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2,705,196

PROCESS FOR DE-OXIDIZING A MOLTEN METAL

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No Drawing. Application February 20, 1952,
Serial No. 272,687

2 Claims. (Cl. 75—58)

This invention relates to a new and improved process for the de-oxidation of molten ferrous metals, such as iron and steel and ferrous alloys.

It has been known that de-oxidation of molten iron and steel is carried out, in general, in several steps. First, the molten steel is treated, mostly in the furnace, with materials having only moderately high affinity to oxygen, for example with ferro-manganese or with ferro-manganese+ferro-silicon, silicon-manganese or with similar alloys. Upon addition of these alloys, liquid and relatively quickly ascending oxides are formed and these oxides remove the bulk of oxygen from the molten steel. For the sake of brevity, this de-oxidation step with metallic materials having only moderately high affinity to oxygen, is denoted hereinafter "pre-de-oxidation." In a subsequent phase, i. e. during the step of pouring into the ladle, or in some cases into the mold or casting form, de-oxidizing means are used, which contain elements having a high affinity to oxygen, such as aluminum, calcium, titanium, magnesium, cerium and other earth metals, alkalimetals or their alloys with each other or with iron.

It has now been found that these de-oxidizing elements having a high affinity for oxygen, react not only with free oxygen present in the molten steel, but also with particles or drops of molten oxides which have been formed during pre-de-oxidation and have not risen yet to the surface of the molten steel. By the reaction of said elements having high affinity to oxygen with said molten oxides, undesired, mostly solid inclusions are formed, which cannot be removed from the steel. For this reason, the desired effect of pre-de-oxidation is mostly either not obtained, or only to a rather unsatisfactory extent. This disadvantage occurs to a still higher extent if not only a de-oxidizing effect, but also alloying of the steel with the above mentioned elements is desired. The situation is similar in the de-oxidation of iron (including cast-iron).

It has now been found that in the de-oxidation of molten steel, the above mentioned disadvantages can be avoided by bringing about reaction with oxygen of said elements having a high affinity to oxygen, in the molten mass at a time when the oxide particles formed during pre-de-oxidation of the steel, have already risen in and have been removed from the molten steel. This condition is attained by allowing the molten steel to stand in the melting vessel for a sufficient period of time after pre-de-oxidation. However, such procedure would lead to considerable difficulties caused by the fact that the metallic materials used in the second phase of de-oxidation have a relatively low specific gravity and, therefore, cannot be satisfactorily distributed in the molten steel of high specific gravity. This is obviously the reason why up to date these de-oxidizing metallic materials have been added to the molten steel during its pouring into the ladle or to the steel flowing into the casting mold.

It has been tried in some cases, to add said de-oxidizing metallic materials to the molten steel after its introduction into the mold. This procedure did not have the desired effect, because, during its introduction into the mold, the pre-de-oxidized molten steel absorbs again oxygen. With the excess of the pre-de-oxidizing metals present in the molten steel, this oxygen forms fluid oxide particles or drops, which then react with the de-oxidizing metallic materials having high affinity to oxygen, and

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cause the occurrence of the above described harmful inclusions.

If, however, in contrast to the above procedure, steel, which has been treated in the ladle with a sufficient amount of metallic elements having high affinity for oxygen, is introduced into the mold, oxide films are formed during casting, which prevent additional absorption of oxygen by the molten material.

The main object of the present invention is a process for bringing about distribution and reaction of de-oxidizing means having high affinity to oxygen, in the pre-de-oxidized molten steel in the ladle, at the desired moment, i. e. after separation from the molten steel of the fluid oxide particles formed during pre-de-oxidation.

According to the present invention, this object is attained by (A) allowing the pre-de-oxidized molten steel to stand for a sufficient period of time and (B) introducing the de-oxidizing metals or alloys of high affinity for oxygen, in a condition protected from premature oxidation into, and distributing them in, the molten steel.

According to the invention, protection of said de-oxidizing metallic materials is effected by placing these materials in high-melting protective containers of iron or other suitable metals and introducing them in these containers into desired portions of the molten steel bath. The protective containers will melt in the steel bath, and after their melting the de-oxidizing metals will react at the desired locations in the molten steel. Said containers containing the de-oxidizing materials can be introduced into the molten steel by means of suitable instruments, for example bars, to the end of which the containers are welded, by hand or suitable mechanical devices.

The material, dimensions, design and wall thickness of the container or wrapping for the de-oxidizing agents can be adjusted to the conditions of the individual cases. A container of small wall-thickness or having a relatively low melting point, is, for example, used if quick action of the de-oxidizing agent is desired, while higher wall-thickness and/or container materials of higher melting point are applied if slower action is of advantage. The container may consist of iron tubes having any desired shape or profile and produced in any suitable manner and the de-oxidizing agent can be filled into the container by suction, pouring, stamping, or the like. The de-oxidizing metals may have rolled profiles.

The invention results in essential savings in de-oxidizing metals. Apart from this, its primary advantage consists in the production of steel which is free from included oxides or the like and in the possibility of an exact dosage of the de-oxidizing means, owing to safe control or elimination of waste by burning. A safe and exact dosage is of particular importance for example in cases in which a de-oxidizing metal, which has a high affinity also to another ingredient of iron, e. g. nitrogen, must be used in such amount that, in addition to oxygen, it combines also with nitrogen, without leaving an excess of the de-oxidizing agent as an alloyed component in the steel.

The introduction of metals and alloys having high affinity to oxygen, in accordance with the present invention can be used with advantage also by adding said metals or alloys in the furnace. The same is true in connection with the introduction of these materials in molds or casting forms. The invention can be applied to steel, iron, alloy steels, cast-iron, cast steel, and to the de-oxidation of non-ferrous metals.

The following examples illustrate some embodiments of the invention, to which the invention is not limited.

Example 1

50,000 kg. of molten steel in the ladle are pre-de-oxidized in conventional manner by introductions into the molten bath of 500 kg. of manganese and 200 kg. of silicon. The molten metal is now allowed to stand until the molten products formed from manganese and silicon ascend into the slag. This requires about 10 minutes. Further de-oxidation is now carried out by addition of 25 kg. of aluminum filled into a closed cylindrical iron container having a length of about 3 m., a diameter of about 2 inches and a uniform wall thickness of 5 mm.

The iron container protects the aluminum from premature oxidation, for example during its passage through the slag, so that it will react with the molten bath without any loss, after the container is molten. Melting of the container takes place in about 1-2 minutes and de-oxidation takes place subsequently.

It will be understood that the material, dimensions, and wall thickness of the container used for introducing the aluminum or the like into the molten bath, depend on when it is desired to start reaction between aluminum and the bath and on the amount of the de-oxidizing material applied. Furthermore, the container may have other than cylindrical shape and a non-uniform wall thickness, and may consist of metals other than iron, for example of nickel or of steel alloys. The container is preferably welded to a metallic rod or bar, by means of which it can be immersed in and placed at the desired depth of location in the metal bath. Two or more containers may also be applied to one bath. The above described de-oxidation with aluminum may be carried out also in the furnace.

Example 2

3,000 kg. of cast-iron containing 1 p. c. of manganese is pre-de-oxidized in a casting mold by adding thereto 25 kg. of silicon. The molten iron is allowed to stand for about 5-6 minutes, during which the molten oxide products formed, rise to the surface. In order to effect further de-oxidation 2.5 kg. of CaSi and 2.5 kg. of aluminum are now added to the molten metal in a closed cylindrical container consisting of cast iron, having a circular cross-section of 10 cm.², a length of 1 meter and a wall thickness of 3-5 mm. This container is welded to the end of an iron rod, by means of which the container is placed centrally near the bottom of the casting mold. The container melts in about 3 minutes, and reaction of the de-oxidizing materials with oxygen takes place then.

Example 3

In order to prepare a titanium-alloyed low-carbon steel free from oxide inclusions 10,000 kg. of molten steel are pre-de-oxidized in conventional manner by introduction into the molten bath of 60 kg. of manganese and 20 kg. of silicon. The molten metal is now allowed to stand until the molten products formed from manganese and silicon ascend into the slag. This requires about 10 minutes. Further de-oxidation is now carried out by addition of 10 kg. of aluminum filled into a closed cylindrical iron container having a diameter of about 1.5 inch and a wall thickness of 4 mm. and a length of 2 meters. It melts in about 1 minute. After this de-oxidation there are added 100 kg. of ferrotitanium also closed into two cylindrical iron containers having a length of 1.5 meters, a diameter of 8 cm., and a wall thickness of 2 mm. The melting of these containers takes place in about 5-10 minutes.

Example 4

5,000 kg. of molten chromium-alloyed steel are pre-de-oxidized in conventional manner by addition of 40

kg. of manganese and 10 kg. of silicon. This requires about 6 minutes. After this pre-de-oxidation 50 kg. of silicon containing 10 p. c. of aluminum are added. They are filled into two closed cylindrical iron containers having a length of 1.5 meters, a circular cross-section of 100 cm.² and a wall thickness of about 5 mm. The melting of the containers takes place in about 1-2 minutes.

It will be understood that the present invention is not limited to the above described specific metals, alloys, proportions, dimensions and other details specifically described, and can be carried out with various modifications without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. In a process for deoxidizing molten iron and ferrous alloys, in combination a sequence of the following steps: (a) pre-deoxidizing the molten metal with a deoxidizing agent having moderate affinity to oxygen; (b) allowing the molten metal resulting from (a) to stand until oxide products formed from said deoxidizing agent rise to the surface of the molten metal; (c) introducing below the surface of the molten metal a de-oxidizing agent of high affinity to oxygen in a container, consisting of a metal which is adapted to melt upon its introduction into the molten metal and has no objectionable effect on the treated ferrous metal, said steps (b) and (c) being carried out in the same vessel for the molten metal.

2. A process as claimed in claim 1, in which pre-de-oxidation is carried out with a material selected from the group consisting of ferro-manganese, ferro-silicon, silicon-manganese, and subsequent de-oxidation is carried out with a material selected from the group consisting of aluminum, calcium, titanium, magnesium, cerium, other earth alkali metals and alkali metals.

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