

[54] **METHOD FOR ADDING A GRANULAR OR POWDERED REACTION COMPONENT TO A MOLTEN METAL, AS WELL AS AN IMPROVED GRANULAR OR POWDERED REACTION COMPONENT FOR CARRYING OUT A CORRECTIVE REACTION ON A MOLTEN METAL**

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[58] **Field of Search**..... **75/53-60, 93, 75/3**

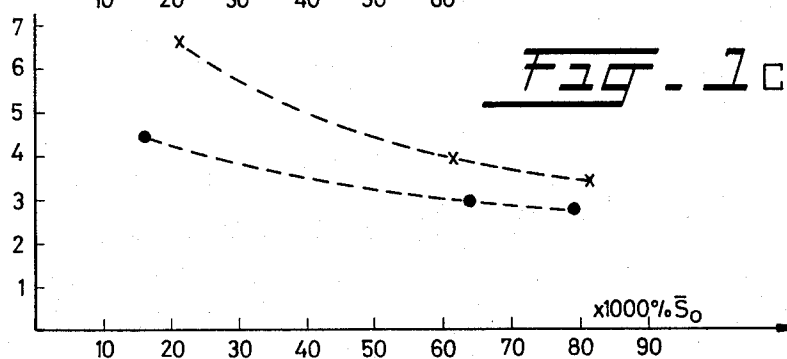
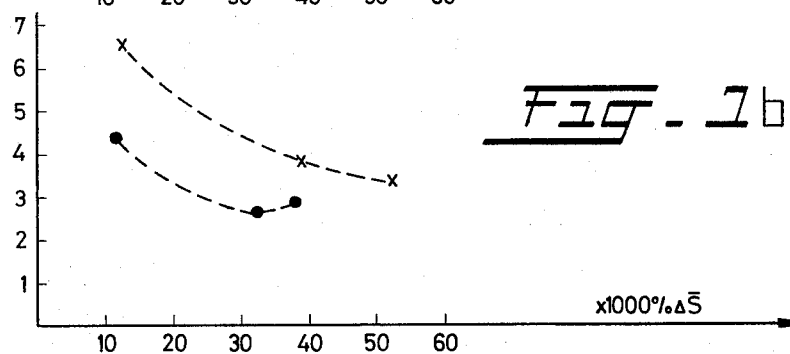
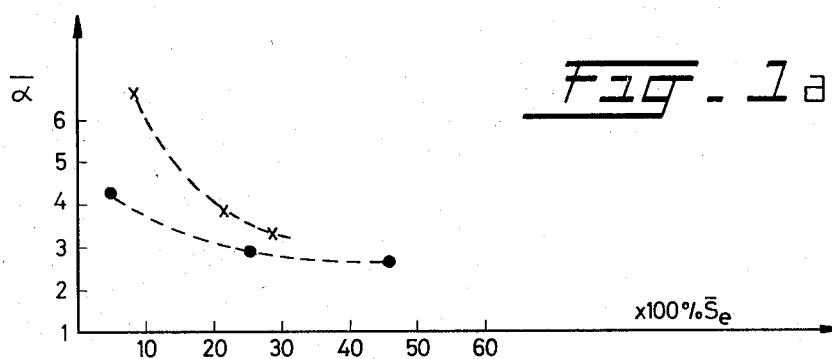
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[57] **ABSTRACT**

In the supply of solid granular or powdered reaction components to molten metal, preliminary to such supply, the reaction component (e.g., desulfurizing agent) is mixed with a solid, finely powdered material (e.g., 0.1 percent colloidal SiO<sub>2</sub>), resulting in less cohesion, more intimate contact, and a saving of the reaction component. The novel composition is also claimed.

**10 Claims, 3 Drawing Figures**



**METHOD FOR ADDING A GRANULAR OR  
POWDERED REACTION COMPONENT TO A  
MOLTEN METAL, AS WELL AS AN IMPROVED  
GRANULAR OR POWDERED REACTION  
COMPONENT FOR CARRYING OUT A  
CORRECTIVE REACTION ON A MOLTEN METAL**

The present invention relates to a method for adding a granular or powdered reaction component to a molten metal, said reaction component remaining solid at the temperature of the molten metal. The invention relates in addition to a granular or powdered reaction component of a kind which may be used for carrying out a corrective reaction on a molten metal.

In the accompanying drawings, FIGS. 1a, 1b and 1c are graphs illustrating advantages of the invention based on test data hereinafter tabulated.

During many refining processes on molten metals, a granular or powdered reaction component is added to the bath of molten metal, said reaction component reacting mostly with the molten metal through the slag stage. A few examples of such a process are the feeding of lime to pig iron in a steel furnace for refining pig iron into steel, and the feeding of a desulfurizing agent, such as calcium carbonate, calcium carbide etc. to molten pig iron, in order to withdraw dissolved sulfur from said pig iron.

The effect of such reactions between a solid substance and a molten metal depends on many factors. In many cases it appears that one of the factors which influences most the effect of the reaction is formed by the extent to which one succeeds in bringing the reaction component into contact with the molten metal. To that end, it has been tried to bring the reaction component in a very fine powdered condition and to spray it through a lance into the metal by means of a gaseous bearing medium. Good results may be attained herewith, however, it has appeared that difficulties may arise which may limit the effect of the measures taken considerably.

For the grains or the powder of the reaction component tend in many cases to coagulate considerably, which is even increased by the fact that many of the materials being used are more or less hygroscopic, as a result of which proper distribution between the solid reaction component and the liquid metal will not be realized, which, in turn, necessitates an excessive amount of solid reaction component to achieve a desired termination of the reaction.

It is noted that it is also possible to bring the solid reaction component in intimate contact with the molten metal by stirring the entire mass during a long period of time. However, with very high melting metals in particular, such as iron compositions and steel alloys, an intensive mechanical stirring operation gives serious technological problems, for which reason it is tried as a rule to have the reaction between the solid reaction component and the metal proceed by merely pouring or blowing the reaction component into the bath.

It may be noted that a proper distribution between a reaction component and a metal bath may be achieved by choosing a reaction component which is also molten at the temperature of the molten metal and which will go into dissolution fast, as is the case when adding soda to a pig iron bath. However, it appears frequently that this method has disadvantages, such as in the case of soda in pig iron, when a slag is obtained which is partic-

ularly objectionable to the refractory lining of the receptacle for the molten metal.

In addition, soda gives off objectionable fumes and liberates a large amount of carbon dust from the reaction, as a consequence of which a nuisance for the environment is formed.

It is the object of this invention to remove said disadvantages and particularly when supplying a solid granular or powdered reaction component to make the contact between said component and the molten metal more intimate. The invention consists in that preliminary to the supply to the melt, the reaction component is mixed with a solid, fine powdered material, which reduces the cohesion of the grains of the reaction component and does not in substance affect unfavourably the termination of the reaction with the molten metal.

As a favourable example of such a process in accordance with the invention, the mixing of the reaction component with a powdered material may be mentioned, said powdered material consisting substantially of colloidal  $\text{SiO}_2$ . In this connection, it is understood by colloidal  $\text{SiO}_2$  the powder which is obtained by the deposit of a colloidal solution of a silicon compound, whereby the deposited powder has as chemical composition  $\text{SiO}_2$ . Said material has an extremely low bulk density. It is put on the market under the name Ketjen-sil by the firm Ketjen and under the name Aerosil by the firm Degussa. It is not fully clear according to which physical or chemical mechanism addition of this powder to a reaction component reduces the cohesion of the grains of said reaction component. However, it appears that even very small quantities of said colloidal  $\text{SiO}_2$  powder are able to make substances such as lime and calcium carbide thin "liquid" as it were. If such a mixture is poured out or is blown by a gaseous medium, it appears that the grains or the powder thereof hardly show a tendency to coagulate any longer.

Thanks to the considerably more intimate contact which, consequently, may be obtained between the reaction component and the molten metal it appears in many cases that a similar reaction result may be obtained with a quantity of granular or powdered reaction component which is up to 25 to 30 percent less.

Consequently, good results have been attained by adding colloidal  $\text{SiO}_2$  to the additives, particularly lime, which are added during the refining of a steel melt in a steel furnace.

In accordance with the invention, good results were attained in particular if according to the invention desulfurizing agents were added which are supplied to a pig iron melt for reducing the percentage of sulfur thereof.

The saving in lime in the steel refining process obtained according to the invention or the saving in desulfurizing agent in the desulfurizing process for pig iron may already be obtained by adding a minimum amount of the colloidal  $\text{SiO}_2$  powder. It has appeared that good results may be attained already with an addition of 0.1 percent of said powder to the additive or to the desulfurizing agent. The increase in cost price of the additive with addition of the desulfurizing agent is neglectable with respect to the saving obtainable.

It has been noted before that said improvements may be achieved by adding a reaction component and by pouring said component into the molten metal. In accordance with the invention, optimum results appear to be attainable by blowing the added reaction compo-

nent through a lance into the molten metal by means of a gaseous floating medium. During the conveyance of the reaction component to and through a lance system, also less inconvenience of fouling and clogging of the apparatus is experienced if the reaction component is added in the manner indicated in accordance with the invention.

The invention not only relates to a method for adding a granular or powdered reaction component to a molten metal but also to said reaction component itself, whereby a solid, fine-powdered material is added to said reaction component in accordance with the invention, said solid material being suitable for reducing the cohesion of the grains of the reaction component. It has been noted before that in this connection good results are obtainable by adding colloidal  $\text{Si O}_2$  powder, preferably in a quantity of approximately 0.1 percent by weight. In this manner, an improvement of granular or powdered reaction components may be achieved, said components being used as additives during the refining of steel melt or having been chosen from the group of desulfurizing agents known as such for the desulfurization of pig iron.

The effectiveness of a desulfurizing agent under certain circumstances is indicated mostly by a value  $\alpha$ . Said value  $\alpha$  indicates the amount of kilograms of desulfurizing agent which is required for reducing the sulfur content in a ton of pig iron by 0.01 percent. Naturally, the magnitude  $\alpha$  depends considerably on a large number of factors, such as the initial contents of sulfur, the final contents of sulfur, etc.

Tests have been carried out with various desulfurizing agents to examine to what extent the  $\alpha$  value could be reduced by adding colloidal  $\text{Si O}_2$ . The tests were carried out each time with a quantity of about 0.1 percent of added  $\text{Si O}_2$ , for which a product was used which is put on the market by the firm Ketjen, Amsterdam Nederland under the trade name Ketjensil 201.

With a large number of desulfurizing tests with CaO under rather normal desulfurizing conditions,  $\alpha$  values were measured which lie mainly between 4 and 6. By desulfurization with CaO with 0.1 percent of Ketjensil 201 added thereto, comparable desulfurizing results were attained, however, with  $\alpha$  values which were lower on an average of approximately  $1\frac{1}{2}$  kg per ton.

Corresponding results were attained when using a mixture of calcium carbide and diamide lime which is put on the market as desulfurizing agent by the firm Suddeutsche Kalkstickstoff Werke in Germany.  $\alpha$  Values were found of about 1.5 to 2 kg per ton from a large number of desulfurizing tests. By adding 0.1 percent of Ketjensil to said desulfurizing agent, these  $\alpha$  values could be reduced by approximately 0.2 to 0.3 kg/ton.

Excellent desulfurizing results could be attained by applying the invention to a desulfurizing agent, known as such, which consists of a mixture of approximately 70 parts of technical lime nitrogen and 30 parts of a calcium carbonate contaminated with carbon in the form of so-called diamide lime. Lime nitrogen contains approximately 60 percent of  $\text{CaNCN}$ , approximately 12 percent of carbon, CaO of 15 to 20 percent, calcium carbonate of 1 to 6 percent and traces of other contaminations. When processing lime nitrogen into melamine, in a first stage cyanamide is formed from the calcium cyanamide in a watery environment, when passing through  $\text{CO}_2$ , in which the calcium hydroxide being

formed reacts with the carbon dioxide to a fine-grained calcium carbonate, which will subsequently flocculate. This by-product is called diamide lime, which, consequently, consists of very fine-grained calcium carbonate and which furthermore contains approximately 10 percent of carbon, derived from the lime nitrogen. With said desulfurizing agent desulfurizing tests were made with pig iron species, the sulfur content of which is below 0.030 percent; between 0.050 and 0.069 percent and between 0.070 and 0.099 percent respectively.

The tests were carried out with the above-mentioned desulfurizing agent, that is 0.1 percent of Ketjensil 201 was added with part of the tests, whereas said additive was omitted with the remaining tests. The subjoined table indicates the results of these tests, in which the following symbols have the following signification:

$\bar{S}_0$  = initial percentage of sulfur in pig iron, on an average over several tests

$\bar{S}_e$  = final percentage of sulfur in pig iron, on an average over several tests.

$\Delta S$  = lowering percentage of sulfur in pig iron, on an average over several tests.

$\alpha$  = effectiveness of desulfurizing agent, in terms of kilograms per ton of pig iron and per 0.01 percent reduction of sulfur content.

$\eta$  = number of tests which showed an average of

$\bar{S}_0$	$\Delta S$	$\bar{S}_e$	$\eta$	$\alpha$	Ketjensil 201
0.020	0.012	0.008	53	6.7	without
0.016	0.011	0.005	16	4.2	with
0.060	0.039	0.021	112	3.9	without
0.063	0.038	0.025	6	2.9	with
0.080	0.052	0.028	80	3.2	without
0.078	0.032	0.046	3	2.6	with

In the accompanying FIGURE, the results of the tests which have been compiled in this table are plotted in a graph, in which each time  $\alpha$  is depicted separately as function of both  $\bar{S}_0$ ,  $\Delta S$  and  $\bar{S}_e$ , and in which each time the pictures of the tests without Ketjensil have been indicated by crosses and the pictures of the tests with Ketjensil have been indicated by dots.

It can be seen clearly from said table and from said graphic representation that the addition of Ketjensil 201 led to a considerable reduction of the  $\alpha$  values.

Finally, it may be noted that  $\text{Si O}_2$  in itself is not a desulfurizing agent and that all substances of the general formula  $(\text{CaO} \cdot n\text{Si O}_2)$  have no desulfurizing effect either or a very bad one. Therefore, the improvement of the desulfurizing results should be sought in the better "flowing" properties of the mixture described.

What is claimed is:

1. A method for treating a molten metal with a reaction component which is solid at the temperature of the molten metal comprising mixing a dry granular reaction component prior to addition of same to the melt to be treated with a minor amount of a dry and finely powdered solid material capable of reducing the tendency of the reaction component granules to cohere with one another and to form a granular reaction component mixture in which said solid material is intimately dispersed throughout said reaction component insuring that said reaction component will be in a non-agglomerated state, said finely powdered solid material having substantially no effect on the termination of the

reaction of said reaction component with the molten metal, and thereafter mixing said formed reaction component mixture with the molten metal to achieve a reaction between said reaction component and the molten metal.

2. A method in accordance with claim 1, wherein the molten metal is molten steel and the reaction component includes CaO, said resulting reaction component mixture effecting a refining of said molten steel.

3. A method in accordance with claim 1, wherein the molten metal is molten pig iron and the reaction component is a desulfurizing agent, said resulting desulfurizing agent mixture effecting a desulfurization of said molten pig iron.

4. A method in accordance with claim 1, wherein the formed reaction component mixture is combined with a gaseous carrier and blown through the molten metal.

5. A method in accordance with claim 1, wherein the finely powdered solid material is  $\text{SiO}_2$  obtained by depositing  $\text{SiO}_2$  in powdered form from a colloidal solution of a silicon compound.

6. A method in accordance with claim 1, wherein said finely powdered solid material is present in an amount of about 0.1 percent.

7. A reaction component material mixture for use as a reaction component in the processing of molten

metal comprising a major amount of a dry granular reaction component which is solid at the temperature of the molten metal and is capable of reacting with said molten metal to effect a processing thereof and a minor amount of a dry and finely powdered solid material capable of reducing the tendency of said reaction component granules to cohere with one another and forming a reaction component material mixture in which said solid material is intimately dispersed throughout said reaction component granules, insuring that said reaction component will be in a non-agglomerated state, said finely powdered solid material having no substantial effect on the reaction of the reaction component with the molten metal.

8. A reaction mixture in accordance with claim 7, wherein the finely powdered solid material is  $\text{SiO}_2$  obtained by depositing  $\text{SiO}_2$  in powder form from a colloidal solution of a silicon compound.

9. A reaction mixture in accordance with claim 8, wherein said reaction component is a desulfurizing agent.

10. A reaction mixture in accordance with claim 9, wherein the  $\text{SiO}_2$  is present in an amount of about 0.1 percent and the desulfurizing agent comprises about 70 parts of technical lime nitrogen and about 70 parts of calcium carbonate contaminated with carbon.

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