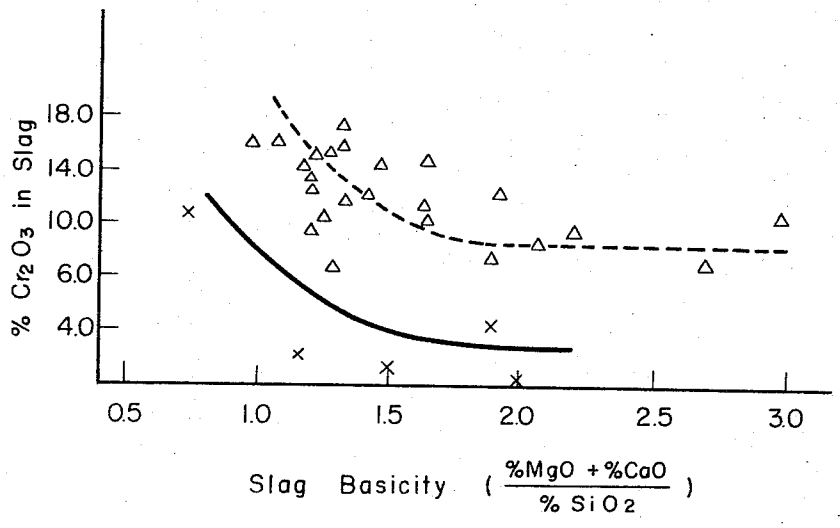
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PROCESS FOR THE PRODUCTION OF CHROME SERIES AND NICKEL-CHROME SERIES STAINLESS STEELS

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PROCESS FOR THE PRODUCTION OF CHROME SERIES AND NICKEL-CHROME SERIES STAINLESS STEELS

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This invention relates generally to a process for the production of stainless steel, and more particularly to a process for the production of chrome series and nickel-chrome series stainless steels.

Stainless steel is generally produced by melting in an electric furnace stainless steel scraps, ordinary steel scraps, high-carbon ferrochrome (or coke breeze), etc., followed by the steps of oxidation, recovery and finishing. In a conventional method of producing stainless steel ingots in an electric furnace, a large amount of ferrosilicon or ferroalloy is generally used to carry out the reducing reaction for the recovery of metal from metal oxide. But, due to the presence of a close relationship between the recovery yield of chrome in slags and the basicity thereof, a large amount of lime, a large electric power and a considerable long period of time are required to maintain the necessary basicity, if the amount of chrome oxide becomes large. In such a case. the formation of slags will further increase and the fluidity of slags will deteriorate, thereby making the operation difficult and the loss of chrome will become large due to the low recovery yield of chrome. Consequently, the use of chromite in an operation of a conventional electric furnace was hardly permitted. Further, as regards the desulfurization in an electric furnace it is impossible to obtain a more economic and better desulfurization in a shorter time than usual in the conventional method without resort to some other means.

Thus, under the present conditions in any conventional method of producing stainless steels, particularly chrome series and nickel-chrome series stainless steels, an increase in productive efficiency, an improvement of quality of product and a reduction of production costs can not be expected, though they are strongly desired.

Therefore, an object of tris invention is to provide a process for producing in a short time stainless steel with extremely high chrome-recovery yield and desulfurization rate.

Another object of this invention is to provide a process for producing stainless steel using a large amount of chromite.

Still another object of this invention is to provide a process for producing stainless steel with a low basicity and a high chrome-recovery yield, even if chrome ore is used as a raw material.

A further object of this invention is to provide a process for producing stainless steel with a facilitated procedure and an extremely low cost, without need of using a large amount of electric power.

These and other objects of this invention and the contents of this invention will be understood by the following description and the claims with reference to the accompanying drawing.

The drawing is a graph showing the relations of "basicity of slag and Cr_2O_3 content in slag" in a conventional process of using an electric furnace and in the process of this invention.

The inventors have found, that in the production of stainless steel ingots, if molten steel added with a reducing agent is sufficiently agitated, chrome oxide in the slag

formed after oxygen blowing is well reduced and the thus obtained chrome is transferred into the molten steel.

In the drawing showing Cr_2O_3 content in the slag on the ordinate and the basicity of the slag

$$(MgO\% + CaO\% / SiO_2\%)$$

on the abscissa, the conventional case of reducing the material in an electric furnace is plotted with sign (Δ) and the case of this invention is plotted with sign (x). As shown in the graph, in the conventional case of using an electric furnace the Cr_2O_3 content in the slag reaches the equilibrium at 8.5% when the basicity of the slag is 1.5 to 2.0, while in the present invention the same equilibrium of Cr_2O_3 may be obtained at the basicity of 0.9 to 1.0, indicating that a considerable amount of chromite may be economically used even at a lower basicity. Moreover, in the present invention the equilibrium state of the Cr_2O_3 may be also obtained at the basicity of 1.5 to 2.0, and in this equilibrium state the Cr_2O_3 content amounts to about 3%, which shows that the recovery yield of chrome is much higher as compared with that of the conventional process. That is to say, according to the process of the present invention, even with a small amount of reducing agent for chrome oxide and of lime for adjusting the basicity the high recovery yield of chrome may be achieved, and as metallic chrome may be effectively recovered by adjusting the basicity to 1.5 to 2.0, with a relatively small amount of slag formation, even though a considerable amount of chromite is used as a material. The present invention is thus best carried out between a slag basicity of 0.9–1.0, at which the Cr_2O_3 is present in the slag in an amount of about 8.5%, and a basicity of 1.5–2.0, at which the Cr_2O_3 is in equilibrium at about 3%. Therefore, the method aciording to the present invention may be said to be very advantageous in producing stainless steel of high chrome content such as chrome series and nickel-chrome series stainless steel.

In the process of the present invention, molten metal is rotated at a high speed. For example, a molten metal is charged in a shaking ladle that moves eccentrically and the molten metal is decarburized by oxygen blowing (or a molten metal previously decarburized by oxygen blowing may be charged in the afore-mentioned type ladle). Then, into the molten metal is added a reducing agent, such as, silicon-chrome or ferrosilicon to recover metallic chrome at an improved contact condition between the molten metal and the reducing agent. After removing the slag, a desulfurizing agent is added into the molten steel to carry out the desulfurization by a solid reaction, then the molten metal is returned into a melting furnace for final refining (for temperature and component adjustment) or is directly poured to obtain stainless steel ingot if the molten metal has a suitable pouring temperature and there is no need of adjusting the composition.

The process of this invention will be explained in detail below.

(1) First of all, a suitable amount of iron, steel scraps, ferro alloys and ores is charged as a raw material in a melting furnace, for instance, an electric furnace, together with slag-forming materials.

In this specification, iron refers to pig iron and iron sand; steel scrap refers to stainless steel scrap, and ordinary steel scrap; ferro alloys refer to ferronickel, ferrochrome, ferromolybdenum and molybdenum briquette; ore includes chromite, nickel oxide, iron ore and laterite. When charging, a suitable amount of the selected above materials is calculated so that the content of chrome may not be insufficient by oxygen blowing.

That is, the raw materials as well as the amounts to

be added must be selected to give sufficient sources for Fe, Ni, and Cr for obtaining desired chrome series or nickel-chrome series stainless steel. In this invention, a large amount of chromite, e.g., about 300–350 kg./ton of ingot can be used, which is one of the characteristics of the process of the present invention.

The raw materials charged in the melting furnace are then completely melted in the furnace. However, as the molten bath is to be subjected to an oxygen blowing in the next step of the process according to the present invention, a great part of the raw materials should be so far melted as to obtain a sufficient fluidity, by which the raw materials may be transferred to the shaking ladle.

(2) Thereafter, the above molten metal is transferred into the ladle and the ladle is moved eccentrically at a high rotation of 40–50 r.p.m. In this case, the ladle is not rotated around a vertical central axis but is moved eccentrically by submitting the ladle to draw a small circle to give an eccentricity of e.g. 90 mm. The value shown as the eccentricity is the radius in millimeters of a small circle drawn by the center of the ladle.

Thus, oxygen blowing is carried out while agitating the molten metal and hence the decarburization can be finished in a considerably short period of time.

It is also possible to put the remaining raw materials into the ladle before pouring the molten metal therein to melt them and simultaneously to carry out the decarburization by utilizing the heat generated when subsequently blowing oxygen into the ladle.

(3) Then, in order to reduce chrome oxide in the slag formed after oxygen blowing and to transfer the chrome into the molten steel, a suitable reducing agent such as, siliconchrome or ferrosilicon is added into the molten metal and the ladle is again moved eccentrically at a high speed to cause an extremely good agitation, so that the reducing reaction for chrome may be conducted effectively.

Thus, by rotating eccentrically the ladle after adding a calculated amount of siliconchrome or ferrosilicon, chrome oxide is reduced with silicon and the reaction is finished in 7–10 minutes. The ratio (by weight) of the amount of chromium transferred into the molten steel resulting from the reduction of Cr_2O_3 contained in the slag by means of a reducing agent to the amount of chromium as Cr_2O_3 contained in the slag is above 90%.

(4) After end of the reducing reaction, the formed slag is removed and the remaining molten steel is agitated again in the shaking ladle which is moved eccentrically with the addition of a desulfurizing agent. The desulfurizing agent is dispersed uniformly in the molten steel and the desulfurization is conducted with a good rate in a short period of time. The ratio of the amount of sulfur liberated by the desulfurization treatment of the invention to the amount of sulfur contained in the molten steel is about 60–80%.

If the temperature of the molten bath is still high after the reduction reaction has ended, it is transferred again in the electric furnace after having carried out the desulfurization in the ladle in order to perform only the adjustment of the composition and temperature of the bath in the electric furnace. But, if the temperature of the molten bath is low after the reduction reaction has ended, it should be immediately transferred into the electric furnace to perform not only the adjustment of the composition and temperature of the bath, but also the removal of slag and desulfurization in the electric furnace. Further, it is also possible to exchange the order of the steps by carrying out the desulfurization immediately after the melting step, antecedently to the oxidation and reduction steps. That is, the same result can be obtained by the process wherein a desulfurizing agent is added into the molten metal in the ladle after having removed the slag, said molten metal being obtained by melting the raw materials together with a suitable slag-forming agent in the melting furnace and then transferred into the ladle, or by the process wherein a desulfurizing agent is added in the molten bath in the melting furnace after having removed the slag therefrom. Therefore, such a modification in the order of the steps is also included in this invention.

As mentioned above, by the process of this invention, the content of Cr_2O_3 in the slag shows a very low value at a basicity of 1.5 to 2.0. But, even at such a low basicity of slag the reduction of chrome oxide can be carried out in an extremely short period of time and with a high percentage of transfer of chromium into the melt. Therefore, in the process of this invention, a considerable amount of a chromite can be used, by which the reduction in the costs for main and subsidiary raw materials and in the production costs can be realized. Further, as a reducing agent and lime may be used only in a small amount, the formation of slag is kept in a less amount and the fluidity of slag is bettered, whereby the period for producing steel may be shortened and the production efficiency may be improved.

Moreover, the desulfurization performed by the process of this invention shows always a stable and good result and gives no unstable desulfurizing reaction as usual when such desulfurizing agents are used in conventional processes, such as, a soda ash ladle pouring process or a carbide- or lime-blowing process. Also, in the method of the present invention there are no such shortcomings of various kinds encountered in carrying out the conventional processes, such as troubles in handling apparatus, marked reduction in the temperature of molten metal and long period of time required for the desulfurization.

In other words, by the process of the present invention, the decarburization, the reduction of chrome oxide and the desulfurization can be carried out effectively in an extremely short time, and consequently stainless steel having a desired composition can be produced with a much reduced cost, accompanied with a good recovery of chromium from the slag and a high percentage of sulfur removal.

The invention will be explained further with reference to the following examples.

EXAMPLE 1

In a 5 ton Hérout-type electric furnace were charged stainless steel scraps (13 Cr), ordinary steel scraps, and high-carbon ferrochrome (Cr 63.72%) together with slag-forming materials such as lime, fluorite, and river sand. After melting, the molten metal was poured into a shaking ladle and was submitted to oxygen blowing (the oxygen being at a pressure of 4.2 kg./cm.^{2}, and in an amount of 668 N m.^{3}/hr., the height of a lance above the level of the slag being 300 mm.) for 10 minutes while moving eccentrically the ladle at 10 r.p.m. After the oxygen blowing, 200 kg. of SiCr (Si 44.48% and Cr 36.42%) and 45 kg. of FeSi (Si 76.19%) were added and the ladle was moved eccentrically for 7 minutes at 50 r.p.m. Immediately after the reduction was finished, the slag was removed and the desulfurization was carried out by adding 5 kg./ton of soda ash while moving the ladle for 10 minutes at 50 r.p.m. After the desulfurization was finished, the formed molten metal was transferred into the electric furnace and after adjusting the composition and the temperature of the metal, the molten steel was tapped.

Amount charged in the electric furnace

	Kilograms
Stainless steel scraps	1,750
Ordinary steel scraps	2,715
High-C ferrochrome	560
Lime	100
Fluorite	20
River sand	100

In the shaking ladle
Added amount of—

	Kilograms
SiCr	200
FeSi	45
Soda ash	25

Besides the above materials, low-carbon ferrochrome, low-carbon ferromanganese and a suitable amount of a slag-forming agent were used for adjusting the composition of the molten steel.

Amount of produced steel, 5,200 kg.

Ladle analysis: C, 0.07; Si, 0.45; Mn, 0.35; P, 0.037; S, 0.005; Cr, 17.66.

Slag composition (end of recovery): Total Fe, 2.05; SiO_2, 30.66; CaO, 16.16; MgO, 41.82; Cr_2O_3, 4.20.

Basicity ($MgO\%+CaO\%/SiO_2$)	1.90
Chromium recovered ——percent——	95
Sulfur removed ——do——	80

EXAMPLE 2

Stainless steel scraps (13 Cr), ordinary steel scraps, chromite (Cr_2O_3, 49.34%; Fe_2O_3, 21.17%, SiO_2, 2.76%; MgO, 15.14%; Al_2O_3, 8.9%; P, 0.003%; S, 0.084%; water 2.60% and Mn trace) and high-carbon ferrochrome (Cr 63.72%) were charged into an electric furnace together with coke breeze, lime, fluorite, and river sand, and they were melted and then poured into the shaking ladle, wherein oxygen blowing was carried out for 10 minutes (the oxygen being at a pressure of 5 kg./cm.^{2}, and in an amount of 738 N m.^{3}/hr., and the height above the slag level being 400 mm.). After oxygen blowing was finished, 440 kg. of SiCr (Si 44.48% and Cr 36.42%) was added into the molten metal and the ladle was moved eccentrically at 50 r.p.m. for 7 minutes. After the reduction was finished, the molten metal was transferred into the electric furnace, wherein the slag was removed and the temperature and the composition were adjusted, and the molten steel was tapped.

Amount charged in the electric furnace

	Kilograms
Stainless steel scraps	1,780
Ordinary steel scraps	2,640
High-C ferrochrome	580
Chromite	500
Coke breeze	30
Lime	150
Fluorite	40
River sand	300

Amount charged in the shaking ladle

	Kilograms
Added amount of SiCr	440

Besides the above materials, lime was used as a desulfurizing agent in the electric furnace after removing the slag and a suitable amount of low-C FeCr and low-C FeMn was used for adjusting the composition of the molten metal.

Amount of produced steel, 5,630 kg.

Ladle analysis: C, 0.10; Si, 0.56; Mn, 0.32; P, 0.038; S, 0.016; Cr, 17.41.

Slag composition (end of recovery): Total Fe, 1.23; SiO_2, 36.92; CaO, 15.28; MgO, 40.02; Cr_2O_3, 1.49; Al_2O_3, 2.68.

Basicity ($MgO\%+CaO\%/SiO_2\%$)	1.50
Chromium recovered ——percent——	95

It will be understood that the above specific explanation for this invention is illustrative only and that various modifications may be made without departing from the spirit and the scope of this invention claimed as follows.

What is claimed is:

1. A method of producing chrome series and nickel-chrome series stainless steels, comprising the steps of charging a melting furnace with a charge which at least includes stainless scraps, ordinary steel scraps and high carbon ferrochrome together with slag-forming agent in an amount so as to form a slag of high Cr_2O_3 content, completely melting the charge in the melting furnace, pouring the melt from the melting furnace into a shaking ladle, blowing oxygen into the melt to effect decarburization of the melt while agitating the melt in the shaking ladle, adding a reducing agent to the melt to reduce the Cr_2O_3 while agitating the melt in the shaking ladle, carrying out the reduction of the Cr_2O_3 contained in the slag to metallic chromium which is transferred into the molten steel until the resultant slag contains a maximum 8.5% of Cr_2O_3, said slag forming agent being charged in amount so as to result in a slag of a basicity of 0.9 to 2.0 on the melt at the end of reduction, and then removing the resultant slag from the melt.

2. The process according to claim 1 wherein the slag is removed after carrying out the reduction of chrome oxide in the ladle, the molten steel is agitated with the addition of a desulfurizing agent in an amount sufficient to carry out the desulfurization, and then the molten steel is tapped.

3. The process according to claim 1 wherein the reduction of chrome oxide is carried out in the ladle, the molten metal is returned into the melting furnace again wherein the desulfurizing reaction is carried out after removing the slag, and then the molten steel is tapped.

4. The process according to claim 1 wherein the reduction of chrome oxide is carried out in the shaking ladle followed by removing the slag, the molten steel is agitated after the addition of a desulfurizing agent, the molten steel is returned, after carrying out the desulfurization, into the melting furnace to adjust the temperature and the composition of the molten steel, and then the molten steel having a desired quality is tapped.

5. The process according to claim 1 wherein said charge comprises an amount of stainless steel scraps, ordinary steel scraps, high-C ferrochrome, and a chromite sufficient to give a desired amount of chrome to the molten steel, and said charge is charged in the melting furnace together with the slag-forming materials for adjusting the basicity to 0.9–2.0, and the mixture is melted in the furnace.

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