3. A process according to claim 1, in which the first blow is limited so that the metal has a phosphorus content comprised between 0.06 and 0.2%.

4. A process according to claim 1, in which the second slag is a slag prepared in a converter by quickly blowing a steel and adding lime.

5. A process according to claim 1, in which the second slag is a synthetic slag prepared in a special slag melting furnace.

6. A process according to claim 1, in which the second slag is a slag of the group consisting of Martin and electric steel refining slag, if necessary corrected by additions of oxides.

7. A process according to claim 1, in which the final oxidized and slightly phosphatized slag is reincorporated, after use as an element of the charge, in a similar process in another Thomas converter.

ALLARD, MARC LOUIS.

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