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TREATMENT OF MOLTEN METAL

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ABSTRACT OF THE DISCLOSURE

High-line content exothermic slags for desulphurisation and inclusion removal, and deoxidation of molten ferrous metals.

This invention relates to the treatment of molten ferrous metals, and particularly to the desulphurising of molten steel, in which connection it will be more particularly described. Most refining processes for ferrous metals are carried out in furnaces or converters, for example in open hearth or arc furnaces, or in the Bessemer converter. It is, however, frequently necessary to treat the molten ferrous metal after it has left the furnace. Such treatments as desulphurisation, dephosphorisation and non-metallic inclusion removal are often practiced just prior to teeming of the molten metal. The treatments generally take the form of additions to the molten metal in the ladle of slag forming materials, which flux away sulphur, phosphorus, non-metallic inclusions and the like from the molten metal. The amount of treatment agent which may be added is, however, severely limited by the chilling of the molten metal produced by the addition of the treatment agent. Conventional treatment agents for steel cannot be added in such fashion in amounts greater than about 2 lbs. per ton of metal to be treated without causing material chilling.

The treatment agent may be used in greater quantity if it is heated before it is added to the metal, but this method necessitates the use of a separate furnace to heat the treatment agent and is generally inconvenient. It has also been proposed to provide that the treatment agent includes components which, under the action of the heat of the molten metal, react exothermically. By this means the chilling effect on the molten metal may be greatly reduced.

The desulphurisation of molten ferrous metal with which subject matter the present invention is concerned, is a long-standing problem, especially insofar as treatment of the molten metal in the ladle is concerned.

There is no method currently used in the steel industry to remove sulphur efficiently from steel in the ladle. In various parts of the world sulphur is reduced in the furnace by injection methods. These usually employ such materials as magnesium and lime, introduced below the metal surface, in powder form carried in a stream of inert gas.

In the case of liquid iron, where sulphur levels are usually very much higher than in steel, sodium carbonate is widely used as a desulphurising agent. Similar treatment in steel ladles would be unacceptable due to the severe erosion of the refractory ladle lining which would result from the use of sodium carbonate at the higher temperatures.

Extensive research has been carried out by the applicants to develop a product which would permit efficient ladle desulphurisation without undesirable side-effects.

A careful study of associated problems suggested that lime additions would be cheap and probably effective. However, when used in sufficient quantities to absorb sulphur to a satisfactory degree, there is the disadvantage of excessive heat removal from the liquid steel and the failure to form the fluid slag necessary for desulphurising. Research was directed towards developing a self-melting slag with the correct characteristics to absorb sulphur.

It has been found, as a result of considerable research and experiment, that highly satisfactory results can be obtained in the desulphurising of molten ferrous metal, particularly of molten steel, in the ladle, by the use of additive compositions of defined character as hereinafter described.

According to the present invention there is provided an additive for use in the desulphurising of molten ferrous metal in the ladle or in an ingot mould, which comprises the following ingredients in the following proportions:

	Parts by weight
Lime (CaO)	40–80
Iron oxide	5–30
Oxidisable material	5–20

the weight of lime in the mixture being at least twice the weight of the iron oxide which is present in a quantity stoichiometrically insufficient to oxidise all the oxidisable material.

The iron oxide and oxidisable material present constitute an exothermically reacting mixture. The iron oxide is the oxidising agent and is preferably present as Fe_3O_4 (magnetite, Itabira ore or iron millscale), although Fe_2O_3 (haematite) is also suitable. The oxidisable material is preferably a finely divided metal or mixture of metals, or silicon or a silicide. The finely divided metal used is preferably aluminium, either as such or in the form of ball mill dust. Other oxidisable materials which may be used are calcium silicide, ferrosilicon, calcium/aluminium, magnesium, silicon, and calcium/silicon or mixtures of alloys thereof. The oxidising agent, as noted above, is essentially iron oxide but any other oxidising agents known for use in the foundry industry, such as sodium nitrate, potassium nitrate, sodium chlorate, manganese dioxide and various perchlorates may also be present.

The relative proportions of the essential ingredients of the composition set forth above are critical. The substance lime is known for use in the desulphurising of steel and is believed to function by direct interaction with iron sulphide present in the steel, the lime being converted to calcium sulphide which enters the slag and the iron sulphide being correspondingly converted to iron oxide. It has been found that this reaction is adversely affected by the presence of added iron oxide (i.e. present in the additive) and that satisfactory results are only obtained in terms of desulphurising effect if the proportion of lime in the additive is at least twice that of the iron oxide.

Further, it has been found desirable to provide that some of the oxidisable material is present over and above that which will be oxidised by the iron oxide present (to afford an exothermic reaction), the excess of such oxidisable material then acting as a sink for the collection of oxygen from the molten metal under treatment, i.e. to support the desulphurising effect with a deoxidising effect. It is probable, in fact, that iron oxide produced by the desulphurising reaction is converted back to iron by reaction with the excess of oxidisable metal.

The optimum composition of the treatment agent will vary with the treatment site. When treatment is effected in the mould, high proportions of alkali metal compounds may be included, though these may be unsuitable for treatment of molten metal in the ladle since they tend to attack the refractory linings of such ladles.

Further ingredients may be incorporated in the compositions to serve auxiliary functions. For example, siliceous slags (e.g. blast furnace slag) may be added to promote the removal of oxide inclusions from the steel. A fluoride preferably fluorspar, may be incorporated to increase fluidity of the molten slag and assist in inclusion removal. Alumina decreases the melting point of the lime-bearing slag and thus improves its fluidity. (Lime melts at about 2400° C. whereas 50/50 eutectic mixture with alumina melts at less than 1600° C.)

Thus a treatment agent suitable for use in the ingot mould might have the following composition (parts by weight):

Oxidisable material	5–20
Alkali metal nitrates and chlorates	Up to 20
Iron oxide	5–30
Lime (for desulphurisation)	40–80
Fluoride	5–40
Silicate slags (for inclusion removal)	Up to 30
Alumina	Up to 80

while a treatment agent suitable for use in the ladle might have the composition (parts by weight):

Oxidisable material	5–20
Iron oxide	5–30
Lime (for desulphurisation)	40–80
Fluoride	Up to 10
Alumina	Up to 80

The fluoride used may be selected from sodium and potassium fluorides cryolite and fluorspar. Of these, fluorspar is preferred. The iron oxide used is generally in the form of haematite or millscale.

Using the treatment agents of the present invention, addition rates of up to 50 kg. per ton of metal to be treated may be used without any important adverse chilling effects on the molten metal but addition rates of 20–30 kg. per ton of metal are preferred.

The invention will be further illustrated in the following examples, in which all parts and percentages are by weight.

EXAMPLE 1

A composition for use in ingot moulds for desulphurising and removing inclusions in the cast metal has the following composition:

	Percent
Aluminium powder	10
Sodium nitrate	8
Millscale (iron oxide)	10
Calcium oxide (lime)	47
Fluorspar	10
Ball mill dust (20% Al content)	15

This composition was applied at the rate of 30 kg. per ton of steel treated by adding the appropriate quantity to the ladle prior to teeming. The lime confers basicity to the slag formed and effects sulphur removal while the fluorspar increases fluidity of the slag and assists in fluxing the non-metallic (i.e. oxide) inclusions.

A large number of trials made with the use of the foregoing composition have shown that the composition so added effects removal of sulphur from steel in proportions which, while varying with the particular circumstances are invariably better than 30% and often approach 60% of the total of sulphur present in the steel under treatment.

EXAMPLE 2

The following composition was formulated and used as in Example 1.

	Percent
Calcium oxide (lime)	55
Iron millscale	7
Sodium nitrate	7
Fluorspar	9
Calcined alumina	8
Silica flour	4
Aluminium powder	10

This composition was used at a rate of up to 30 kg. per ton of steel to be treated, either by placing it on the bottom of the ladle prior to tapping or by feeding it into the tapping stream.

An application rate of 20 kg. per ton resulted in a desulphurisation to the extent of 47%.

EXAMPLE 3

A composition for use in ingot moulds for desulphurising and removing inclusions in the cast steel has the following composition:

	Percent
Lime	30
Calcium/silicon	25
Sodium nitrate	8
Millscale (iron oxide)	8
Sodium carbonate	17
Fluorspar	10

This composition was applied at the rate of 20 to 30 kg. per ton of steel. A 26% reduction in the sulphur content of the steel was obtained.

I claim as my invention:

1. An additive for use in the desulphurising of molten ferrous metal in the ladle or in an ingot mould which comprises the following ingredients in the following proportions:

	Parts by weight
Lime (CaO)	40–80
Iron oxide	5–30
Oxidisable material selected from the group consisting essentially of aluminum, calcium silicide, ferrosilicon, calcium/aluminum, magnesium, silicon, calcium/silicon and mixtures and alloys thereof	5–20

the weight of lime in the mixture being at least twice the weight of the iron oxide and the weight of the iron oxide in the mixture being stoichiometrically insufficient to oxidise all the oxidisable material present.

2. An additive according to claim 1 which further contains an alkali metal nitrate in amounts up to 10 parts by weight.

3. An additive according to claim 1 which further contains fluorospar in amount from 5–40 parts by weight.

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