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

Schieberfüllmasse für metallurgische Gefäße

Matière de charge pour poches métallurgiques

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Description

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.

In EP-A-0137734 is disclosed a flux for use particularly in the continuous casting of steel. The flux is formed as granules of a composition containing carbonaceous powder, binder and metallic oxides, the latter being in combined form, e.g. calcium oxide and silicon dioxide as calcium silicate in synthetic wollastonite. An essential feature of the granules is that they have a higher proportion of carbonaceous powder in their surfaces than the overall proportion of carbonaceous powder in the granules, i.e. there is a non-homogeneous distribution of the constituents throughout the granules.

In FR-A-2550126 is disclosed an anti-skulling material in granular form, the granules comprising a particulate core principally composed of quartz and

having a coating layer of a multiplicity of fine particles. The fine particles of the coating layer are principally made of materials selected from the feldspar per group and the coating material has a lower melting point than the core material. Again, there is a non-homogeneous distribution of the constituents throughout the granules.

It is an object of the present invention to provide an improved anti-skulling agent in granular form in which the granules have a substantially homogeneous distribution of their particulate constituents.

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 up to 10% binder and/or sintering aid and particulates comprising 0 to 10% carbon or carbonaceous material, the anti-skulling material being in granular form and the balance of the composition of the granules being sinterable or partially sinterable refractory filler material and wherein the particulate constituents of the granules are distributed substantially homogeneously therein.

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.

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 heteropolysaccharide (Biopolymer) or a carboxy-methyl-cellulose.

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°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. As indicated above, binder is present in an amount up to 10% by weight, e.g. from 1 to 10%, especially 2 to 5% by weight.

Also, as indicated above, the composition may 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.

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 up to 10% binder and/or sintering aid and particulates comprising 0 to 10% carbon or carbonaceous material, the anti-skulling material being in granular form and the balance of the composition of the granules being sinterable or partially sinterable refractory filler material and wherein the particulate constituents of the granules are distributed substantially homogeneously therein.
2. An anti-skulling material according to Claim 1, characterised in that the binder is selected from the group consisting of sodium polyphosphates, sodium metaphosphates, aluminium phosphate and sodium silicate.
3. An anti-skulling material according to Claim 1 or 2, characterised in that the binder is present in an amount of from 2 to 5% by weight.
4. An anti-skulling material according to any preceding

ing claim, 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.

5. An anti-skulling material according to any preceding claim, 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.

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

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

Patentansprüche

1. Antirückstandsmaterial zur Verwendung in der Auslaßbohrung eines metallurgischen Gebrauchsgefäßes, wobei das Material bis zu 10% Bindemittel und/oder Sinterhilfsmittel sowie Feststoffteilchen enthält, die 0 bis 10% Kohlenstoff oder kohlenstoffhaltiges Material aufweisen, wobei das Antirückstandsmaterial in Granulatform vorliegt und der Rest der Zusammensetzung der Granulate ein sinterbares oder teilweise sinterbares feuerfestes Füllstoffmaterial ist sowie die teilchenförmigen Bestandteile der Granulate im wesentlichen darin homogen verteilt sind.
2. Antirückstandsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Bindemittel aus der Gruppe ausgewählt ist, die aus Natriumpolyphosphaten, Natriummetaphosphaten, Aluminiumphosphat und Natriumsilicat besteht.
3. Antirückstandsmaterial nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Bindemittel in einer Menge von 2 bis 5 Gew% vorliegt.
4. Antirückstandsmaterial nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Granulate zwei oder mehr der Materialien Chromitmehl, Quarzmehl, Olivin, calcinierter Magnesit, Bauxit, Schamotte, Zirkon und feuerfeste Aluminosilicate in Teilchenform enthalten.
5. Antirückstandsmaterial nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Granulate ein oder mehrere teilchenförmige feuerfeste Materialien enthalten, die zusammen mit einer kleineren Menge eines Sinterhilfsmittels bei der Handhabungstemperatur von geschmolzenem Material nicht leicht sintern.

6. Antirückstandsmaterial nach Anspruch 5, dadurch gekennzeichnet, daß das teilchenförmige feuerfeste Material Aluminiumoxid oder Magnesiumoxid ist.

7. Antirückstandsmaterial nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß das Sinterhilfsmittel ein Alkali- oder Erdalkalimetallsilicat, -phosphat oder -borat ist.

Revendications

1. Matière anti-loup ou -calotte destinée à être utilisée dans l'alésage de sortie d'une cuve de traitement métallurgique, laquelle matière contient jusqu'à 10 % de liant et/ou d'adjuvant de frittage et des matières particulières comprenant 0 à 10 % de carbone ou de matière carbonée, la matière anti-loup ou -calotte étant sous forme granulaire et le complément de la composition des granules étant de la matière de charge réfractaire frittage ou partiellement frittage et dans laquelle les ingrédients particuliers des granules y sont distribués de façon essentiellement homogène.
2. Matière anti-loup ou -calotte selon la revendication 1, caractérisée en ce que le liant est choisi dans le groupe constitué par les polyphosphates de sodium, les métaphosphates de sodium, le phosphate d'aluminium et le silicate de sodium.
3. Matière anti-loup ou -calotte selon la revendication 1 ou 2, caractérisée en ce que le liant est présent en une quantité de 2 à 5 % en poids.
4. Matière anti-loup ou -calotte selon l'une quelconque des revendications précédentes, caractérisée en ce que les granules contiennent deux constituants ou plus choisis parmi la farine de chromite, la farine de silice, l'olivine, la magnésite calcinée, la bauxite, la chamotte, le zircon et les aluminosilicates réfractaires sous forme particulière.
5. Matière anti-loup ou -calotte selon l'une quelconque des revendications précédentes, caractérisée en ce que les granules contiennent une ou plusieurs matières réfractaires particulières qui ne se frittent pas facilement à la température de traitement du métal fondu, ensemble avec une proportion mineure d'un adjuvant de frittage.
6. Matière anti-loup ou -calotte selon la revendication 5, caractérisée en ce que la matière réfractaire particulière est de l'alumine ou de la magnésie.
7. Matière anti-loup ou -calotte selon la revendication 5 ou 6, caractérisée en ce que l'adjuvant de frittage est un silicate, phosphate ou borate de métal alcalin ou alcalino-terreux.