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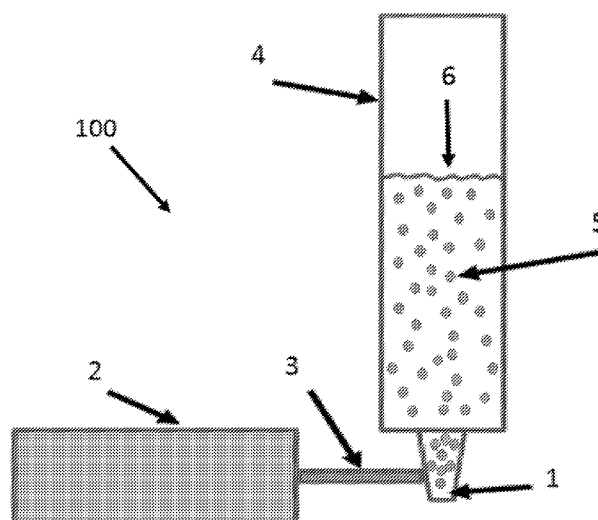


FIG. 1

(57) Abstract: This disclosure generally relates to methods and apparatus for 3D printing of highly viscous materials, especially to high amplitude ultrasonic vibration facilitated lower temperature 3D printing of highly viscous materials with a viscosity of at least 1000 Pa·s.



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Methods and apparatus for 3d printing of highly viscous materials

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims benefit of U.S. Provisional Patent Application Serial No. 62/418,874 filed November 8, 2016, which is incorporated herein by specific reference.

TECHNICAL FIELD

[0002] This disclosure generally relates to methods and apparatus for the 3D printing of highly viscous materials, especially to high amplitude ultrasonic vibration facilitated lower temperature 3D printing of highly viscous materials with a viscosity of at least 1000 Pa·s.

BACKGROUND

[0003] This section introduces aspects that may help facilitate a better understanding of the disclosure. Accordingly, these statements are to be read in this light and are not to be understood as admissions about what is or is not prior art.

[0004] Additive manufacturing methods have been increasingly receiving attention due to their numerous advantages over traditional methods like forming and machining. The most significant of these advantages is the ability to fabricate intricate, highly detailed parts on demand with little material waste. The immense industrial potential of these methods resulted in numerous alternative

approaches and brought some of the initially highly specialized systems into commercial products that became ubiquitous. Nowadays, high quality plastic parts can be produced even at home with very little investment using a 3D printer system that employs fused deposition modeling (FDM) or digital light processing (DLP). It is highly desirable to expand the type of materials that can be printed. These materials include heterogeneous composites, such as clays that are precursors to ceramics, and also metals. Several of these materials have desirable structural and thermal properties compared to polymers.

[0005] Current 3D printing methods for additive manufacturing such as FDM, DLP, stereolithography (SL), selective laser melting (SLM), selective laser sintering (SLS) and ultrasonic consolidation (UC) are limited in their applicability. Specifically, heterogeneous composites and metal powders are very challenging to process with conventional approaches. FDM in its existing form can only work for polymers well above their melting/glass transition temperatures, due to their high viscosity, and for low melting temperature metals. In addition, the deposition rates are low, especially with small nozzle sizes, due to the viscosity of the materials. The use of low viscosity materials is problematic as well, because the printed parts do not retain their shapes until they are cured or solidified. SLM and SLS generally suffer from high porosity in the finished metal parts and low processing rates. SL and DLP are very fast and have good print resolutions, up to 30 μm , but are limited to UV curable polymers with low viscosity.

[0006] The printing of highly viscous materials is a challenge. The only available method known to the applicant uses very high pressure flow to push the material through the nozzle. Such systems are highly specialized and expensive and cannot be integrated with commercial systems. The 3D

printing of clays and other viscous materials has been successfully performed using a pressurized reservoir with a nozzle. However, the required pressures are very high and the nozzle diameters are much bigger, on the order of many centimeters, to overcome the large reaction forces due to viscosity and wall friction and to get reasonable printing rates. The clays also require solvent additions up to 5% to decrease viscosity.

[0007] There are commercially available systems that use low amplitude ultrasonic vibrations to induce the flow of very low viscosity fluids through nozzles for inkjet printing. However, they cannot work for viscous fluids.

[0008] Some prior art disclosed the ultrasonic-assisted extrusion of metal materials. Such a method requires higher temperature, such as about 200 °C, which is not suitable for many materials that are sensitive to high temperatures. See United States Patent No. 9,156,072 B2.

[0009] New approaches for enhancing print quality and rates, while being applicable to different material systems, especially to highly viscous and high temperature sensitive material systems, are therefore of critical industrial need. Thus there exists an unmet need for methods and apparatus for the 3D printing of materials, especially highly viscous materials with less cost and at print resolutions of 100 μm or less.

SUMMARY

[0010] The present disclosure provides novel methods and apparatus for the 3D printing of highly viscous materials, especially to a high amplitude ultrasonic vibration facilitated lower temperature 3D printing method and apparatus for highly viscous materials with a viscosity of at least 1000 Pa·s.

[0011] In one embodiment, the present disclosure provides a three-dimensional (3D) printing method for highly viscous materials comprising:

- a) providing a 3D printer comprising a reservoir, a nozzle, and a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle; and the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration;
- b) providing a highly viscous material substantially free of any thinning material, wherein the highly viscous material has a viscosity of at least 1000 Pa·s and/or a solid content of at least 60%; and
- c) 3D printing the highly viscous material at a temperature lower than 100 °C to provide a 3D printed material with a porosity of less than 10%.

[0012] In one embodiment, the present disclosure provides a 3D printing system comprising a reservoir, a nozzle, a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle, and the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration.

BRIEF DESCRIPTION OF DRAWINGS

[0013] Some of the figures shown herein may include dimensions. Further, some of the figures shown herein may have been created from scaled drawings or from photographs that are

scalable. It is understood that such dimensions or the relative scaling within a figure are by way of example, and not to be construed as limiting. Objects and features of this disclosure will be better understood from the following description taken in conjunction with the drawing, wherein:

[0014] FIG. 1 is a schematic representation of the operation principle of the 3D printer of this disclosure in the case of a heterogeneous viscous material such as clay.

[0015] FIG. 2 is a partial view of an apparatus suitable for vibratory printing according to the present disclosure with a ring-shaped configuration for an ultrasonic probe or actuator (3).

[0016] FIG.3. provides some 3D printed samples. a) Polymer clay 20 mm long pirate ship printed with no supports (nozzle size 600 μm , layer height of 250 μm , print speed 5 mm/s, back pressure 0.69 MPa, print temperature 50 °C). b, c) 3D models (base width is 20 mm) and their 3D printed forms using a fondant mix (nozzle size 600 μm , layer height of 250 μm , print speed 5 mm/s, back pressure 0.15 MPa, print temperature 30 °C). The scale bars are 10 mm.

DETAILED DESCRIPTION

[0018] For the purposes of promoting an understanding of the principles of the disclosure, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the disclosure is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the disclosure as illustrated therein being contemplated as would normally occur to one skilled in the art to which the disclosure relates.

[0019] In the present disclosure the term “about” can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0020] In the present disclosure the term “substantially” can allow for a degree of variability in a value or range, for example, within 90%, within 95%, or within 99% of a stated value or of a stated limit of a range.

[0021] In the present disclosure, the term “close vicinity of a node of ultrasonic vibration” may refer to a position or a reasonable range of position that is sufficiently close to the node of the ultrasonic vibration to ensure the printing quality, especially the resolution of the 3D printed product to be no more than 100 μm under a temperature lower than 100 $^{\circ}\text{C}$.

[0022] In this disclosure, methods and apparatus for 3D printing of highly viscous materials are disclosed. This disclosure describes a novel method for the 3D printing of highly viscous materials ($\mu > 1000 \text{ Pa}\cdot\text{s}$) by the application of high-amplitude vibrations at the nozzle connected to a reservoir filled with the material of interest as the controlling mechanism, which can lower the

effective viscosity allowing an applied pressure differential, i.e. compressed gas, feed screw, etc. to feed material out for the desired increment. The reservoir can be separated from or part of the system utilized to impart vibrations to the nozzle. The rest of the system is similar to an FDM printer or other similar systems, where the nozzle is moved in 3D to print out the material in an additive fashion. The method can be described as vibratory printing (VP) and an apparatus that accomplishes VP as vibratory-printing apparatus. Vibratory printing (VP) utilizes the unique effects of high-amplitude (such as 1-200 μm) ultrasonic vibrations that can reduce apparent friction and effective flow stress of highly viscous materials such as clays that are precursors for ceramics, composite propellants or explosives, viscous food slurries, and numerous others. For purposes of this disclosure, materials with a viscosity higher than 1000 Pa·s are considered highly viscous.

[0023] FIG. 1 is a schematic illustration of the operating principle of the VP apparatus of this disclosure which can be used for the VP method of this disclosure to effectively print high viscosity materials such as, but not limited to, clay. Referring to FIG. 1, system (100) comprises a nozzle (1), a high amplitude vibration generator (2), an ultrasonic probe or actuator (3), and a reservoir (4) for highly viscous materials (5). During the 3D printing, a pressure (6) is applied to the highly viscous materials (5). Materials in the reservoir other than the highly viscous materials, such as a fluid medium in which the particles are suspended are not shown in FIG. 1. High amplitude vibrations are applied in a way that the nozzle (1) is positioned at or in the close vicinity of a node of the high amplitude vibration, while a sufficient pressure (6) is applied to the material to maintain a pressure differential across the printing end of the nozzle and the other wider end. A non-limiting range for the amplitude of these vibrations may be 1-200 μm . These vibrations can be applied to

the nozzle by means of an ultrasonic probe or actuator (3). The ultrasonic probe or actuator (3) may have any configuration at the end that is used to pass the vibration to the nozzle (1). As shown in FIG 2, a ring-shaped configuration that can be applied to surround the nozzle may provide advantage since it provides more evenly distributed vibration to the nozzle (1) when the nozzle is positioned within the ring. There can be one or more ultrasonic probes or actuators (3) as far as the nozzle (1) is positioned at or in the close vicinity of a node of the ultrasonic vibration generated by one or more ultrasonic probe or actuator (3). Ensuring that the nozzle (1) is positioned at or in the close vicinity of a node of the ultrasonic vibration may provide unexpected advantages. For example, there is a much lower temperature need to achieve the successful low porosity 3D printing. Prior art disclosures normally require a much higher temperature to make the to-be-printed material a molten material. For certain high-temperature sensitive materials, the present disclosure provides a much safer method of material deposition. In the present invention, the extruded materials are not molten since they are far below their melting temperatures. In some instances, the ultrasonic probe itself can be the nozzle (1). These vibrations reduce the viscosity of the printing material by decreasing its flow stress. Further these vibrations reduce the inter particle friction as well as the friction between the walls of the nozzle and the particles in the printing material. Also, in the methods and apparatus of the present disclosure, the ultrasonic vibrations are used to induce flow and also as the on-off trigger for material deposition.

[0024] The application of the vibration enables the use of fine nozzles with diameters less than 100 μm , in addition to larger nozzles, with very high feed rates for the rapid printing of a wide variety of materials with high resolution (100 μm or less). The higher resolutions, apart from the

obvious advantage of higher quality parts, can also reduce the porosity. The required pressure differential for pushing the feed stock or the thick fluid is reasonable when such vibrations are employed. For example, here a pressure of 25 psi was sufficient. In the absence of vibrations, even at 100 psi (the maximum pressure that could be applied in the current setup), the flow rates were less. Furthermore, the less viscous fluid in the heterogeneous mixture tends to get preferentially squeezed out between the particles and extrude, eventually clogging the nozzle with the solids left behind. There was also no control of flow. For reducing the friction, the use of ultrasonic frequencies is much more effective and high amplitudes such as those in the non-limiting range of 1-200 μm are also required, as submicron amplitudes appear to have negligible effect. The field of high-intensity ultrasonic vibration is not broadly studied, and the transducers and electronics required are highly specialized. High amplitude vibrations at ultrasonic frequencies are fundamentally different from those that are low amplitude lower frequency due to unique contribution of inertial effects in these regimes.

[0025] Vibratory printing, as disclosed herein, can be extremely significant and useful in light of current additive manufacturing methods, because the presently disclosed approach can be readily integrated into existing systems. The relative simplicity of the process and the equipment and the small cost associated keeps the initial and operating costs to a minimum compared to other methods that require expensive equipment and material specific consumables. VP can create new potential opportunities for industrial applications, such as the large scale metal printing of near-net shape parts, which are not feasible and cost-effective using the existing methods.

[0026] High amplitude ultrasonic vibrations can reduce apparent friction between surfaces, due to the vibration amplitudes being comparable to asperity dimensions..

[0027] The system can be easily integrated into existing commercial printing systems, by nozzle or reservoir modification. Importantly, the flow of the material is controlled very precisely by turning on/off the ultrasonic vibrations for tight tolerances on printed parts. This is not possible with just the application of pressure, as the material continues to flow when the pressure is reduced or shut off. The possibility of printing ceramics enables the near-net shape printing of biomedical parts such as porcelain teeth and implants. Another possible application is the printing of metals with low porosity. Methods that use nozzles utilize a mixture of metal powder with a polymer which is melted and extruded. However, high viscosities limit the solid fraction that can be attained. Such prints need to be treated at elevated temperatures to drive off the polymer and provide adhesion between metal particles, but the dimensions of the prints vary considerably due to the low volume fraction of the metal powder. VP can use high viscosity mixtures of metals and plasticizers with >60 vol% solids and thus the prints do not change shape after elevated temperature treatments, because the individual metal particles are already in intimate contact.

[0028] As described above, the vibratory printing detailed in this disclosure uses a modified nozzle for 3D printing systems, which applies high amplitude vibrations to the printed material to reduce the flow stress and friction. This enables the printing of highly viscous materials through fine nozzles with diameters down to at least a few hundred micrometers at high flow rates. The technology also enables the on-off control of the flow to deposit precise amounts of materials such as thick pastes that consist of mixtures and ceramics that are highly viscous. The combination of

high flow rate with fine nozzle dimensions enables previously prohibitive high resolution printing with reasonable printing durations.

[0029] The general term vibration generator can be used for the vibration-generating element of the VP printing apparatus. Thus an ultrasonic probe or an ultrasonic actuator fall into the general class of vibration generators. It should be noted that the VP printing apparatus of FIG. 1 can be further modified to integrate the vibration probe or actuator, which one can generally term as vibration generator, into the reservoir-nozzle system. This is accomplished by an arrangement, wherein the vibration generator is mechanically coupled to the reservoir.

[0030] It should be noted that the methods and apparatus of the present disclosure provide the ability to print highly viscous materials through reduced flow stress and friction. They also enable very high resolution printing at very high speeds due to the increased flow rate that enables the use of fine nozzles. The presently disclosed method and apparatus also provide precise on/off digital control of the flow that provides better printing control with high resolution.

[0031] It should be further recognized that the methods and apparatus of this disclosure also enable on-off control of the flow to deposit precise amounts of materials such as thick pastes that consist of mixtures, ceramics and semi-solid metals that are highly viscous. The combination of high flow rate with fine nozzle dimensions enables previously prohibitive high resolution printing with reasonable printing durations.

[0032] The methods and apparatus of this disclosure are also applicable to novel material systems that were not successfully printed before. Metals and ceramics with high resolution can be printed

using these methods and apparatuses. The method can also be easily integrated into existing 3D printing systems.

[0033] Because most 3D printed parts are built layer-by-layer, a previous layer to build upon is required. Depending on the specific 3D printing technology and the complexity of the 3D model, this can mean that a 3D print requires support structures. The present disclosure, however, provides a method that can print highly viscous materials with no support or minimal support while still maintain the excellent printing quality due to the high yield strength of such materials.

[0034] Materials and Methods

[0035] A commercial 3D printer (Monoprice Mini) was modified by replacing the print head with a pneumatically operated low-density polyethylene syringe with a nozzle opening of 600 μm rated up to 0.69 MPa (Mcmaster Carr Semi-Clear Syringe 66305A55). The syringe was attached to a custom ultrasonic mini probe with a threaded hole at the end, which was driven by a function generator (Fluke 294 Waveform Generator) and an amplifier connected to a transformer (turn ratio 1:20) to switch on the high-amplitude vibrations for flow control of the material. The peak-to-peak voltage applied to the transducer was up to 500 V at a frequency of 30.3 kHz which produced nozzle displacements of 16 μm in this configuration. The source waveform was switched on and off using a relay attached to the filament feed stepper motor output, which was controlled by turning the stepper motor on and off in the printer GCode. Duty cycles were used for controlling temperature rises. The ultrasonic vibrations were turned on 1 second and turned off 1 second (or within a range from 500 ms to 2 s in general). When they were turned off, the print waited for that amount. This prevented excessive heating. The syringe was pressurized using a commercial air

compressor (Fini Advanced 2 gallon 125 psi air compressor). The materials investigated were a commercial polymer clay (Sculpey Oven Bake), natural clay (AMACO Air Dry Natural Clay), a stiffened fondant mix (66 wt.% Wilton Decorator Preferred Fondant, 26 wt.% C&H powdered sugar, 8 wt.% Clover Valley Light Corn Syrup), and a propellant (85 wt.% of ammonium perchlorate particles in the size range 60-130 μm , 15% of hydroxyl terminated polybutadiene (HTPB) as a polymer binder). The viscosity and yield strength of the materials were measured with a capillary rheometer (Bohlin Rosand RH2000) at shear rates in the range of 2-50 s^{-1} with two capillaries with diameters of 4 mm and lengths of 16 mm and 32 mm to apply Bagley correction. The flow rate of the material in the printing syringe was measured with a high-speed camera (Vision Research Phantom V 7.3) at varying pressures. The temperatures of the nozzle and materials during printing were measured using a FLIR A325 infrared camera at 30 Hz. A fan and a lower duty cycle for the vibrations were used to keep the temperature rise below 30 $^{\circ}\text{C}$.

[0036] Table 1 provided the 3D printing conditions and the outcome of the 3D printed materials.

Example No.	Materials	Viscosity (Pa·s)	T ($^{\circ}\text{C}$)	P (MPa)	Vibration amplitude (μm)	Porosity	Printing speed (mm/s)	Nozzle size (μm)
1	polymer clay	about 9,000	50	0.48	16	<5%	5	600
2	stiffened fondant mix	about 14,000	30	0.15	16	<5%	5	600
3	propellant	about 10,000	30	0.15	16	<5%	5	600

[0037] FIG.3 provides some 3D printed products with highly viscous materials.

[0038] In one embodiment, the present disclosure provides a three-dimensional (3D) printing method for highly viscous materials, wherein the method comprises:

- a) providing a 3D printer comprising a reservoir, a nozzle, and a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle; and the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration;
- b) providing a highly viscous material substantially free of any thinning material, wherein the highly viscous material has a viscosity of at least 1000 Pa·s and/or a solid content of at least 60%; and
- c) 3D printing the highly viscous material at a temperature lower than 100 °C to provide a 3D printed material with a porosity of less than 10%.

[0039] In one embodiment, the present disclosure provides a three-dimensional (3D) printing method for highly viscous materials, wherein the method comprises:

- a) providing a 3D printer comprising a reservoir, a nozzle, and a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the tip of the nozzle; and the tip of the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration;

b) providing a highly viscous material substantially free of any thinning material, wherein the highly viscous material has a viscosity of at least 1000 Pa·s and/or a solid content of at least 60%; and

c) 3D printing the highly viscous material at a temperature lower than 100 °C to provide a 3D printed material with a porosity of less than 10%.

[0040] In one embodiment of the present disclosure, the 3D printing temperature is lower than 75 °C at the nozzle. In one aspect, the 3D printing temperature is lower than 50 °C. In one aspect, the 3D printing temperature is lower than 30 °C. In one aspect, the 3D printing temperature is between 0-100 °C, 0-50 °C, or 0-30 °C.

[0041] In one embodiment of the present disclosure, the 3D printed materials have a porosity of less than 20%, 15%, 10%, 5%, 4%, 3%, 2%, or 1%. In one aspect, the 3D printed materials have a porosity of about 0-20%, 0-15%, 0-5%, 0-4%, 0-3%, 0-2%, or 0-1%.

[0042] In one embodiment of the present disclosure, the 3D printing is carried out by applying a pressure under 30, 25, 20, 15, 10, 5, 4, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 MPa.

[0043] In one embodiment of the present disclosure, the 3D printed material has a 3D printing resolution of 100 μm or less, 90 μm or less, 80 μm or less, 70 μm or less, 60 μm or less, 50 μm or less, 40 μm or less, 20 μm or less. In one aspect, the 3D printing resolution is about 20-100 μm, 40-100 μm, 50-100 μm, 60-100 μm, 70-100 μm, 80-100 μm, or 90-100 μm.

[0044] In one embodiment of the present disclosure, the amplitude of the ultrasonic vibration is about 0.5-200 μm, 1-200 μm, 5-200 μm, 0.5-100 μm, 1-100 μm, 5-100 μm, 0.5-75 μm, 1-75 μm, or 5-75 μm.

[0045] In one embodiment of the present disclosure, the frequency of the ultrasonic vibration is about 10-200 kHz, 10-150 kHz, 10-100 kHz, 10-75 kHz, 10-50 kHz, 20-200 kHz, 20-150 kHz, 20-100 kHz, 20-75 kHz, or 20-50 kHz.

[0046] In one embodiment of the present disclosure, the diameter of the nozzle is about 5-1000 μm , 5-500 μm , 5-100 μm , 10-1000 μm , 10-500 μm , 10-100 μm , 20-1000 μm , 20-500 μm , 20-100 μm .

[0047] In one embodiment, the present disclosure provides a 3D printing method to print a highly viscous material with minimum or no support.

[0048] In one embodiment, the present disclosure provides a 3D printing method wherein the vibration probe has a ring-shaped configuration to keep the nozzle run through and within the ring-shaped configuration to provide evenly distributed vibration.

[0049] In one embodiment, the present disclosure provides a 3D printing system comprising a reservoir, a nozzle, a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle, the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration. In one aspect, the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the tip of the nozzle, the tip of the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration.

[0050] In one embodiment, the vibration probe has a ring-shaped configuration to keep the nozzle run through and within the ring-shaped configuration to provide evenly distributed vibration.

[0051] While the present disclosure has been described with reference to certain embodiments, it will be apparent to those of ordinary skill in the art that other embodiments and implementations are possible that are within the scope of the present disclosure without departing from the spirit and scope of the present disclosure. Accordingly, it should be understood that the disclosure is not limited to any embodiment described herein. It should also be understood that the phraseology and terminology employed above are for the purpose of describing the disclosed embodiments, and do not necessarily serve as limitations to the scope of the disclosure.

WE CLAIM:

1. A three-dimensional (3D) printing method for highly viscous materials, wherein the method comprises:

- a) providing a 3D printer comprising a reservoir, a nozzle, and a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle; and the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration;
- b) providing a highly viscous material substantially free of any thinning material, wherein the highly viscous material has a viscosity of at least 1000 Pa·s and/or a solid content of at least 60%; and
- c) 3D printing the highly viscous material at a temperature lower than 100 °C at the nozzle tip to provide a 3D printed material with a porosity of less than 10%.

2. The method of claim 1, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the tip of the nozzle; and the tip of the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration.

3. The method of claim 1 or 2, wherein the 3D printing temperature is lower than 50 °C.

4. The method of any preceding claim, wherein the 3D printed material has a porosity of less than 5%.

5. The method of any preceding claim, wherein the 3D printing is carried out by applying a pressure under 1 MPa.
6. The method of any preceding claim, wherein the 3D printed material has a porosity of less than 2 %.
7. The method of any preceding claim, wherein the 3D printed material has a 3D printing resolution of 100 μm or less.
8. The method of any preceding claim, wherein the 3D printing is carried out with minimum or no support.
9. The method of any preceding claim, wherein the vibration probe has a ring-shaped configuration to keep the nozzle run through and within the ring-shaped configuration to provide evenly distributed vibration.
10. A 3D printing system comprising a reservoir, a nozzle, a high amplitude ultrasonic vibration generator, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the nozzle, the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration.
11. The 3D printing system of claim 10, wherein the high amplitude ultrasonic vibration generator is configured to generate an ultrasonic vibration through a vibration probe with an amplitude of 1-200 μm near the tip of the nozzle; and the tip of the nozzle is positioned at or in the close vicinity of a node of the ultrasonic vibration.

12. The 3D printing system of claim 10, wherein the vibration probe has a ring-shaped configuration to keep the nozzle run through and within the ring-shaped configuration to provide evenly distributed vibration.

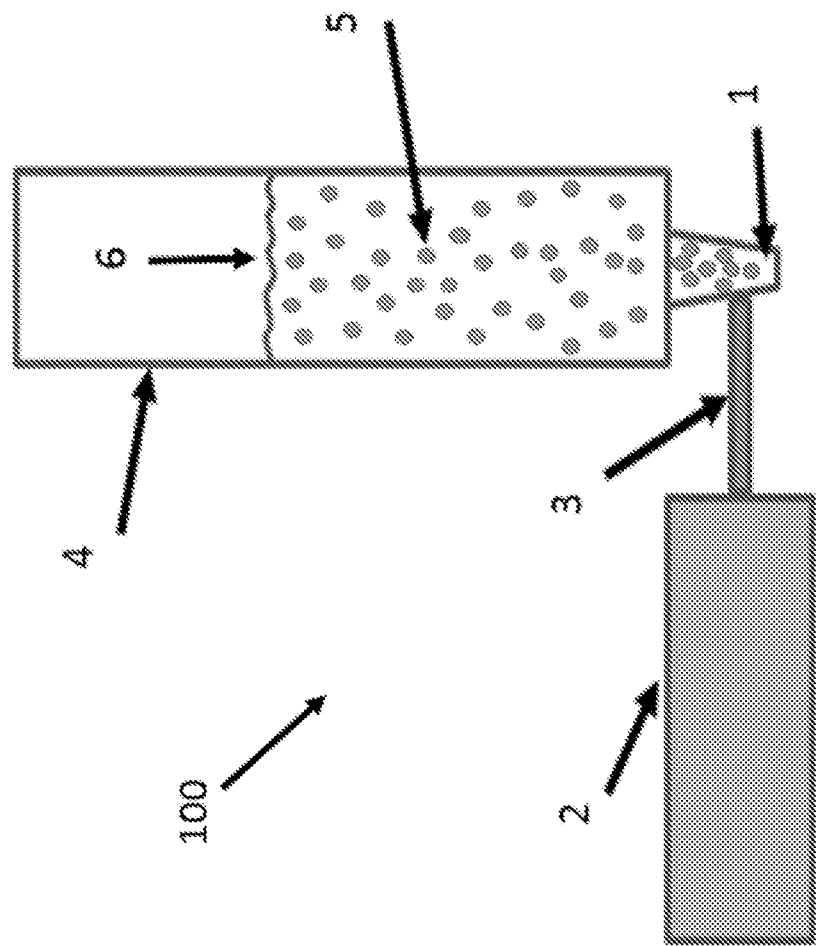


FIG. 1

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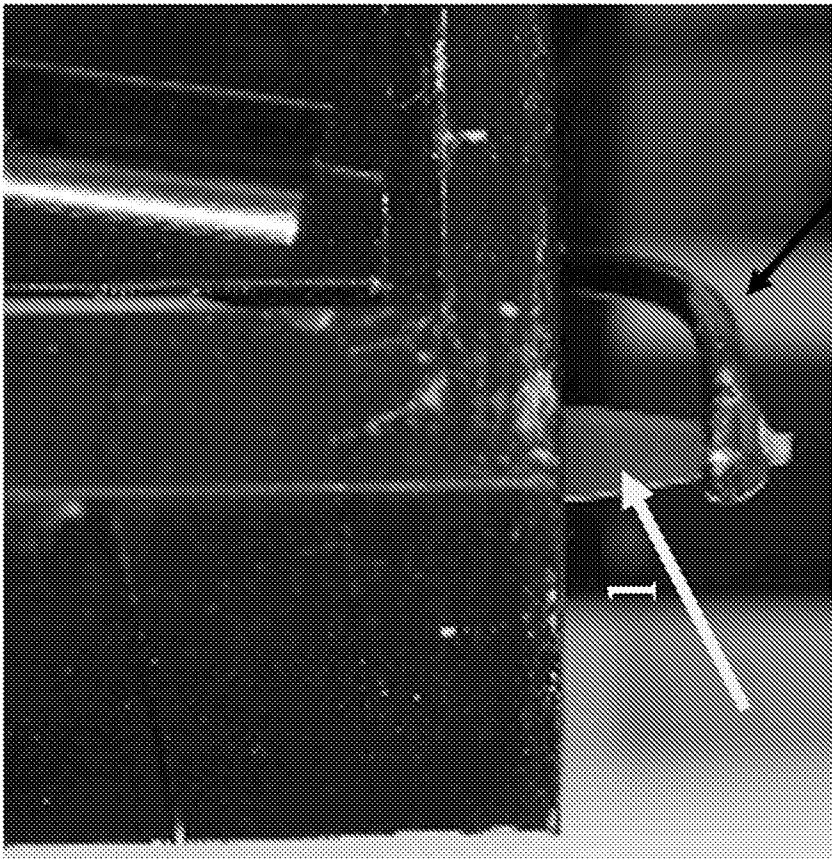
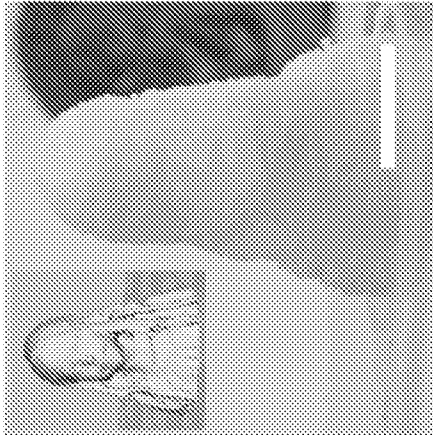
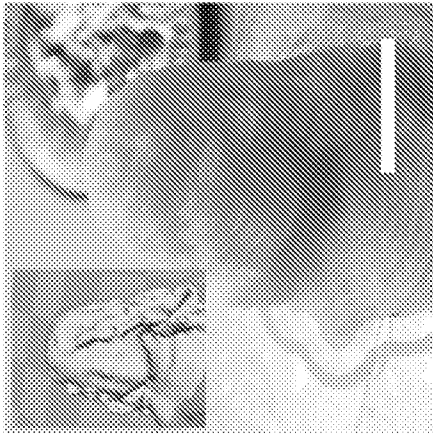


FIG. 2

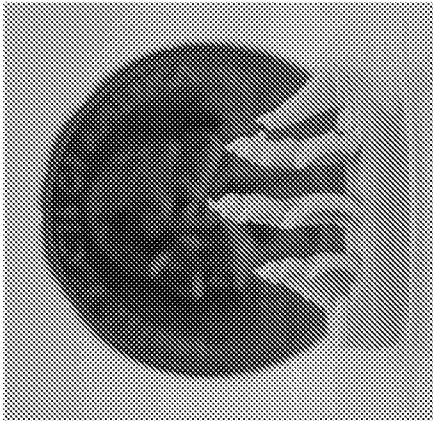
3/3



c



b



a

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/060346

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-9
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/060346

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B33Y 70/00; B05B 17/06; B29C 64/00; B29C 64/20; B33Y 10/00; B33Y 40/00 (2017.01)
 CPC - B33Y 70/00; B05B 17/06; B21C 23/004; B28B 1/001; B29C 64/00; B29C 64/106; B29C 64/124;
 B29C 64/165; B29C 64/188; B29C 64/20; B29C 64/209; B33Y 10/00; B33Y 40/00 (2017.08)

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)

See Search History document

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

USPC - 72/253.1; 228/110.1; 700/119 (keyword delimited)

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/0199158 A1 (MUHLBAUER TECHNOLOGY GMBH) 14 July 2016 (14.07.2016) entire document	10-12
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Y		1-3
Y	WO 2016/071241 A1 (WACKER CHEMIE AG) 12 May 2016 (12.05.2016) entire document	1-3
Y	US 2016/0200045 A1 (HOPKINS et al) 14 July 2016 (14.07.2016) entire document	1-3
A	US 6,450,393 B1 (DOUMANIDIS et al) 17 September 2002 (17.09.2002) entire document	1-3, 10-12
A	US 2015/0064047 A1 05 March 2015 (05.03.2015) entire document	1-3, 10-12
A	WO 2016/140906 A1 (GRAPHENE 3D LAB INC.) 09 September 2016 (09.09.2016) entire document	1-3, 10-12
A	US 2014/0252668 A1 (LOUGHBOROUGH UNIVERSITY) 11 September 2014 (11.09.2014) entire document	1-3, 10-12
A	WO 2016/090286 A1 (UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC. et al) 09 June 2016 (09.06.2016) entire document	1-3, 10-12

☐ 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

"I" 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

15 December 2017

Date of mailing of the international search report

04 JAN 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
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