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[54] METHOD OF REFINING IRON MELTS CONTAINING CHROMIUM

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[58] **Field of Search** 75/60, 130.5

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[57] ABSTRACT

Molten iron containing chromium is refined by oxygen being blown onto the surface of the molten metal while said surface is being kept free of slag; at the same time as the oxygen is being blown onto the surface of the metal, a molten iron is also subjected to vigorous stirring or agitation.

7 Claims, No Drawings

METHOD OF REFINING IRON MELTS CONTAINING CHROMIUM

The present invention relates to a method of refining carbon out of iron melts containing chromium. The refining is performed with oxygen in an open vessel or ladle or converter in which the iron melt forms a bath.

During such refining processes special precautions must be observed because of the high affinity of chromium to oxygen, so that not too much chromium is oxidized and must then be recovered by repeated reduction using expensive reducing agents. By successively increasing the temperature as the carbon content in the melt decreases the chromium oxidation can be kept in check but in order to achieve low carbon contents it has in practice been necessary to use temperatures which are too high.

The conditions for refining steel melts containing chromium to low C contents are substantially determined by the temperature and the partial pressure for CO.

For each Cr content and C content in the bath there is for a certain CO partial pressure a limit temperature which must be exceeded if the supply of oxygen is to result in refining away carbon. Below this temperature, the oxygen instead reacts with Cr to form Cr_2O_3. This limit temperature, which must thus be exceeded, if the carbon in the bath is to be removed, is lower, the lower the partial pressure for CO is in the gas which is in contact with the steel bath. The examples below are given for the lowest carbon content to which it is possible according to equilibrium diagrams for refining a melt with 17% Cr at corresponding temperature and CO-partial pressure before substantial chromium oxidation commences.

Temp. C°	P_{CO}atm	Carbon Content %
1550	1	0.65
1900	1	0.065
1650	0.35	0.06
1650	0.10	0.02

In order to achieve low carbon contents in steel baths having high chromium contents without oxidizing the chromium, therefore, either the refining can be performed at greatly increased temperatures which results in the refractory material being vigorously attacked, and therefore should be avoided if possible, or it can be performed under reduced partial pressure achieved by vacuum or the supply of inert gas.

One known method makes use of the latter principle in such a way that a mixture of argon and oxygen gas is blown through nozzles below the surface of the bath. The proportion argon:oxygen increases gradually towards the end as the carbon content falls, and in this way low carbon contents can be achieved at reasonable refining temperatures without the chromium of the bath being oxidized to any great extent. The surface of the bath is covered by a slag which takes up the silicon and the chromium which is oxidized. The disadvantage with this method is that it requires a large quantity of expensive argon and special regulating and other equipment in order to maintain such conditions while the gas is being blown so that the nozzles are not quickly destroyed. Even with such precautions, maintenance, and replacement of the nozzles is a considerable expenditure.

From the equipment point of view a more attractive solution is blowing oxygen gas against the surface of the bath from above. However, it has been found that, without special precautions, it is impossible to get less than 0.2 – 0.3 percent C in the bath and still retain a reasonable chromium content, even if the temperature is permitted to reach the higher temperature range, about 1,900°, where according to the equilibrium conditions it should be possible to reduce the carbon content easily to < 0.10 percent. The use of extremely highly basic slag has been recommended for this process. Attempts have also been made blowing the oxygen gas from above with varying quantities of argon in order to achieve low CO partial pressure, without nearly achieving the carbon contents (still maintaining the Cr content) achieved when blowing in the same gas mixture below the surface of the bath.

However, it has now been found that even when blowing oxygen gas from above it is possible to achieve low carbon contents without noticeable chromium oxidation, as predicted by the equilibrium conditions, if according to the invention the bath is vigorously stirred during the refining process so that melt containing carbon is conveyed to the reaction zone at the same rate as oxygen gas is supplied, so that this oxygen is not free to oxidize the chromium to any great extent, and also the surface of the bath is kept substantially free from slag. It seems that for reasons which are not apparent, the presence of slag encourages chromium oxidation at the cost of carbon refining.

A surprising result of the absence of slag from the surface of the bath during the refining process is that the production of smoke and dust is considerably lessened when compared to refining with a slag cover. This is also true at higher temperatures near 1,900°C. Another advantage is that the attack on the refractory lining becomes milder since there is no floating slag which might attack the lining. Since the oxygen gas is supplied from above, even the corrosion problems connected with nozzles and the adjacent lining, in the methods in which oxygen gas is supplied below the surface of the melt, are eliminated.

The stirring can be produced in conventional manner either by so-called vibratory (shaking) ladle in which the melt is set in rotating movement in the refining vessel, or by blowing in inert gas, for example argon, krypton, xenon, helium, below the surface of the melt, suitably through openings or porous brick in the bottom or side walls of the refining vessel. The requirement of stirring is of course particularly strong during the final stage of the refining process when the average carbon content of the melt approaches the limit at which time oxygen has greater tendency to oxidize chromium than carbon.

The slag-free surface of the bath is achieved by removing silicon, and other substances having greater affinity to oxygen than chromium, from the bath, suitably by oxidation and pre-slagging, and then drawing off all slag before the start of the carbon refining process. The content of Si and similar substances, for example Al and V, should suitably be less than 0.05 percent. Due to the cooperation of the vigorous stirring and the bath surface free from slag at the start of the process, no noticeable new formation of slag takes place and the surface is kept slag-free.

By blowing oxygen from above against a substantially slag-free bath surface and stirring with argon-blowing through the bottom of the refining vessel, for example, with chromium contents of about 17 % C it has been possible to get down to <0.05 percent at bath temperatures of about 1,800°. The argon gas supplied for stirring may also contribute to acquiring a low final carbon content by lowering the CO partial pressure at the gas-emitting surfaces of the bath. This effect is more marked the larger the quantity of argon used in relation to the quantity of oxygen gas. The refining is thus carried out with very small chromium losses right up to a well-defined end point when there is a steep decline in the CO content in the exhaust — which is continuously analyzed — indicating that the carbon refining process is ending and that further addition of oxygen substantially oxidizes the chromium in the bath.

Good results have been obtained using only the vibratory ladle movement, but it is of particular advantage to combine stirring with vibratory ladle movement and the supply of inert gas. The latter helps to lower the CO partial pressure, but need only be used in comparatively small quantities.

In many cases the C content thus achieved is satisfactorily low and the steel can be finished by means of deoxidation and the addition of the required alloying substances, for example Mn and Si. The amount of slag which may then occur on the surface of the bath is small in quantity and firm in consistency, and it may not be necessary to reduce it completely in order to achieve a satisfactorily low oxygen content in the steel bath.

According to a variation of the method, however, in order to further facilitate deoxidation, the steel melt may be tapped into a special completion vessel preferably after the refining, keeping back any slag.

In order to acquire even lower carbon content without oxidizing the chromium it is possible, when the exhaust analysis has shown that the CO-development has noticeably decreased and the final stage in the carbon refining process has been reached in the normal refining process described above, to continue to supply inert gas and oxygen gas but with a considerably decreased ratio between the volumes of oxygen and inert gas. In principle only so much oxygen should be supplied so that it corresponds to the quantity of carbon monoxide removed when the inert gas is flushed through the bath (plus the increased oxygen solubility in the melt due to the decreased carbon content in the bath).

The decrease in the ratio oxygen:inert gas can be done gradually but in practice it is probably suitable to decrease the ratio immediately after the drop in CO-content in the exhaust, from a maximum of 20:1 — applying to the latter part of the refining process with a high CO content in the exhaust — in one or two steps to 1:1 or 1:2, this being maintained until the desired carbon content has been attained in the region of 0.01 – 0.05 percent.

The carbon content in the low carbon content range can be lowered still further in known manner by continued inert gas flushing without the supply of oxygen.

The steel refined in this way is deoxidized and alloyed in the same way as described above.

OPERATIVE EXAMPLE

2030 kg molten pig iron containing 4.0 % C, 1.6 % Si and 0.7 % Mn was refined to remove Si in a vibratory ladle, after which most of the slag was removed. 750 kg ferrochromium carburé was melted with an oxygen oil burner while being stirred according to the vibratory ladle principle, after which more slag was removed so that the steel surface was bare. Analysis according to the table, sample No. 1.

Carbon refining was then initiated at 1,450°C, the vibratory movement being continued to effect stirring and the bath being flushed through with 0.4 nm^3/min, argon supplied through two slits in the brickwork of the bottom of the ladle. After 18 minutes of blowing with 4.0 nm^3/min. oxygen, the temperature had increased to 1,670°C and the steel bath had a composition according to the table, sample No. 2. The steel surface was still bare.

The blowing was now continued in a stationary ladle with 4.0 nm^3/min. oxygen being blown on and 1.0 nm^3/min. argon being flushed through. The CO content of the exhaust was analysed continuously. When this dropped noticeably after 12 minutes blowing, the flow of oxygen gas was reduced to 1.0 nm^3/min, the argon flow remaining the same. Without interrupting the blowing, steel sample No. 3 was taken and the temperature measured as 1,875°C. The oxygen blowing was interrupted after 5 minutes of the reduced flow. The temperature was then 1,880°C and the steel composition according to the table, sample No. 4. A negligible quantity of molten slag was found close to the wall of the ladle, but most of the steel bath was still bare.

All the time oxygen was being blown in after sample No. 1 had been taken, there was no noticeable iron smoke. As can be seen from the table, no noticeable chromium oxidation was obtained either. After the oxygen blowing had ceased, argon gas was flushed through for another 5 minutes. The steel was then tapped into another ladle for conventional deoxidation, adjustment of the Si, Mn and Cr contents, and casting. Sample No. 5 was taken after deoxidation with 4 kg Al, and sample No. 6 during casting.

Analysis:	Test No.	C	Si	Mn	Cr	O	
	1	3.87	0.00	×	18.8	×	per cent by weight
	2	1.60	0.00	×	18.7	×	
	3	0.09	0.00	×	18.4	×	× = not analyzed
	4	0.03	0.00	0.05	18.2	0.136	
	5	0.02	0.05	0.04	18.2	0.070	
	6	0.03	0.61	0.32	18.8	0.007	

In the examples shown above, molten pig iron and ferrochromium carburé have been used as raw materials for producing stainless steel. However, pig iron, crude chromium and scrap which have been melted in electric arc furnaces and transferred to a vibratory ladle are all within the scope of the invention. All silicon is preferably oxidized and all slag removed in the vibratory ladle before the carbon refining process is carried out according to the invention. Of course it is possible to oxidize all silicon straight away in the arc furnace and tap over a slag-free melt to a ladle or converter where the carbon refining is performed according to the invention. The required carbon content of the steel prior to carbon refining according to the invention is dependent on the size of the charge, the temperature before blowing is started, and the specified final carbon content. In the example shown above the refining was performed from a remarkably high carbon content. This was caused by the requirement of an extremely low carbon content in the finished steel and the very great heat loss caused by low charge weight in relation to the reaction heat. In order to achieve a satisfactory final temperature, however, the carbon refining according to the invention should start at at least 0.5 percent by weight C in the steel. One of the advantages of the method is that it is possible to have a relatively high carbon content at the start of the refining, as an inexpensive crude chromium and FeCr carburé may then be used for the manufacture of stainless steel having a low C content.

Another advantage of the carbon refining according to the invention over normal oxygen blowing against slag-covered steel, or an emulsion of slag and steel, is the improved heat exchange achieved due to the partial burning of the carbon monoxide to carbon dioxide above the surface of the bath. According to exhaust analysis up to 30 percent of the carbon was oxidized to CO_2 during the experiments, and a considerable portion of this heat was transmitted to the slag-free steel melt.

The invention is exemplified here in the manufacture of chromium steel, but can also be used for the manufacture of other types of steel having a high chromium content, for example stainless steel containing Cr, Ni and possibly other alloying substances.

What is claimed is:

1. A method for refining carbon from an iron melt containing chromium comprising the steps of: maintaining said melt substantially free of surface slag, blowing oxygen gas from above onto said substantially slag free surface of said melt and subjecting said melt during carbon refining simultaneously to vigorous stirring by means of an inert gas being blown from under the surface of said melt as its surface is being kept substantially free of slag.

2. The method according to claim **1,** and wherein an oxygen to inert gas ratio is reduced during said refining when according to the CO content of the exhaust gas carbon refining requires less oxygen for oxidation of carbon.

3. The method according to claim **1,** and wherein before the start of the carbon refining process, the content of Si and other substances having higher oxygen affinity than Cr is reduced to below 0.05 percent by weight, and thereafter removing slag as completely as possible from the surface of said melt.

4. The method according to claim **1,** and wherein the carbon refining process starts at a carbon content of at least 0.5 percent by weight.

5. The method according to claim **1,** and wherein stirring is effected in a shaking ladle zone.

6. The method according to claim **5,** and wherein the inert gas which is blown from under the surface of the melt is argon.

7. The method according to claim **6,** and wherein the ratio between the flow of oxygen gas supplied from above and the inert gas supplied for stirring purposes is reduced continuously when according to the CO content in exhaust gas the supplied oxygen demand for oxidation of carbon decreases.

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