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(54) **Metallurgical treatment agents.**

(57) Metallurgical treatment agents for molten ferrous metals e.g. iron and steel and suitable for desulphurising molten iron and steel comprise particulate magnesium coated with a first coating of a hydrophobic liquid and a second coating of particulate soda ash. The coated magnesium possesses improved flowability and is less prone to premature reaction when subjected to high temperatures. The soda ash provides enhanced desulphurisation of molten ferrous metals than may be obtained by e.g. refractory coated magnesium.

EP 0 328 270 A2

METALLURGICAL TREATMENT AGENTS

This invention relates to metallurgical treatment agents for molten metals particularly for the desulphurisation of ferrous metals and their method of production.

In addition to desulphurisation of ferrous metals other effects may be obtained such as deoxidation, inclusion shape modification and nodularisation.

It has been proposed to desulphurise molten ferrous metals such as iron and steel by use of treatment agents containing magnesium. More recently it has been proposed to treat molten iron with magnesium by injecting the metal beneath the surface of the iron and satisfactory results have been obtained although problems with material flow and lance blockage have sometimes been encountered.

Although magnesium has gained acceptance as a useful treatment agent it possesses disadvantages which create problems during its production and/or use. A particular disadvantage of magnesium relates to its high vapour pressure and the violence with which it reacts on contact with molten ferrous metals.

There are many suggestions in patent literature in respect of means to control the reaction of magnesium with molten ferrous metals. However, only a relatively few of these proposals have gained any significant measure of commercial success. Notably there is a treatment agent described in United States Patent Publication No. 3321304 of American Cast Iron Pipe Company comprising porous metallurgical coke impregnated with magnesium and there is a treatment agent described in United States Patent Publication No. 4186000 of the Dow Chemical Company comprising salt-coated magnesium granules. The salt-coating comprises predominately an admixture of alkali metal halides and alkaline earth metal halides, particularly chloride. The latter proved to be a significant advance because the salt-coated magnesium could be injected on its own i.e. without any filler material such as lime or ball-mill-dust, without excessive violence and without the high risk of lance blockage when injecting uncoated magnesium particles. Due to the high thermal conductivity and low melting point of magnesium adherence of magnesium in the vicinity of the exit of an injection lance can occur when injecting uncoated magnesium and this can contribute to lance blockage. Nevertheless, the salt-coated magnesium product suffers from the disadvantage of environmental pollution emanating from the metal halide coating material which may give rise to e.g. hazardous chlorine fumes polluting the work place. In addition such products are hygroscopic and tend to agglomerate during storage.

Particulate magnesium having an adherent coating of refractory material having a very small particle size is known. By using a refractory material having a very small particulate size a tenacious refractory coating can be produced on the particulate magnesium without the need for a binder.

The coating improves the smooth flow of the coated granules and most effectively protects the magnesium against premature reaction when subjected to high temperatures. However, such coated magnesium suffers the disadvantage of generating non-adherent fine particles from the outer coating when the product is e.g. pneumatically conveyed in a steelworks for distances in excess of about 75 metres leading to blockages in the material transport system.

Such treatment agents are particularly suitable for injection into molten metal with e.g. a carrier gas such as e.g. argon.

An improved coated magnesium injectable treatment agent of the above type is described in EP-A-0292205.

It has now been found that a still further improved coated magnesium treatment agent may be produced where the particulate magnesium is coated with a first coating of a hydrophobic liquid and a second coating containing soda ash. Such treatment agents have been found to provide enhanced desulphurisation of molten ferrous metals.

According to the present invention there is provided a treatment agent for molten ferrous metal comprising particulate magnesium coated with a first coating of a hydrophobic liquid and a second coating comprising a major proportion of soda ash.

It is to be understood that the second coating may be a single layer or it may consist of more than one layer e.g. two or more layers.

Suitable hydrophobic liquids for coating the magnesium particles include synthetic resins or aliphatic or aromatic oils, for example oils derived from petroleum or from coal. Paraffin based oils of low or medium grade generally used as compressor oils, bearing oils or for machine lubrication are satisfactory. Other hydrophobic liquids which may be used are vegetable oils such as rape seed oil, olive oil or corn oil.

Particularly preferred hydrophobic liquids for use in the present invention are epoxy or novolak type synthetic resins.

In order that the hydrophobic liquid may be readily coated onto the magnesium particles the hydrophbic liquid preferably is of relatively low viscosity i.e. within a range from about 10 to about 70 centipoise at 25° C.

For epoxy resins and hardeners therefor and novolak type synthetic resins it has been found that a hydrophobic liquid of suitable low viscosity may be prepared by mixing the resin with a suitable solvent. In this respect the amount of resin to solvent may be about 20 to 30% and 70 to 80% respectively. The preferred solvent for an epoxy resin and hardener therefore is methylene chloride used in the ratio of 25 parts resin/hardener to 75 parts solvent and for a novolak resin the preferred solvent is propanol the ratio of which is also 25 parts resin to 75 parts solvent.

The application of the resin coating onto the particulate magnesium may be effected using spraying or atomising equipment.

The resin may be heated e.g. up to about 50° C to 60° C which further reduces its viscosity which in turn enhances the ability of the resin to coat the particles of magnesium even at low application rates.

The quantity of resin needed to coat the particulate magnesium is relatively small and usually about 3% by weight based on the total weight of the treatment agent will be sufficient.

The soda ash referred to above is sodium carbonate which has the chemical formula Na_2Co_3. The soda ash of the second coating may comprise up to about 40% of the total treatment agent but more preferably is within the range of from about 15 to 35%. The soda ash coating may comprise a minor proportion of other materials which assist the soda ash to adhere to the first coating. Such other materials may be selected from one or more of bentonite, other clays containing up to 2% combined water, sodium silicate, low molecular weight waxes, calcium stearates and methyl cellulose. Of these bentonite is particularly preferred which may be present in a proportion of from 5 to 30% by weight of the second coating preferably about 10-20% by weight and more preferably about 15% by weight.

Preferably the particle size of the magnesium particles does not exceed 1 mm.

The coated magnesium treatment agent may be produced by mixing the particulate magnesium thoroughly with the hydrophobic liquid for example in a high energy mixer and then adding the particulate soda ash and continuing the mixing process until the particles of soda ash are thoroughly dispered and coated on to the liquid coated magnesium particles.

The weight average particle size of the soda ash coating is preferably less than 50 microns, more preferably less than 30 microns.

The hydrophobic liquid produces a surface film on the magnesium particles thus providing additional protection against hydration compared to the protection achieved by a soda ash coating alone. Accordingly, the stringent packaging regulations (normally steel drums or nitrogen sealed containers are used) may be dispensed with thus giving easier bulk transportation of treatment agents according to this invention.

The hydrophobic liquid coating also enables the application of the coating of particles of soda ash to be carried out more efficiently by reducing the amount of wastage of particles of soda ash which do not become coated onto the magnesium particles.

In addition the use of the hydrophobic liquid permits the use of coarser particles of soda ash than is the case when the liquid coating is omitted.

It has been found in accordance with the present invention that the quantity of non-adherent particles is less than 1% by weight of the coating composition. In the event that this source of non-adherent particles exceeds 1% by weight the resultant treatment agent thus formed suffers from poor flowability through e.g. injection equipment which may be employed to e.g. desulphurise molten ferrous metals with the result that lance blockage may occur.

In one embodiment of the present invention a further coating may be applied to the second coating, said further coating comprising a synthetic resin selected from any one or more of those specified above. It has been found that the further coating imparts a hard attrition resistant surface which in turn reduces the incidence of non-adherent particles emanating from e.g. the material of the second coating.

The treatment agent of the invention in particulate form is suitable for injection into molten ferrous metals such as iron or steel in a carrier gas such as argon, nitrogen, air, methane or propane. The preferred carrier gas is argon. If desired the treatment agent may be mixed with other treatment agents such as lime, ball-mill-dust, magnesium oxide, alumina, calcium aluminate, calcium carbonate, calcium carbide or sodium carbonate. Alternatively, the treatment agent of the invention may be used in the so-called co-injection process. In this process two separate silos contain different treatment agents and these agents are simultaneously injected into the molten metal held in a vessel such as a ladle.

The treatment agent may be in the form of the particles contained within an elongate metal casing e.g. in the form of a wire-like product. The wire may be injected into iron in the production of S.G. iron.

According to a further aspect of the present invention there is provided a method of treating a molten ferrous metal which comprises treating the metal with a treatment agent according to the invention.

The following Examples will serve to illustrate the invention:-

EXAMPLE 1

A coated particulate magnesium treatment agent was prepared in the laboratory having the following composition by parts by weight:-

Magnesium	80
Liquid Novolak resin (25% solids dissolved in 75% propanol)	1
Soda Ash	17
Wyoming Bentonite	3

The magnesium had a weight average particle size of 0.5. mm and the soda ash and bentonite together had a weight average particle size of 20 microns.

The resin and the particulate magnesium were mixed together for 3 minutes in a high energy mixer (manufactered by Eirich G.m.b.H.) using fume extraction equipment to exhaust the organic solvent safely away from the mixer then the soda ash was added and the mixing was continued for a further 15 minutes.

The coated magnesium particles were separated from the fine particles of soda ash which had not become coated and the quantity of non-adherent fine particles was determined as 0.2% by weight. By comparison production of a similar treatment agent having no coating of resin by the same method resulted in non-adherent fines of 11% by weight.

EXAMPLE 2

Another coated particulate magnesium treatment agent was prepared in the laboratory having the following composition by parts by weight:-

Magnesium	70
Liquid epoxy resin/hardener (19.2% resin and 5.8% hardener in 75% methylene chloride)	3
Soda Ash	25.5
Bentonite	4.5

The properties of the particulate magnesium, soda ash and bentonite and the method of preparation were in accordance with Example 1. The viscosity of the resin/solvent mixture was approximately 55 centipoise at 25 $^{\circ}$C.

A comparison of the amount of non-adherent fine particles was repeated as in Example 1 with the following results:-

a) non-adherent fines with resin 0.22% by weight
b) non-adherent fines without resin 16% by weight

The degree of protection against hydration afforded to the magnesium particles having a resin coating and the soda ash coating was assessed by standing the treatment agent described in Example 1 and Example 2 in a laboratory atmosphere for 14 days following which the increase in weight was negligible.

In order to illustrate the enhanced desulphurising efficiency of treatment agents according to the present invention Table 1 represents a comparison between an agent according to Example 2 and two other proprietory magnesium treatment agents. In Table 1 the % Mg efficiency values were calculated using the following formula:-

$$EMg = \frac{\text{Initial Sulphur} - \text{Final Sulphur}}{1.32 \times \text{Mg added}} \times 100\%$$

where 1.32 = stoichiometric equivalents of Mg and S.

NUMBER OF TESTS	TREATMENT AGENT	INITIAL SULPHUR %	FINAL SULPHUR %	% Mg ADDED	% Mg EFFICIENCY
5	UNCOATED 80% Mg, 20% Ball Mill Dust	0.059	0.0025	0.1515	28.25
		0.058	0.013	0.1315	25.92
		0.053	0.0053	0.135	26.77
		0.071	0.0040	0.137	37.05
		0.053	0.0020	0.149	25.93
	AVERAGE RESULTS	0.059	0.0054	0.1408	28.84
7	COATED 80% Mg, 2% SiO_2, 18% Al_2O_3	0.039	0.0033	0.1056	25.61
		0.058	0.0031	0.1232	33.76
		0.059	0.0029	0.1285	33.07
		0.058	0.0028	0.1162	35.99
		0.052	0.0038	0.1321	27.64
		0.067	0.0016	0.1412	35.09
		0.053	0.0067	0.1053	33.31
	AVERAGE RESULTS	0.055	0.0035	0.1217	32.07
13	COATED AS INVENTION 68% Mg, 3% liquid epoxy resin, 24.8% Soda Ash 4.2% Bentonite	0.051	0.007	0.083	40.16
		0.043	0.0075	0.083	32.40
		0.047	0.0096	0.087	32.57
		0.057	0.011	0.087	40.06
		0.054	0.0075	0.084	41.94
		0.102	0.049	0.092	43.64
		0.068	0.02	0.098	37.11
		0.036	0.0056	0.088	26.17
		0.029	0.006	0.085	20.50
		0.044	0.0067	0.089	31.75
		0.055	0.013	0.093	34.21
		0.051	0.018	0.088	28.41
		0.054	0.0089	0.087	39.27
	AVERAGE RESULTS	0.053	0.012	0.088	35.30

Claims

1. A treatment agent for molten ferrous metals comprising particulate magnesium having a first coating of a hydrophobic liquid and a second coating of particulate material characterized in that the second coating comprises a major proportion of particulate soda ash.

2. A treatment agent according to claim 1 characterized in that the soda ash comprises up to 40% of the total treatment agent.

3. A treatment agent according to claim 1 or claim 2 characterized in that the second coating comprises a plurality of layers.

4. A treatment agent according to any one of the preceding claims characterized in that the soda ash comprises a proportion of a material which assists the soda ash to adhere to the hydrophobic liquid.

5. A treatment agent according to any one of the preceding claims characterized in that the weight average particle size of the soda ash is less than 50 microns.

6. A treatment agent according to any one of the preceding claims characterized in that the hydrophobic liquid is selected from one or more of synthetic resins, aliphatic oils, aromatic oils and vegetable oils.

7. A treatment agent according to claim 6 characterized in that the resin is an epoxy resin or novolak type resin.

8. A treatment agent according to claim 6 or claim 7 characterized in that the viscosity of the hydrophobic liquid is within the range from 10 to 70 centipoise at 25° C.

9. A treatment agent according to any one of the preceding claims characterized in that a coating comprising a synthetic resin is applied to the soda ash coating.

10. A treatment agent according to any one of the preceding claims characterized in that the particle size of the magnesium does not exceed 1 mm.

11. A treatment agent according to any one of the preceding claims characterized in that the treatment agent is contained within an elongate metal casing.

12. A method of treating molten ferrous metal characterized by injecting into the molten ferrous metal a treatment agent according to any of claims 1 to 11.