3,681,050
AGENT FOR DESULFURIZING MOLTEN
IRON
Kazufusa Ueki, Yamato-Takada, Japan, assignor to
Aikoh Co., Ltd., Tokyo, Japan
Filed Aug. 27, 1970, Ser. No. 67,356
Claims priority, application Japan, Mar. 27, 1970,
45/25,237
Int. Cl. C21c 7/02
U.S. Cl. 75--58

1. This invention relates to a desulfurizing agent for molten iron characterized by placing into a container a molding of a homogeneous composition which contains 53 to 58% by weight of sodium carbonate (soda ash), 5 to 18% by weight of portland cement, 3 to 10% by weight of sodium hydroxide and 0 to 4% by weight of water glass as solid component and a proper quantity of water.

2. The present invention relates to a desulfurizing agent for molten iron. It is already known to use a desulfurizing agent for molten iron such as, for example soda ash and the like. It is useful that a powdery, granular or lumpy desulfurizing agent is thrown into a ladle at the time of pouring a molten iron into it. However, the difference of specific gravity between the desulfurizing agent and the molten iron is so large that as soon as the desulfurizing agent is added into the ladle, it floats up to the surface of the molten iron and becomes a slag, its contact reaction with the molten iron is conducted only on the boundary surface, and substantially all the desulfurizing agent is wasted without reacting.

Further, particularly, in case of a powdery desulfurizing agent, at the time of a violent reaction with molten iron, it is lost by scattering, deteriorates the desulfurizing rate and at the same time obstructs the operation for treating the melt.

Therefore, in order to carry out an expected desulfurization, an excess amount of desulfurizing agent must be added in anticipation of its waste. However, the unreacting desulfurizing agent added in excess erodes the lining of the ladle, shortens the life of the lining and therefore such must be avoided. After all, the expected desulfurization cannot be conducted.

The present invention is to improve all the above mentioned defects, to provide a molded desulfurizing agent consisting of a specific composition characterized by a desulfurizing agent of one body constituted integrally with single sodium hydroxide arranged in the lower part or the lower interior of the molding and contained in a container to be placed in a ladle of molten iron in advance.

That is to say, the present invention is to provide a molding of a homogeneous composition containing sodium carbonate (soda ash), portland cement and sodium hydroxide and optionally water glass and a proper amount of water and having sodium hydroxide integrally arranged in the lower part or the lower interior of said molding so as to be contained in a container as a desulfurizing agent for molten iron.

The above mentioned molding is that of a homogeneous composition consisting of 53 to 85% by weight of sodium carbonate, 5 to 18% by weight of portland cement, 3 to 10% by weight of sodium hydroxide, 0 to 4% by weight of water glass as the solid component and a proper amount of water.

In the form of the molding, one or more holes vertical to the bottom or recesses can be made.

Further, if necessary, single sodium hydroxide may be put into the lower part or the lower interior of the molding. The amount of such sodium hydroxide to be used is 5 to 30% by weight of the molding.

The form of sodium hydroxide to be put into the lower part or the lower interior of the molding is powdery, granular, flaky, lumpy or solid after molding. Single sodium hydroxide is filled together with the molding directly or as contained in a bag in the above mentioned container.

The container containing a desulfurizing agent consisting of the above mentioned molding of homogeneous composition and single sodium hydroxide is made of formed steel, steel plate, hardboard, wooden plate, plastic and the like.

According to necessity, steel plate, damp-proof paper or the like may be placed between the above mentioned molding and single sodium hydroxide. According to necessity, the upper part of the above mentioned steel container filled with desulfurizing agent is covered with steel or any other kind of plate.

The above mentioned desulfurizing agent is placed in the ladle for molten iron in advance and molten iron is poured onto the desulfurizing agent in the ladle and the desulfurization is conducted.

Some embodiments of the form of the desulfurizing agent according to the present invention will be explained in the following with reference to the drawings in which:

FIG. 1 is a plane view showing an embodiment of the desulfurizing agent according to the present invention,
FIG. 2 is a vertically sectioned view of the same,
FIG. 3 is a plane view showing another embodiment of the desulfurizing agent according to the present invention,
FIG. 4 is a vertically sectioned view in the position of B--B in FIG. 3,
FIG. 5 is a vertically sectioned view of the bottom part of the ladle for molten iron in which a desulfurizing agent according to the present invention is placed in advance,
FIG. 6 is a plane view showing another embodiment of a desulfurizing agent according to the present invention,
FIG. 7 is a vertically sectioned view in the position of C--C in FIG. 6,
FIG. 8 is a plane view showing still another embodiment of a sulfuring agent according to the present invention,
FIG. 9 is a vertically sectioned view in the position of D--D in FIG. 8,
FIG. 10 is a plane view showing still another embodiment of a sulfurizing agent according to the present invention.

FIG. 11 is a vertically sectioned view in the position of E—F in FIG. 10.

FIG. 12 is a plane view showing another embodiment of a sulfurizing agent according to the present invention, and

FIG. 13 is a vertically sectioned view in the position of E—F in FIG. 12.

According to FIGS. 1 and 2, a molding 1 of one body consisting of sodium carbonate (soda ash), Portland cement, sodium hydroxide, water glass and water is contained in steel container 3.

According to FIGS. 3 and 4, 1 is the same molding having a homogeneous composition in FIGS. 1 and 2 and having a recess 5 in the center part.

According to FIG. 5, the steel container 3 which is filled with the molding 1 of desulfurizing agent having a homogeneous composition according to the present invention is placed on the bottom of the ladle 8 for molten iron in advance.

According to FIGS. 6 and 7, sodium hydroxide 2 is placed on the bottom of a steel container 3 and the molding 1 of desulfurizing agent having homogeneous composition as mentioned above is charged on the sodium hydroxide 2 to unite therewith.

According to FIGS. 8 and 9, the hole 5 vertical to the bottom is made in the center part of the molding 1 having a homogeneous composition as mentioned above and sodium hydroxide is placed under a steel plate or a damp-proof plate 6 in the steel container 3 so as to make it one body, and if necessary the upper part of the molding is covered with a steel plate or the like 4.

According to FIGS. 10 and 11, a certain amount of single sodium hydroxide is placed in the interior of the lower part of the molding 1 as mentioned above.

According to FIGS. 12 and 13, plural number of recesses 5 are made in the same molding 1 of homogeneous composition as mentioned above and single sodium hydroxide 2 contained in polyethylene bag 7 is placed in the lower part of the molding 1.

As soda ash used conventionally as a desulfurizing agent is powdery, it scatters at the time of addition, is high in the addition loss and floats to the surface of molten iron due to the light specific gravity. Accordingly, it desulfurizes only the surface of molten iron and nearly all of the amount of addition may be made a slag. In order to prevent the above mentioned defects, a molded soda ash made into lumps by pressing is used. However, as it is industrially impossible to make the bulk specific gravity of a molding to more than 2 only by a pressure molding of soda ash. Therefore, in order to improve these defects, there have been suggested such methods as close contact with molten iron and desulfurizing agent by using rotary furnace or by jetting the desulfurizing agent into molten iron by a gas flow or by shaking ladle, but the above method is undesirable on the standpoint of economy, as equipments are necessary for this method.

The desulfurizing agent according to the present invention has in specific composition and form as mentioned above and is therefore very suitable as a desulfurizing agent for molten iron. That is to say, the molding of desulfurizing agent which can give the fixed adding quantity by the use of one or two of the molding is placed in the ladle for molten iron in advance. Therefore, there is no necessity in the operation for continuously or discontinuously adding desulfurizing agent to the ladle as seen in the conventional method.

Therefore, there is no need of approaching the molten iron to the ladle during molten iron pouring where a smoke and dust are generated by the desulfurizing agent, and also this makes the operation easy and safe.

Differing from the conventional method which uses powdery or lumpy soda ash, as the desulfurizing agent according to the present invention can be molded to make it a fixed amount of addition by using less than several pieces, it does not float to the surface of molten iron, and improves the desulfurizing ratio. Nearly the same extent of desulfurization is obtained, even if the amount used decreases to ½ to ⅔ of soda ash. Therefore, as it is desirable on the economical standpoint and the desulfurizing efficiency is high, it is not necessary to add in excess and the erosion of the furnace wall is less than before, and thus the life of the furnace can be prolonged.

Further, in case a proper amount of sodium hydroxide is singly placed in the lower part or the lower interior of the molding, no violent reaction occurs at the early stage of molten iron which is poured into the ladle. Therefore, the operation is easy. The single sodium hydroxide gradually reacts after a considerable amount of molten iron is poured into the ladle, therefore the desulfurization is carried out effectively and a violent reaction state is inhibited.

The reaction mechanism of the desulfurization in molten iron is as follows:

\[
\text{FeS} + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{S} + \text{CO}_2 + \text{Fe} + \text{CO}
\]

\[
\text{Na}_2\text{S} + \text{CaO} \rightarrow \text{CaS} + \text{Na}_2\text{O}
\]

Portland cement produces stable CaS by the substituent reaction of CaO occupying the greater part of its composition with Na$_2$S produced by the above mentioned reaction Formula 1 prevents the resulfurization, and at the same time acts as a binder and is thus an appropriate material for the present invention.

Further, as shown in the drawings, in case the hole going to the bottom or recess is made in the molding, as the contact area of molten iron and desulfurizing agent becomes larger, the desulfurizing rate can be further increased.

The present invention is illustrated by the following examples.

**EXAMPLES 1 TO 4**

The desulfurizing agent having the composition and forms as shown in the following Table 1 according to the present invention were placed in a 60 tons ladle in advance and a molten iron were desulfurized with them.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Example</strong></td>
</tr>
<tr>
<td><strong>Materials</strong></td>
</tr>
<tr>
<td>Sodium carbonate (soda ash)</td>
</tr>
<tr>
<td>Portland cement</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Water glass (as solid component)</td>
</tr>
<tr>
<td>Water content</td>
</tr>
</tbody>
</table>

The results obtained were shown in the following Table 2 comparing with the results obtained by the use of soda ash.
The desulfurizing agent having the composition and forms as shown in the following Table 3 according to the present invention were placed in a 60 tons ladle in advance and a molten iron were desulfurized.

<table>
<thead>
<tr>
<th>Example</th>
<th>Material</th>
<th>Amount of molten iron (tons)</th>
<th>Kind of desulfurizing agent</th>
<th>Desulfurizing method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium carbonate (soda ash)</td>
<td>80</td>
<td>Placed in the ladle.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Sodium hydroxide</td>
<td>80</td>
<td>Placed in the ladle.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Water glass (as solid component)</td>
<td>80</td>
<td>Placed in the ladle.</td>
<td></td>
</tr>
</tbody>
</table>

1. Single placed sodium hydroxide (flame state) was placed in the lower part of a steel container and a molding of the above mentioned composition was placed on it. (The form shown in FIGS. 6 and 7.)
2. Single placed sodium hydroxide was placed in the lower part of a steel container and a molding of the above mentioned composition was placed on it. (The form shown in FIGS. 8 and 9.)
3. Flaked sodium hydroxide was placed in the lower interior of a steel container and the molding of the above mentioned composition was placed on it. (The form shown in FIGS. 10 and 11.)
4. Flaked sodium hydroxide contained in a polyethylene bag was placed in the lower interior of a steel container and the molding of the above mentioned composition having four recesses was placed on it. (The form shown in FIGS. 12 and 13.)

The results obtained were shown in the following Table 4 comparing with the results obtained by the use of soda ash.

<table>
<thead>
<tr>
<th>Example</th>
<th>Added amount of desulfurizing agent (per ton of molten iron)</th>
<th>9 percent before desulfurizing</th>
<th>9 percent after desulfurizing</th>
<th>Desulfurizing rate per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>130 kg X (2 kg.)</td>
<td>0.069</td>
<td>0.048</td>
<td>60.3</td>
</tr>
<tr>
<td>6</td>
<td>130 kg X (2 kg.)</td>
<td>0.069</td>
<td>0.048</td>
<td>60.3</td>
</tr>
<tr>
<td>7</td>
<td>130 kg X (2 kg.)</td>
<td>0.069</td>
<td>0.048</td>
<td>60.3</td>
</tr>
<tr>
<td>8</td>
<td>130 kg X (2 kg.)</td>
<td>0.069</td>
<td>0.048</td>
<td>60.3</td>
</tr>
</tbody>
</table>

As shown in Table 4, it was recognized that the desulfurizing agent according to the present invention is more remarkable in the desulfurizing effect than soda ash used conventionally and can increase the desulfurizing rate in any case.

In the present invention, sodium carbonate acts as the main part of the desulfurizing effect. However, its content is limited to be 53 to 85% by weight in order to further contain other effective components.

Portland cement of which CaO in the composition conducts replacement reaction with Na₂S produced by the above mentioned reaction Formula 1 and changes to a stable CaS to prevent any resulfurization and is used as a filler. Portland cement must be used in a range of 5% to 18% by weight. When less than 5% by weight of Portland cement is used there is a case of not being able to prevent the desulfurization as mentioned above and also the strength of the molding is weak and undesirable. Further it is not necessary to use more than 18% by weight of Portland cement.

Sodium hydroxide contained in the molding which gives the same result as soda ash must be used in a range of 5% to 10% by weight and must be used in the said range depending upon the quantity of soda ash in molten iron. Because soda ash is mixed with the other materials and is previously placed in the ladle in a form of molding according to the present invention and also contacts with molten iron at the initial period of the pouring. When more than 10% by weight of soda ash is used a violent
reaction is occurred so that it is not preferable. When less than 3% by weight of soda ash is used the aimed result cannot be obtained.

In case of using water solution containing about 5% by weight of solid component, as sodium hydroxide to be contained in the molding, it is more desirable as it uniformly disperses into the molding.

If necessary, water glass may be used in a quantity of 0 to 4% by weight of it as a solid component. When a comparatively large quantity of sodium carbonate (soda ash) and portland cement are used or when sodium hydroxide is in the form of powder, it is preferable to use 0 to 4% by weight of water glass as a solid component.

In the present invention, single sodium hydroxide to be placed as required together with the molding of the above-mentioned composition range comes into contact with molten iron, violently reacts, gives a stirring motion to molten iron and has a desulfurizing effect. It is appropriate to use such single sodium hydroxide in a range of 5 to 30% by weight based upon the weight of the above mentioned molding. In case of using it less than 5%, the above effect is not obtained and it is not necessary to use sodium hydroxide in the molding more than 30% by weight. Further, it should avoid to use more than 30% by weight of sodium hydroxide because the reaction of it with molten iron becomes only violent.

The present invention is to use known sodium carbonate as a desulfurizing agent for molten iron. However, this is a desulfurizing agent which is made to a molding having a specific composition by mixing other effective components to sodium carbonate and in which sodium hydroxide is placed and made into one body and which, can considerably increase the desulfurizing rate compared with the conventional desulfurizing agents as shown in the before-mentioned examples.

The modes of the practice of the present invention is as follows:

1. Desulfurizing agent for molten iron is a molding of a homogeneous composition containing sodium carbonate (soda ash), portland cement, sodium hydroxide, if necessary water glass and water and if any necessary sodium hydroxide being placed in the lower part or the lower interior of said molding so as to make it one body and the molding being placed in container.

2. The composition of said molding is a homogeneous one containing 53 to 85% by weight of sodium carbonate, 5 to 18% by weight of portland cement, 3 to 10% by weight of sodium hydroxide, 0 to 4% by weight of water glass as a solid component and a suitable quantity of water.

3. The shape of said molding is one which is if necessary provided with one or more of holes reaching the bottom or of recesses.

4. Single sodium hydroxide which is placed in the lower part or the lower interior of said molding may be if necessary used in a range of 5 to 30% by weight of said molding.

5. The shape of the single sodium hydroxide which is placed in the lower part or the lower interior of said molding is powdered, granular, flaky, humpy or solid after melting and the single sodium hydroxide is directly placed into the before-mentioned container or is charged into polyethylene bag, resin-treated paper bag or other container and then is placed into the container.

6. As the container which integrally contain the above-mentioned molding having a homogeneous composition and if necessary single sodium hydroxide, a container made of a formed steel, steel plate, hardboard, wooden plate or plastics and the like.

7. The upper part of said container may be if necessary covered with a plate.

8. The present invention consists of a desulfurizing agent having said composition and form and consists of such desulfurizing method for molten iron as the desulfurizing agent contained in a container and is placed in the ladle for molten iron which is poured to the ladle from the top of said agent.

What I claim is:

1. A desulfurizing agent for molten iron comprising a molding in a container, the molding consisting of a homogeneous composition comprising 53 to 58% by weight of sodium carbonate (soda ash), 5 to 18% by weight of portland cement, 3 to 10% by weight of sodium hydroxide and 0 to 4% by weight of water glass, and a proper quantity of water and united with 5 to 30% of sodium hydroxide based upon the weight of the molding at the lower interior of the molding and with the molding being providing with at least one recess.

References Cited

UNITED STATES PATENTS
2,117,348 5/1938 Muskat 75—58 X
2,462,871 3/1949 Kinsel 75—58 X
2,550,735 5/1951 Tour 75—58 X
3,051,564 8/1962 Drenning 75—58 X

L. DEWAYNE RUTLEDGE, Primary Examiner
J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

75—53