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(54) Title: DRY MIX FOR TREATING REFRACTORY SUBSTRATES AND PROCESS USING SAME

(54) Titre : MELANGE SEC POUR LE TRAITEMENT DE SUBSTRATS REFRACTAIRES ET PROCEDE LE METTANT EN OEUVRE

(57) Abstract: Dry mix for treating refractory substrates, comprising combustible particles of at least one oxidizable substance which, in the presence of oxygen, gives rise to an exothermic reaction, and particles of at least one other substance, wherein these particles form together, during said exothermic reaction, a coherent mass capable of adhering to and/or interacting with the treated substrate, characterized in that it comprises, as particles of at least one other substance, particles of at least one expanding substance, in that the dry mix without the particles of this at least one expanding substance has a first bulk density and in that the mix comprising said at least one expanding substance has a second bulk density lower than said first bulk density.

(57) Abrégé : Mélange sec de traitement de substrats réfractaires, comprenant des particules combustibles d'au moins une substance oxydable qui, en présence d'oxygène, donne lieu à une réaction exothermique, et des particules d'au moins une autre substance, ces particules formant ensemble, au cours de ladite réaction exothermique, une masse cohérente capable d'adhérer et/ou d'interagir avec le substrat traité, caractérisé en ce qu'il comprend, comme particules d'au moins une autre substance, des particules d'au moins une substance d'expansion, en ce que le mélange sec sans les particules de cette au moins une substance d'expansion présente une première densité apparente et en ce que le mélange comprenant ladite au moins une substance d'expansion présente une seconde densité apparente inférieure à ladite première densité apparente.

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Dry Mix for Treating Refractory Substrates and Process Using Same

The present invention relates to a dry mix for treating refractory substrates, comprising:

- combustible particles of at least one oxidisable substance which, in the presence of oxygen, gives rise to an exothermic reaction, and
- particles of at least one other substance,

wherein these particles together form, during said exothermic reaction, a coherent mass capable of adhering to and/or interacting with the treated substrate, this mix comprising, as particles of at least one other substance, particles of at least one expanding substance, the dry mix without the particles of this at least one expanding substance having a first bulk density and the dry mix comprising said at least one expanding substance having a second bulk density lower than said first bulk density,
and a process using such a mix.

Refractory walls used in certain production installations suffer damage during service due to erosion, corrosion, thermal shock etc., which renders their surface rough, porous or marked with defects (scaling, cracking, cavities etc.). This can have various consequences for the operation of the production installations: hindering the circulation of solid products, incrustation, leakage of fluid or gas, penetration of corrosive agents; in particular in coke ovens, walls of refractory silica in the carbonisation chambers become lined with carbon which over the course of time transforms into graphite and swells; it must be eliminated regularly to avoid a power overload on discharge of the coke. Similarly, the coal charging zone is also subject to such carbon deposits, which require manual removal at regular intervals. Also, continuous cracks between the carbonisation chamber and the heating flues allow the passage of organic matter towards the chimney, with the resulting ecological consequences.

These various faults and damage phenomena have led to the development of several methods of repair or treatment of refractory substrates.

For example, patent application FR-A-2202053 describes a method of projection onto a damaged wall, at high temperature, of an aqueous solution containing for the majority a refractory granular material of the same nature as the wall (silica), a binder (alkali metal borate or carbonate type), a colloidal thickener (bentonite) and a compound to lower the melting point (sodium silicate).

Patent application WO 2004/085341 also discloses the application to the substrate by dry gunning of a mixture comprising for the majority grains of vitreous silica, an aluminous granulate, a clay and a chemical binder.

Patent application FR-A-2524462 describes a method of flame spraying of a mixture comprising for the great majority particles of silica, calcium oxide and an addition of lithium oxide.

Reference may also be made to the family of patents relating to ceramic welding, which comprises the projection against a wall, at high temperature and in a flow of oxygen, of a mixture comprising for the majority refractory grains (silica, alumina, zirconia, etc.) and oxidisable particles (Si + Al) which, by exothermic reaction (combustion), form a coherent refractory mass on the wall to be repaired (see amongst others FR-A-2066355, FR-A-2516915 and BE-1005914).

These four methods allow application to the refractory substrate to be treated or repaired, of a thick, coherent refractory layer or mass which adheres to the surface of the substrate and/or interacts with this. These methods all use, for the composition of the mixture, a granular refractory material bonded by fusible components or components melted with a flame.

Also a process of ceramic welding is known which allows formation of a porous refractory mass, the mix to be projected containing, in addition to refractory particles and combustible particles, particles of a material able to give rise to the formation of a porosity inside the refractory mass formed by the projection (see GB-A-2233323).

During the operation of repair by reactive projection, the quality of the coating obtained on the generally refractory wall depends on several parameters, including in particular the temperature of the support, the speed of projection and the mass flow of the mixture.

In this type of process, and in particular in the case of ceramic welding, the carrier gas is a gas which is reactive with at least one of the elements of the powdery material. On contact with the hot wall, the mixture reacts spontaneously and a series of chemical reactions leads to the formation of an adhesive refractory material, the characteristics of which are compatible with those of the treated support.

The speed of projection is therefore a preponderant element. If this is too high, the quantity of material may not react (as it does not participate in the exothermic reaction), and may rebound too strongly on the wall, to the detriment of the quality of the magma formed by projection.

The object of the present invention is to develop a dry mix for treating refractory substrates and a process for its use which allows a slower and controlled projection speed, avoiding the possibility of flame back, so as to produce a suitable surface treatment, using a simple and effective compound.

To achieve this object, according to the invention a dry mix can be used such as described initially which comprises also, as the particles of at least one other substance, particles of at least one silica glass as the majority part by weight of the mix.

Due to its high specific volume (grain density preferably less than 2, advantageously less than 1.5, and in particular less than 1), the expanding substance gives the mix for projection a lower bulk density, which helps slow the projected mass flow and hence reduce the thickness of the layer deposited (of the order of millimetres) on the surface of the refractory on each passage of the spray jet. Application can be made in a single passage (surface treatment) or in several passages (filling a crack or cavity).

Said at least one expanding substance can be selected from expanded perlite, expanded vermiculite, powdered wood or coke, and their mixtures.

Preferably expanded perlite is used. Perlite is a granular silica glass of volcanic origin, which can be expanded thermally in order to obtain particles of expanded perlite. Preferably the size of the expanded perlite particles is less than or equal to 1 mm.

Unexpectedly, it has also been found that the presence of expanded perlite in the mix improves its stability (no segregation due to vibration). In fact it has been found that, during storage or transport of the mix when it may be subjected to shaking or vibration, the mix shows no sign of downward segregation of the combustible particles of the mix, which is the case if there are no expanded perlite particles.

Suitable oxidisable substances could be fine particles of one or more metals or metalloids capable of burning in the presence of oxygen, in particular at the normal operating temperature of the furnace to be repaired. Preferred substances may be particles of silicium, aluminium, zirconium, magnesium, calcium or even iron, chromium, titanium, or their mixtures or alloys. Preferably the size of the combustible particles is less than or equal to 100 µm.

In another embodiment of the invention, the mix also comprises, as the particles of at least one other substance, particles of at least one substance selected from the group comprising vitreous or fused silica, and crystalline silica such as quartz, tridymite and cristobalite; alumina, zircona, magnesia, lime, alkaline compounds and their mixes or mixed compounds. Preferably the size of the silica particles is less than or equal to 0.5 mm, preferably between 0.1 and 0.3 mm.

Silica glass here means any glass containing silicium. Preferred glasses are silico-sodo-calcic glasses, borosilicates, cullet or broken glass advantageously obtained from untinted glass, and mixtures of these materials. Preferably the size of the particles of silica glass is less than or equal to 1 mm so as to ensure total fusion of the particles. Advantageously their size is between 0.3 and 0.6 mm.

A mix according to the invention contains silica glass as the majority by weight of the dry mix. This term means that the weight fraction of the silica glass is greater than that of any other constituent in the mix.

Such a mix is perfectly suitable for a treatment process of the well known and controlled type of ceramic welding, where the addition of heat results mainly from an exothermic oxidisation of the combustible particles of the mix. In the presence of oxygen and at the operating temperature of the furnace, combustion is spontaneous and the silica glass particles melt completely to form an amorphous mass capable of being spread in a thin layer on the refractory wall to be repaired, and infiltrating into the cracks formed in this wall. The layer deposited is thin and has a smooth aspect which does not promote the adhesion of carbon deposits. The Ra roughness is of the order of 50 - 100 µm. Calculation of the roughness complies with standard ISO 11652 and ISO 4287-1997. This Ra value is the arithmetic standard deviation of the surface profile, i.e. the arithmetic mean of the absolute values of the profile deviations (as peaks or hollows) within the limits of a base length L.

The coherent mass applied to the refractory wall to be treated constitutes either a surface treatment to smooth a rough refractory wall, for example at the coal charging opening in a coking plant, or a means for filling fine cracks without applying excess thickness to the damaged refractory wall.

The refractoriness or high temperature strength of the resulting amorphous mass may advantageously be adapted to the service temperature via the proportion of silica added in relation to that of the crushed silica glass.

By adjustment of the weight proportion between the particles of silica glass and the particles of silica, a deposit can be obtained of extremely thin layers of a thickness of less than 2 mm per passage of the spraying machine. These layers have an extremely smooth surface which does not promote the adhesion of carbon deposits during operation of the furnace treated. Advantageously, this weight ratio may be between 3/1 and 6/1.

In a refined embodiment of the invention, the mixture contains:

a) 45 to 60% by weight of silica glass particles,

b) 10 to 40%, in particular 20 to 30% by weight of combustible particles,

c) 2 to 40%, in particular 5 to 10% by weight of expanded perlite particles,

d) 10 to 25% by weight of silica particles,

the sum of the percentages by weight of constituents a) to d) giving 100% by weight.

The invention also concerns a process for treatment of a refractory substrate of the type of ceramic welding process. It comprises projection onto this substrate of a jet of dry mix according to the invention in the presence of oxygen and at a temperature at which said combustible particles give rise to an exothermic reaction with said oxygen, and an at least partial fusion of particles of the mix in the form of a coherent amorphous mass which adheres to and/or interacts with the substrate. By using for example silica glass as the majority by weight of the mix, advantageously a complete fusion of the particles can be obtained. Advantageously the process comprises movement of the jet of dry mix during projection, forming a deposit of a uniform thin layer on the substrate. Successive repeated passages can also be performed at the same place on the substrate in order to obtain a superposition of thin smooth layers, one upon the other.

In a refined embodiment of the invention, the process comprises, after projection, annealing of said mass adhering to the substrate at a temperature at least greater than its vitreous transition temperature. This allows the amorphous mass deposited to complete its densification and perfect the smooth state of the surface.

This ability to create a molten mass on the surface of the refractory wall leads to another field of application of the invention, namely a process for descaling and/or machining of a refractory wall. The process according to the invention can in fact be applied to a glass-making furnace to descale a refractory wall in the superstructure or to cut perforations in blocks in order to later anchor a product which will be deposited by ceramic welding. The coherent mass formed interacts with the substrate to the point of causing it to melt and flow, with the aim of modifying its profile or hollowing it out (perforation for anchoring).

The present invention will be explained in more detail with reference to the examples given below which are non-limitative.

Example 1

The mixture to be projected comprises:

- 76% crushed silico-sodo-calcic glass (0.2 - 1 mm)
- 18% crushed silicium (< 50 μm)
- 6% fine aluminium (< 63 μm)

and its specific volume after homogenisation is 0.75 litre/kg.

The refractory wall to be treated has a temperature of around 900°C; the mixture sprayed in the oxygen flow combusts spontaneously and gives rise to an exothermic reaction; a uniform deposit is formed on movement of the jet of powdery mix (mass flow = 64.3 kg/hour).

The layer deposited has a relatively smooth aspect (roughness Ra = 50 - 100 μm) and results from complete fusion (no residual grains); the thickness is around 3 mm per passage of the spray jet; it adheres strongly to the refractory wall without detaching or cracking after cooling.

Example 2

The mixture this time comprises:

- 68% crushed silico-sodo-calcic glass (fraction 0.2 - 1 mm)
- 19% crushed silicium (< 50 μm)
- 6% fine aluminium (< 63 μm)
- and 7% expanded perlite (fraction < 1 mm).

Thanks to the addition of the expanded perlite, the specific volume is substantially higher (1.8 litre/kg) than that of the mix in the previous example.

After projection under the same conditions, the formed material is found to have spread very well [smoother surface (roughness Ra = 25 μm) and lower thickness

(2 mm)]. The lower volume mass of the mix allows a slower flow of the mix (58 kg/hour) from the spraying machine, which contributes to an improvement in quality and fineness of the deposit.

It is found that the fraction consisting of oxidisable particles (Si + Al) is no longer subject to segregation (downward concentration) when the mix is exposed to shaking or vibration. In contrast to the dry mix of the previous example in which the combustible particles do not adhere to the surface of the particles of silica glass, the mix in example 2 no longer has this tendency to segregation.

Example 3

In relation to example 2, part of the crushed silica glass has been replaced by a fine silica sand in order to increase the refractoriness of the resulting mass.

The mix therefore comprises:
- 55% crushed silico-sodo-calcic glass (0.2 - 1 mm)
- 10% silica sand (quartz) (0.1 - 0.3 mm)
- 20% silicium (< 50 μm)
- 8% aluminium (< 63 μm)
- 7% expanded perlite (fraction < 1 mm)

and its specific volume is 1.6 litre/kg.

Here, as in example 2, the mass flow has been slowed (56 kg/hour), which leads to a thinner deposit and an even more uniform surface (thickness per passage = 1.5 mm; roughness Ra = 20 μm).

The resulting deposit is then annealed at 1250°C for 5 hours which completes the densification; it has retained its vitreous aspect and has no tendency to flow up to this temperature; it still adheres perfectly to the refractory support, even after cooling.

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Finally, it has also been found that, on projection, the mass generated in molten state penetrates deeply into fine cracks, which facilitates their filling without forming extra thickness on the surface of the damaged refractory.

It must be understood that the present invention is in no way restricted to the embodiments and processes described above, and that modifications may be made to this without leaving the framework of the attached claims.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

Claims

1. Dry mix for treating refractory substrates, comprising
   - combustible particles of at least one oxidisable substance which, in the presence of oxygen, gives rise to an exothermic reaction, and
   - particles of at least one other substance,

   wherein these particles together form, during said exothermic reaction, a coherent mass capable of adhering to and/or interacting with the treated substrate,

   this mix comprising, as particles of at least one other substance, particles of at least one expanding substance, the dry mix without the particles of this at least one expanding substance having a first bulk density and the dry mix comprising said at least one expanding substance having a second bulk density lower than said first bulk density,

   characterised in that said mix also comprises, as particles of at least one other substance, particles of at least one silica glass, as the majority part by weight of the mix.

2. Mix according to claim 1, characterised in that said at least one expanding substance consists of grains of a density of less than 2.

3. Mix according to one of claims 1 and 2, characterised in that said expanding substance is selected from expanded perlite, expanded vermiculite, powdered wood or coke, and their mixtures.

4. Mix according to any of claims 1 to 3, characterised in that it also comprises, as particles of the at least one other substance, particles of at least one substance selected from silica, alumina, zircona, magnesia, lime, alkaline compounds and their mixtures or mixed compounds.

5. Mix according to claim 4, characterised in that the silica is selected from vitreous or fused silica, and crystalline silica and their mixtures.

6. Mix according to one of claims 1 to 5, characterised in that the silica glass is selected from the group comprising silico-sodo-calcic glasses, borosilicates, cullet or broken glass, and their mixtures.

7. Mix according to any of claims 4 to 6, characaterised in that it has a weight ratio between the particles of silica glass and the particles of silica of between 3/1 and 6/1.

8. Mix according to any of claims 1 to 7, characterised in that said at least one oxidisable substance is selected from the group comprising Si, Al, Zr, Mg, Ca, Fe, Cr, Ti or their combinations or alloys.

9. Mix according to any of claims 1 to 8, characterised in that it contains:
a) 45 to 60% by weight of silica glass particles,
b) 10 to 40% by weight of combustible particles,
c) 2 to 40% by weight of expanded perlite particles,
d) 10 to 25% by weight of silica particles,
the sum of the percentages by weight of constituents a) to d) giving 100% by weight.

10. Mix according to claim 9, characterised in that it contains:
a) 45 to 60% by weight of silica glass particles,
b) 20 to 30% by weight of combustible particles,
c) 5 to 10% by weight of expanded perlite particles,
d) 10 to 25% by weight of silica particles,
the sum of the percentages by weight of constituents a) to d) giving 100% by weight.

11. Mix according to any of claims 1 to 10, characterised in that the maximum size of the particles of expanding substance is less than or equal to 1 mm.

12. Mix according to any of claims 1 to 11, characterised in that the maximum size of the combustible particles is less than or equal to 100 μm.

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13. Mix according to any of claims 4 to 12, characterised in that the maximum size of the silica particles is less than or equal to 0.5 mm.

14. Mix according to any of claims 1 to 13, characterised in that the maximum size of the silica glass particles is less than or equal to 1 mm.

15. Process for treatment of refractory substance, comprising projection onto this substrate of a jet of dry mix according to any of claims 1 to 14 in the presence of oxygen and at a temperature at which said combustible particles give rise to an exothermic reaction with said oxygen, and an at least partial fusion of particles of the mix in the form of a coherent mass which adheres to and/or interacts with the substrate.

16. Process according to claim 15, characterised in that it comprises movement of the jet of dry mix during projection, forming a deposit of a uniform thin layer on the substrate.

17. Process according to one of claims 15 and 16, characterised in that it comprises, after projection, annealing of said mass adhering to the substrate at a temperature at least greater than its vitreous transition temperature.

18. Process according to claim 15, characterised in that it comprises also, by interaction of the coherent mass formed with the refractory substrate, a fusion and flow thereof with modification of the profile or hollowing of this substrate.

19. A dry mix for treating refractory substrates substantially as herein described with reference to the accompanying examples, excluding comparative examples.