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[54] COMPOSITE MEANS FOR TREATING CAST IRON

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Related U.S. Application Data

[62] Division of Ser. No. 724,960, April 29, 1968, Pat. No. 3,598,575.

[30] **Foreign Application Priority Data**

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March 4, 1968 France....................68142187

[52] U.S. Cl....................75/130 A, 75/58
[51] Int. Cl....................C22c 33/00
[58] Field of Search........75/58, 130 R, 130 A, 130 B

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[57] **ABSTRACT**

Compact composite means for treating molten iron.

The composite means is in the form of a solid piece of an inoculating product having a coating of a non-metallic refractory material totally covering the inoculating product. The piece has a plurality of faces and the coating covering one of these faces is thinner than the coating on the other faces so that when the composite means is placed in the molten iron, the piece melts progressively along a front roughly parallel to said one face.

Alternatively, the composite means is in the form of a plurality of solid compact pieces of inoculation product. The pieces are wholly coated with non-metallic refractory coatings of different thicknesses so that the piece melt successively in the molten-iron in the order to increasing thicknesses of the coatings.

6 Claims, 8 Drawing Figures

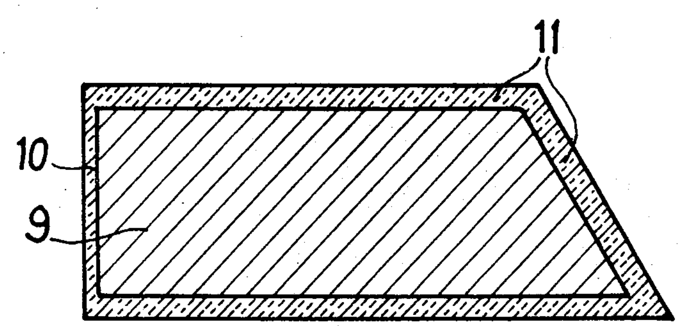

Fig.1

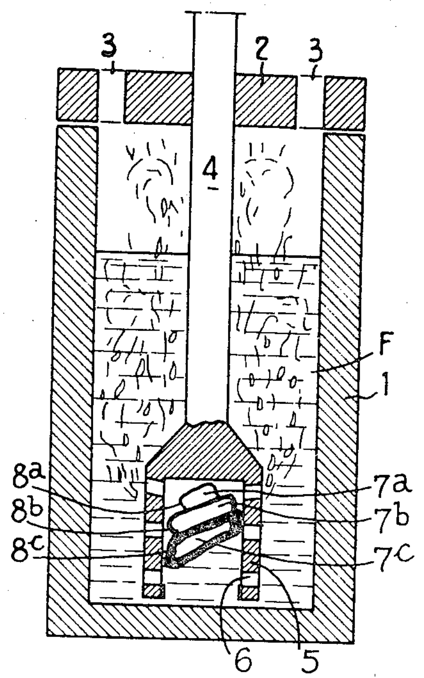

Fig.2

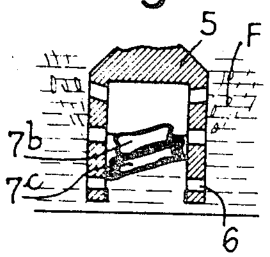

Fig.3

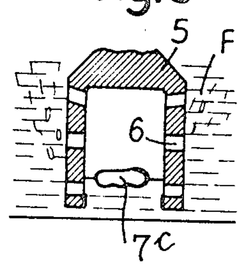

Fig.4

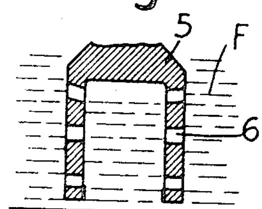

Fig.5

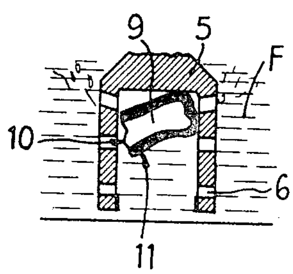

Fig.6

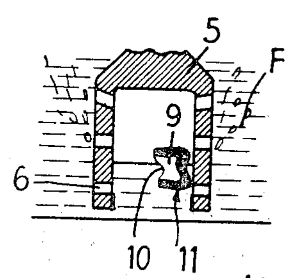

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Fig.7

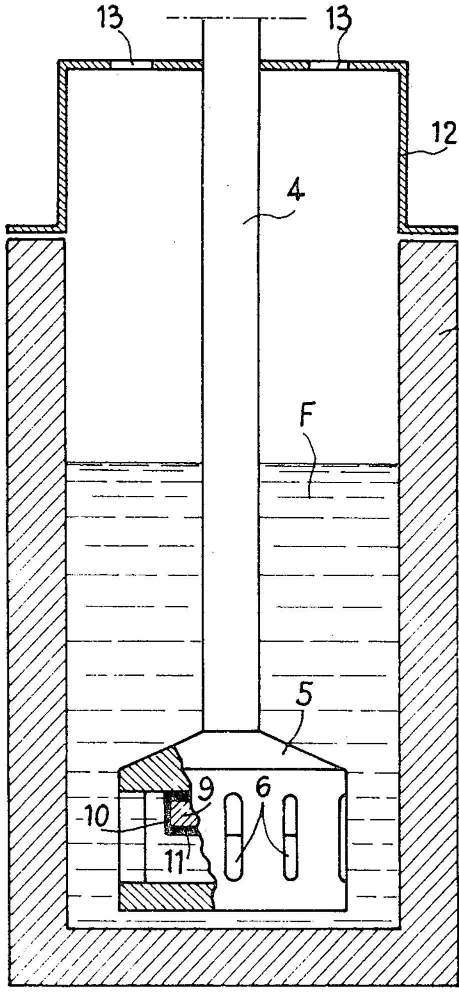
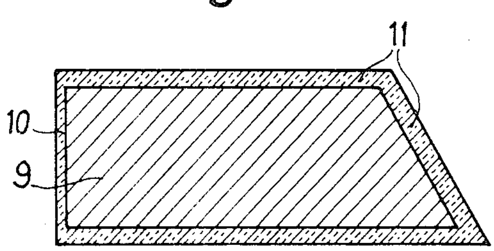


Fig. 8



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COMPOSITE MEANS FOR TREATING CAST IRON

This is a division of my copending application entitled: "Process for treating cast iron" Ser. No. 724,960 filed Apr. 29, 1968, now U.S. Pat. No. 3,598,575 which issued Aug. 10, 1971.

The present invention relates to the treatment of cast iron and more particularly to the introduction into the liquid iron of an inoculating metal for the purpose of obtaining a spheroidal graphite cast iron.

It is known that the reaction of a very volatile inoculating metal, such as magnesium, with the iron in which it is introduced is very rapid and very violent and the yield or the result is poor if precautions are not taken for controlling this reaction.

Various known processes tend in fact to control this reaction, lessen the violence and improve the yield.

Thus a process is known which comprises introducing pure magnesium in a hermetically closed ladle the interior of which is subjected to a certain pressure of air or neutral gas. This process is advantageous and gives good results, but it is more particularly suitable for the treatment of small amounts of iron, for example **500 – 1,500** kg.

Processes are also known which comprise the utilization, not of pure magnesium, but of alloys having a variable magnesium content, of the order of **5–30** percent. Generally ferrosilicomagnesium is employed. The disadvantage of these processes is that, for a given amount of magnesium, the cost of such an alloy is much higher than that of pure magnesium. Further, from the metallurgical point of view, if the amount of silicon that the alloy contains is excessive, it can be harmful in certain cases since it is not always desirable to introduce silicon into iron in excess of a certain amount.

The object of the invention is to provide composite means for inoculating molten iron which is immersed in the iron with the aid of an immersed apertured container, said means being so arranged as to remedy the aforementioned drawbacks and is suitable for the treatment of any amount of iron.

The invention provides composite means for inoculating molten iron comprising an amount of at least one metallic inoculation product in the form of at least one solid compact piece of said product, a coating of a non-metallic refractory material totally covering said inoculation product, said coating having at least one part which is thinner than a remaining part of said coating so that a part of said amount of inoculation product covered by said thinner part of said coating comes in contact with the iron before another part of said amount of inoculation product whereby said inoculation product comes into contact with the iron in a progressive manner and the duration of contact is prolonged.

With this composite means, no violent reaction occurs at the moment of introduction of the piece or pieces of coated inoculation product into the iron so that it is possible to employ treating ladles of conventional type or ladles which require only low-cost adaptations. The duration of the reaction, on which the yield of the treatment depends, is prolonged as a function of the duration of consumption of the coated piece or pieces which results in a satisfactory yield at low cost.

Further features and advantages of the invention will be apparent from the ensuing description with reference to the accompanying drawings.

In the drawings:

FIG. **1** is a diagrammatic vertical sectional view of equipment for carrying out the process employing the composite means according to the invention;

FIGS. **2**, **3** and **4** are partial detail sectional views of the bell forming part of said equipment, these views illustrating the progressive consumption of the inoculating composite means in the form of coated pieces;

FIGS. **5** and **6** are views similar to FIGS. **2–4** showing another form of the composite means consisting of a single piece of coated inoculating product;

FIG. **7** is a diagrammatic sectional view of another modification of the equipment for carrying out the process employing the composite means according to the invention, and

FIG. **8** is a sectional view of composite means in the form of a coated cake or ingot employed for the inoculation.

The invention can be carried out in accordance with two types of reactions each of which will be described in turn:

a. The so-called "reaction by stages" (FIGS. **1–4**), thus termed since a plurality of pieces of magnesium or other metal or alloy are consumed in succession which results in a plurality of reaction stages.

b. The so-called "progressive reaction" (FIGS. **5–7**), thus termed since a single piece of magnesium or other metal or alloy is consumed over a rather long period of time so that the reaction, which is initially weak, is amplified in accordance with a certain progression.

In the example shown in FIG. **1**, which illustrates a reaction in stages, the process is carried out with the following equipment: a ladle or vessel **1** which has a refractory lining, contains liquid metal, for example iron F, and is closed in its upper part by a cover **2** which is merely laid on the ladle. Preferably, the ladle has great height relative to the area of its base.

The cover **2** has an opening **3** for the escape of fumes resulting from the treatment.

Extending through the cover **2** is a rod **4** which terminates at its lower end in a treating bell or apertured container **5** having a wall provided with apertures **6**. In a known manner, the bell **5** serves to introduce an amount of inoculating metal at the bottom of the ladle **1**.

According to the invention, this amount of inoculating metal, which is pure magnesium, is in the form of pieces of metal 7^a, 7_b, 7^c coated with a coating of refractory material 8^a, 8^b, 8^c, for example of the silico-aluminous type.

The composition of such a coating product may vary somewhat for technical or economical reasons. But it contains about 65 percent of silica and 22 percent of alumina, the balance being such elements as CaO, MgO, Fe_2O_3 and Na_2O.

As an example, the following analysis is given:

SiO_2	64,96%
Al_2O_3	21,81%
CaO	1,6%
MgO	0.6%
Fe_2O_3	1,3%
Na_2O	4%
Losses	the balance

The magnesium pieces 7^a, 7^b, 7^c, are produced merely by breaking up small pigs or ingots of commercially available magnesium. If desired, these pigs or ingots of magnesium can be employed wholly without being broken into pieces. The pure magnesium pieces are immersed in a pulp of refractory material and dried in air. They are in this way coated with a refractory crust 8 and the resulting cakes can be used once this crust has hardened.

In the embodiment shown in FIG. 1, cakes of different sizes and masses provided with different thicknesses of refractory coatings are advantageously employed. These different thicknesses are achieved by dipping the metal pieces in refractory pulps of different viscosities or by dipping them successively different numbers of times in the same pulp subsequent to intermediate drying between the successive dippings. FIG. 1 shows, from top to bottom, pieces 7^a, 7^b, 7^c of increasing sizes coated with refractory coatings 8^a, 8^b, 8^c of increasing thicknesses.

The process is carried out in the following manner with this equipment:

The ladle 1 having been filled with liquid iron F, the cover 2 is placed on this ladle after having mounted on this cover the rod 4 on the bell 5 in which are wedged, for example, three pieces of magnesium provided with their coatings. When the cover 2 has been placed on the ladle 1, the bell 5 is located at the bottom of the ladle.

At the start, for a few seconds, no reaction occurs owing to the fact that the refractory coating of the pieces prevents the pure magnesium from coming in contact with the iron. However, the thinnest crust (8^a) of one (7^a) of the magnesium pieces heats up more rapidly and, owing to the transmission of heat through this crust, as soon as the surface temperature of the magnesium reaches the melting and vaporizing temperature, the magnesium vaporizes and this breaks the thin crust and sets off the well-known reaction. As can be seen in comparing FIGS. 1 and 2, the smallest piece 7^a at the top (FIG. 1) whose crust 8^a is the first to break, is rapidly consumed in a violent reaction which lasts for about 10 seconds. In the course of this reaction, the smallest magnesium piece 7^a is rapidly vaporized and the magnesium vapor passes through the apertures 6 of the bell 5 and rises to the surface of the liquid iron F. The inoculation reaction occurs in the course of this rise through the iron F. It is advantageous that the ladle 1 have a great height so as to afford a rising path of the magnesium which is as long as possible which results in a duration of contact between the magnesium and the iron which is as long as possible. This is the first stage of the reaction.

While the first piece 7^a is being consumed, the crust 8^b of the piece 7^b is heated more slowly since it is thicker than the crust 8^a. The choice of the crust thicknesses is such that it is about when consumption of the first piece 7^a has finished that the magnesium of the second piece 7^b is brought superficially to the melting and vaporizing temperature and its crust 8^b is broken. Thus, the start of the second reaction stage follows on the end of the first.

Likewise, the third reaction stage, which corresponds to the consumption of the piece 7^c having the thickest crust 8^c, starts at the end of the second stage, that is, after the complete melting and vaporizing of the piece 7^b having the crust 8^b of medium thickness.

In employing three cakes of magnesium pieces coated with protective crusts of increasing thicknesses, three successive reactions are produced, each of which lasts a few seconds, the total reaction time being substantially longer than the time of the melting of pure magnesium pieces of known type uncoated with a refractory coating. This is why it is possible to obtain a very satisfactory inoculation yield by prolonging the duration of contact between the magnesium and the iron.

The start of the reaction in stages is acertained a few seconds after the bell 5 has been placed at the bottom of the ladle 1 owing to the abundant amount of white fumes given off and the end of the treatment is revealed when the emission of fumes through the openings 3 diminishes in intensity and stops.

As a numerical example, 2 tons (French) of iron were treated with 2.4 kg of pure magnesium consisting of a piece 7^a of 700 g coated with a refractory crust 8^a having a thickness of 1 mm, a piece 7^b of 800 g coated with a refractory crust 8^b of 2 mm thickness, and a piece 7^c of 900 g having a crust 8^c of 3 mm thickness. This corresponds to the introduction of 0.120 percent of magnesium.

The iron had at 1,400°C before treatment the following analysis: carbon 3.60 percent, silicon 2 percent, sulphur 0.010 percent, and contains after treatment 0.028 percent of magnesium and a negligible final sulphur content and graphite entirely in the spheroidal form. The yield R of magnesium is calculated from the following formula:

$$R=\frac{\text{retained magnesium}+\frac{12}{16}\,(\text{initial sulphur-final sulphur})}{\text{added magnesium}}\times 100$$

The coefficient 12/16 represents the ratio between the respective atomic weights of the magnesium and sulphur.

If the components of this formula are replaced by their magnitudes in the considered example, there is obtained:

$$R=[(0.028+0.007)/0.120]+100=29\%$$

This yield of 29 percent is very satisfactory and results in spheroidal graphite cast iron under economical conditions which are much more advantageous than when ferrosilicomagnesium alloys are employed.

According to the modification shown in FIGS. 5 and 6, which illustrate the progressive reaction method, instead of employing the amount of inoculation products in the form of three pieces coated with crusts of different thickness, a single small pig 9 is employed which is coated on one of its faces with a thin refractory crust 10 and on all the other faces with a thick refractory crust 11.

Under these conditions, after having immersed the cake consisting of the pig 9 and the refractory coatings 10 and 11 at the bottom of the iron ladle, as in the foregoing example, the reaction starts with a certain delay due to the resistance to the transmission of heat of the thin refractory coating 10. But the latter is the first heated and subsequently broken when the wall of magnesium it covers has reached the melting and vaporizing temperature. Consumption of the pig 9 starts on the face thereof which was previously coated with the thin crust 10 while the other faces coated with the thick crust 11 are still in the heating stage and there is not yet transmitted to the wall of magnesium covered by this crust 11 sufficient temperature to cause the magnesium to vaporize and break the crust; the melting of the pig 9 thus progresses along a front which is roughly parallel to the face which was initially coated with the thin crust 10. Consequently, the surface of contact between the pure magnesium and the iron is very advantageously limited to the extent of the face previously coated with the thin crust 10, which permits prolonging the reaction so that it is much less rapid and violent than if the pure magnesium had been attacked on all faces simultaneously under the usual conditions when no refractory coating is provided.

In this way, a good yield is obtained which is higher than that obtained under the conditions of the preceding example. Thus, by way of a trial, for treating 1,200 kg of iron, a pig of 1,400 g was employed which was coated on one face with a thin crust 10 having a thickness of 1 mm and on the other faces with a thick crust 11 having a thickness of 3 mm. The reaction started 5–6 seconds after immersion of the pig at the bottom of the ladle. This time corresponds to the duration of attaCk of the thin crust 10 and the reaction lasted about 1 min. The yield was of the order of 32–33 percent.

With reference now to the embodiment shown in FIG. 7, the equipment comprises a ladle 1 which has a refractory lining and contains the liquid metal, for example iron F. This ladle is capped by a vertically extended cover 10 which increases the height of the ladle. This cover has openings 13 for the escape of fumes which result from the treatment and a refractory rod 4 extends through the cover and terminates at its lower end in a bell or container 5 provided with slots or other openings 6 allowing the escape of the vaporized magnesium.

Placed in the bell 5 is a cake mainly consisting of an inoculation piece or ingot 9, for example of pure magnesium (FIG. 8). This piece is for example produced by severing an ingot straight from casting into pieces of the desired length by means of shears, the ingot having a circular, rectangular, trapezoidal or other section.

The severed face of the piece 9 is coated with a thin refractory crust 10 and all the other faces of the ingot are coated with a thick uniform refractory crust 11 whose thickness is 2–20 times greater than that of the thin crust 10. The refractory crusts are, for example, of silico-aluminous material having, preferably, excellent adherence characteristics when cold and when hot and an excellent resistance to mechanical and thermic shocks.

The duration of the inoculation with the progressive reaction method is variable and can be selected, in accordance with needs, between 15–20 seconds and about 2 minutes by regulating the thickness of the main coating, that is, the thickness of the thick crust 11 and by judiciously choosing the area of the cross-section receiving the thin refractory crust 10. The duration of the reaction must be as long as the layer 11 is thick. This is explained by the fact that the vaporization of the cake of magnesium 9 starts after the rapid cracking of the thin crust 10 coating the end face and increases progressively along a front parallel to this end face.

Note that for a given effective amount of magnesium, an ingot 9 of pure magnesium has a volume which is about one-sixteenth that of a piece of magnesium alloy of known type (iron, silicon, magnesium having 15 percent magnesium for example). Consequently, it is possible to employ a bell 5 which is shorter than the bells usually employed for the same amount of treated iron and this enables the vaporized magnesium to travel through a greater height of liquid iron up to the free surface of the iron. The yield of the treatment is thereby improved.

For example, in treating amounts of iron between 1 ton and 4 tons at a temperature of 1,410°C by means of the cake shown in FIG. 8, the yield R of magnesium is at least equal to 60 percent and there is obtained an iron having a graphite wholly in the spheroidal form.

It must be understood any amount of iron, that is, less or more iron, can be treated in this way.

The main advantages of the invention are the following:

As can be seen, while being more progressive than the reaction produced by uncoated pure magnesium pieces of known type, the reaction produced by cakes of magnesium pieces protected by a refractory coating according to the invention remains sufficiently rapid for treating successive pouring ladles employed in mass-production casting sites.

The process employing the composite means according to the invention is very economical since it allows the utilization of crude small pigs in the state in which they are bought with no preparation other than the breaking thereof into pieces, the classifying of the pieces into different sizes and the immersion of whole pigs and pieces in pulps of refractory materials. These operations are simple and cheap to carry out.

The small pigs can be in the form of ingots having trapezoidal faces or in the form of round-section billets. Owing to the use of treating ladles of suitable dimensions affording a suitable height of iron above the treating bell 5, an excellent inoculation yield is achieved.

The process results in great economy as concerns the metallic inoculation product since it is employed in the pure state.

The duration of the reaction, and therefore the yield, can be controlled by employing cakes of magnesium having refractory crusts of suitably diminishing thickness, as in the first embodiment, or by employing a single ingot having a suitable mass and a thin crust 10 on a small part of its outer surface and a thick crust 11 on the rest of its surface, as in the second embodiment.

It is possible to control not only the duration but also the progressivity of the treatment and therefore achieve a satisfactory yield while attenuating the violence of the reaction without utilization of special and costly equipment.

Thus, it is possible to employ cakes of magnesium coated with a refractory coating in accordance with the invention in special ladles of known type allowing a treatment in a retort under pressure, which considerably increases the yield of the treatment, that is, the yield of magnesium relative to treatments in these same special ladles with pure magnesium uncoated with a refractory coating.

Further, the two types of reaction, namely the reaction in stages and the progressive reaction, can be employed simultaneously in combination, by employing a single pig 9, such as that shown in FIG. 5, and a plurality of cakes 7, such as those shown in FIG. 1, to make up the weight of magnesium necessary for the treatment of a given amount of iron.

Further, instead of employing silicoaluminous refractory coatings or coatings containing refractory clay, it is possible to employ refractory coatings containing silica or asbestos.

The invention is also applicable to the treatment of iron with cerium or alkali metals, such as sodium and calcium, and to the treatment of iron with metal alloys, such as misch metal. The invention permits the staggering of reactions by, for example, reacting in accordance with a preferential order metals and/or metal alloys by coating the pieces which must react first with a thinner refractory coating and the pieces which must react last with a thicker coating.

It must be understood that the process can be carried out by putting the pieces of magnesium coated with a refractory crust in contact with the iron by means of any device other than the bell 5.

Having now described my invention what I claim and desire to secure by Letters Patent is:

1. Composite means for inoculating molten iron consisting essentially of an amount of at least one metallic inoculation product in the form of at least one solid compact piece of said product, and a continuous coating of a non-metallic refractory material covering the whole of the outside of said amount of said inoculation product, said coating having at least one part which is thinner than a remaining part of said coating so that a part of said amount of inoculation product covered by said thinner part of said coating comes in contact with the iron before another part of said amount of inoculation product whereby said inoculation product comes into contact with the iron in a progressive manner and the duration of contact is prolonged.

2. Composite means for inoculating molten iron, consisting essentially of at least one metallic inoculation product in the form of a solid piece of said product, and a continuous coating of a non-metallic refractory material covering the whole of the outside of said solid piece of inoculation product, said piece having a plurality of faces, said coating covering one of said faces being thinner than said coating covering other faces of said piece so that said piece melts progressively in said molten iron along a front which is roughly parallel to said one face.

3. Composite means as claimed in claim 2, wherein said coating covering said one face has a thickness which is between one-twentieth and one-half of the thickness of said coating covering said other faces of said piece.

4. Composite means for inoculating molten iron, consisting essentially of at least one metallic inoculation product in the form of a plurality of solid pieces of said inoculation product, the whole of the outside of each of said pieces being coated with a non-metallic refractory continuous coating, the coatings being of different thicknesses so that said pieces melt successively in said molten iron in the form of a reaction in stages proceeding in the order of increasing thicknesses of said coatings.

5. Composite means for treating molten iron consisting essentially of an amount of a metallic treating product in the form of at least one solid compact piece of said product and a continuous crust of a non-metallic refractory material covering the whole of the outside of said amount of treating product, said crust having at least one part which is thinner than a remaining part of said crust so that a part of said amount of treating product covered by said thinner part of said crust comes in contact with the iron before another part of said amount of treating product whereby said treating product comes into contact with the iron in a progressive manner and the duration of contact is prolonged.

6. Composite means for treating molten iron consisting essentially of an amount of a product consisting essentially of magnesium in the form of at least one solid compact piece of said product and a continuous crust of a non-metallic refractory material covering the whole of the outside of said amount of treating product, said crust having at least one part which is thinner than a remaining part of said crust so that a part of said amount of treating product covered by said thinner part of said crust comes in contact with the iron before another part of said amount of treating product whereby said treating product comes into contact with the iron in a progressive manner and the duration of contact is prolonged.

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