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(54) A compound for producing foundry moulds and cores

(57) A compound for manufacturing through rapid prototyping foundry moulds and cores which can be used for melting metallic alloys castings comprising a structural base component made of granular inert material and at least one binder suitable to increase the mechanical strength of said structural base component in respect to the hydrostatic pressure of the molten metallic alloy. In particular, the compound comprises at least one hygroscopic component suitable to at least partly absorb the humidity present in said structural base component, at least one reactant suitable to react with the oxygen present into the mould upon contact with the molten metallic alloy in order to trigger a combustion and at least one catalyst suitable to reduce the starting time of the combustion of said at least one reactant and increase the propagation rate of the combustion.

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Description

[0001] The present invention can be generically applied in the technical foundry field ad has particularly as object a compound for manufacturing moulds and cores, especially through prototyping, which can be used for melting metallic alloys castings.

[0002] As known, foundry moulds are constituted by at least one female die having an inner cavity reproducing in negative the casting to be melt and one or more cores intended to be housed inside said cavity. Both portions of the mould are made with sands, binders and other additives-based granular compounds.

[0003] A particularly critical aspect of this equipment is represented by the difficulty of achieving complex castings with undercuts or internal cavities. Indeed, in order to get these geometries it is necessary to prepare cores of considerable complexity and cost, and in some cases it is necessary to perform on the finished casting expensive and complicated mechanical workings.

[0004] In order to reduce these drawbacks, it is possible to use the technique of rapid prototyping, obtained through solidification of a plurality of superimposed layers of a granular compound.

[0005] In particular, the rapid prototyping allows to make a foundry core by overlapping a plurality of layers of a sand or proper resin-based compound, each having a thickness of some tenths of millimetre.

[0006] Every single layer is solidified by controlled application of a heat source, for instance by a laser beam suitable to produce a local temperature higher than the melting one of the resinous part of the compound.

[0007] Moreover, the high temperature produced by the laser beam will allow the melt areas of each layer to melt with the solified areas of the underlying layers thus giving origin to a high accuracy foundry core.

[0008] By suitably varying the composition of the compounds and the melting temperature of the laser beam it is possible to provide cores with mechanical and chemical-physical properties more suited to the alloy used for casting.

[0009] A mould or core produced by the technology of rapid prototyping is described in the prior art patent document US6,155,331 and in the scientific literature documents entitled respectively *"Investigation on casting mold (or core) making with coated sand by the selective laser sintering",* on behalf of ZITIAN FAN and others (CHINA FOUNDRY JOURNAL), and *"An investigation of rapid prototyping of sand casting molds by selective laser sintering",* on behalf of CASALINO and others (LASER INSTITUTE OF AMERICA), in which the mould is obtained starting from sands and binders-based granular compounds.

[0010] A drawback of such a solution is represented by the fact that the compound currently used in the process of rapid prototyping presents a relatively low melting temperature which hinders use thereof with castings of metallic alloys having relatively high melting temperatures.

[0011] A further drawback of such a solution is represented by the fact that in order to get the uniform melting of the compound during the process of rapid prototyping it is necessary to keep the speed of advance of the laser beam low, consequently considerably lengthening time of completion of the mould.

[0012] A further drawback of such a solution is represented by the fact that the compounds currently used do not allow to make moulds and cores with particularly extensive internal cavities or walls with undercuts of particularly complex geometries.

[0013] Main purpose of the present invention is to overcome the above encountered drawbacks, by providing a compound for foundry cores that allows to manufacture foundry moulds and cores which can be used with a high melting temperature of the molten material.

[0014] A particular purpose of the present invention is to provide a compound particularly suitable for manufacturing moulds and cores through rapid prototyping and which allows to significantly increase the speed of advance of the laser beam with respect to the state of the art of the technical field of the foundry.

[0015] A further particular purpose of the present invention is to make available a compound which allows to manufacture cores with particularly complex geometries.

[0016] These purposes, as well other ones which will appear more clearly hereinafter, are achieved by a compound for manufacturing through rapid prototyping foundry moulds and cores which can be used for melting metallic alloys castings according to the attached claim 1: more precisely, the compound of the present invention comprises a structural base component made of granular inert material, at least one hygroscopic component suitable to at least partly absorb the humidity present in said structural base component, at least one reactant suitable to react with the oxygen present in the mould upon contact with the molten metallic alloy in order to trigger a combustion, at least one catalyst suitable to reduce the starting time of the combustion of said at least one reactant component and increase the propagation rate of the combustion, at least one binder suitable to increase the mechanical strength of said structural base component in respect to the hydrostatic pressure of the molten metallic alloy.

[0017] The compound obtained by the aforesaid combination allows to produce foundry moulds and cores with mechanical and chemical-physical properties suitable to facilitate its use with foundry castings having high melting temperature (included between 680°C, in case of aluminum alloys, and 1,900°C, in case of steel alloys) and with high specific weight. Advantageous embodiments of the invention are indicated in the corresponding dependent claims.

[0018] The composition according to the invention is used to provide moulds and cores for the melting of metallic alloys castings such as, for example, aluminum alloys, steel, cast iron, bronze, titanium.

[0019] The compound, substantially in the granular or powdery shape, lends itself to be used in rapid prototyping, that is in the production of moulds and cores by controlled solidification of superimposed layers without intermediate three-dimensional models, that is without using physical moulds but directly processing a virtual image.

[0020] The mould will have an inner female cavity and the core will constitute a male element to be inserted into the inner cavity so as to provide the final casting.

[0021] According to the invention, the compound for manufacturing foundry moulds and cores includes:

a) a structural base component made of granular inert material;
b) at least one hygroscopic component suitable to at least partly absorb the humidity present in the structural base component;
c) at least one reactant suitable to react with the oxygen present in the mould upon contact with the molten material in order to trigger a combustion, typically at a temperature included between 50°C and 150°C;
d) at least one catalyst suitable to reduce the starting time of the combustion of the reactant and increase the propagation rate of the combustion in the same and
e) at least one binder suitable to increase the mechanical strength of the structural base component in respect to the hydrostatic pressure of the molten metallic alloy.

[0022] Suitably, the inert material of the structural base component a) could be selected from the group of siliceous sands (otherwise known as natural sands, typically though not exclusively having a content of silicon equal to 97.4%) and/or in the group of synthetic sands (natural sands thermally treated) and could present an index of fineness between 50AFA and 170AFA.

[0023] In particular, the percentage of the structural base component a) could be included between 82% and 99% of the total weight of the compound, preferably between 85% and 98.5% of the total weight of the compound, and still more preferably between 93.7% and 94.2% of the total weight of the compound.

[0024] By purely indicative and preferred, but not limiting, title, the siliceous sands and/or synthetic sands are in percentage included between 94% and 98.5% of the total weight of said structural base component.

[0025] Preferably, the granules of siliceous sand and/or synthetic sand used for the structural inert material could be pre-coated with a partly polymerized and lubricated phenolic resin which, by being heated in contact with the melting casting, contributes to amalgamate the structural base component.

[0026] The phenolic pre-coating resin could be chosen from the group comprising the novolac with free phenol lower than 1% and will be present in a percentage between 1.5% and 7% of the total weight of the inert structural component.

[0027] Advantageously, the use of a phenolic resin of novolac type will allow to manufacture cores with higher accuracy since the thermoplastic polymers contained into such a resin allow to increase the ductility and formability of the compound when the latter solidifies. Furthermore, the use of novolac with a percentage of phenol lower than 1% as phenolic resin advantageously allows to limit the emission of reaction gas during the melting of the metallic alloy casting into the mould (or core) made with the compound of the invention, while retaining the advantages just mentioned above.

[0028] In particular, when the inert granular material is selected from the group of the siliceous sands, the index of fineness of the same will be preferably included between 120AFA and 140AFA with a tolerance of about +5AFA and could present a resinous part equal to about 3% of its total weight.

[0029] Use of siliceous sands will allow to get a compound particularly suitable to manufacture through rapid prototyping foundry moulds and/or cores with a maximum melting temperature close to 1,800°C and a use temperature included between approximately 250°C and approximately 350°C.

[0030] The hot flexural strength of the final mass will be close to 700 N/cm^2 with a tolerance of $\pm$80 N/cm^2, cold resistance close to 1,100 N/cm^2 and tolerance of $\pm$120 N/cm^2 and loss by calcination of 3.5% with a tolerance of $\pm$ 0.2%.

[0031] When the granular inert material is selected from the group of the synthetic sands, for example of the type cerabit® or similar, the index of fineness will be preferably included between 60AFA and 120AFA with a tolerance of about +5AFA, and the resinous coating will be included between 2% and 5% of its total weight.

[0032] The use of an inert component selected from the group of the synthetic sands will allow to get a compound suitable to manufacture foundry cores for cast iron castings of limited section or for aluminum, steel or an alloy thereof castings.

[0033] In this case, the operating temperature will be included between about 60°C and about 100°C, the hot flexural strength close to 360 N/cm^2 with tolerance of +50 N/cm^2, cold resistance close to 600 N/cm^2 with tolerance of +80 N/cm^2 and the loss by calcination included between 2.4% and 2.8% with tolerance of +0.1%.

[0034] The structural base component a) could be solidified by application of a concentrated heat source, for instance by a laser beam of predetermined power and frequency.

[0035] For example, the laser could be of the $C0_2$ type with maximum power in the range of values from 80W to 300W. The amplitude of such a beam could be approximately 0.2 mm and the maximum speed of movement of the same could be included between 100 m/s and 10,000 m/s.

[0036] The laser beam will cause a partial melting of the phenolic resin which coats the sand. The subsequent cooling will lead to solidification of the phenolic resin which will contribute to increase the compactness of the compound in the area treated by the laser beam and, in particular, will allow to uniformly mix the compound at the outer peripheral edges of the core without forming shrinkages or imperfections.

[0037] With regard to the hygroscopic component b) identified above, it will be chosen in such a way as to absorb the humidity present in the structural base component in a percentage ranging between 10% and 60% of the total humidity present in such an inert base component (the total humidity, coincident with the environmental humidity, depends on the conditions of the environment in which the process of manufacturing the mould or core using rapid prototyping and melting of the metallic alloy casting takes place), and avoid formation of lumps or clumps during the combination of the components.

[0038] Suitably, the hygroscopic component b) could be chosen from the group comprising calcium stearate. This material will be particularly suitable to prevent the thickening or lumps of the inert component and presents a self-ignition temperature not lower than 400°C.

[0039] Suitably again, the hygroscopic component b) could be present in a percentage included between 0.03% and 0.35%, more preferably included between 0.05% and 0.25% of the total weight of the compound.

[0040] Preferably but not exclusively, the reactant c) could be selected from the group of esammines which are a highly flammable and allergenic heterocyclic organic compound (they have a boiling temperature equal to 280°C), and assure the proper and uniform trigger of the combustion of the reactant component when they are placed into contact with the melting casting.

[0041] More in detail, the hexamine is a particular type of amine highly soluble in water and polar organic solvents (such as alcohol and chloroform), useful in the synthesis of other chemical compounds, such as for instance plastic materials and pharmaceuticals.

[0042] Alternatively, the reactant c) could be chosen from the group comprising the amines or similar obtained by the chemical reaction of formaldehyde and ammonia.

[0043] Reactant c) could be present in a percentage included between 0.1% and 1%, more preferably between 0.4% and 0.5% of the total weight of the compound.

[0044] Preferably but not necessarily, the catalyst d) can be chosen within the group comprising salicylic acid ($C_7H_6O_3$) or similar.

[0045] Salicylic acid is a carboxylic acid, identified as a plant hormone, notoriously used for years in fields far from that one of the present invention, such as for example the food industry, medicine and cosmetics, and mostly known for its healing properties: salicylic acid is, indeed, the essential component of some products for the treatment of the skin, especially for the treatment of acne and warts, and can also be used in cases of psoriasis in order to eliminate exfoliation and thus facilitate the topical treatment.

[0046] More specifically, such a catalyst d) could be present in a percentage included between 0.05% and 1% of the total weight of the compound of the invention.

[0047] Salicylic acid could present a melting temperature included between 150°C and 180°C and a temperature of beginning of the sublimation included between 70°C and 80°C. Furthermore, salicylic acid could present a minimum ignition temperature included between 470°C and 500°C.

[0048] Binder e) could be preferably selected from the group of the phenolic resins or similar. More precisely, binder e) could be selected from the group of the phenolic resins of resol-novolac type in alcoholic solution.

[0049] In a preferred but not binding manner, binder e) just identified could be present in a percentage included between 1.5% and 10% of the total weight of the compound.

[0050] Such a type of phenolic resins has a density at 20°C comprised between 1.11 g/cm^3 and 1.13 g/cm^3 and a viscosity comprised between 1,300 mPas and 2,000 mPas. Furthermore, the phenolic resins have a pH included between 2.2 and 3.5 and an induction time of the resin at 150°C included between 50 sec and 90 sec.

[0051] The foundry mould and/or the core that is obtained through the compound according to the invention could have a substantially porous structure so as to allow air to fill the interstices present in the mass and facilitate trigger of the reactant component when the same is placed into contact with the molten metal.

[0052] Moreover, the combustion triggered by the reactant c) identified above when the same is placed into contact with the molten metal could extend to the binder component, the catalyst component and the hygroscopic component.

[0053] The partial combustion of the compound could cause the partial or total destruction of the structure of the mould and/or core as a result of the introduction of the melting casting into the mould itself.

[0054] Suitably, the combustion triggered by the reactant c) does not affect the inert structural base component a) which will maintain substantially unaltered its physical-chemical properties even after the introduction of the melting casting and could be reused later to form again the compound.

[0055] Indeed, during the melting of the metallic alloy in the mould obtained with the compound of the invention, a percentage equal to about 20% of the structural base component made of inert material is burned upon contact with the melting casting. This percentage is immediately reusable, subject to specific and appropriate separation by sieving, while the remaining percentage is subsequently recoverable by calcination.

[0056] It has been verified by the applicant that the compound according to the invention, once solidified, has a flexural strength not less than hot 350 N/cm^2 with a tolerance of approximately $\pm$50 N/cm^2 and a cold flexural strength not less than 550 N per unit of square centimetre with a tolerance of approximately ±80 N/cm^2.

[0057] Furthermore, the compound solidified could present a loss by calcination - understood as the difference between the total weight of the compound before the introduction of the melting casting and the total weight of the compound remaining after the introduction of the melting casting -: this loss by calcination will be not more than 3.5% with a tolerance of ±0.2%.

[0058] A change in the percentage of the binder e) and reactant c) on the total weight of the compound could generated a change in the hot flexural strength of the compound and a change in the speed of movement (or advance) of the laser beam used for the rapid prototyping of the core and/or mould.

[0059] In particular, a percentage increasing of the binder e) and reactant c) could cause an increase of the hot flexural strength.

[0060] Conversely, the percentage decrease of the binder and reactant could cause a decrease in hot flexural strength.

[0061] In addition, the higher the percentage of the binder e), such as phenolic resin or similar, on the total weight of the compound the higher the mechanical strength of the structural base component in respect to the hydrostatic pressure of the melting casting.

[0062] Besides that, the higher the percentage of the catalyst b), such as preferably the salicylic acid ($C_7H_6O_3$) or similar, on the total weight of the compound the lower the trigger time of the combustion of the reactant.

[0063] Furthermore, a limited increase in percentage of only the reactant c) could result, the power used for the laser beam being equal, in an increase of maximum speed of movement of the beam itself.

[0064] Suitably, the percentage change of the reactant could be normally included within a range of about ± 3%.

[0065] Conversely, a limited decrease in percentage of only the reactant could result, the power used for the laser beam being equal, in a reduction of the maximum speed of movement of the laser beam.

[0066] The maximum speed of movement of the laser beam must be intended as the maximum speed of movement of the beam on the compound suitable to cause melting of the resinous part and of the components present in the same in order to obtain a subsequent solidification suitable to confer the core (and/or mould) the desired mechanical and chemical-physical properties.

[0067] In any case, the applicant was able to verify that the compound of the invention is able to increase the speed of advance of the laser beam even up to 200% compared to the levels allowed by the technologies currently used.

EXAMPLES

__Example 1__

[0068] In order to get approximately 450 Kg of compound an amount of siliceous sand equal to about 420 Kg, pre-coated with a partly polymerized and lubricated novolac type phenolic resin has been mixed with calcium stearate in an amount equal to approximately 0.8 Kg, in percentage corresponding to 0.17% of the total weight of the compound. Examine in amount equal to about 2 Kg and a catalyst consisting of salicylic acid in amount equal to about 1.2 Kg has been added to the mixture. Finally, a binder consisting of resol-novolac type phenolic resin in solution alcoholic has been added to the mixture in amount equal to 25 Kg. The final compound has been used to especially prepare moulds and cores for steel, cast iron and bronze and non-ferrous materials castings, using a laser beam for the solidification of the mass. The maximum temperature of the melting casting allowed by the moulds and cores obtained with the aforesaid composition of the compound of the invention is equal to about 1,800°C.

__Example 2__

[0069] In order to get approximately 400 Kg of compound an amount of cerabit® synthetic sand equal to approximately 375 Kg, pre-coated with a partly polymerized and lubricated phenolic resin of novolac type, has been mixed with calcium stearate in amount equal to approximately 0.8 Kg, hexamine in amount equal to approximately 2 Kg and a catalyst consisting of salicylic acid in amount equal to approximately 1.15 Kg. Finally, a phenolic resin of resol-novolac type in alcoholic solution has been added in amount equal to 21 Kg. The final compound has been used to specifically prepare moulds and cores for steel and aluminum alloys castings, using a laser beam for the solidification of the mass. The maximum temperature of the melting casting allowed by the moulds and cores obtained with the aforesaid composition of the compound of the invention is equal to approximately 1,700°C.

[0070] From what previously described, it appears evident that the invention achieves the prefixed purposes and in particular the purpose of providing a compound for manufacturing foundry moulds and cores which allows to be used with a wide range of melting castings, even with particularly high melting temperatures.

[0071] The compound according to the invention is liable to several modifications and variants falling within the inventive concept expressed by the appended claims. All the details could be replaced by technically equivalent elements, and the materials could be different depending on the needs, without departing from the scope of the invention.

Claims

1. Compound for manufacturing through rapid prototyping foundry moulds and cores which can be used for melting metallic alloys castings, said compound comprising:

- a structural base component made of granular inert material;
- at least one binder suitable to increase the mechanical strength of said structural base component in respect to the hydrostatic pressure of the molten metallic alloy,

characterized in that it comprises:

- at least one hygroscopic component suitable to at least partly absorb the humidity present in said structural base component;
- at least one reactant suitable to react with the oxygen present into the mould upon contact with the molten metallic alloy in order to trigger a combustion;
- at least one catalyst suitable to reduce the starting time of the combustion of said at least one reactant and increase the propagation rate of the combustion.

2. Compound according to claim 1) **characterized in that** the inert material of said structural base component is selected in the group comprising siliceous sands and/or in the group comprising the synthetic sands with index of fineness between 50AFA and 170AFA.

3. Compound according to claim 1) or 2) **characterized in that** said structural base component is in percentage included between 82% and 99%, preferably between 85% and 98,5% and even more preferably between 93,7% and 94,2% of the whole weight of the compound.

4. Compound according to claim 3) **characterized in that** said siliceous sands and/or said synthetic sands are in percentage included between 94% and 98,5% of the whole weight of said structural base component.

5. Compound according to claim 4) **characterized in that** said siliceous sands and/or said synthetic sands are pre-coated with an at least partly polymerized and lubricated phenolic or similar resin.

6. Compound according to claim 5) **characterized in that** said phenolic or similar resin is selected from the group comprising novolac with phenol lower than 1%.

7. Compound according to claim 5) or 6) **characterized in that** said phenolic or similar resin is in percentage included between 1,5% and 7% of the whole weight of said structural base component.

8. Compound according to any of the preceding claims **characterized in that** said at least one hygroscopic component is selected form the group comprising calcium stearate.

9. Compound according to claim 8) **characterized in that** said at least one hygroscopic component is in percentage included between 0,03% and 0,35% of the whole weight of the compound.

10. Compound according to any of the preceding claims **characterized in that** said at least one reactant is selected from the group comprising the examines or the amines or similar obtained from the chemical reaction of formaldehyde and ammonia.

11. Compound according to claim 10) **characterized in that** said at least one reactant is in percentage included between 0,1% and 1% of the whole weight of the compound.

12. Compound according to any of the preceding claims **characterized in that** said at least one catalyst is selected from the group comprising salicylic acid ($C_7H_6O_3$) or similar.

13. Compound according to claim 12) **characterized in that** said at least one catalyst is in percentage included between 0,05% and 1% of the whole weight of the compound.

14. Compound according to any of the preceding claims **characterized in that** said at least one binder is selected from the group comprising the phenolic resins or similar.

15. Compound according to claim 14) **characterized in that** said at least one binder is in percentage included between 1,5% and 10% of the whole weight of the compound.

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EUROPEAN SEARCH REPORT

Application Number
EP 13 42 5098

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	7 April 2014	Lombois, Thierry

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X : particularly relevant if taken alone
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A : technological background
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Application Number
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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