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(54) **MOULDING OR CORE SANDMIX**

(57) The moulding or core sandmix with inorganic binder, the matrix of which is the fireproof granular material, which contains the inorganic loosening additive and possibly a hardener, which is characterized by this, that as a loosening additive it contains fine-grained ver-

miculite, a material which is a magnesium, iron and lithium hydrated aluminosilicate or fine-grained pearlite ore which is a transformed igneous rock in a form of potassium-sodium aluminosilicate glass.

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Description

[0001] The object of the invention relates to a moulding or core sandmix with an inorganic binder, which is used for making castings of all types of alloys.

[0002] The moulding and core sandmixes prepared with use of inorganic binders are used in founding engineering for many years. Their main advantage is low emission of harmful gases during pouring with liquid metal compared to moulding sandmixes with organic binders. The main disadvantage is poor knock-out properties, which makes them unsuitable for making complex castings with varying thicknesses of walls. In addition to poor knock-out properties these sandmixes are considered to be difficult to regenerate mechanically.

[0003] The moulding sandmix with inorganic binder consists of: granular matrix, which is usually formed by generally available quartz sand, binder and hardener. The hardening process of cores is carried out with use of gaseous carbon dioxide, influence of increased temperature or electromagnetic radiation from the microwave temperature range. In making the moulds the liquid organic hardeners are usually used, consisting of glycerol esters and ethylene glycol, mainly glycerol mono-, di- and triacetates and ethylene glycol diacetates. In Poland, the method of preparing sandmixes with use of liquid esters is called floster technology and the hardener is called flodur.

[0004] In order to improve the knock-out properties of the sandmixes with inorganic binders they are introduced with so-called loosening organic additives such as: coal dust, carbon black, peat coke, mazout, pitch, substances containing the phthalic anhydride, polyvinyl chloride, polyethylene, polypropylene, kaolin, treacle and other substances which significantly impairs the ecological properties of a sandmixes.

[0005] The easy to knock-out moulding or core sandmix is known from the Polish patent description no. 106 510, which consists of quartz sand and water glass, where the calcium carbonate in the amount of 0.5 to 25% of sand weight is used to facilitate the knock-out of sandmix.

[0006] The moulding or core sandmix based on quartz sand is also known from the Polish patent description no. 128 721, which contains coal dust or other bright coal carrier in the amount of 0.5 to 8 parts by weight, preferably in the amount of 2.0 to 6.0 and bauxite dust in the amount of 0.5 to 8.0 parts, preferably 2.0 to 4.0 parts and the water glass in the amount of 2.0 to 10.0 per 100 parts by weight of sand.

[0007] Moreover, the moulding or core sandmix with water glass and inorganic loosener is known from the patent description PL 166 929 B1, which contains calcium phosphate in the amount of 50-150% by weight compared to amount of the binder, which is used as an agent improving the knock-out properties.

[0008] The moulding or core sandmix is also known from the patent description PL 206 691 B1 which contains water glass and mineral porous additive with granular structure as a loosening additive, previously subjected to thermal treatment in temperature of 950 - 1150°C in the amount of 0.1 to 2.0 parts by weight per 100 parts by weight of the matrix. This additive consists of by weight: 70 - 80% of silica, 10 - 20% of aluminium oxide, 1 - 3% of ferric oxide, 1 - 8% of calcium and magnesium oxide and 5 - 8% of sodium and potassium oxide. The main disadvantage of such additive is the large difference of density compared to granular matrix, which inhibits the mixing process of moulding sandmix components.

[0009] The attempts to modify the structure of water glass with use of nanoparticles of metal oxides are known from literature, including the articles: A. Bobrowski, A. Kmita, M. Starowicz, B. Stypuła, B. Hutera titled "Effect of magnesium oxide nanoparticles on water glass structure", Archives of Foundry Engineering 2012, vol. 12 iss. 3, pages 9-12 and A. Bobrowski, B. Stypuła, B. Hutera, A. Kmita, D. Drożynski, M. Starowicz titled "FTIR spectroscopy of water glass - the binder moulding modified by ZnO nanoparticles" Metalurgija = Metallurgy 2012, vol. 51 no. 4, pages 477-480, what in consequence contributes to, inter alia, the improvement of knock-out properties of sandmixes.

[0010] The aim of this invention is to eliminate the disadvantage of state of the art in the scope of technology of sandmixes with inorganic binder, which is poor knock-out property, related to the phenomenon of sandmix strengthening under the influence of heating as a result of a contact with high temperature of casting alloy poured into the casting mould.

[0011] The object of the invention is moulding or core sandmix with inorganic binder, the matrix of which is the fireproof granular material, which contains the inorganic loosening additive and possibly a hardener, which is characterized that as a loosening additive it contains fine-grained vermiculite, a material, which is a magnesium, iron and lithium hydrated aluminosilicate or fine-grained pearlite ore which is a transformed igneous rock in a form of potassium-sodium aluminosilicate glass.

[0012] The vermiculite is formed by hydrolysis and then weathering of biotite or phlogopite, i.e. potassium-magnesium mica. It is introduced at the sandmix preparation stage, during which the fine-grained fraction of vermiculite is covered with a binder layer and evenly distributed within the entire volume.

[0013] On the other hand, the pearlite ore was formed from volcanic lava, originating from the eruption of undersea volcanoes in ancient geological eras. As a result of rapid cooling and contact with sea water, the lava has closed drops of water inside it. The pearlite ore is introduced at the stage of preparation of moulding or core sandmix, during which the pearlite ore grains are distributed evenly among the matrix grains and are covered with a layer of a binder.

[0014] In the course of researches on moulding and core sandmix containing the vermiculite as one of its components,

it turned out surprisingly, that as a result with liquid metal, the phenomenon of rapid transformation of water trapped in porous material into steam, which results in a 15 - 30-fold increase in its volume, takes place as a result of high temperature exposure. This reaction results in destruction of silicate glaze formed in the sandmix, thus lowering the final strength of the sandmix, what contributes to facilitating the castings knock-out process as a result of eliminating the strengthening of the sandmix.

[0015] The analogous phenomenon takes place in case of use of the pearlite ore in moulding or core sandmix. As a result of contact with liquid metal, the small grains of pearlite ore covered with silicate glaze formed in the sandmix increase their volume as a result of transformation of water trapped in the structure of pearlite ore into water steam. The rapid increase of pearlite causes destruction of hardened binder, thus lowering the final strength of a sandmix, what contributes to facilitating the castings knock-out process.

[0016] The preferable effect of using the solution according to the invention is that the introduction of fine-grained loosening additive in the form of vermiculite or pearlite ore eliminates the secondary reinforcements of sandmixes with inorganic binders, thus improving the knock-out process. The additive is being introduced at the stage of preparation of a sandmix and has no negative influence on sandmixes mixing process and does not cause deterioration of their basic mechanical and technological properties, as well as the quality of castings' surfaces. The sandmix is characterized by very low harmfulness for the environment, since the loosening additive is inorganic mineral material, and its introduction also improves the sandmix's compliance to mechanical regeneration.

[0017] The solution according to the invention is shown in the following embodiments.

Example 1. The moulding sandmix containing the following components:

[0018]

| | |
|---|---|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| geopolymer binder called Geopol 618, containing by weight: 14,5-15,5% Na ₂ O, 25,5-27,0% SiO ₂ , the rest is water | - 2,5 parts by weight |
| liquid hardener: the mixture of esters from SA series produced by SAND TEAM company from Czech Republic | - 8% parts by weight compared to the amount of geopolymer binder |
| loosening additive: vermiculite | - 1,0 part by weight |

Example 2. The moulding sandmix containing the following components:

[0019]

| | |
|---|-----------------------|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| sodium water glass | - 3,0 parts by weight |
| liquid hardener: flodur (ester of ethylene glycol diacetate) | - 8% parts by weight |
| compared to the amount of geopolymer binder loosening additive: vermiculite | - 1,0 part by weight |

Example 3. The moulding sandmix containing the following components:

[0020]

| | |
|---|---|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| geopolymer binder called Geopol 618, containing by weight: 14,5-15,5% Na ₂ O, 25,5-27,0% SiO ₂ , the rest is water | - 2,5 parts by weight |
| liquid hardener: the mixture of esters from SA series produced by SAND TEAM company from Czech Republic | - 8% parts by weight compared to the amount of geopolymer binder |
| loosening additive: vermiculite | - 2,0 parts by weight |

[0021] The tensile strength of a sandmix with geopolymer binder prepared without the loosening additive after 24 hours of rest is about 0.7 MPa. After heating the sandmix in temperature of 900°C the strength increases to about 0.85 MPa. On the other hand, the sandmix prepared of components mentioned in example 1, after 24 hours of rest was characterized by similar strength value, and after heating in temperature of 900°C the tensile strength rapidly dropped to the value less than 0.1 MPa.

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[0022] The compressive strength after 24 hours of rest of the sandmix with geopolymer binder, which was prepared without the loosening additive, is higher than 3 MPa. The sandmix prepared of components mentioned in example 1, after 24 hours of rest was characterized by similar strength value. The strength of sandmix with geopolymer binder after heating in the temperature of 900°C increases to about 5 MPa, while the strength of this sandmix prepared according to example 1, after heating in the temperature of 900°C rapidly drops to the value less than 0.1 MPa.

Example 4. The moulding sandmix containing the following components:

[0023]

| | |
|---|---|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| geopolymer binder called Geopol 618, containing by weight: 14,5-15,5% Na ₂ O, 25,5-27,0% SiO ₂ , the rest is water | - 2,5 parts by weight |
| liquid hardener: the mixture of esters from SA series produced by SAND TEAM company from Czech Republic | - 8% parts by weight compared to the amount of geopolymer binder |
| loosening additive: pearlite ore with the main fraction 0,16 - 0,10 - 0,071 | - 1,0 part by weight |

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Example 5. The moulding sandmix containing the following components:

[0024]

| | |
|---|----------------------------------|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| geopolymer binder called Geopol 618, containing by weight: 14,5-15,5% Na ₂ O, 25,5-27,0% SiO ₂ , the rest is water | - 2,5 parts by weight liquid |
| hardener: the mixture of esters from SA series produced by SAND TEAM company from Czech Republic | - 8% parts by weight compared to |
| the amount of binder loosening additive: pearlite ore with the main fraction 0,40 - 0,32 - 0,20 | - 2,0 parts by weight |

Example 6. The moulding sandmix containing the following components:

[0025]

| | |
|--|--|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| binder: sodium water glass | - 2,5 parts by weight |
| liquid hardener: flodur (ester of ethylene glycol diacetate) | - 8% parts by weight compared to the amount of binder |
| loosening additive: pearlite ore with the main fraction 0,16 - 0,10 - 0,071 | - 1,0 part by weight |

Example 7. The moulding sandmix containing the following components:

[0026]

| | |
|--|--|
| matrix: quartz sand from Szczakowa | - 100 parts by weight |
| binder: sodium water glass | - 2,5 parts by weight |
| liquid hardener: flodur (ester of ethylene glycol diacetate) | - 8% parts by weight compared to the amount of binder |
| loosening additive: pearlite ore with the main fraction 0,16 - 0,10 - 0,071 | - 2,0 parts by weight |

Example 8. The moulding sandmix containing the following components:

[0027]

- 5 matrix: quartz sand from Szczakowa - 100 parts by weight
geopolymer binder called Geopol 618, containing by weight: 14,5-15,5%
Na₂O, 25,5-27,0% SiO₂, the rest is water - 2,5 parts by weight
liquid hardener: the mixture of esters from SA series produced by SAND
TEAM company from Czech Republic - 8% parts by weight compared to the
10 loosening additive: pearlite ore with the main fraction 0,16 - 0,10 - 0,071) - 3,0 parts by weight

[0028] The tensile strength of a sandmix with geopolymer binder prepared without the loosening additive after 24
15 hours of rest is about 0.7 MPa, and after heating the sandmix in temperature of 900°C the strength increases to about
0.85 MPa. The sandmix prepared of components mentioned in example 4, after 24 hours of rest was characterized by
similar strength value, and after heating in temperature of 800°C the tensile strength rapidly dropped to the value less
than 0.25 MPa. On the other hand, the sandmix prepared of components mentioned in example 5, after 24 hours of rest
was characterized by similar strength value, and after heating in temperature of 800°C the tensile strength rapidly dropped
to the value less than 0.40 MPa.

20 [0029] The compressive strength after 24 hours of rest of the sandmix with geopolymer binder, which was prepared
without the loosening additive, is higher than 3 MPa, and after heating in the temperature of 800°C it increases to about
5 MPa. On the other hand, the sandmix prepared according to example 8, after 24 hours of rest was characterized by
similar strength value, and after heating in temperature of 800°C the tensile strength rapidly dropped to the value of 1.4
MPa

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Claims

- 30 1. The moulding or core sandmix with inorganic binder, the matrix of which is the fireproof granular material, which
contains the inorganic loosening additive and possibly a hardener, **characterized in that** it contains fine-grained
vermiculite as a loosening additive, a material, which is a magnesium, iron and lithium hydrated aluminosilicate or
fine-grained pearlite ore which is a transformed igneous rock in a form of potassium-sodium aluminosilicate glass.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 20 2842

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
| X | US 2009/025606 A1 (GREFHORST CORNELIS [NL] ET AL) 29 January 2009 (2009-01-29) * abstract * * paragraphs [0010], [0012], [0017], [0022], [0024], [0038] * | 1 | INV. B22C1/02 B22C1/18 B22C9/02 |
| X | ST. M DOBOSZ ET AL: "Development tendencies of moulding and core sands", CHINA FOUNDRY, vol. 8, no. 4, 1 November 2011 (2011-11-01), pages 438-446, XP055177917, * abstract * * section 1.1 * | 1 | |
| X | "Sand mould additive which promotes disintegration after use - consists of unsintered high temp. expandable clay mineral", WPI / THOMSON,, vol. 1977, no. 1, 18 November 1976 (1976-11-18), XP002680293, * the whole document * | 1 | TECHNICAL FIELDS SEARCHED (IPC) B22C |
| X | DE 30 17 119 A1 (HEINZE GMBH DR [DE]) 5 November 1981 (1981-11-05) * page 5, line 15 - line 21 * * page 7, line 1 * | 1 | |
| X | FR 2 377 244 A1 (NYNAES PETROLEUM AB [SE]) 11 August 1978 (1978-08-11) * claims 10,12,13,15 * | 1 | |
| The present search report has been drawn up for all claims | | | |
| Place of search The Hague | | Date of completion of the search 24 April 2019 | Examiner Grave, Christian |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |

EPO FORM 1503 03/82 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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24-04-2019

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|---|--|
| US 2009025606 A1 | 29-01-2009 | DE 102007027621 A1 EP 2014391 A2 US 2009025606 A1 | 18-12-2008 14-01-2009 29-01-2009 |
| ----- | ----- | ----- | ----- |
| DE 3017119 A1 | 05-11-1981 | NONE | |
| ----- | ----- | ----- | ----- |
| FR 2377244 A1 | 11-08-1978 | BE 862928 A FR 2377244 A1 IT 1161388 B NL 7800509 A SE 413997 B | 17-07-1978 11-08-1978 18-03-1987 19-07-1978 07-07-1980 |
| ----- | ----- | ----- | ----- |

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- PL 106510 [0005]
- PL 128721 [0006]
- PL 166929 B1 [0007]
- PL 206691 B1 [0008]

Non-patent literature cited in the description

- **A. BOBROWSKI ; A. KMITA ; M. STAROWICZ ; B. STYPUTA ; B. HUTERA.** Effect of magnesium oxide nanoparticles on water glass structure. *Archives of Foundry Engineering*, 2012, vol. 12 (3), 9-12 [0009]
- **A. BOBROWSKI ; B. STYPUTA ; B. HUTERA ; A. KMITA ; D. DROŻYNSKI ; M. STAROWICZ.** FTIR spectroscopy of water glass - the binder moulding modified by ZnO nanoparticles. *Metallurgija = Metallurgy*, 2012, vol. 51 (4), 477-480 [0009]