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(54) Anti-skulling material for use in a metallurgical handling vessel.

(57) The invention provides an anti-skulling material for use in the outlet nozzle of a metallurgical vessel, e.g. a tundish.

By providing a particulate, sinterable or partially-sinterable filler material in granulated form, the granules containing the desired proportion of the particulate constituents, the invention enables greater consistency and uniformity of sintered crust to be formed in the nozzle area during contact with the molten metal in the vessel.

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This invention relates to the inhibition of skull in the outlet nozzles of metallurgical handling vessels.

The invention is of particular importance in respect of metallurgical handling vessels such as furnaces, for example, ladle furnaces, ladles, tundishes and the like which have nozzles comprising opening and closing means which may be used to control the rate of flow of molten metal, e.g. steel, from the vessel. One means known in the metallurgical industry is the so-called sliding gate and slide-gates are increasing in prominence throughout the metallurgical industry.

Molten steel in, e.g. a ladle, having a closed sliding-gate outlet nozzle tends to cool and solidify in the nozzle bores to form what is known as "skull" and this may partly or completely block the outlet when the outlet is opened. It is known to try to avoid this problem by putting into the nozzle zone from its inner side, particulate high melting point matter generally referred to as 'anti-skulling material' to provide a barrier before steel is introduced into the ladle. Such anti-skulling material is known and typically comprises one or more particulate filler materials and may optionally include a sintering agent and/or carbon. In use of the material in a nozzle outlet, sintering of the material occurs at the material/molten metal interface. The sintering effect progresses away from the area of contact to form, e.g. a crust or bridge of sintered material and beneath this crust the remainder of the material is unsintered. On opening the nozzle, the loose material beneath the sintered crust flows out and the crust is dislodged owing to the metallostatic pressure and thus free-opening of the nozzle is effected.

However, known particulate anti-skulling materials can suffer the drawback of segregation owing to the different particle size and density of each constituent of the mixture. Segregation occurs in transit of the material and results in the anti-skulling material giving inconsistent and unreliable results. One problem relates to the formation of a crust which is uneven in thickness. This defect can promote areas of crust which are too thick to be dislodged by the metallostatic pressure with the result that complete free-opening of the nozzle is prevented which is clearly most undesirable.

According to the present invention there is provided an anti-skulling material for use in the outlet bore of a metallurgical handling vessel which material contains particulates and comprises granules containing the desired proportion of particulates so that the granules partially sinter at the material/molten metal interface at molten metal handling temperatures.

The granulated anti-skulling material of this invention is a material which, in use, will provide a physical barrier to molten metal entering the bore of a metallurgical handling vessel nozzle when the nozzle is closed and yet permit free-opening of the nozzle when the nozzle is opened and provides these properties in a more reliable and consistent manner than the prior art materials.

The granules comprising the granulated mixture may be produced by any of the known granulation processes but preferably the granules are formed by means of a spray-drying granulation process.

Each granule of an anti-skulling material, according to the invention, has the particulate constituents thereof distributed substantially homogeneously and thereby compensates for any differences in the particle size and/or density of its constituents. Accordingly, the material possesses enhanced resistance to segregation which, in turn, leads to significantly more uniform and reliable opening of the slide-gate mechanism of a metallurgical handling vessel.

The granulated anti-skulling material composition of the invention may comprise a mixture of two or more particulate refractory materials which partially sinter, i.e. form a bridge or crust, when subjected to elevated temperatures, e.g. in excess of 1500 $^{\circ}$ C. For example, the composition may comprise two or more of the following refractory materials:
chromite flour, silica flour, olivine, calcined magnesite, bauxite, chamotte, zircon and refractory aluminosilicates mixed in proportions appropriate to ensure that partial sintering occurs.

Such proportions for a particular composition may be readily determined by the average skilled man of the art.

Alternatively, the anti-skulling composition may comprise one or more particulate refractory materials such as alumina or magnesia which do not readily sinter at molten metal handling temperatures but which may be caused to partially sinter at said temperatures by mixing with such particulate refractory material a relatively minor proportion of a known sintering aid such as alkali or alkaline earth metal silicates, phosphates or borates.

In any event a proportion of an alkali metal silicate or phosphate may be present in the granulated anti-skulling material of the invention as a result of its presence as a binder in the composition as formulated prior to granulation of the composition. Specific examples of binders include sodium polyphosphates, sodium metaphosphates, aluminium phosphate and sodium silicate. The binder may be present in an amount up to 10% by weight, e.g. from 1 to 10%, especially 2 to 5% by weight.

The composition may optionally comprise a proportion of particulate carbon or carbonaceous material such as carbon black or crushed graphite electrode scrap, the inclusion of which, it is believed, is useful in

controlling the degree to which sintering occurs in the material remote from the composition/molten metal interface.

Depending on the size of the handling vessel, the anti-skulling material of the invention has a typical consumption rate of from about 2 kg to about 40 kg/vessel.

In another aspect, the invention provides a method of making an anti-skulling material in which a mixture is formed of particulates, the mixture in water is spray-dried to form granules containing the desired proportion of particulates, the granules being partially sinterable at molten metal handling temperatures.

Typically, the composition of a granulated anti-skulling material of the invention comprises:

% By Weight	Constituent
0 - 10	Particulate carbon or carbonaceous material
Up to 10	Binder/sintering aid
Balance	Sinterable or partially sinterable refractory filler material.

Prior to granulation using spray-drying equipment it is generally preferred to include from about 0.2% to about 1% of a suspension agent such as a heteropolysacharide (Biopolymer) or a carboxy-methylcellulose.

The invention is more particularly described with reference to the following examples:-

EXAMPLE 1

Ingredients	% by Weight
Chromite flour	30
Silica flour	66.3
Carbon black	0.5
Sodium silicate powder	3
Suspension agent	0.2

The dry particulate materials were mixed in a blender/mixer and then sufficient water was added to form a slurry having about 60% solids content. The slurry was sprayed through a fine nozzle into a hot-air spray drying vessel operating on the counter-flow principle. The temperature of the air was between 300 to 600 ° C. The resulting free-flowing granules were discharged into suitable containers for transit.

EXAMPLE 2

Ingredients	% by Weight
Chromite flour	30
Silica flour	61.5
Carbon black	0.5
Electrode scrap	5
Sodium hexa-meta-phosphate	3

The composition was prepared substantially in accordance with Example 1 except that the water added was consistent with that required for use with a high-energy mixer of the type manufactured by the Eirich Company.

In use of an anti-skulling material composition according to Example 1, 30 kg of free-flowing granules were charged into the bore of a slide-gate nozzle of a 200 tonne ladle. On introduction of molten metal steel at 1600°C into the ladle the initial contact with the anti-skulling material promoted partial sintering of the outer surface of the granules thus preventing molten steel or associated skull from entering into the bore. Upon opening of the slide-gate mechanism, all the anti-skulling material was instantly discharged from the bore enabling free-running of the slide gate to be established immediately on initial opening. The formation of any skull in the nozzles zone requiring removal before the steel could egress from the ladle was prevented.

Claims

1. An anti-skulling material for use in the outlet bore of a metallurgical handling vessel, which material contains particulates that partially sinter at the material/molten metal interface at molten metal handling temperatures, characterised in that the material comprises granules, each containing the desired proportion of particulates.

2. An anti-skulling material according to Claim 1, characterised in that the granules have been produced by a spray-drying process.

3. An anti-skulling material according to Claim 1 or 2, characterised in that the granules contain two or more of chromite flour, silica flour, olivine, calcined magnesite, bauxite, chamotte, zircon and refractory aluminosilicates in particulate form.

4. An anti-skulling material according to Claim 1 or 2, characterised in that the granules contain one or more particulate refractory materials which do not readily sinter at the molten metal handling temperature together with a minor proportion of a sintering aid.

5. An anti-skulling material according to Claim 4, characterised in that the particulate refractory material is alumina or magnesia.

6. An anti-skulling material according to Claim 4 or 5, characterised in that the sintering aid is an alkali or alkaline earth metal silicate, phosphate or borate.

7. An anti-skulling material according to any one of the preceding claims, characterised in that particulate carbon or carbonaceous material is included in the granules.

8. An anti-skulling material for use in the outlet bore of a metallurgical handling vessel, which material contains particulates, characterised in that the material comprises granules having the following

composition by weight:

i) 0 to 10% particulate carbon or carbonaceous material

ii) up to 10% binder and/or sintering aid

iii) the balance of the composition being sinterable or partially sinterable refractory filler material.

9. An anti-skulling material according to Claim 8, characterised in that it contains a binder selected from the group consisting of sodium polyphosphates, sodium metaphosphates, aluminium phosphate and sodium silicate.

10. An anti-skulling material according to Claim 8 or 9, characterised in that the binder is present in an amount of from 2 to 5% by weight.

11. A method of making an anti-skulling material in which a mixture is formed of particulates, characterised in that the mixture in water is spray-dried to form granules containing the desired proportion of particulates, the granules being partially sinterable at molten metal handling temperatures.

12. A method according to Claim 11, characterised in that from 0.2% to 1% of a suspension agent is included in the mixture.

13. A method according to Claim 11 or 12, characterised in that the proportions by weight of particles obtained in the granules are:

i) 0 to 10% particulate carbon or carbonaceous material

ii) up to 10% binder and/or sintering aid

iii) the balance being sinterable or partially sinterable refractory material.