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Steinmetz et al.

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[54] **PROCESS FOR THE PRODUCTION OF STEELS HAVING HIGH CHROMIUM CONTENT AND LOWEST POSSIBLE CARBON CONTENT**

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[52] **U.S. Cl.** **75/51;** 75/60; 75/130.5

[51] **Int. Cl.²**...................... **C21C 7/00;** C22C 33/00

[58] **Field of Search** 75/57, 59, 60, 51, 130.5

[56] **References Cited**

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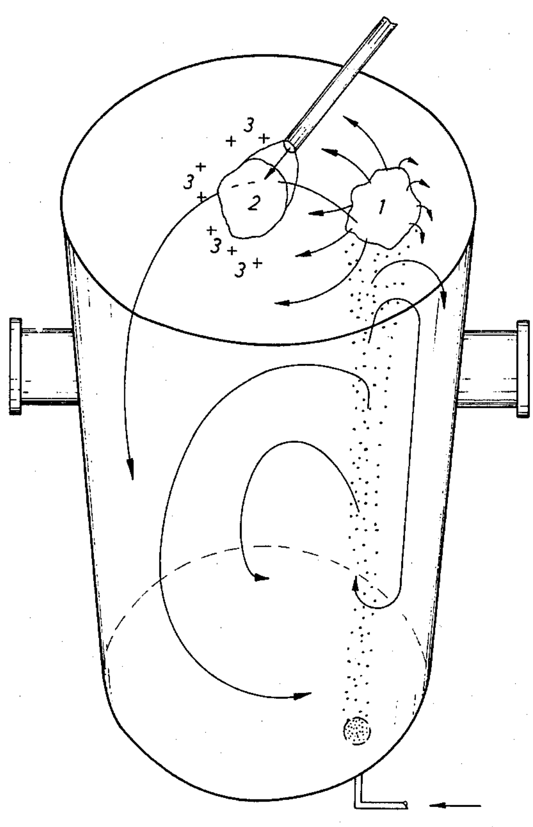
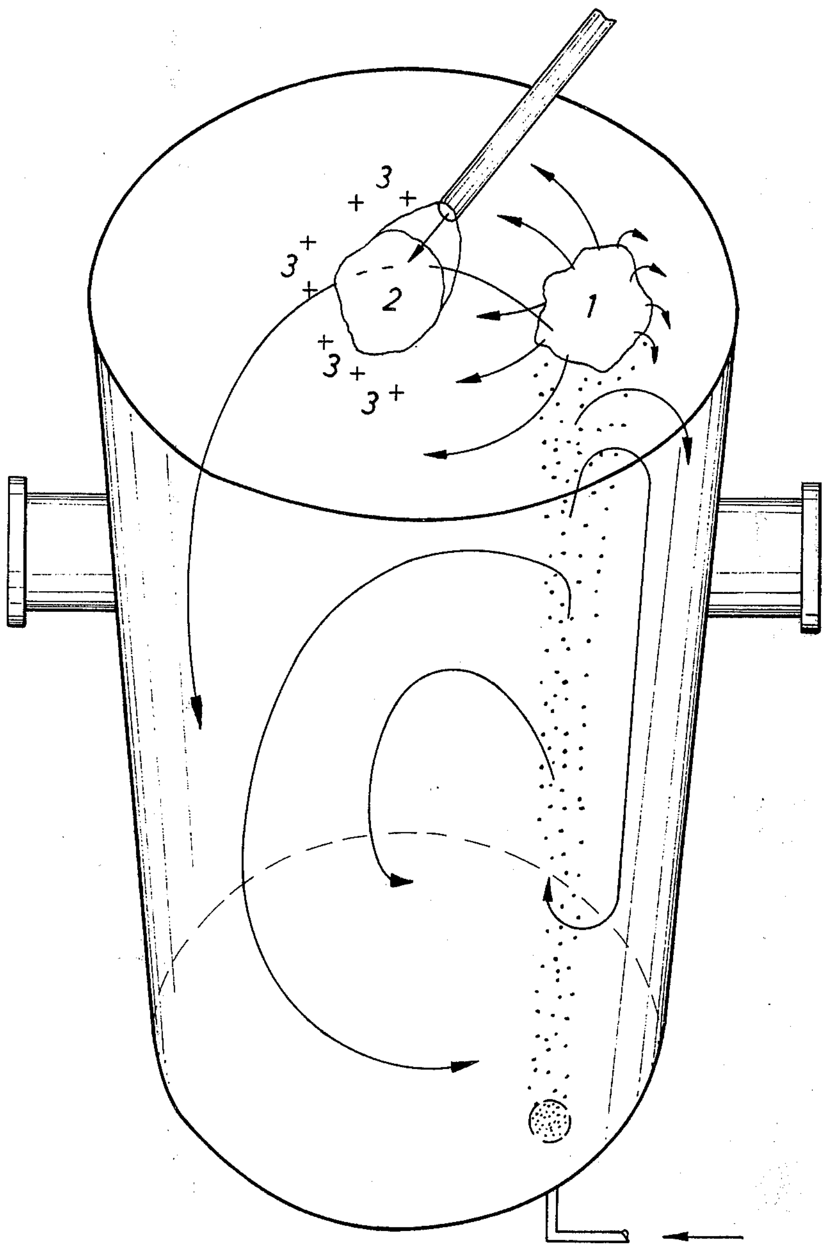
[57] **ABSTRACT**

An improvement in a process for removing carbon from a chromium-containing molten steel wherein an unidirectional flowing stream is maintained within a bath of molten steel by the injection in such molten steel of a gaseous oxidizing stream, which improvement retains high chromium content in the final refined steel while minimizing carbon content, the improvement being provided by a process which comprises introducing a reducing agent into said unidirectional flowing stream at a point downstream of the point wherein said gaseous oxidizing stream contacts said molten steel.

12 Claims, 1 Drawing Figure

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PROCESS FOR THE PRODUCTION OF STEELS HAVING HIGH CHROMIUM CONTENT AND LOWEST POSSIBLE CARBON CONTENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to the production of steel as having high chromium content and lowest possible carbon content. More particularly, this invention is directed to a process for the removal of carbon, as carbon monoxide or carbon dioxide from liquid chromium-containing steels while retaining in such liquid steels the chromium therein. More especially, this invention is directed to a process for refining chromium-containing steels without loss of chromium as the oxide thereof. This invention is especially directed to a one-step process for the production of high chromium-containing steels characterized by low carbon content.

2. Discussion of the Prior Art

It is known to promote the formation of carbon monoxide in steels by lowering the carbon monoxide partial pressure. Such processes are exemplified by vacuum refining processes and argon-oxygen-decarbonization processes. These processes operate by the Le Chatelier principle. A more recent process is described in German Auslegeschrift 2 063 532, in which a steel melt in a plasma induction furnace is heated simultaneously by induction and by the plasma arc. With all known processes, corresponding to the equilibria between carbon an oxygen and also between chromium and oxygen, an extensive lowering of the carbon content can be achieved without substantial chromium slagging. However, it has been found that where the carbon content becomes extensively reduced, an apparently strong simultaneous reaction occurs between the chromium and oxygen. Thus, a chromium oxide is formed.

For this reason, in the known processes for producing steels having high chromium content it is necessary to effect a subsequent chromium recovery by subjecting the slag to the action of a reducing agent. Essentially these processes are two-step processes. One such two-step process for the production of alloy steel is described in Austrian patent 249 714. In this process, at some time following the termination of the introduction of the oxygen to effect carbon removal, a reducing agent, such as aluminum granules or ferrosilicon, is introduced into the slag. As a result of the action of the reducing agent a reverse reduction of the alloying elements in the slag occurs and the chromium is reintroduced into the bath.

It has therefore become desirable to provide a one-step process for the production of steels having a high chromium content wherein the loss of chromium into a slag is precluded. More particularly, it is desirable to provide a one-step process in which the subsequent treatment of a slag to recover the chromium is unnecessary. More especially it has become desirable to provide such a process which is characterized by the maximum removal of carbon from a steel.

SUMMARY OF THE INVENTION

The above objects are attained in an improved process for the removal of carbon from a chromium containing molten steel wherein an unidirectional flowing stream is maintained within a bath of molten steel by the injection in such molten steel of a gaseous oxidizing stream. The improvement resides in introducing a reducing agent into the unidirectional flowing stream at a point downstream of the point wherein the gaseous oxidizing stream first contacts the molten stream. By such improved process there is a high retention of chromium in the final refined steel. Moreover, the carbon content is reduced. Especially no further treatment of slag to recover a chromium is required.

The present invention is based upon a surprising finding that an oxidizing and reduction function can be carried out virtually simultaneously and at points virtually adjacent to one another whereby the carbon content of the steel can be reduced to the lowest possible value without loss of chromium into a slag. According to the invention an unidirectionally flowing stream of an oxidizing substance as H_2O, CO_2, pulverized NiO and, iron oxide especially oxygen or air, is introduced into or onto a molten liquid chromium-containing steel. Into such stream there is introduced a reducing agent as Fe-Si, Ca-Si, Si, Ca, Mg, more especially, aluminum. The aluminum is introduced at a point downstream from the point at which the oxidizing stream first enters into or onto the liquid steel. Generally speaking, the reducing agent is introduced onto or into the unidirectionally flowing stream at a point at least 5 cm. and advantageously up to 100 cm. from the point where the oxidizing stream first makes contact with the molten steel bath.

The unidirectionally flowing stream is caused by the action of the gaseous stream effecting an impulse thereon. The unidirectional bath circulation is also effected by injected substances contained in such stream. One means for affecting unidirectional bath circulation is described in Austrian patent 225 212, the disclosure of which is hereby incorporated herein by reference. According to such patent tangentially directed nozzles are arranged in a refining vessel, distributed uniformly over the periphery. By the action of a gaseous stream flowing through such nozzles a helical bath circulation is effected. This procedure is employed to even out the refining procedure. The rotation of the bath leads to a more uniform and more intensive mixing, with a constant change at the boundary surface between the bath and slag.

According to the invention, the unidirectional bath circulation is necessary for the proper contacting of the bath initially with the oxidant and thereafter with the reducing agent. Thus, in the subject process the addition of oxygen is only within the unidirectionally flowing stream created within the bath and does not take place over a number of points within the entire area of the vessel.

The main bath circulation has to be produced about an imaginary horizontal axis. For example, the introduction of such a stream into the bath can take place at an angle inclined to the bath surface and/or through the bottom or the wall of the melting vessel below the bath surface. It is important that conditions are provided by the unidirectional bath circulation which allows the initial addition of oxidizing agent followed by the addition of reducing agent at the same time but downstream thereof or within a separate region in the unidirectionally flowing stream.

The gases and other substances are advantageously injected into or onto the metal surface without the formation of any droplets. It has been found that the formation of droplets during the introduction of the oxidizing stream adversely affects the chromium/carbon ratio. Droplet formation can be avoided by suitable selection of the process parameters, the blowing pressure of the gaseous stream, the angle at which the stream is introduced in or onto the liquid steel and the shape diameter and relative spacing of the nozzles employed therefore. It is desired that special attention be given to the nozzle diameter. It has been found that noxxle diameters having a relatively large diameter can be beneficially employed to limit the formation of droplets. This is owing to the fact that such large nozzle diameters provide a gentle gas stream.

Thus, one should consider the above factors all of which have an influence on the drop formation. Consideration should also be given to the discussion of process paramaters as they affect drop formation described by R. Gardon and J. C. Akfirat Int. J. Heat Transfer 8 (1965), pages 1261/72, the disclosure of which is hereby incorporated herein by reference.

DISCUSSION OF SPECIFIC EMBODIMENTS

It has been stated that measures should be taken to avoid the formation of drops during the introduction of the substances. It has been found that droplets which form upon introduction of oxygen especially show an unfavorable ratio of chromium to carbon. In other words, the ratio between chromium and carbon in the steel is changed to the disadvantage of the chromium more strongly in those instances where droplets are formed during the process. The extent of the difference is shown from the mass ratios between chromium and carbon as indicated below, these values being mean values of tests heretofore conducted.

	Mass ratio chromium/carbon		
in the drop	180	170	250
in the bath	260	300	370

It is seen from these results that it is of significant importance to avoid formation of drops in the process. This is particularly applicable for the termination of the refining operation when the chromium/carbon ratio in the bath exceeds the value 200, for example, wherein there is a carbon content of 0.09% with a chromium content of 18% by weight. From this moment, the supply of oxygen to the bath surface should be reduced. With an oxygen throughflow remaining the same, the object is achieved by increasing the space between the blowing lance and the bath.

The process of the present invention affects marked reduction in the carbon content by flushing out carbon monoxide. Substances which give off gases or which gasify can also be blown in to the molten steel for this purpose. One can also energize the gas bubble formation by the introduction of solids by way of nucleus formation.

Gas yielding substances, more particularly calcium carbonate in powder form, can advantageously be additionally sprayed into the molten bath by injection. It is of particular advantage if the addition of calcium carbonate and aluminum are so matched to one another that, after the oxidation, the weight ratio between the so-formed calcium oxide and the so formed alumina is between 0.5 and 1.6.

The process is advantageously carried out under vacuum. Particular advantages are produced insofar as the required unidirectional bath circulation is concerned when using electromagnetic or mechanical stirring systems.

An important consideration in the instant refining process lies in the use of oxygen or an oxygen yielding substance and reducing agents which are supplied to the liquid steel at practically the same moment and at relatively close proximity to one another. The addition is, however, made at different points, the reducing agent being supplied at the rim of the oxygen impact spot in the direction of flow at a distance of at least 5 cm. and advantageously up to 100 cm. This can be more readily understood when reference is made to the accompanying drawing.

BRIEF DESCRIPTION OF DRAWINGS

Referring to the drawing herein, the accompanying drawing is an isometric diagrammatical view of a bath of molten steel undergoing decarbonization by the subject process.

DESCRIPTION OF PROCESS

Referring to the drawing there is introduced into the bottom of the vessel containing molten steel an inert gas which bubbles upwardly toward the surface. The bath is caused to rotate somewhat about an imaginary horizontal axis extending through the center of the bath. At the center of the melt surface, an oxygen stream **2** strikes the melt surface at an inclined angle. This oxidizing stream intensifies the required, unidirectional bath circulation. Reducing agent is added to the molten steel at positions within 5–100 cm. from the point where the oxygen strikes the molten surface. The reducing agent is thus added at positions indicated by reference numerals **3**. The speed of supply or injection of the reducing agent, aluminum, is matched of course to the process and the reaction yield.

The process proceeds in contradiction to metallurgical experience which has assumed that oxidation and reduction should be carried out separately from one another. It has been surprisingly found that the undesired chromium oxide formation can be limited if a unidirectional bath circulation is caused when using a reaction vessel and a reducing agent is introduced such that it is arranged to follow immediately upon the addition of the oxygen to the bath at a certain fixed location.

Generally speaking, the amount of reducing agent depends on the initial and final carbon content and on the rate of decarburisation.

The amount of oxidizing substance introduced generally depends upon the amount of carbon being removed from the steel being treated.

A principal advantage of the invention resides in the fact that an immediate and therefore economic chromium reduction is produced while simultaneously a steel with a high degree of purity is obtained. This high degree of purity is assured when limestone is simultaneously introduced with the aluminum such that they are matched so that the weight ratio of calcium oxide to aluminum is between 0.5 and 1.6. The steels produced by the subject invention not only have high chromium content with extremely low carbon content, but the nitrogen contents thereof are also low.

A particularly desirable embodiment of the invention resides in introducing into the metal bath quicklime locally proximate the point of reducing agent introduction whereby a calcium oxide-alumina slag of low melting point is produced. By such all or a part of the calcium oxide proportion introduced as limestone can be supplied.

The introduction of the oxidizing stream to effect unidirectional bath circulation can be accomplished employing gaseous oxygen alone or in admixture with inert gases such as argon. Of course, air can be used as the gaseous medium. Additionally, gas-yielding solids especially those which simultaneously exert a flushing action with the possibility of gas separation. Gaseous constituents liberated by the gas yielding solids include water, carbon monoxide, especially when the gaseous stream contains calcium carbonate. The unidirectional bath circulation is particularly advantageously effected by the use of electromagnetic or mechanical stirring mechanisms. In a desirable embodiment the process is conducted by the addition of components for liquefying the slag.

In order to more fully illustrate the nature of the invention and the manner of practicing the same the following examples are presented.

EXAMPLE 1

Into a liquid steel composition having the assay below there was introduced an oxidizing stream of oxygen through a nozzle inclined at the surface of the liquid steel. The process was conducted under vacuum conditions. The steel analyzed as follows:

0.50% C; 0.15% Si; 0.35% Mn; 18.93% Cr and the usual accompanying elements.

About 40 cm downstream of the rim of the area, where the oxygen first contacts the unidirectional flowing stream of the metal, there were deposited into the unidirectional flowing stream created by the flow of oxygen and by an additional argon bubbling aluminum granules. Calcium carbonate was added to the oxidizing stream through an additional tube. There is set forth below a table showing the duration of the blowing in of the oxygen and the amounts of the added calcium carbonate and aluminum in kg per ton metal melt and blowing minute. The first line in the table means that during the first 15 minutes there were added within each minute 0,040 kg $CaCO_3$ per ton metal melt, i.e. for a melt of 100 tons 4 kg per minute and for the total of 15 minutes 15 × 4 kg = 60 kg caccium carbonate. Likewise to this melt of 100 tons 2 kg aluminum were added per minute, i.e. 30 kg in total within the first 15 minutes.

Blowing time (min.)	Addition in kg/t × min.	
	$CaCO_3$	Al
1. – 15	0.040	0.020
15. – 22	0.090	0.045
22. – 30	0.100	0.050

The steel was decarbonized so that its final carbon content was 0.03%. The amount of chromium in the steel was about 98,2% of the chromium present in the liquid steel prior to the decarbonization process.

EXAMPLE 2

In the manner of Example 1 a steel having the following composition was decarbonized:

0.50% C; 0.15% Si; 0.35% Mn; 18.05% Cr and the usual companion elements.

The same apparatus employed in Example 1 was utilized and the rates of addition of calcium carbonate and aluminum are disclosed in the table shown below. The steel had a final carbon content of only 0.012 weight percent. It retained about 98,0% of its chromium content.

Blowing time (min.)	Addition in kg/t × min.	
	$CaCO_3$	Al
1. – 15	0.040	0.020
15. – 22	0.090	0.045
22. – 30	0.100	0.050
30. – 45	0.120	0.066

In neither Examples 1 or 2 was it necessary to subject the slag to the independent action of a reducing agent to recover chromium.

As this contact point is in reality, as seen in the FIGURE, reference **2**, a contact area the disclosed distance refers to the shortest distance between the rims of the contact area of oxygen and metal and the area of aluminum introduction. Preferably the distance is between 30 cm up to 50 cm.

The invention bases upon the effect that the chromium oxide being just constituted and not yet being part of the slag phase resting on the metal surface, has a good and remarkable reactivity for the reduction. Therefore the immediate reduction leads to a high chromium recovery and therefore the proposed process is very economic.

What is claimed is:

1. In a process for removing carbon from a chromium-containing molten steel wherein an unidirection flowing stream was maintained within a bath of molten steel by the injection in such molten steel of the gaseous oxidizing stream the improvement for retaining high chromium content in the final refined steel while minimizing carbon content therein which comprises introducing a reducing agent in said unidirectionally flow stream at a point downstream of the point wherein said gaseous oxidizing stream contacts said moltent steel.

2. A process according to claim **1** wherein said reducing agent is aluminum.

3. A process according to claim **1** wherein the reducing agent is introduced to the unidirectional flowing stream at a point between 5 and 100 cm. from the point where the unidirectionally flowing stream makes contact with the molten steel.

4. A process according to claim **1** wherein the oxidizing stream contains oxygen gas.

5. A process according to claim **1** wherein the process is carried out in a vacuum.

6. A process according to claim **1** wherein the process is carried out with the concomitant introduction of a stream of inert gas passing upwards through the molten steel.

7. A process according to claim **1** wherein a gas yielding substance is introduced by injection into said molten steel.

8. A process according to claim **7** wherein said substance is calcium carbonate in powder form.

9. A process according to claim **8** wherein said reducing agent is aluminum and the ratio of the addition of the calcium carbonate and aluminum are so matched with one another that, after oxidation, the weight ratio of calcium oxide to alumina is between 0.5 and 1.6.

10. A process according to claim **1** wherein the oxidizing stream and the reducing agent are injected into the steel while avoiding the formation of drops.

11. A process according to claim **10** wherein drop formation is reduced by regulating the pressure of the oxidizing stream being introduced into the molten steel, the angle at which it is introduced, the shape, diameter and spacing of the nozzles employed to produce the unidirectionally flowing stream.

12. A process according to claim **1**, wherein the reducing agent is introduced to the unidirectinal flowing stream at a distance of between 30 cm to 50 cm from the rim of the area where the oxygen first makes contact with the molten steel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,907,548

DATED : September 23, 1975

INVENTOR(S) : Eberhard Steinmetz and Jürgen Berve

It is certified that error appears in the above–identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 6, lines 22-34

The two paragraphs bridging the above should be inserted instead at column 2, after line 27.

Col. 3, line 7

"noxxle" should be "nozzle".

Signed and Sealed this

twenty-third **Day of** *December 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks