



(51) International Patent Classification:

B22C 3/00 (2006.01) *B22C 1/16* (2006.01)
B22C 7/02 (2006.01) *B22C 1/22* (2006.01)
B22C 9/04 (2006.01)

(21) International Application Number:

PCT/IB2018/055359

(22) International Filing Date:

18 July 2018 (18.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/535,020 20 July 2017 (20.07.2017) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

(54) Title: INVESTMENT CASTING COMPOSITIONS, MOLDS, AND RELATED METHODS

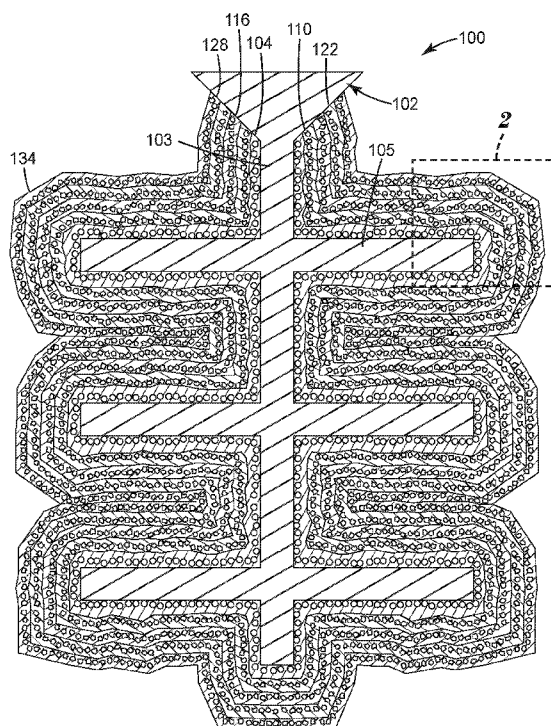


Fig. 3

(57) Abstract: Various embodiments of an injectable slurry composition for investment casting are disclosed. The injectable slurry composition can include a refractory material, a binder, a solvent, and a thixotropic agent that includes fibrillated fibers. The injectable slurry composition can also include a working viscosity of 200-3000 poise when subjected to a yield stress ranging from 1100 dynes/cm² to 1400 dynes/cm².



EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

INVESTMENT CASTING COMPOSITIONS, MOLDS, AND RELATED METHODS

BACKGROUND

5 Investment casting, sometimes referred to as a “lost wax” process, is a well-known method of manufacturing components having intricate and complex shapes. This process is used in diverse large- and small-scale applications, ranging from the manufacture of superalloy gas turbine engine components to tiny customized orthodontic appliances.

10 An investment casting process typically begins with the preparation of a sacrificial wax pattern having a size and shape similar to that of the device to be manufactured. This wax pattern can be made by molding, a rapid prototyping process, or any other method. The pattern then undergoes a shelling process in which it is sequentially dipped into tanks containing coating materials, typically ceramic slurries. Each layer of coating material is given time to dry before the next dip. Additionally, dry refractory granules, or stucco, can be applied between dips to enhance the structural integrity of the shell. This process can be
15 repeated over and over to gradually build up a shell having multiple ceramic layers.

After the shell is thus formed, the pattern is heated, typically using a flash furnace or steam autoclave, to melt the wax and allow it to be extracted from the mold. The end result is a mold with a hollow cavity faithfully reproducing the shape of the pattern. At this point, the mold can be further strengthened by firing. A molten metal alloy can then be introduced into the mold cavity to cast the
20 desired part. Finally, after the alloy has been sufficiently cooled, the mold can be mechanically or chemically disintegrated to separate the cast part from the mold.

In conventional investment casting methods, the finished shell contains six or more layers, each of which could include two or more sub-layers of slurry or stucco. The first layer, known as a prime coat, is applied directly to the wax pattern. The prime coat often includes both a refractory slurry and a
25 refractory stucco. The finished shell can include one or more prime coat layers. The next layer, known as the intermediate coat, is applied over the prime coat and also includes a refractory slurry and a refractory stucco. As with the prime coat, the finished shell can also include one or more intermediate layers. Following application of the prime and intermediate coats, three or more backup coats are generally applied to build up the thickness of the shell. Each backup coat also commonly includes a refractory
30 slurry and a refractory stucco. In many cases, a final seal coat is then applied over the final backup coat to prevent stucco from coming loose from the shell during further processing of the shell.

SUMMARY

35 In general, the present disclosure provides various embodiments of an injection slurry composition for investment casting and a method of forming such composition. The injection slurry composition can include at least one of a refractory material, a binder, a solvent, and a thixotropic agent. In one or more embodiments, the thixotropic agent can include fibers, e.g., fibrillated fibers. Further, in

one or more embodiments, the injection slurry composition can be injected into one or more cavities of a mold and dried or hardened prior to coating the mold with one or more additional slurry compositions.

In one aspect, the present disclosure provides an injectable slurry composition for investment casting. The injectable slurry composition includes a refractory material, a binder, a solvent, and a
5 thixotropic agent including fibrillated fibers. The injectable slurry composition also includes a working viscosity of 200-3000 poise (20 to 300 Pascal-seconds) when subjected to a yield stress ranging from 1100 dynes/cm² to 1400 dynes/cm² (110 to 140 Pascal).

In another aspect, the present disclosure provides a method of making an investment casting mold. The method includes injecting a first slurry composition into a cavity of a sacrificial pattern; at
10 least partially hardening the first slurry composition; forming a first layer including a second slurry composition on the sacrificial pattern; and at least partially hardening the first layer. The first slurry composition includes a first working viscosity and the second slurry composition includes a second working viscosity, where the first working viscosity is greater than the second working viscosity.

15 These and other aspects of the present disclosure will be apparent from the detailed description below. In no event, however, should the above summaries be construed as limitations on the claimed subject matter, which subject matter is defined solely by the attached claims, as may be amended during prosecution.

20 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic perspective view of one embodiment of an investment casting wax pattern.

FIG. 1a is a schematic cross-section view of the investment casting wax pattern of FIG. 1.

FIG. 2 is a schematic perspective cross-section view of the investment casting wax pattern of
FIG. 1.

25 FIG. 3 is a schematic cross-section view of an embodiment of a multilayered investment casting mold.

FIG. 4 is an enlarged fragmentary cross-section view of an inset portion of the investment casting mold of FIG. 3.

FIG. 5 is a schematic cross-section view of another embodiment of a multilayered investment
30 casting mold.

FIG. 6 is a schematic cross-section view of another embodiment of a multilayered investment casting mold.

FIG. 7 is a schematic cross-section view of another embodiment of an investment casting mold.

FIG. 8 is a flowchart of one embodiment of a method of making an investment casting mold.

35 FIG. 9 is a plot of viscosity versus stress for an exemplary investment casting mold.

DEFINITIONS

As used herein:

“injectable” refers to a slurry composition for investment casting that can be injected into small features or cavities of an investment casting mold and dried or hardened to form a portion of the final mold;

“refractory” refers to a heat-resistant ceramic material;

“slurry” refers to a fluid mixture of a solid grain with a liquid;

“stucco” refers to a solid grain having a particle size usually not typically coarser than a U.S. sieve 20 mesh screen;

“thixotropic” refers to a shear-thinning property, where a gel or liquid becomes less viscous when it is shaken, agitated, or otherwise stressed;

“wax” refers to a polymeric substance capable of melting at low temperatures to yield a low viscosity liquid; and

“zircon” refers to zirconium silicate, having the chemical formula ZrSiO_4 .

As used herein, the terms “preferred” and “preferably” refer to embodiments described herein that may afford certain benefits under certain circumstances. Other embodiments may also be preferred, under the same or other circumstances. Further, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

As used herein and in the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a” or “the” component may include one or more of the components and equivalents thereof known to those skilled in the art. Further, the term “and/or” means one or all of the listed elements or a combination of any two or more of the listed elements.

It is noted that the term “comprises” and variations thereof do not have a limiting meaning where these terms appear in the accompanying description. Moreover, “a,” “an,” “the,” “at least one,” and “one or more” are used interchangeably herein.

Reference throughout this specification to “one embodiment,” “certain embodiments,” “one or more embodiments” or “an embodiment” means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as “in one or more embodiments,” “in certain embodiments,” “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

DETAILED DESCRIPTION

The present disclosure describes, by way of illustration and example, slurry compositions used to produce investment casting molds. In one or more embodiments, the slurry composition can be injectable such that the composition can be injected into fine or small features of a mold. The slurry composition can include at least one of a refractory material, a binder, a solvent, and a thixotropic agent. In one or more embodiments, the thixotropic agent can include fibers, e.g., fibrillated fibers. In one or more embodiments, the slurry composition can be injected into one or more cavities of a mold and dried or hardened prior to coating the mold with one or more additional slurry compositions to form one or more layers on the mold.

The illustrated patterns and associated sprues are exemplary, not drawn to scale, and may differ widely in size and shape depending on the application at hand. It is further understood that the refractory materials, solvents, and binders herein described are exemplary and may be substituted or modified according to the knowledge of one skilled in the art.

While the compositions and related methods described herein enable one of skill in the art to make and use investment casting molds with certain advantageous properties, it is appreciated that these compositions and methods could be further combined with additives or enhancements not examined here. For example, slurry compositions could further include gaseous or solvent-based gelling agents, chemically treated refractory materials, and slurry binder systems that interact with one another. In one or more embodiments, other additives such as microsilicas and pozzolans can also be utilized.

Creating the aforementioned layers of the shell involves a substantial amount of time. Substantial amounts of time are involved not only in the dipping process used to apply each of the constituent slurry and/or stucco layers, but also the drying steps that follow the coating of each major layer. The large number of steps in the manufacturing process also heightens the overall risk of inadvertently inducing a defect or causing damage to the shell.

One or more embodiments of the present disclosure can provide various advantages. For example, one or more embodiments of injectable investment casting slurries or compositions described herein can be a premixed, ready-to-use composition or paste that can be injected from a syringe or tube directly into a wax pattern for building detailed core passageways within the pattern. Such premixed compositions can save time at a foundry, where mixing a composition used to fill cores of molds can add additional time to the casting process. Further, one or more embodiments of injectable slurry compositions can also eliminate mixing and batching errors and inconsistencies at the foundry. In addition, such injectable slurry compositions can be more cost-effective to use than pre-made ceramic cores that have to be specially made and then used as a mold to form an investment casting wax pattern.

One or more embodiments of injectable slurry compositions described herein can be used to fill patterns within, e.g., wax molds after such molds have been removed from a metal die or formed using any suitable technique or techniques. Following injection of the injectable slurry composition or compositions and drying or hardening of such compositions, the wax mold can be assembled in precision

investment casting (PIC) trees. One or more layers can then be formed on the wax mold or PIC trees using any suitable technique or techniques.

FIG. 1 is a schematic perspective view of one embodiment of an investment casting wax pattern 10. Further, FIG. 1a is a schematic cross-section view of the investment casting wax pattern 10 of FIG. 1. The wax pattern 10 can take any suitable shape or combination of shapes. The pattern 10 includes a body 12 having a first cavity 20 and a second cavity 22. Although depicted as including two cavities 20, 22, the pattern 10 can include any suitable number of cavities, openings, internal passageways, etc.

The pattern 10 can include any suitable material or materials. In one or more embodiments, the mold includes a wax material. Further, the pattern 10 can be formed using any suitable technique or techniques, e.g., injection molding, 3D printing, machining, etc. In one or more embodiments, the pattern 10 can be formed by disposing or injecting molten wax into a metal (e.g., aluminum) mold and then hardening the molten wax to form the wax mold.

Any suitable slurry composition can be disposed within the pattern 10 using any suitable technique or techniques. For example, FIG. 2 is a schematic perspective cross-section view of a portion of the pattern 10 of FIG. 1. As shown in FIG. 2, a slurry composition 30 has been disposed within at least a portion 14 of the pattern 10. The slurry composition 30 can include any suitable composition or compositions described herein. In one or more embodiments, the slurry composition 30 can be an injectable slurry composition. For example, in one or more embodiments, the slurry composition 30 includes an injectable slurry composition including a refractory material, a binder, a solvent, and a thixotropic agent. In one or more embodiments, the thixotropic agent can include fibrillated fibers.

The refractory material (i.e., refractory flour or powder) is a first major component of the injectable slurry composition. Refractory powders commonly used in the investment casting industry are zircon (ZrSiO_4), silica (SiO_2), both fused and quartz, alumina (Al_2O_3), zirconia (ZrO_2), and aluminosilicate (various combinations of Al_2O_3 and SiO_2 , commonly fired at high temperatures). Refractory materials usable in the slurry and/or stucco can include fused silica, aluminosilicate, zircon, aluminum oxide and mixtures thereof. Although not critical, the refractory powder can have a wide particle size distribution, including sizes as large as 30 mesh along with sub-micron particle sizes.

The binder is a second major component of the injectable slurry composition. For the purposes described herein, the binder may include a refractory binder, an organic binder, or a combination of both. Refractory binders that may be contained in the refractory slurry include a variety of ceramic materials, including silicates, alkali metal silicates, silica sols, aluminum oxychloride, aluminum phosphate, gypsum-silica mixes, cements, tetraethyl orthosilicates (TEOS), and mixtures thereof. In one or more embodiments, the refractory binder includes colloidal silica. Organic binders can be thermally decomposable and include polyvinyl alcohol, polyvinyl butyral, methyl cellulose, carboxymethyl cellulose, ethyl cellulose, and mixtures thereof. Exemplary binders are described, for example, in U.S. Patent Nos. 3,165,799 (Watts), 3,903,950 (Lirones), 5,021,213 (Kato et al.), and 6,020,415 (Guerra). Alternatively, the organic binder could include a mixture of colloidal sol and at least one acrylic latex polymer. The colloidal sol could be, for example, a silica sol, zirconia sol, alumina sol, or yttria sol, while

the latex polymer could be an acrylic latex polymer, acrylic polymer, various styrene-butadiene latex polymers, or a mixture thereof.

The solvent is generally the same as the liquid dispersant used for the binder. In the presently exemplary embodiments, water is the preferred solvent. Many other solvents are available, however, including other polar solvents such as mineral acids, alcohols such as methanol, ethanol, isopropanol, and butanol, glycols and glycol ethers, and mixtures thereof. Commercial binders are often provided in solution form, so the step of adding of a separate solvent may not be necessary. Some of these solvents may provide added benefits in terms of shortening the required dry time for best overall strength.

The composition of at least one of the injectable slurry composition 30 further includes the thixotropic agent (or shear-thinning agent). Any suitable thixotropic agent can be utilized. In one or more embodiments, the thixotropic agent includes one or more fibers. Any suitable fibers can be utilized. For example, in one or more embodiments, the fibers can include fibrillated fibers. As used herein, the term “fibrillated fiber” means a fiber that is a multifilament yarn-like strand having interconnecting, fibrous elements that intermittently unite and separate at irregular intervals through one or more of the width, length, and thickness of the strand. Any suitable fibrillated fibers can be utilized. Although not wishing to be bound by any particular theory, the fibrillated fibers can provide various thixotropic properties to the injectable slurry composition and the refractory slurry.

In one or more embodiments, the fibrillated fibers include organic fibers, e.g., fibers that include at least one of high density polyethylene, polypropylene, fluoropolymers, meta aramid, para aramid, spandex, elastane, ultrahigh molecular weight fibers, wood pulp, and combinations thereof.

In one or more embodiments, the fibrillated fibers can include inorganic fibers, e.g., fibers that include at least one of glass, mineral, polycrystalline ceramic fibers such as alumina and alumina silicate (e.g., 3M™ Nextel™ textiles available from 3M Company, St. Paul, MN), and combinations thereof.

In one or more embodiments, the fibrillated fibers can include both organic and inorganic fibers.

The fibers can be present in the injectable slurry composition 30 in any suitable amount. In one or more embodiments, the fibers present in the injectable slurry composition can be present in an amount of at least 0.005 weight percent and no greater than 1.5 weight percent, based on the overall weight of the composition.

The fibers in the injectable slurry composition can have any suitable dimensions. In one or more embodiments, one or more fibers in the injectable slurry composition can have an average diameter of at least 1 micron and no greater than 10 microns. Further, the fibers in the injectable slurry composition can have any suitable length. In one or more embodiments, one or more fibers can have a length of at least 20 microns and no greater than 500 microns. The injectable slurry composition can include any distribution of fibers, e.g., bimodal, trimodal, etc.

The fibers of the injectable slurry composition can also have any suitable aspect ratio. In one or more embodiments, one or more fibers of the composition can have an average aspect ratio of at least 20 and no greater than 200.

The injectable slurry composition can include a homogeneous distribution of fibers. In one or more embodiments, the composition can include one or more fibers that are different in composition, dimension, etc., than one or more additional fibers in the composition.

In one or more embodiments, the thixotropic agent can also include a polymer emulsion. In one or more embodiments, the polymer emulsion is an acrylic polymer emulsion. In one or more embodiments, the polymer emulsion is an acrylic polymer emulsion in water.

Polymers suitable for this application may be prepared using any of a number of different synthetic routes. Alkali-swellable polymers, for example, are synthesized by copolymerizing different monomers, where at least one monomer contains a carboxyl (-COOH) functional group. These polymers may have a structure that is linear, branched, or crosslinked to form a networked structure. Use of these polymers as thickening agents is described, for example, in U.S. Patent No. 4,226,754 (Whitton et al), which discloses a polymer made by reacting an ester of methacrylic acid, methacrylic acid, and a vinyl ester of a saturated aliphatic carboxylic acid. These thickeners are often referred to as alkali-swellable thickeners because the carboxylic acid groups are sufficient to render the polymer water-soluble when neutralized with a suitable base.

In one or more embodiments, the refractory slurry includes hydrophobic entities covalently bonded to the polymeric backbone. For example, polymers can be formed by reacting an ethylenically unsaturated carboxylic acid monomer, a nonionic vinyl monomer, and a vinyl surfactant ester such as an alkylphenoxypoly (ethyleneoxy) ethyl acrylate terminated on one end with an alkyl phenyl group. Another example derives from a reaction product of an unsaturated carboxylic acid, alkyl (meth)acrylate, and an ester containing an alkyl phenyl group, where the alkyl group has 8 to 20 carbon atoms. These water-soluble polymers modified with hydrophobic moieties are described in U.S. Patent Nos. 4,384,096 (Sonnabend) and 4,138,381 (Chang et al).

In one or more embodiments, the refractory slurry includes an acrylic emulsion copolymer that is prepared using emulsion copolymerization of monomers falling within three of four classes of monomers, namely (meth)acrylic acid, alkyl (meth)acrylate, an ethoxylated ester of (meth)acrylic acid having a hydrophobic group and, optionally, a polyethylenically unsaturated monomer. In still other embodiments, the refractory slurry includes an emulsion copolymer based on the reaction product of monomers including methacrylic acid, ethyl acrylate, optionally a defined copolymerizable ethylenically unsaturated monomer, and a small weight percent of a polyethylenically unsaturated monomer. Advantageously, a wide range of surfactants can enhance the thickening effect on the composition when added to an aqueous system containing the copolymer when the emulsion copolymer is neutralized. The aforementioned copolymers are further described in European Patent No. 13,836 (Chang et al.) and U.S. Patent No. 4,421,902 (Chang et al.).

In one or more embodiments, an alkali-swellable copolymer is synthesized as the reaction product of an ethylenically unsaturated carboxylic acid, a surface-active unsaturated ester, methacrylic acid esters or acrylic acid esters of aliphatic alcohols, and optionally one or more other ethylenically unsaturated comonomers, polyethylenically unsaturated compounds, and molecular weight regulators.

The surface-active ester is terminated at one end with an aliphatic radical, which may be linear or branched, a mono-, di- or tri-alkyl phenyl radical with alkyl groups of 4 to 12 carbon atoms, or a block-copolymeric radical. On partial or complete neutralization, the copolymer becomes water-soluble or colloiddally dispersible, and can be used as a thickening agent. These copolymers are also described in U.S. Patent No. 4,668,410 (Engel et al.).

One particularly advantageous thixotropic agent usable in the refractory slurry 242 is a polymer emulsion based on hydrophobically modified ester of methacrylic acid available from Elementis Specialties in Hightstown, NJ under the tradename RHEOLATE. Methods of making such polymer emulsions are described in detail, for example, in U.S. Patent No. 6,069,217 (Nae et al.).

Another advantageous thixotropic agent, available from the same source and under the same tradename, is based on an aqueous hydrophobically modified alkali-soluble emulsion derived from an acrylic polymer and having about 30% solids by weight. Typically, this acrylic emulsion has a pH value of less than about 5.

The polymer emulsion can be present in an amount that increases the yield stress of the refractory slurry to an extent that enables use of only a single backup layer while preserving strength in the investment casting mold. In one or more embodiments, the polymer emulsion is present in an amount of at least 0.02 weight percent, at least 0.03 weight percent, at least 0.05 weight percent, at least 0.06 weight percent, or at least 0.07 weight percent, based on the overall weight of the composition. In one or more embodiments, the polymer emulsion is present in an amount of at most 1 weight percent, at most 0.9 weight percent, at most 0.8 weight percent, at most 0.75 weight percent, or at most 0.7 weight percent, based on the overall weight of the composition.

Advantageously, using a polymer emulsion as a thixotropic agent allows the injectable slurry composition to be operated within a shear stress regime that is much lower than that of known compositions while achieving a similar working viscosity for investment casting. In one or more embodiments, the composition displays a working viscosity of about 20 poise when subjected to a shear stress of at least 1 dyne per square centimeter, of at least 5 dynes per square centimeter, of at least 10 dynes per square centimeter, of at least 20 dynes per square centimeter, of at least 50 dynes per square centimeter, at least 100 dynes per square centimeter, at least 200 dynes per square centimeter, or at least 400 dynes per square centimeter, as measured using the method described in the Examples.

In one or more embodiments, the same slurry composition displays a working viscosity of about 20 poise when subjected to a yield stress in shear of at most 1000 dynes per square centimeter, at most 950 dynes per square centimeter, at most 900 dynes per square centimeter, at most 850 dynes per square centimeter, or at most 800 dynes per square centimeter.

The injectable slurry composition 30 can have any suitable properties. In one or more embodiments, the injectable slurry composition 30 can include a working viscosity having any suitable value or values. In one or more embodiments, the working viscosity can be at least 200 poise and no greater than 3000 poise when subjected to a yield stress ranging from 1100 dynes/cm² to 1400 dynes/cm². See, e.g., FIG. 9.

The injectable slurry composition 30 can be disposed within any suitable portion or portions of the pattern 10. In one or more embodiments, an entire inner space 16 of the pattern 10 can be filled with the injectable slurry composition 30. In one or more embodiments, only a portion or portions of the inner space 16 of the pattern 10 can be filled with the injectable slurry composition 30.

5 The injectable slurry composition 30 can be dried or hardened (e.g., cured) once disposed within one or more portions of the pattern 10 using any suitable technique or techniques. In one or more embodiments, the injectable slurry composition 30 can remain uncured or partially cured until such time as additional layers or coatings are disposed over the wax mold as is further described herein.

10 After the slurry composition 30 is injected into one or more cavities 20, 22 of the pattern 10, one or more additional layers can be formed on the mold to provide an investment casting. For example, FIG. 3 is a schematic cross-section view of another embodiment of an investment casting mold 100. The mold 100 is shown encapsulating a substantial portion of a sacrificial pattern 102, which has a tree-like structure with a centrally located trunk 103 and a plurality of branches 105 extending outwardly from the trunk 103. The pattern 102 is exemplary and there are no particular restrictions on its size or shape. In one
15 or more embodiments, the mold 10 of FIG. 1 can be utilized to form one or more parts of mold 100. For example, a plurality of molds 10 can be assembled together as PIC trees.

In one or more embodiments, the pattern 102 is made from wax, polymer resin, or other suitable pattern material capable of being subsequently melted, vaporized, burned, or dissolved to leave behind, with minimal residue, a cavity conforming to the exterior contours of the pattern 102.

20 As shown, the mold 100 includes a series of successive layers built up by dipping the pattern 102 into containers of refractory slurry or slurry composition. After withdrawing the pattern 102 following each dip, excess slurry/stucco is allowed to drain off. Optionally, the pattern 102 is manipulated by hand or mechanically to promote uniform coverage. Refractory granules, or stucco, are then applied to the wet slurry coating. Here, the combination of slurry and stucco includes a single major layer, which then is
25 allowed to dry and at least partially harden before the next coat is applied. By repeating this process, the walls of the mold 100 are progressively built up, layer upon layer, until the overall mold 100 has the strength to withstand the physical handling forces induced by metal casting.

Beginning from the innermost layer and ending with the outermost layer, mold 100 includes a prime layer 104, an intermediate layer 110, a first backup layer 116, a second backup layer 122, a third
30 backup layer 128, and a seal layer 134.

While the mold 100 of FIG. 3 represents a six-layered construction, additional or fewer layers may also be used depending on the nature of the application. For example, factors such as the molten metal head pressure and the size of the casting to be poured from the final mold can influence the number of backup layers used. Common commercial investment casting shells often use four backup layers. Any
35 suitable number of backup layers can be utilized to form the mold 100.

Each of the six layers enumerated herein are described in further detail in reference to the inset, FIG. 4. The prime layer 104 is an innermost layer extending across and contacting the pattern 102. The prime layer 104 is intended to come into direct contact with molten metal after the finished mold 100 has

been de-waxed and fired. As shown, the prime layer 104 includes two sub-layers—an inner layer of refractory slurry 106 and an outer layer of refractory stucco 108. In one or more embodiments, both the refractory slurry 106 and refractory stucco 108 include zircon particles (shown here as round particles) although this need not be the case. In one or more embodiments, one or more additional prime layers may be used. This may be the case, for example, where there is no intermediate slurry layer capability.

The intermediate layer 110, and successive backup layers 116, 122, 128 also include two sub-layers each, i.e., a layer of refractory slurry 112, 118, 124, 130 and an adjacent layer of refractory stucco 114, 120, 126, 132, respectively. The refractory slurry 112, 118, 124, 130 can include any suitable slurry composition, e.g., the compositions described regarding the injectable slurry composition 30 of FIGS. 1-2. In one or more embodiments, the slurry composition includes a refractory material, a binder, a solvent, and a thixotropic agent. In one or more embodiments, the thixotropic agent includes fibers, e.g., fibrillated fibers. While the slurry composition is described regarding the backup layers 116, 122, 128, such slurry composition can be utilized for any suitable layer used to form the mold 100, e.g., one or more of the prime layer, the intermediate layer, and the seal layer. The refractory stucco (represented in the figures as jagged-edged particles) may include a fused silica, alumino-silicate, zircon, aluminum oxide, or mixture thereof. The stucco can be applied either by sprinkling it onto a freshly coated slurry by hand or by rainfall sander, or by immersion into a fluidized bed of stucco. In one or more embodiments, the size of the stucco particles generally increases from the inside to the outside of the mold 100.

Optionally and as shown, a seal layer 134 is located on the outermost periphery of the mold 100. The seal layer 134 serves the purpose of preventing stucco from the backup layer 128 from coming loose during subsequent processing of the finished mold 100 and can have a composition identical or similar to that of the intermediate or backup slurries. In exemplary embodiments, the seal layer 134 contains a fused silica, alumino-silicate, zircon, aluminum oxide, or a mixture thereof.

In an exemplary method, the resulting structure as shown in FIGS. 3-4 can then be fully dried and heated to melt the pattern 102 and remove the pattern 102 from the finished investment casting mold 100. To add greater strength, the finished mold 100 can be fired in a curing oven at temperatures of about 980 degrees Celsius.

As mentioned herein, any suitable slurry composition or compositions can be utilized for the refractory slurry utilized to form one or more layers of the mold 100, e.g., the same composition or compositions described regarding the injectable slurry composition 30 of FIGS. 1-2. Other suitable compositions are described, e.g., in co-owned PCT Application Publication No. WO 2015/168233. In one or more embodiments, the slurry composition for the layer or layers of the mold 100 can have the same material properties (e.g., viscosity) as the material properties of the injectable slurry composition 30 or material properties that are different from those of the injectable slurry composition.

In one or more embodiments, the slurry composition can be provided as a dry composition that includes the refractory material and the thixotropic agent, e.g., fibrillated fibers. In such embodiments, the dry composition can be shipped more easily. At least one of a binder and a solvent and any other desired

compositions or components can be added to the dry composition to provide the final slurry refractory material.

In one or more embodiments, the slurry composition can also include a filler. Any suitable filler may be utilized. In one or more embodiments, the filler can include one or more bubbles. Any suitable bubbles can be utilized, e.g., glass bubbles. Suitable glass bubbles include 3M™ Glass Bubbles (available from 3M Company, St. Paul, MN). The glass bubbles can have any suitable density, e.g., at least 0.12 g/cc and no greater than 1.2 g/cc. Further, the glass bubbles can be present in any suitable amount in the slurry composition. In one or more embodiments, the glass bubbles can be present in the slurry composition in an amount of at least 0.25 weight percent and no greater than 5 weight percent, based on the overall weight of the composition.

Further, the glass bubbles can have any suitable dimensions. In one or more embodiments, the glass bubbles can have a particle size distribution of at least 60 µm and no greater than 120 µm in the effective top 95th percentile of size distribution. The glass bubbles can have a single size distribution or two or more size distributions, e.g., a bimodal distribution.

The glass bubbles can include any suitable material or combination of materials. Further, in one or more embodiments, the glass bubbles can be hollow. The glass bubbles can also be disposed in any suitable matrix.

Investment casting shells generally have large porosity as a result of the stuccoing process, which can adversely affect strength. For the strength to be deemed adequate for a given application, it must be capable of withstanding potentially high internal pressure and thermal stress, especially during the de-waxing process and when pouring metal into the free standing ceramic shell. Cracking can occur when the stress on the mold is greater than the modulus of rupture of the mold material. In some embodiments, the investment casting mold has non-fired modulus of rupture of at least about 1 MPa, or at least 1.75 MPa, after being fully hardened. In some embodiments, the investment casting mold has non-fired modulus of rupture of at most 5 MPa after being fully hardened.

In one or more embodiments, the slurry composition further includes an aluminum phyllosilicate clay. In one or more embodiments, the aluminum phyllosilicate clay is present in an amount ranging from a weight ratio of at least 1:15, at least 1:10, at least 1:8, at least 1:7, or at least 1:6, relative to that of the polymer emulsion. In one or more embodiments, the aluminum phyllosilicate clay is present in an amount ranging from a weight ratio of at most 6:1, at most 5:1, or at most 4:1, relative to that of the polymer emulsion.

Combining a thixotropic thickener that includes a polymer emulsion, particularly an acrylic emulsion, with an aluminum phyllosilicate clay may provide certain synergistic effects in the investment mold. For example, inclusion of both the polymer emulsion thickener and the aluminum phyllosilicate clay in the backup refractory slurry may substantially increase the working time of the slurry as compared with including only the aluminum phyllosilicate as thickener. When the aluminum phyllosilicate clay is used on its own, the backup slurry may continue to drain off of the pattern. Moreover, inclusion of both the polymer emulsion and the aluminum phyllosilicate clay may be preferred over inclusion of the

polymer emulsion alone as the latter may produce slurries that can be too viscous. Such high viscosities in turn can cause delicate patterns to crack or break when inserted into the slurry. In sum, the combination of a polymer emulsion thickener and an aluminum phyllosilicate clay may provide an unexpected and advantageous balance of flowability along with a long working time.

There are no particular restrictions on the overall solids present in the slurry composition, but this measure should fall within a range sufficient to enable a stable colloidal suspension and yield a robust final investment casting mold 100. In one or more embodiments, the slurry composition has an overall solids content of at least 45 weight percent, at least 50 weight percent, or at least 55 weight percent, based on the overall weight of the composition. In one or more embodiments, the slurry composition has an overall solids content of at most 85 weight percent, at most 80 weight percent, or at most 75 weight percent, based on the overall weight of the composition.

FIG. 5 is a schematic cross-section view of another embodiment of an investment casting mold 200. All of the design considerations and possibilities regarding the mold 100 of FIGS. 3-4 apply equally to the mold 200 of FIG. 5. The mold 200 shares some characteristics of the mold 100. For example, one or more molds 10 that have been injected with the injectable slurry composition 30 can be utilized to form mold 200. Further, like mold 100, the mold 200 includes a prime layer 204 disposed on a wax pattern 202 and an intermediate layer 210 disposed on the prime layer 204. The pattern 202, prime layer 204, and intermediate layer 210 generally share the aforementioned features, options, and advantages described regarding the mold 100. Here, the prime layer 204 includes an inner coating of zircon-containing slurry 206 followed by an outer layer of zircon stucco 208. The intermediate layer 210, in the illustrated embodiment, includes an inner coating of refractory slurry 212 and an outer layer of refractory stucco 214. The intermediate slurry layer 210 may also contain a zircon refractory.

A single backup layer 240 is disposed on the intermediate layer 210. As shown, the backup layer 240 has a spatial thickness considerably greater than either of the prime or intermediate layers 204, 210. Advantageously, and as shown, the backup layer 240 can fill in open undercuts and cavities presented by the branches of the pattern 202, thereby simplifying subsequent coating processes. As a further major benefit, the configuration of the mold 200 eliminates the need for multiple backup layers in common investment casting applications. The backup layer 240, as shown, includes an inner coating of a refractory slurry 242 followed by a layer of refractory stucco 244. Finally, a seal layer 234 is disposed over the backup layer 240, whereby the two layers 234, 240 directly contact each other. The seal layer 234, which serves the same purposes as those of the seal layer 134, can also be omitted if desired.

Alternative embodiments are shown in FIGS. 6 and 7. FIG. 6 depicts an investment casting mold 300 according to another embodiment in which an outermost seal layer is omitted. All of the design considerations and possibilities regarding the mold 100 of FIGS. 3-4 apply equally to the mold 300 of FIG. 6. This three-layered construction includes a prime layer 304 extending across and contacting a sacrificial pattern 302, an intermediate layer 310 extending across and contacting the prime layer 304, and a single backup layer 340 extending across and contacting the intermediate layer 310. Like in the

embodiment previously described, each of the layers 304, 310, 340 includes an inner sub-layer of refractory slurry adjoining an outer sub-layer of a refractory stucco.

Absent from the mold 300 is an outermost seal layer; in FIG. 6, the layered construction ends with the refractory stucco for the backup layer 340. While sharing most of the functional properties of the mold 200, the mold 300 requires even fewer processing steps to fabricate.

FIG. 7 illustrates an investment casting mold 400 according to yet another embodiment. All of the design considerations and possibilities regarding the mold 100 of FIGS. 3-4 apply equally to the mold 400 of FIG. 7. Compared with prior embodiments, the mold 400 is notably even further simplified in its two-layered construction. Showing merely a prime layer 404 and backup layer 440 disposed on a pattern 402, the mold 400 can advantageously be made using only two dips—one for each of layers 404, 440. Other aspects of the mold 400 and its constituent layers are essentially the same as those described with respect to the three- and four-layered embodiments above.

In the above method, each slurry layer is optionally disposed on the pattern or underlying layer using a dipping process. When a dipping process is used, it is advantageous for the slurry to have a sufficient viscosity to be retained on the pattern or underlying layer over an acceptable working time, yet also having sufficient flowability to fill essentially all of the voids in the dipped assembly to preserve high fidelity in the mold shape. Acceptable working times generally range from about 12 seconds to about 60 seconds. The required working time for this slurry will depend upon the process and foundry but generally is the time required for the slurry to stop draining and then be moved from above the slurry pot into the stucco application area. Using suitable techniques, this time period is on the order of 2-3 minutes. These competing properties can be simultaneously achieved using the investment casting molds and methods described herein.

In one or more embodiments, the investment casting mold 200 is fabricated using methods of layer-by-layer construction analogous to those used to fabricate the investment casting mold 100, but with certain deviations as noted herein. Generally, departures from known techniques include differences in the composition of the refractory slurry used for the backup layer(s) and, advantageously, reduction in the number of processing steps required to produce the finished investment casting mold 200.

Ideally, an investment casting refractory slurry displays a yield stress that is sufficient to prevent excessive drainage of the slurry from a pattern after the pattern is withdrawn from a bath of the slurry. This characteristic should be tempered, however, by its flowability—essentially, its ability to flow into and around complex pattern geometries, including narrow cavities that have not been filled with the injectable slurry composition 30, when the pattern is dipped into the slurry. The refractory slurries provided here operate in a solid-like regime at the low shear rates associated with gravity, but operate in a liquid-like regime at higher shear rates associated with dipping the pattern into a bath of the slurry. By minimizing gravity-induced drainage while simultaneously achieving good flowability in the dipping process, the provided compositions reduce the number of required dips while preserving the fidelity of the final molded product.

In some embodiments, the yield stress of the slurry composition is at least 0.2 dynes/cm², at least 0.5 dynes/cm², at least 1 dyne/cm², at least 5 dynes/cm², at least 10 dynes/cm², or at least 50 dynes/cm². In the same or alternative embodiments, the yield stress of the refractory slurry can be at most 100 dynes/cm², 200 dynes/cm², at most 250 dynes/cm², at most 500 dynes/cm², at most 750 dynes/cm², or at most 1000 dynes/cm². Exemplary refractory slurries or compositions, at the onset of flow, can display a viscosity at the onset of flow of at least 20 cP and no greater than 40,000 cP.

Any suitable technique or combination of techniques can be utilized to form investment casting mold that includes the refractory slurries described herein. In one or more embodiments, a sacrificial pattern can be coated with a prime layer that includes a first refractory slurry and a first refractory stucco. The prime layer can be at least partially hardened using any suitable technique or combination of techniques. The prime layer can be coated with an intermediate layer that includes a second refractory slurry and a second refractory stucco. Such intermediate layer can be at least partially hardened using any suitable technique or combination of techniques. The intermediate layer can be coated by a backup layer that includes a thixotropic agent that includes, e.g., fibrillated fibers. The backup layer can be at least partially hardened using any suitable technique or combination of techniques. In one or more embodiments, one or more glass bubbles can be included in the backup layer.

As mentioned herein, one or more embodiments of refractory slurries can be provided as dry compositions and then mixed with one or more solvents or liquids using any suitable technique or combination of techniques. For example, a dry composition that includes a refractory material, glass bubbles, and a thixotropic agent (e.g., fibrillated fibers) can be provided to form a dry composition using any suitable technique or combination of techniques. The dry composition can be combined with at least one of a binder and a solvent to form a refractory slurry using any suitable technique or combination of techniques.

Returning to FIGS. 1-2, the mold 10 that includes the injectable slurry composition 30 can be utilized to form an investment casting mold using any suitable technique or techniques. For example, FIG. 8 is a flowchart of one embodiment of a method 500 of making an investment casting mold. In one or more embodiments, a first slurry composition can be injected into one or both cavities 20, 22 of the mold at 502. The first slurry composition can include any suitable composition described herein, e.g., injectable slurry composition 30 of FIGS. 1-2. Further, any suitable technique or techniques can be utilized to inject the first slurry composition into one or both cavities 20, 22. For example, in one or more embodiments, the first slurry composition can be disposed within a syringe, and the syringe can be utilized to inject the composition into the cavities 20, 22. Further, in one or more embodiments, a pressurized hose or tube can be connected to an injection device for continuously providing injectable slurry composition 30 from a tank or container. In one or more embodiments, a tool such as a spatula can be utilized to press injectable slurry composition 30 into the cavities 20, 22.

At 504, the first slurry composition can be at least partially hardened using any suitable technique or techniques. A first layer (e.g., prime layer 104 of FIG. 3) including a second slurry composition can be formed on the sacrificial pattern or mold at 506. The second slurry composition can include any suitable

composition described herein, e.g., the slurry composition described regarding mold 100 of FIGS. 3-4. Further, any suitable technique or techniques can be utilized to form the first layer on the sacrificial pattern, e.g., the techniques described regarding FIGS. 3-4. The first layer can be at least partially hardened at 508 using any suitable technique or techniques.

5 The first composition can be the same composition as the second composition or a different composition. Further, the first composition can have the same physical characteristics or material properties as those of the second composition or different characteristics and material properties. For example, in one or more embodiments, the first slurry composition can include a first working viscosity and the second slurry composition can include a second working viscosity. In one or more embodiments, 10 the first working viscosity is the same as the second working viscosity. In one or more embodiments, the first working viscosity is greater than the second working viscosity. Further, in one or more embodiments, the first working viscosity is less than the second working viscosity.

The first working viscosity of the first slurry composition can have any suitable value or values. In one or more embodiments, the first working viscosity is at least about 200 poise and no greater than 15 about 3000 poise when subjected to a yield stress ranging from 1100 dynes/cm² to 1400 dynes/cm². Further, the second working viscosity of the second slurry composition can have any suitable value or values. In one or more embodiments, the second working viscosity is at least about 2 poise and no greater than about 20 poise when subjected to a yield stress ranging from 1 dyne/cm² to 400 dynes/cm².

20 EXAMPLE

Materials

“NALCO 1030”, silica sol, 30 weight % SiO₂, 11-16 nm particle size, was obtained from Nalco Chemical Company, Naperville, IL, under trade designation “NALCO 1030”.

25 “LATEX”, a styrene butadiene latex polymer, 50 weight% solids, was obtained from 3M Midway, Midway, TN, under trade designation “Minco HP”.

“200F Zircon flour was obtained from Continental Minerals.

“200F Fused Silica flour was obtained from 3M Midway.

30 “BENTONE EW”, highly beneficiated, easily dispersible powdered clay thickener, was obtained from Elementis, Specialties, Inc., Hightstown, NJ, under trade designation “BENTONE EW”.

“RHEOLATE 475”, an alkali swellable thickener, was obtained from Elementis, Specialties, Inc., Hightstown, NJ, under trade designation “RHEOLATE 475”.

Fibrillated fibers, a high-density polyethylene (HDPE) fibrillated fibers 0.1 mm length and 5 micrometers diameter, obtained from Minifibers, Inc., Johnson City, TN under trade designation 35 “SHORT STUFF FIBRILLATED HDPE”.

General Method for Preparing Injectable Slurry Composition

The injectable slurry composition was made by first blending the colloidal silica (NALCO 1030) and latex with a high shear mixer, followed by the BENTONE EW. When fully dispersed, the refractory flours were added. Upon reaching uniform appearance, the fibers were next added. Once uniformity was again achieved the RHEOLATE 475 was last added. Syringes were then filled with the slurry for later use in wax patterns. Total mix time was approximately 30 minutes.

The following table is a summary of the composition of each of the injectable slurry compositions that were tested for yield stress.

Material	(g)	(%)
200F zircon	7100	36.6%
200F fused silica	7100	36.6
Colloidal Nalco 1030	4750	24.5
Latex 50/50 styrene/butadiene	375	1.9
Rheolate 475	25	0.1
EW bentone	60	0.3
Fibrillated fibers	25	0.1
Surfactant Nalco 8815	10	0.1

As a result, the injectable slurry composition included 7.3% of the liquid was latex, 28% of the liquid was NALCO 1030, and 73% refractory solids.

Method for evaluation of the yield stress

Samples were loaded between 40-mm diameter parallel plates affixed to a stress-controlled rotational rheometer. Temperature was controlled at 23 °C. The sample gap was lowered to 1.05 mm, the sample edge was trimmed, and then sample gap was lowered to 1 mm. Testing was conducted within a saturated water solvent trap, to reduce the effect of evaporation during testing. The samples were subjected to a pre-shear at shear rate of 1 1/sec for 1 minute, followed by 1 minute of equilibration.

Sample viscosity was then measured as a function of shear stress, linearly ramping the stress from 10 dynes/cm² to 3000 dynes/cm² over the course of 300 seconds. The yield stress was determined as the stress at which viscosity rapidly decreased over a narrow stress range. The working viscosity at yield was the viscosity measured just above the yield stress, at the onset of flow.

FIG. 9 is a plot of viscosity in poise versus stress A in dynes/cm². The injectable slurry composition was tested three times to provide curves 602, 604, and 606 using the techniques described herein.

All references and publications cited herein are expressly incorporated herein by reference in their entirety into this disclosure, except to the extent they may directly contradict this disclosure.

Illustrative embodiments of this disclosure are discussed and reference has been made to possible variations within the scope of this disclosure. These and other variations and modifications in the disclosure will be apparent to those skilled in the art without departing from the scope of the disclosure, and it should be understood that this disclosure is not limited to the illustrative embodiments set forth herein. Accordingly, the disclosure is to be limited only by the claims provided below.

5

What is claimed is:

1. An injectable slurry composition for investment casting, comprising:
a refractory material;
5 a binder;
a solvent; and
a thixotropic agent comprising fibrillated fibers;
wherein the injectable slurry composition has a working viscosity of 20-300 Pascal-seconds when
subjected to a yield stress ranging from 110 Pascal to 140 Pascal.
10
2. The injectable slurry composition of claim 1, wherein the thixotropic agent further comprises a
polymer emulsion.
3. The injectable slurry composition of any one of claims 1-2, wherein the fibrillated fibers
15 comprise organic fibrillated fibers.
4. The injectable slurry composition of any one of claims 1-3, wherein the fibrillated fibers are
present in an amount of at least 0.1 weight percent and no greater than 0.5 weight percent, based on the
overall weight of the composition.
20
5. The injectable slurry composition of any one of claims 1-4, wherein the thixotropic agent further
comprises an alkali-swellaable polymer.
6. The injectable slurry composition of any one of claims 1-5, further comprising an aluminum
25 phyllosilicate clay.
7. The injectable slurry composition of any one of claims 1-6, wherein the composition has an
overall solids content ranging from 65 weight percent to 80 weight percent, based on the overall weight of
the composition.
30
8. The injectable slurry composition of any one of claims 1-7, wherein the binder comprises
colloidal silica.
9. The injectable slurry composition of any one of claims 1-8, wherein the binder comprises a latex.
35
10. The injectable slurry composition of any one of claims 1-8, wherein the binder comprises a
polyvinyl butyral resin.

11. The injectable slurry composition of any one of claims 1-10, wherein the refractory material comprises zircon particles.

12. An investment casting mold made using the composition of any one of claims 1-11.

13. A method of making an investment casting mold comprising:
injecting a first slurry composition into a cavity of a sacrificial pattern;
at least partially hardening the first slurry composition;
forming a first layer comprising a second slurry composition on the sacrificial pattern; and
at least partially hardening the first layer;
wherein the first slurry composition has a first working viscosity and the second slurry composition has a second working viscosity, wherein the first working viscosity is greater than the second working viscosity.

14. The method of claim 13, wherein the first working viscosity is at least 20 Pascal-seconds and no greater than 300 Pascal-seconds when subjected to a yield stress ranging from 110 Pascal to 140 Pascal, and further wherein the second viscosity is at least 0.2 Pascal-seconds and no greater than 2 Pascal-seconds when subjected to a yield stress ranging from 0.1 Pascal to 40 Pascal.

15. The method of any one of claims 13-14, wherein prior to forming the first layer on the sacrificial pattern, the method further comprises:
coating the sacrificial pattern with a prime layer comprising a first refractory slurry and a first refractory stucco; and
at least partially hardening the prime layer.

16. The method of any one of claims 13-15, further comprising:
coating the first layer with a second layer comprising a third slurry composition; and
at least partially hardening the second layer.

17. The method of any one of claims 13-16, wherein the first slurry composition comprises:
a refractory material;
a binder;
a solvent; and
a thixotropic agent.

18. The method of claim 17, wherein the thixotropic agent comprises fibrillated fibers.

19. The method of any one of claims 13-18, wherein the second slurry composition comprises a thixotropic agent comprising a polymer emulsion.

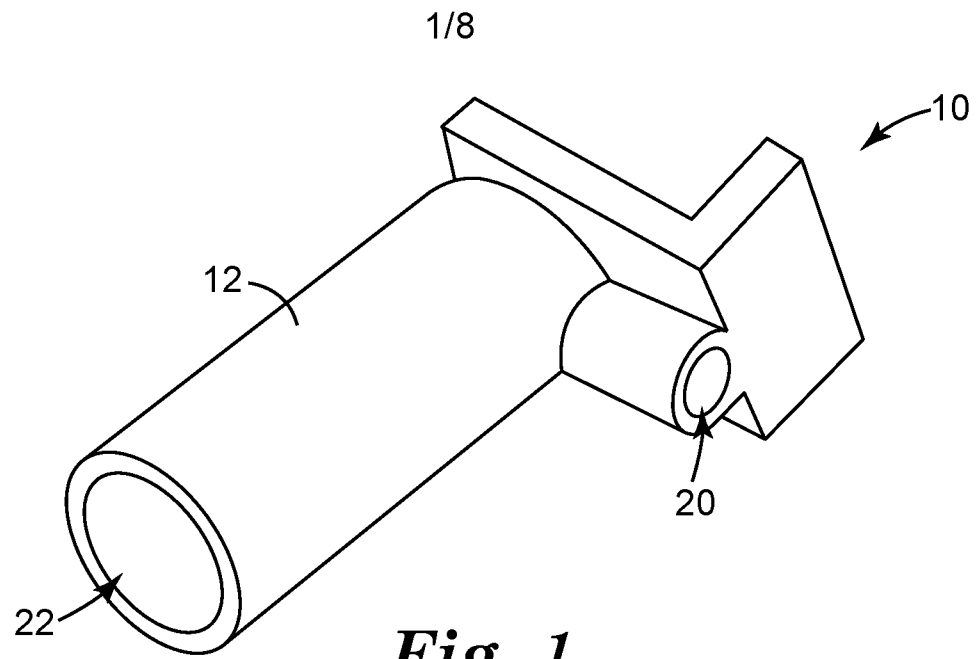


Fig. 1

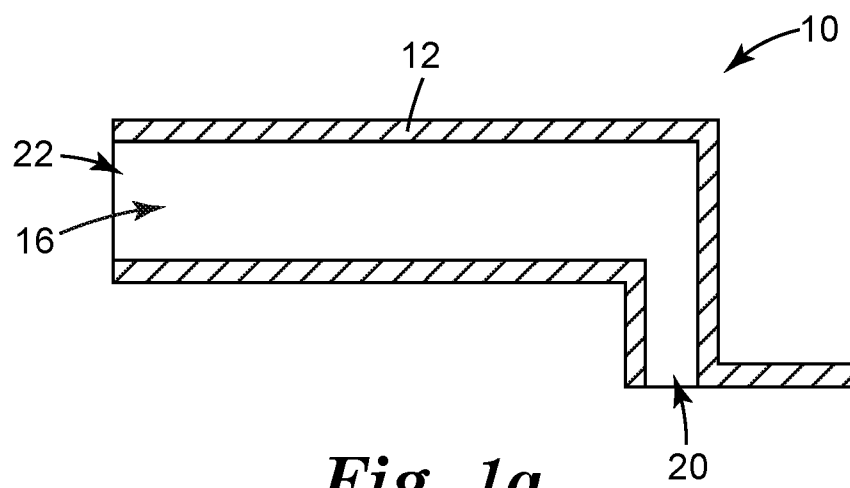


Fig. 1a

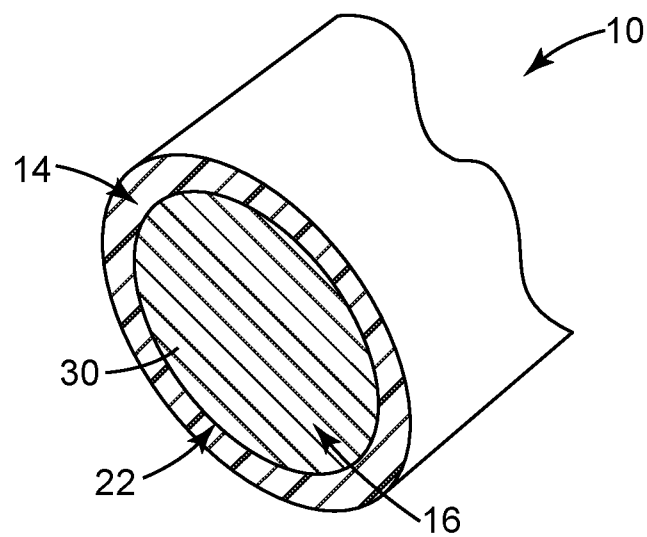


Fig. 2

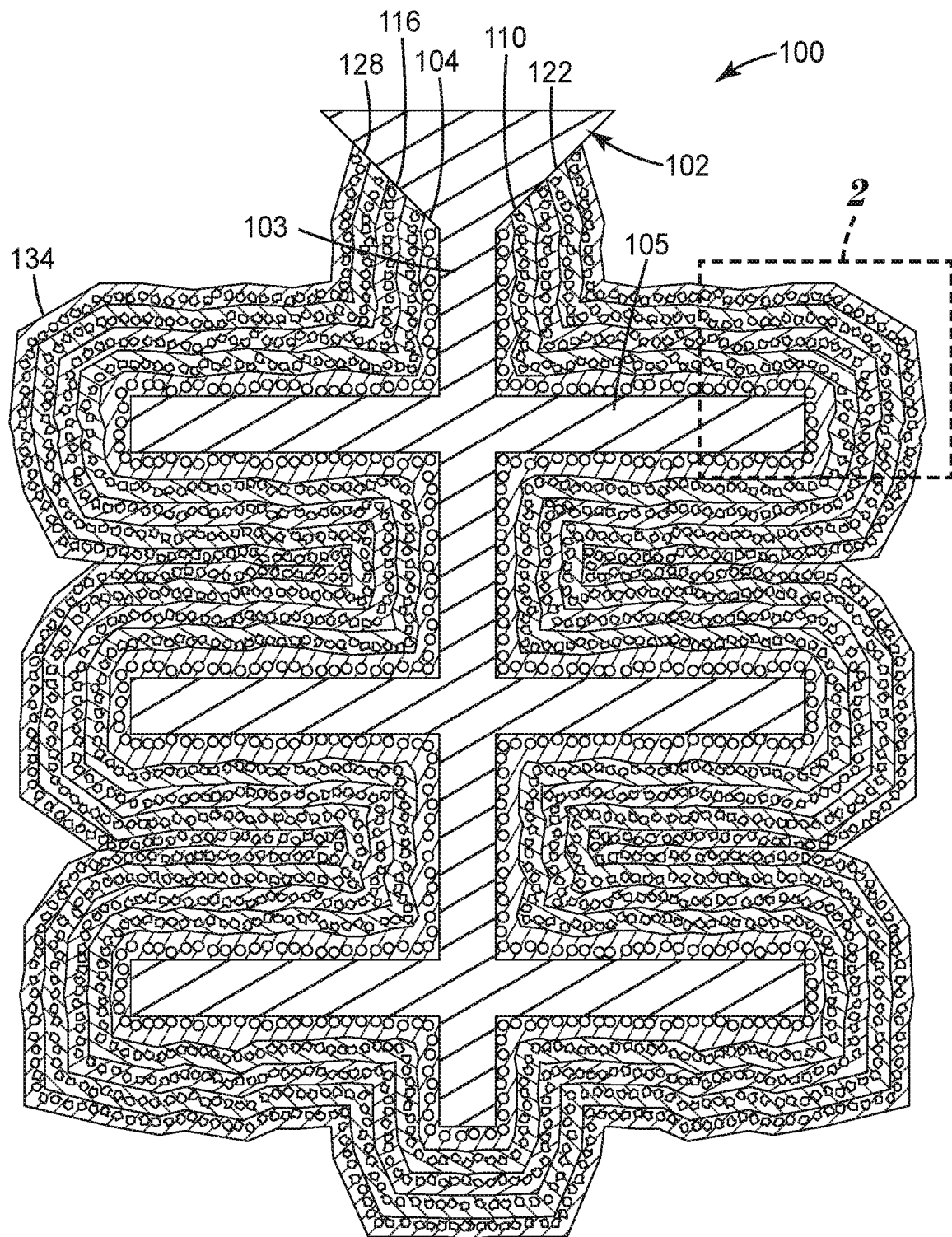
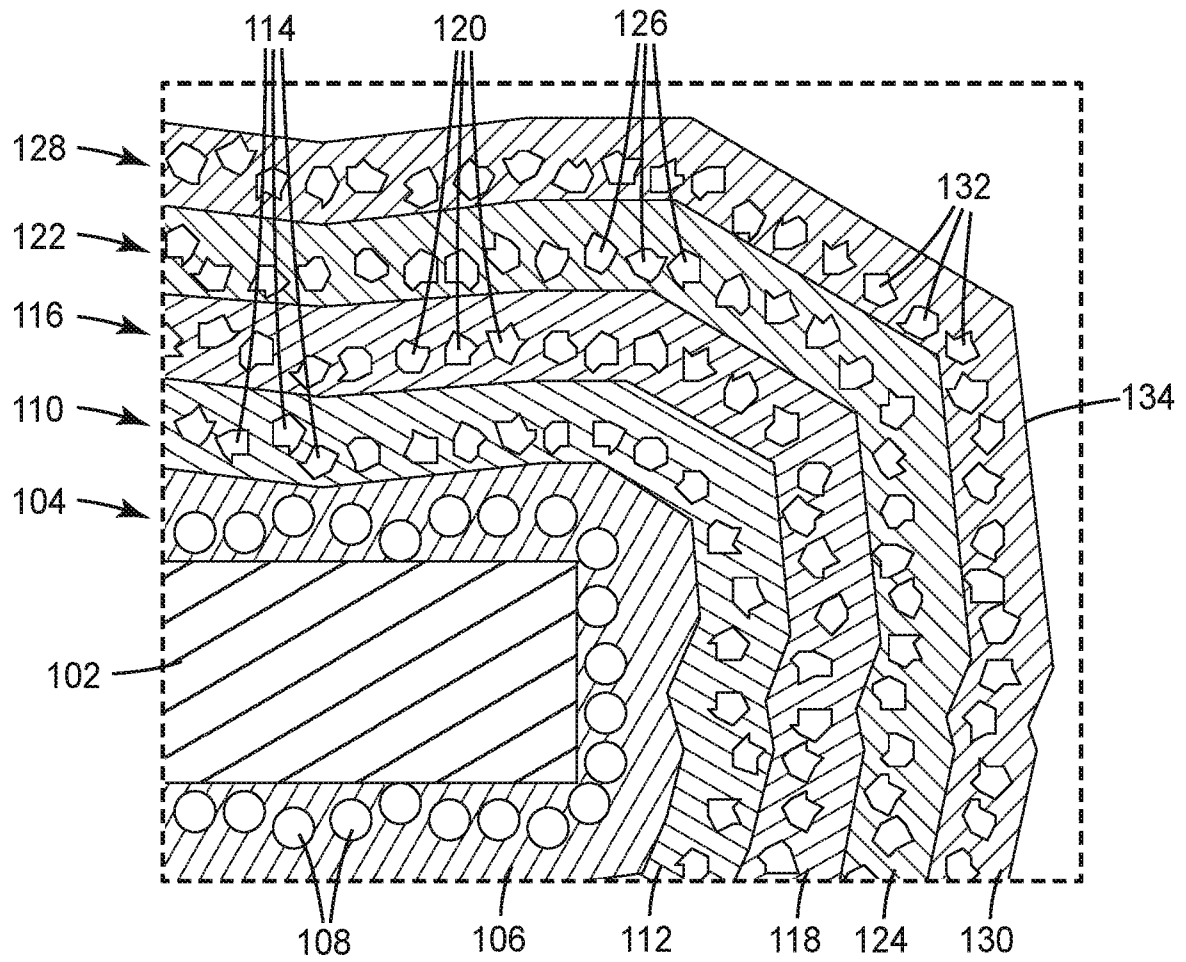
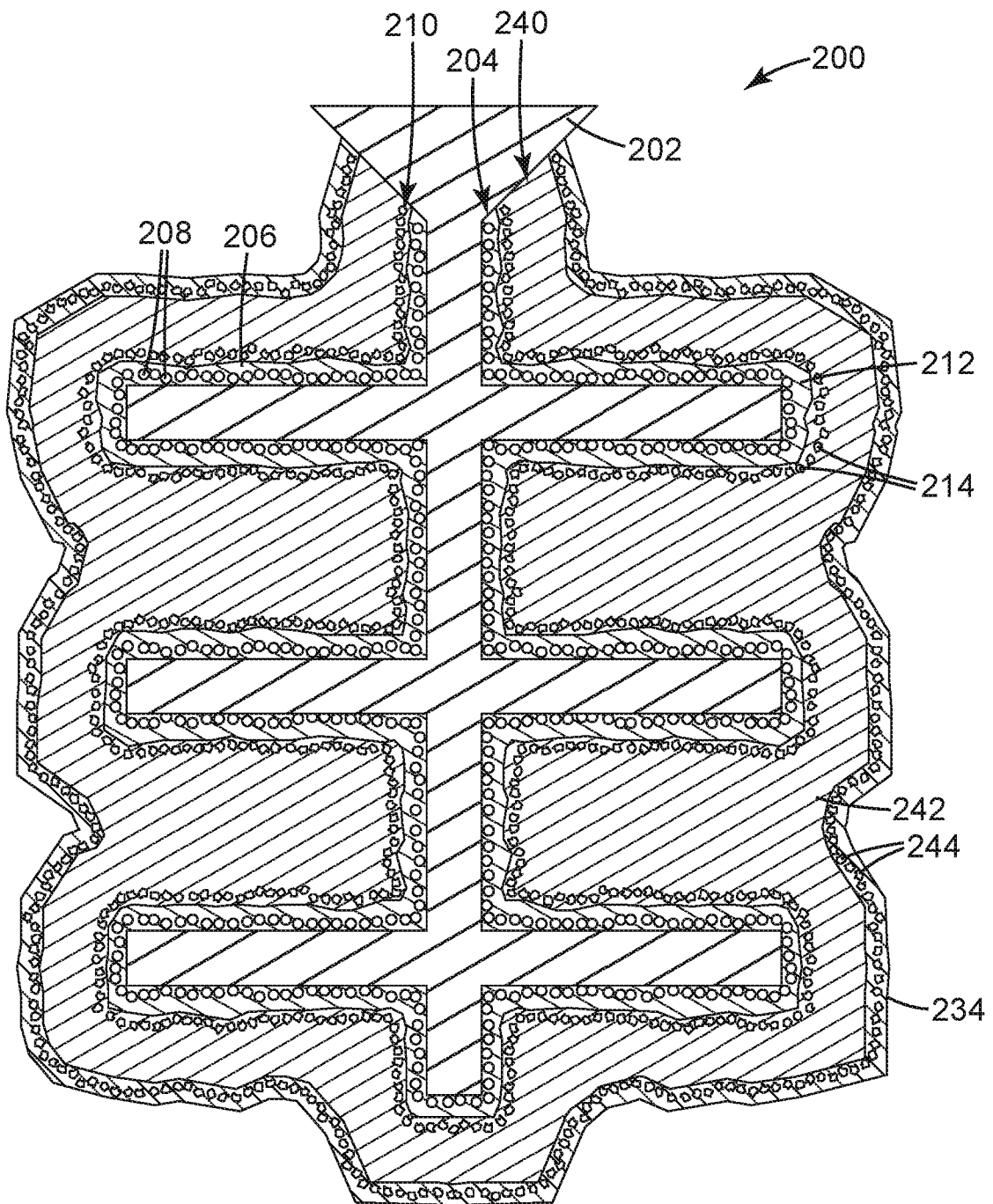


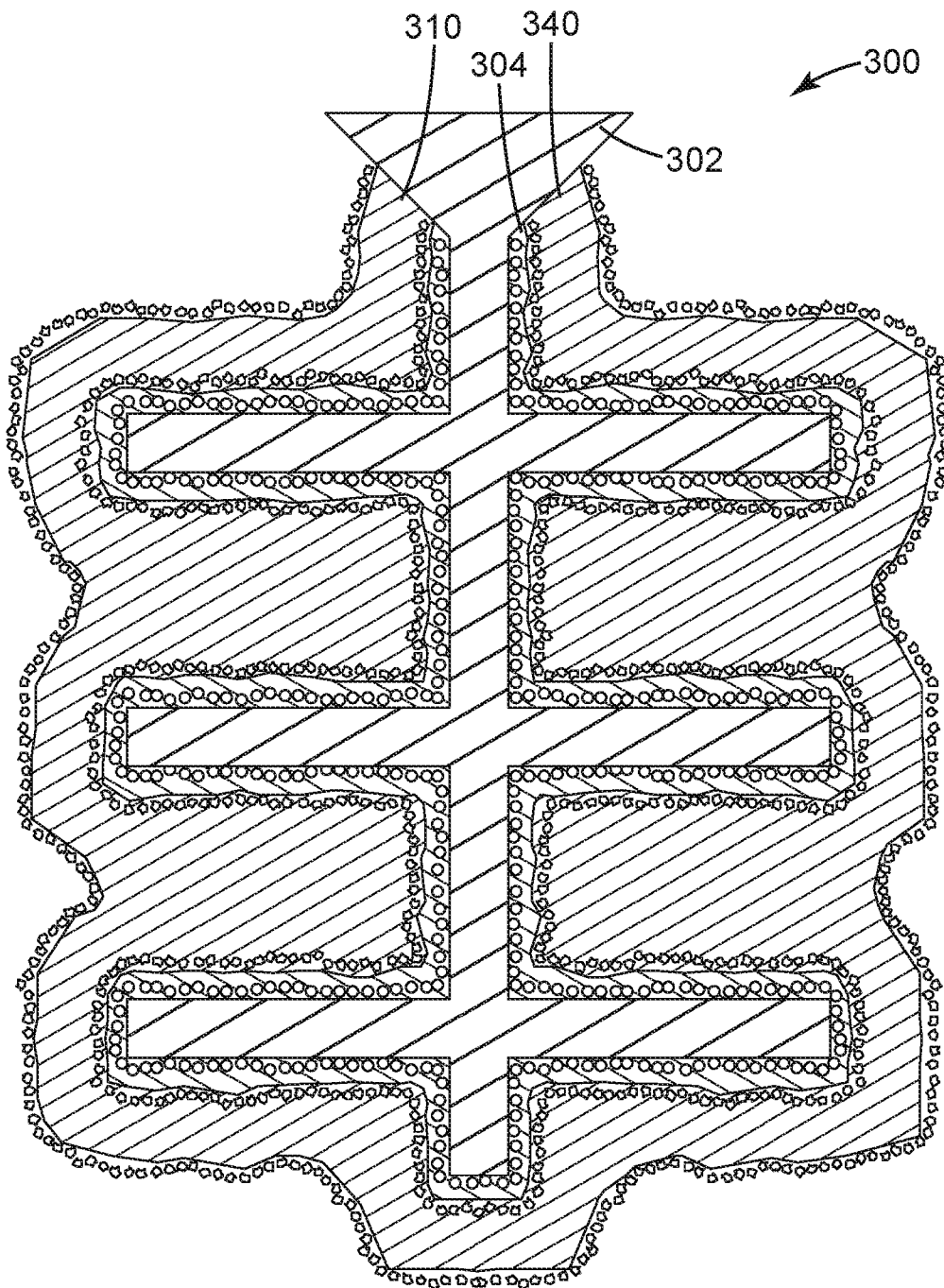
Fig. 3

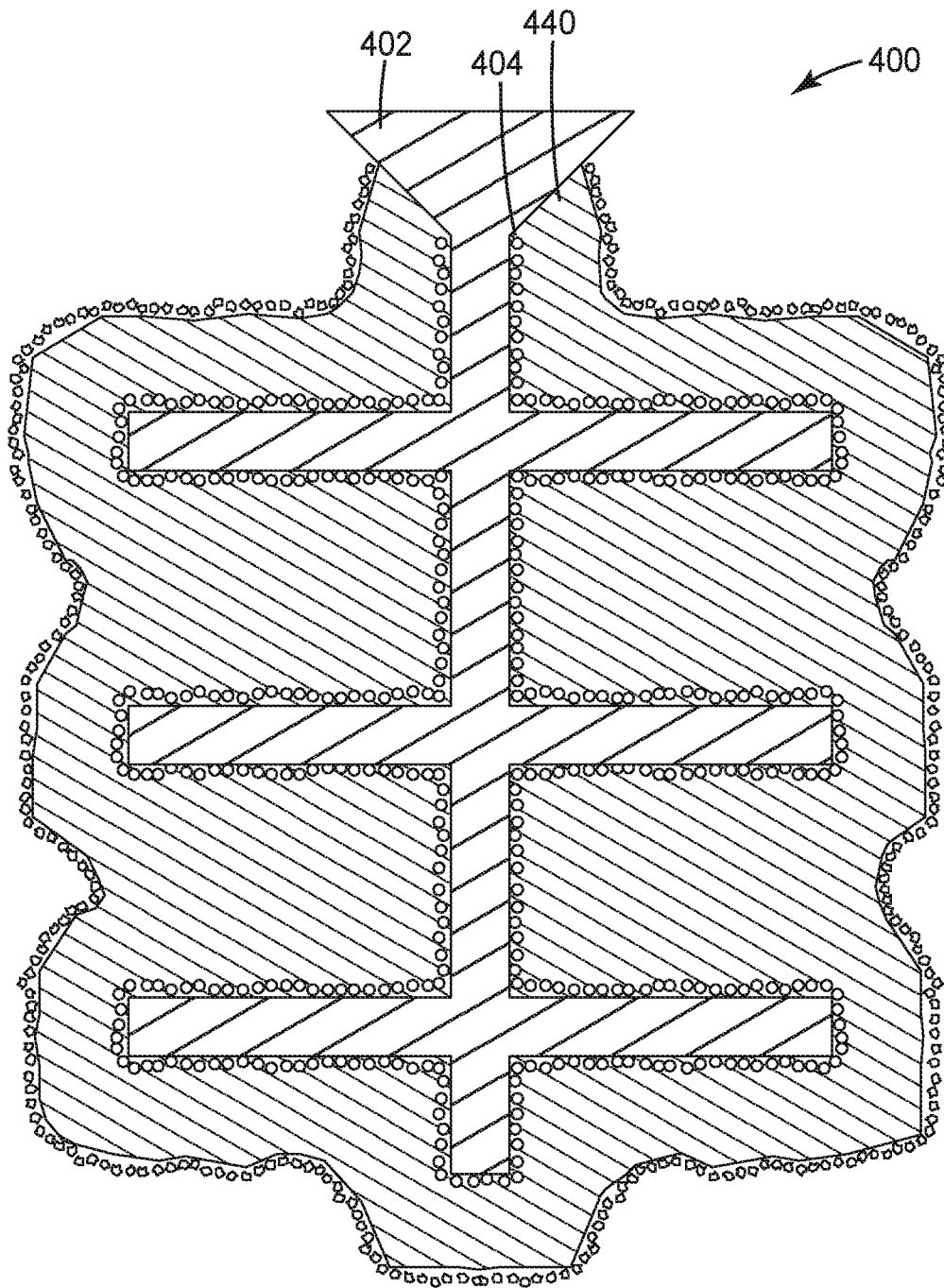
*Fig. 4*

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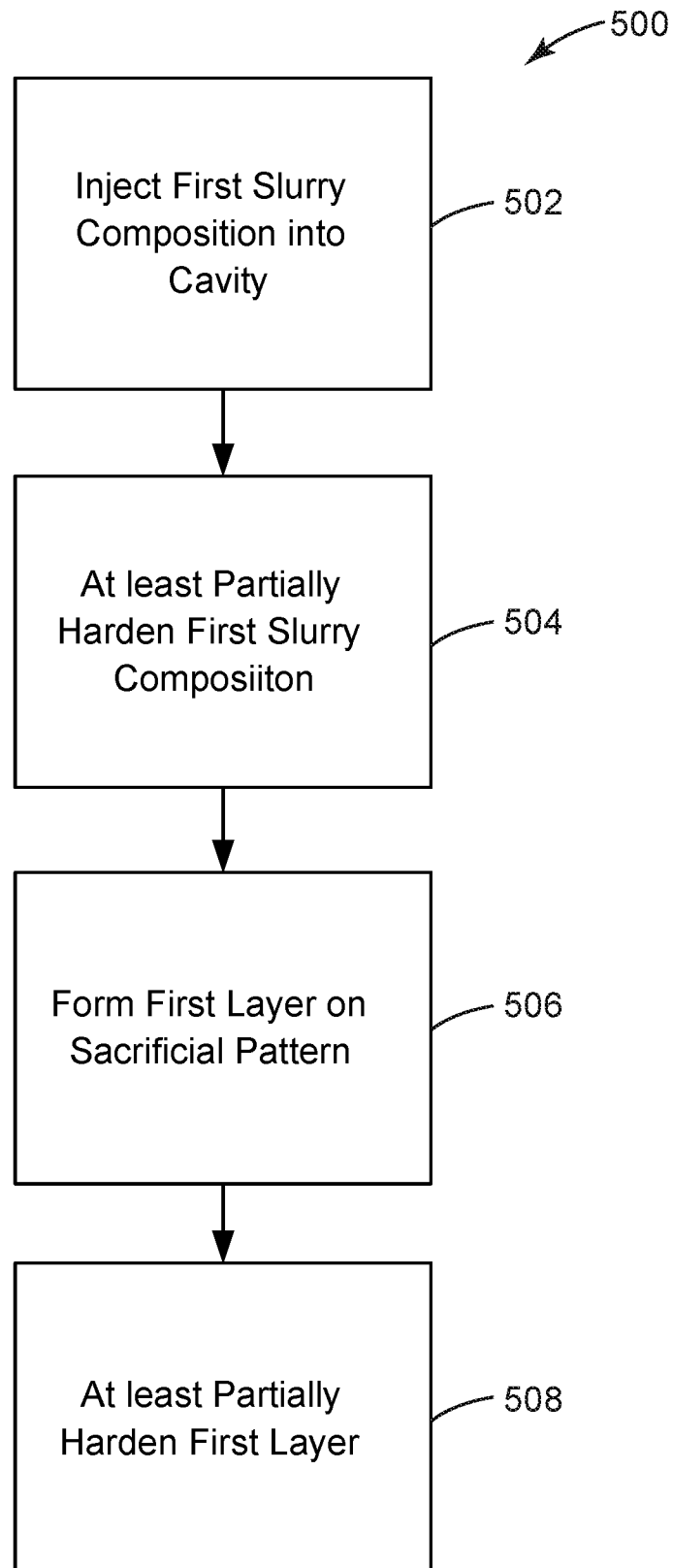
*Fig. 5*

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*Fig. 6*

*Fig. 7*

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*Fig. 8*

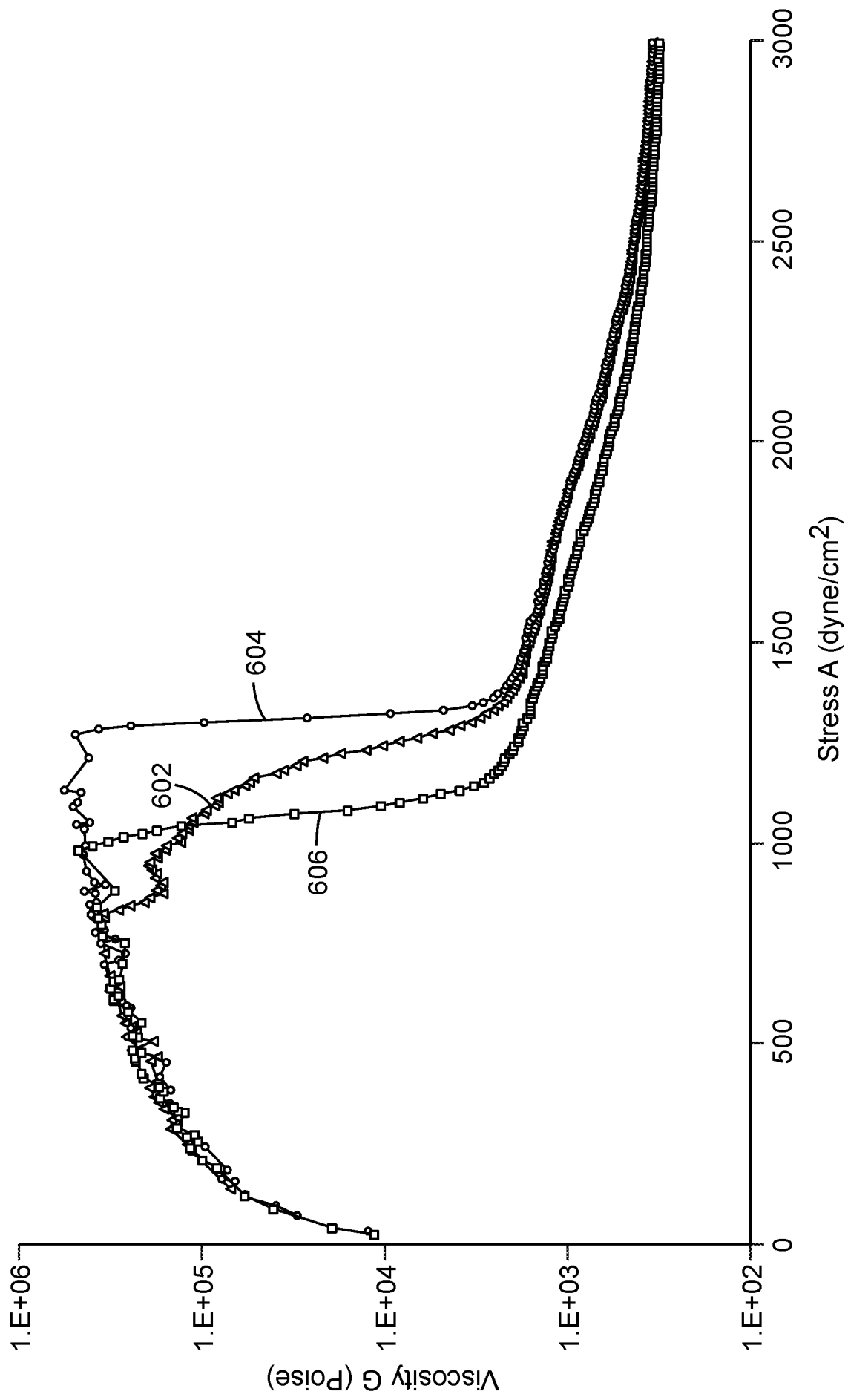


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/055359

A. CLASSIFICATION OF SUBJECT MATTER

INV. B22C3/00 B22C7/02 B22C9/04 B22C1/16 B22C1/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/114279 A1 (SCOTT DAVID H [US]) 19 May 2011 (2011-05-19)	1,3,4, 6-9, 11-18
Y	examples 1-5, 8-15, 18-20 paragraph [0015] - paragraph [0020] paragraph [0027] - paragraph [0037] paragraph [0043] paragraph [0046]	2,5,10, 19
Y	----- WO 2015/168233 A1 (3M INNOVATIVE PROPERTIES CO [US]) 5 November 2015 (2015-11-05) cited in the application page 5, line 19 - page 28, line 28	2,5,10, 19
A	----- EP 1 207 975 A1 (DENTSPLY INT INC [US]) 29 May 2002 (2002-05-29) page 4, line 24 - page 9, line 33 -----	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

8 October 2018

Date of mailing of the international search report

17/10/2018

Name and mailing address of the ISA/

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Authorized officer

Pipoli, Tiziana

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/055359

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