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[54] **METHOD OF PREPARING VACUUM-TREATED STEEL FOR MAKING INGOTS FOR FORGING**

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[57] **ABSTRACT**

A process for preparing a vacuum-treated steel for making forging ingots of great weight and high purity as required for rotors, turbine shafts, inductor shafts and other, usually annealed, large steel parts, which comprises:

1. Subjecting molten raw iron to blowing with oxygen and at least one slagging operation to form a foremetal containing 0.10 to 1 percent by weight carbon and less than 0.010 percent by weight phosphorus, at temperatures not exceeding 1650°C;
2. Separating said foremetal formed in step 1 from slag and directing an oxygen down-blast onto the surface of said molten metal while maintaining it molten to raise the temperature thereof to a temperature greater than 1700°C;
3. Simultaneous to said oxygen down-blast, injecting gas into said molten metal through at least one laterally disposed gas inlet terminating in a nozzle, the amount of gas being sufficient only to keep the nozzle free of said metal;
4. After said molten metal has reached a temperature in excess of 1700°C, discontinuing said oxygen down-blast;
5. Introducing an alloying component to said foremetal and increasing the injection of oxygen and inert gas to said molten metal;
6. Adding reducing agent to said molten metal;
7. Adding a desulfurizing agent to said molten metal to reduce sulfur content to less than 0.010 weight percent and introducing to said molten metal inert gas; and
8. Subjecting said molten metal to a vacuum treatment and teeming said molten metal.

8 Claims, No Drawings

METHOD OF PREPARING VACUUM-TREATED STEEL FOR MAKING INGOTS FOR FORGING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to a method of preparing vacuum-treated steel for making forging ingots of great weight and high purity as required for rotors, turbine shafts, inductor shafts, and other, usually annealed, large steel parts. In particular, the present invention is directed to preparing relatively pure, vacuum-treated steel having a phosphorus content less than 0.010 weight percent, a carbon content of between 0.10 and 1 weight percent and a sulfur content less than 0.010 weight percent. In particular, the present invention is directed to steels in which the sulfur and phosphorus content is kept at a minimum.

2. Discussion of the Prior Art

Steel for the preparation of such ingots, especially in the case of steels whose weight exceeds 30 tons, are to have as low a phosphorus and sulfur content as possible so as to forestall, insofar as possible, the phosphorus and sulfur segregations which inevitably occur while the cast ingot is solidifying. If such steels with prescribed low phosphorus and sulfur contents are melted in the electric furnace, extensive slagging work is required in the furnace (e.g., the so-called refining time for the removal of sulfur), which, on the one hand, considerably increases the total batch time and reduces the economy of operation of the furnace, and, on the other hand, also severely attacks the refractory lining of the furnace due to the very high temperatures, exceeding 1700°C, which must be utilized owing to the vacuum treatment that follows.

On account of this high temperature, a post-desulfurization (in the form of a Perrinization, for example) cannot be performed in the ladle during the tapping operation on account of the heat losses involved. Additionally, to achieve the lowest possible final sulfur content, expensive lowsulfur types of scrap steel have to be selected for use in this process. The same difficulties are encountered with respect to low phosphorus and sulfur contents when such steels are made in the openhearth furnace.

The production of these steels by the Linz-Donowitz process utilizing raw iron of normal composition is possible. However, the phosphorus content cannot be maintained reliably low. Since after the addition of the principal alloying agents, chromium and nickel, in the form of ferrous alloys, temperatures above 1700°C must prevail before the melt is tapped, in order to compensate for the temperature losses which occur during the subsequent vacuum treatment, the phosphorus contents of the steel are very high at these high temperatures on account of the well known phosphorus equilibrium. The phosphorus content can amount often to more than 0.040 weight percent phosphorus which is incompatible with the production of high-quality ingots for forging.

It has, therefore, become desirable to provide a process for the preparation of high-quality ingots useful for forging from normal composition raw iron stock which steel have a phosphorus content well below 0.040 weight percent phosphorus. In particular, it has become desirable to provide a steel whose phosphorus content is below 0.010 weight percent phosphorus. Particularly desirable is such a low phosphorus steel having a sulfur content also below 0.010 weight percent sulfur.

SUMMARY OF THE INVENTION

The long-felt desideratum in the art is answered by a process, in accordance with the invention, for preparing a vacuum-treated steel for making forging ingots of great weight and high purity as required for rotors, turbine shafts, inductor shafts, and other, usually annealed, large steel parts, which process comprises:

1. Subjecting molten pig iron to blowing with oxygen and at least one slagging operation to form a foremetal containing 0.10 to 1 percent by weight carbon and less than 0.010 weight percent phosphorus at temperatures not exceeding 1650°C.

2. Separating said foremetal formed in step 1 form slag and directing an oxygen down-blast onto the surface of said molten metal while maintaining it molten to raise the temperature thereof to a temperature of greater than 1,700°C;

3. Simultaneous to said oxygen down-blast, injecting a gas mixture of oxygen and inert gas into said molten metal through at least one laterally disposed gas inlet terminating in a nozzle, the amount of said gas mixture being sufficient only to keep the nozzle free of said metal;

4. After said molten metal has reached a temperature in excess of 1700°C, discontinuing said oxygen down-blast;

5. Introducing an alloying component to said foremetal and increasing the injection of oxygen and inert gas to said molten metal;

6. Adding reducing agent to said molten metal;

7. Adding a desulfurizing agent to said molten metal to reduce the sulfur content to less than 0.010 weight percent and introducing to said molten metal inert gas; and

8. Subjecting said molten metal to a vacuum treatment and teeming said molten metal.

The present invention has as its object obtaining relatively pure steel whose sulfur and phosphorus contents are both less than 0.010 weight percent for each component. This is done by selecting a usual pig iron stock whose composition can fall within the following range:

TABLE 1

COMPOSITION OF PIG IRON

Components	Weight Percent Broad			Preferred		
carbon	3.5	to	4.5	3.8	to	4.3
silicon	0	to	1.5	0.8	to	1.2
manganese	0.5	to	1.5	0.8	to	1.2
phosphorus	0.1	to	2.0	0.10	to	0.15
sulphur	0.010	to	0.060	0.010	to	0.030

The pig iron is heated preferably in a mixer to a temperature between 1150° and 1300°C. It is subjected to blowing with oxygen in a LD-vessel or the like. The oxygen contacts the surface of the molten raw iron at a lance pressure of between 9 and 12 atm. Generally between 45 and 60 normal liters gas per kilogram of metal contact the raw iron. At the end of this oxygen blowing operation the temperature of the foremetal should not exceed 1650°C. In the slagging operation a slag composition falling within Table 2 is desirably utilized, although other slag compositions can also be employed:

TABLE 2

SLAG COMPOSITION

Components	Weight Percent Broad			Preferred		
CaO	46.0	to	65.0	50.0	to	60.0
SiO_2	6.0	to	17.0	8.0	to	10.0
MnO	8.0	to	12.0	8.0	to	10.0
Fe in slag	3.0	to	10.0	4.0	to	5.0
P_2O_5	1.3	to	2.0	—	—	—
MgO	1.0	to	3.0	about 2.0		

After the carbon and phosphorus are adjusted, there can be added to the foremetal so prepared, of desired, an alloying element such as nickel and/or molybdenum. If nickel is added, it is added in an amount of between 17 and 40 grams nickel per kilogram of foremetal. If molybdenum is added, it is added in an amount between 4 and 6 grams per kilogram of foremetal. The combined amount of alloying elements added at this stage is between 21 and 46 grams per kilogram of foremetal. The alloying elements added at this stage are those which are inoxidizable under the prevailing conditions and include alloying elements other than nickel and molybdenum.

After addition of any alloying elements, if desired, or after the foremetal has obtained the desired carbon and phosphorus levels, it is separated from the slag and transferred slag-free to a converter-like vessel which is provided with two different blowing systems. In the converter-like vessel, there are nozzles which pass laterally through the converter wall close to the bottom, say within about 0.15 to 0.45 meters from the bottom of the vessel. These nozzles are suitable for the injection of controllable mixtures of oxygen and inert gas. Vessels which can be used for this purpose which are provided with such nozzles are known and described, for example, in the Union Carbide Magazine, 33, June 1972, pages 40–45.

The vessel is furthermore provided with an oxygen down-blast system. When the hot foremetal is passed into the converter-like vessel, there can be added to the metal heat carriers such as carbon and ferrosilicate. The temperature of the foremetal which has been transferred slag-free to the converter-like vessel is raised by virtue of the oxygen down-blast to a temperature of more than 1700°C. During the oxygen down-blast, a gas mixture of oxygen with inert gas is simultaneously injected through the lateral nozzles but only to a sufficient extent to keep the nozzles free of the foremetal. During the oxygen and oxygen/inert gas mixture treatment of the foremetal in the converter-like vessel, between 20 and 60 normal liters oxygen per kilogram of metal pass from the down-blast gas exit. Generally speaking, the ratio of oxygen in the down-blast to gas injected laterally is between 5 and 20, preferably between 10 and 12 on a volume basis. Similarly, the pressure of the gas introduced through the laterally disposed nozzles is between 3 and 7 atmospheres. Here, the pressure is only that amount which is required to keep the nozzles free of the foremetal. In this lateral injection of gas the volume ratio of oxygen to onert gas is from 1.5 to 3.0.

Silicon dioxide formed by the combustion of silicon is preferably bound by lime (CaO). When the melt has

reached the required high temperature of about 1750°C, the oxygen down-blast is shut off and alloying components are added to the molten foremetal on the basis of a sampling. Preferable alloying components used at this stage are those which are easily oxidizable and can contain elements such as chromium, titanium, vanadium, tantalum, niobium, and the like required in the final analysis. Although the alloying is done on the basis of the assay of the foremetal, between 20 and 30 grams alloying element per kilogram of foremetal are generally introduced depending on the percents by weight of the alloying elements.

During the addition of the alloying elements, the injection of the mixture of oxygen and inert gas is intensified as the alloying elements are mixed with the components of the metal bath. Generally speaking, between 8 and 15 normal liters of gas mixture per kilogram of metal are added at this stage. Similarly, the oxygen to inert gas ratio on a volume basis is between 1.5 and 3.0, preferably 2.25.

Thereafter, reducing agents such as aluminium, ferrosilicon and the like are also added to the molten metal. These reducing agents are added in amounts between 0.1 and 1.5 grams reducing agent per kilogram of molten metal. Naturally, the quantity of the reducing agent will depend upon the components of the foremetal.

A desulfurizing agent is introduced into the molten metal bath, and then inert gas alone is blown in. Suitable desulfurizing agents for this purpose include lime, especially in powder form or a mixture of about 60 percent by weight CaO, 5 percent CaF_2, 15 percent CaC_2 and 20 percent CaSi. The desulfurizing agent is added to the metal in an amount between 5 and 20 grams desulfurizing agent per kilogram of foremetal. During addition of the desulfurizing agent, only an inert gas is blown into the molten metal bath in the converter-like vessel. This inert gas enters the bath through the nozzles disposed laterally in the wall of the vessel. Treatment of the molten metal bath by desulfurizing agent and inert gas is continued until the sulfur content of the metal is less than 0.010 weight percent, preferably less than 0.005 weight percent.

The steel is subjected to a vacuum treatment once it has attained a sulfur content of less than 0.010 weight percent. The vacuum treatment can be any one of a number of known conventional vacuum treatment methods, preferably, the falling stream degassing process. The vacuum treatment is generally carried out using pressures of between 0.1 and 3.0 Torr and temperatures between 1650° and 1600°C. Following the vacuum treatment, the molten metal is teemed, the teeming temperature (measured in the teeming stream) being between 1540° and 1550°C.

DISCUSSION OF PREFERRED EMBODIMENTS

The present invention is particularly useful for preparing highly pure steel stocks from raw iron whose phosphorus content ranges from 0.10 to 2.0 weight percent phosphorus. Such a composition can contain up to 4.3 weight percent carbon, up to 1.5 weight percent silicon, up to 1.5 weight percent manganese, 0.020 to 0.60 weight percent sulfur, the balance being iron with the usual impurities.

Steels made by the above-described process can generally contain 0.05 to 0.50 weight percent carbon, 0 to 2.8 weight percent chromium, 0 to 4.0 weight percent nickel, 0 to 1.5 weight percent molybdenum and 0 to 0.5 weight percent silicon. Preferred steels made by the process of the invention have chromium present in an amount between 0.5 and 2.8 weight percent. A steel having a nickel content of 0.5 to 4.0 weight percent is particularly preferred.

In the operation of the present invention, numerous gases can be used in the oxygen-inert gas mixture. Preferably, the inert gas is argon or nitrogen, although virtually all inert gases are useful.

In order to more fully illustrate the nature of the invention and the manner of practicing the same, the following example is presented:

EXAMPLE

(60 metric ton ingot, quality NiCrMoV/So)

In a Linz-Donowitz crucible, 70 tons of raw iron of the following analysis were blown: 4.3% C; 0.91% Si; 0.65% Mn; 0.140% P; 0.039% S; 0.20% Cr, with the addition of 65kg/t of CaO, 17 kg/t of fluorspar, 10 kg/t of ore, 21 kg/t of nickel and 5 kg/t of ferromolybdenum, to form a foremetal with the following values:

0.5% C; less than 0.01% Si; 0.43% Mn; 0.007% P; 0.024% S; 2.7% Ni; 0.05% Cr; 0.39% Mo, final temperature 1645°C.

This foremetal was then tapped without slag from the Linz-Donawitz crucible and transferred to the second, converter-like vessel.

Starting at 1580°C, this foremetal, with the addition of coke and ferrosilicon as heat carriers plus lime CaO, was then raised by oxygen blowing to 1750°C. Thereafter, the following analysis was obtained:

0.38% C; 0.31% Si; 0.42% Mn; 2.07% Ni; 0.05% Cr; 0.009% P; 0.019% S; 0.38% Mo.

Then, 23 kg/t of 75 percent ferrochromium with a carbon content of 6 percent was added while a mixture of oxygen and argon (ratio 2:1) was blown in, and then, after the addition of ferrosilicon and aluminium, the bath and slag were intensively blown with argon alone. After the addition of 1.5 kg/t of ferrovanadium, the analysis, prior to the tapping of the steel at a temperature of 1700°C, was:

0.29% C; 0.29% Si; 0.37% Mn; 0.008% P; 0.004% S; 2.03% Ni; 1.53% Cr; 0.36% Mo; 0.12% Va; 0.004% Al.

The steel was vacuum treated in a ladle-to-ladle-pouring-stream-degassing process. Temperature before degassing: 1650°C; temperature after degassing: 1580°C, measured in each case at the top of the ladle. The steel was poured at pouring stream temperatures of 1540° to 1550°C to form a 60-ton bloom by filling the ingot mold from the top. The temperature would also have permitted to fill the ingot mold by pouring the steel through the bottom via runner bricks.

Other methods for vacuum treatment of the steel in accordance with step 8 include:

All vacuum processes for treating molten steel before or during pouring are applicable well known in the art, especially stream degassing (ladle-to-ladle or ladle-to-mold) or ladle-degassing or circulating vacuum degassing process or the so-called DH-process (Dortmund-Hoerde).

What is claimed is:

1. A process for preparing a vacuum-treated steel for making forging ingots of great weight and high purity as required for rotors, turbine shafts, inductor shafts, and other, usually annealed, large steel parts, which comprises:

A. Subjecting molten pig iron in a vessel to blowing with oxygen and and at least one slag which reduces the phosphorus content thereof to form a foremetal containing 0.10 to 1 weight percent carbon and less than 0.010 weight percent phosphorus, the foremetal having a temperature at the end of said blowing not exceeding 1650°C;

B. Separating said foremetal formed from step A from said slag and directing an oxygen down-blast onto the surface of said molten metal while maintaining it molten to raise the temperature thereof to a temperature of greater than 1700°C;

C. Simultaneous to said oxygen down-blast, injecting a gas mixture of oxygen and inert gas into said molten metal through at least one laterally disposed gas inlet terminating in a nozzle, the amount of gas being sufficient only to keep the nozzle free of said metal;

D. After said molten metal has reached a temperature in excess of 1700°C, discontinuing said oxygen down-blast;

E. Introducing an alloying component to said foremetal and increasing the injection of oxygen and inert gas to said molten metal;

F. Thereafter adding reducing agent to said molten metal;

G. Adding a sufficient amount of a desulfurizing agent to said molten metal to reduce the sulfur content to less than 0.010 weight percent and introducing to said molten metal an inert gas; and

H. Subjecting said molten metal to at least one vacuum treatment and teeming said molten metal.

2. A process according to claim **1** wherein said pig iron has a content of up to 4.3 weight percent carbon, up to 1.5 weight percent silicon, up to 1.5 weight percent manganese, 0.10 to 2.0 weight percent phosphorus, 0.040 to 0.060 weight percent sulfur, the remainder iron and the usual impurities.

3. A method according to claim **1** wherein subsequent to step A and prior to directing said oxygen down-blast into the surface of said molten metal, there is added to said molten metal an alloying element which is non-oxidizable under the prevailing conditions.

4. A method according to claim **3** wherein said alloying element is nickel or molybdenum.

5. A method according to claim **1** wherein subsequent to the raising of the temperature of said foremetal to temperature greater than 1700°C, there is added to said foremetal an oxidizable alloying agent.

6. A method according to claim **5** wherein said alloying agent is one having an element selected from the group consisting of chromium, manganese, titanium, vanadium, tantalum and niobium.

7. A method according to claim **6** wherein there is prepared a steel having a carbon content of 0.05 to 0.50 weight percent, a chromium content of 0 to 2.8 weight percent, a nickel content of 0 to 4 weight percent, a molybdenum content of 0 to 1.5 weight percent, a silicon content of 0 to 0.5 weight percent with the remainder of said composition being iron with the usual impurities.

8. A method according to claim **7** wherein the steel contains 0.5 to 2.8 weight percent chromium and 0.5 to 4 percent by weight nickel.

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