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# Method and Apparatus for Fabricating Ceramic and Metal Components via Additive Manufacturing with Uniform Layered Radiation Drying

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(54) **METHOD AND APPARATUS FOR FABRICATING CERAMIC AND METAL COMPONENTS VIA ADDITIVE MANUFACTURING WITH UNIFORM LAYERED RADIATION DRYING**

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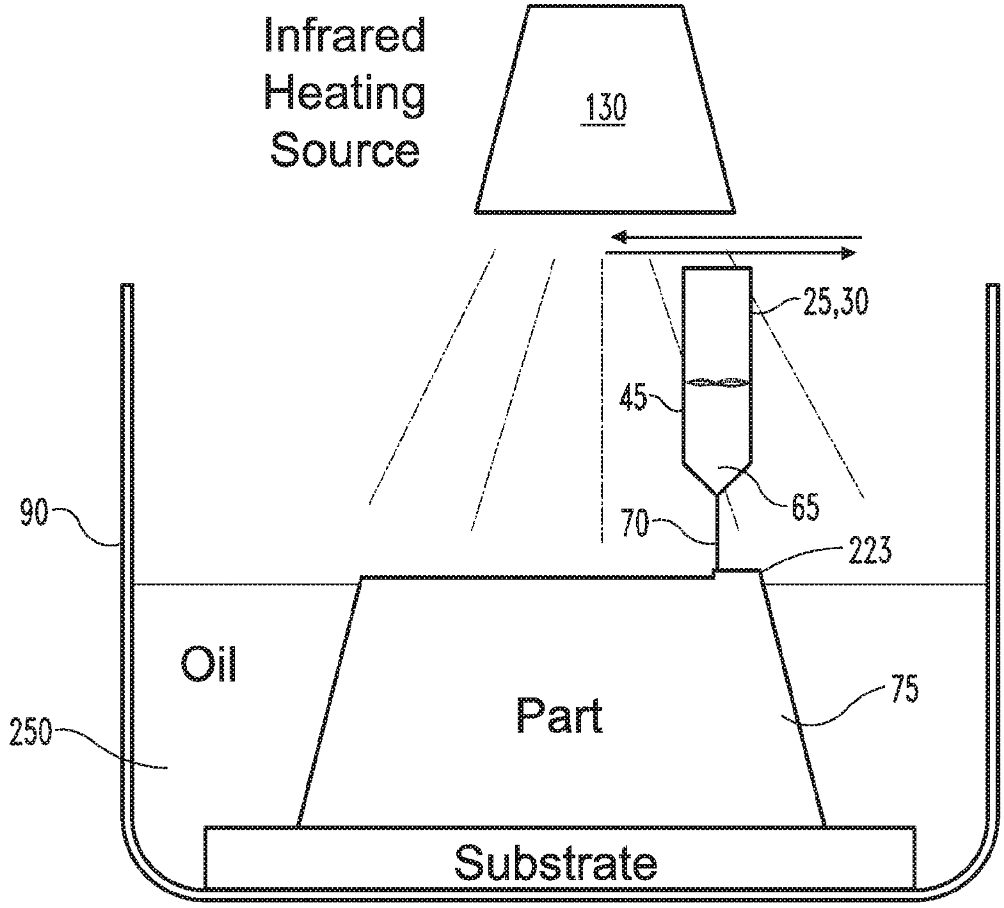
(57) **ABSTRACT**

A freeform extrusion fabrication process for producing three-dimensional ceramic, metal and functionally gradient composite objects, including the steps of filling a plurality of paste sources with a respective plurality of aqueous paste compositions, operationally connecting respective syringes containing respective aqueous paste compositions to a mixing chamber, moving a first aqueous paste composition from a first respective paste source into the mixing chamber, moving a second aqueous paste composition from a second respective paste source into the mixing chamber, mixing the first and second aqueous paste compositions to define a first admixture having a first admixture composition, extruding the first admixture onto a surface to define an extruded layer having a first admixture composition, surrounding the sides of the extruded layer with an oil bath, radiatively drying the extruded layer.



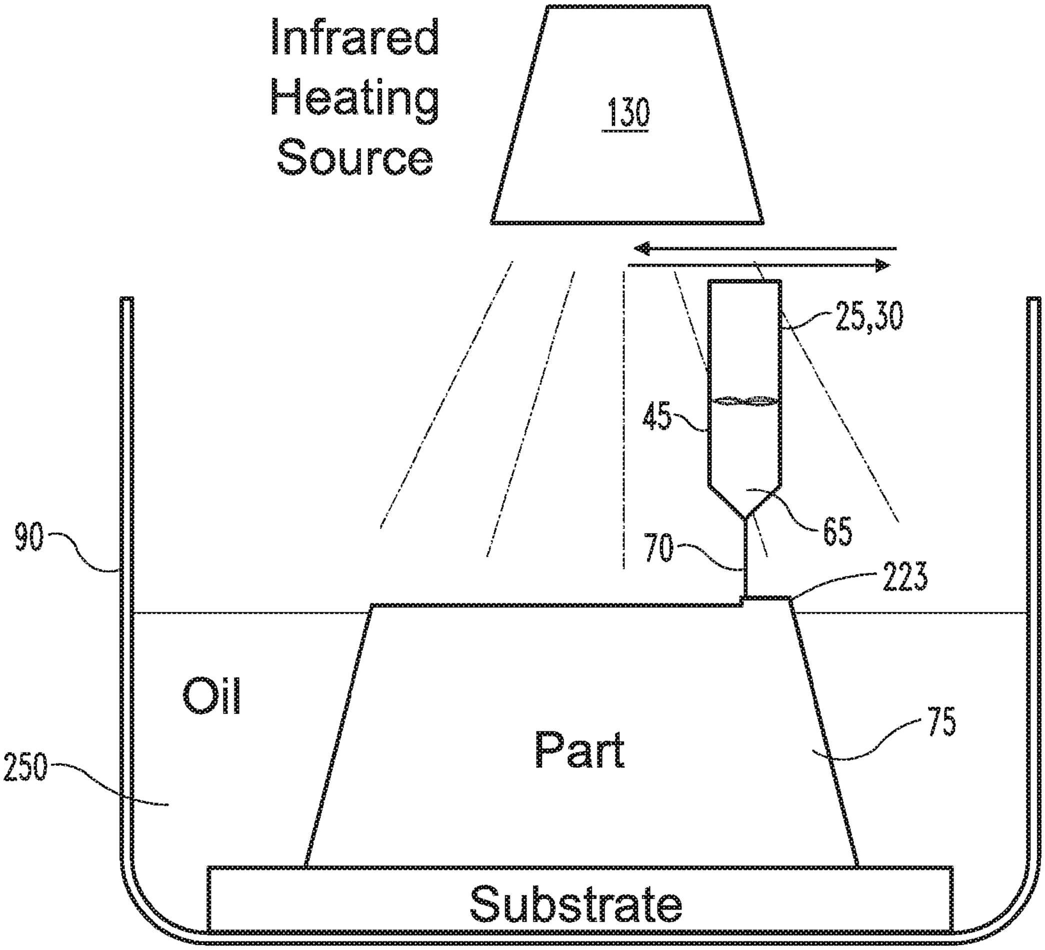

Infrared
Heating
Source
130
25,30
45
65
70
223
90
Oil
250
Part
75
Substrate

Fig. 1

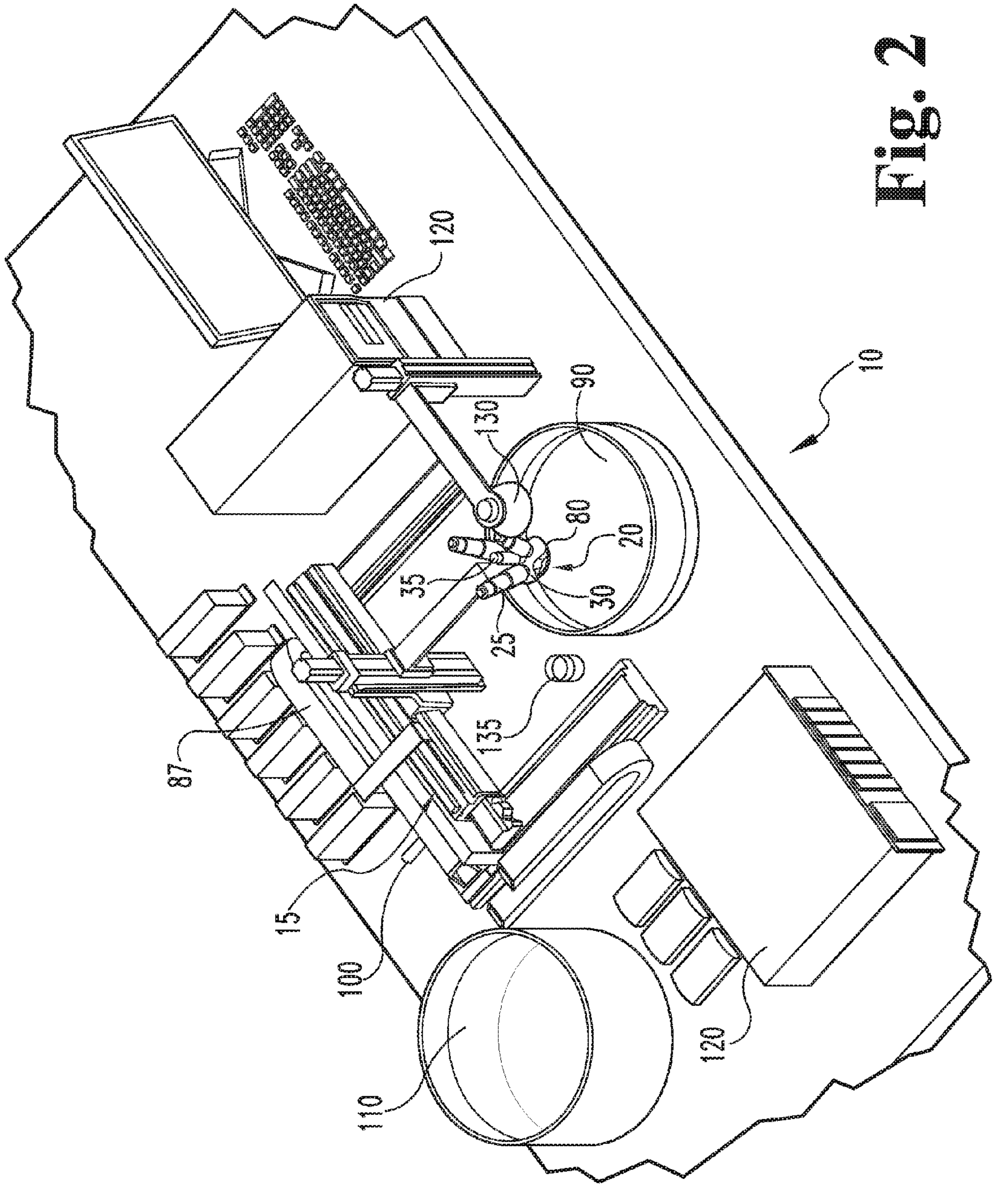


Fig. 2

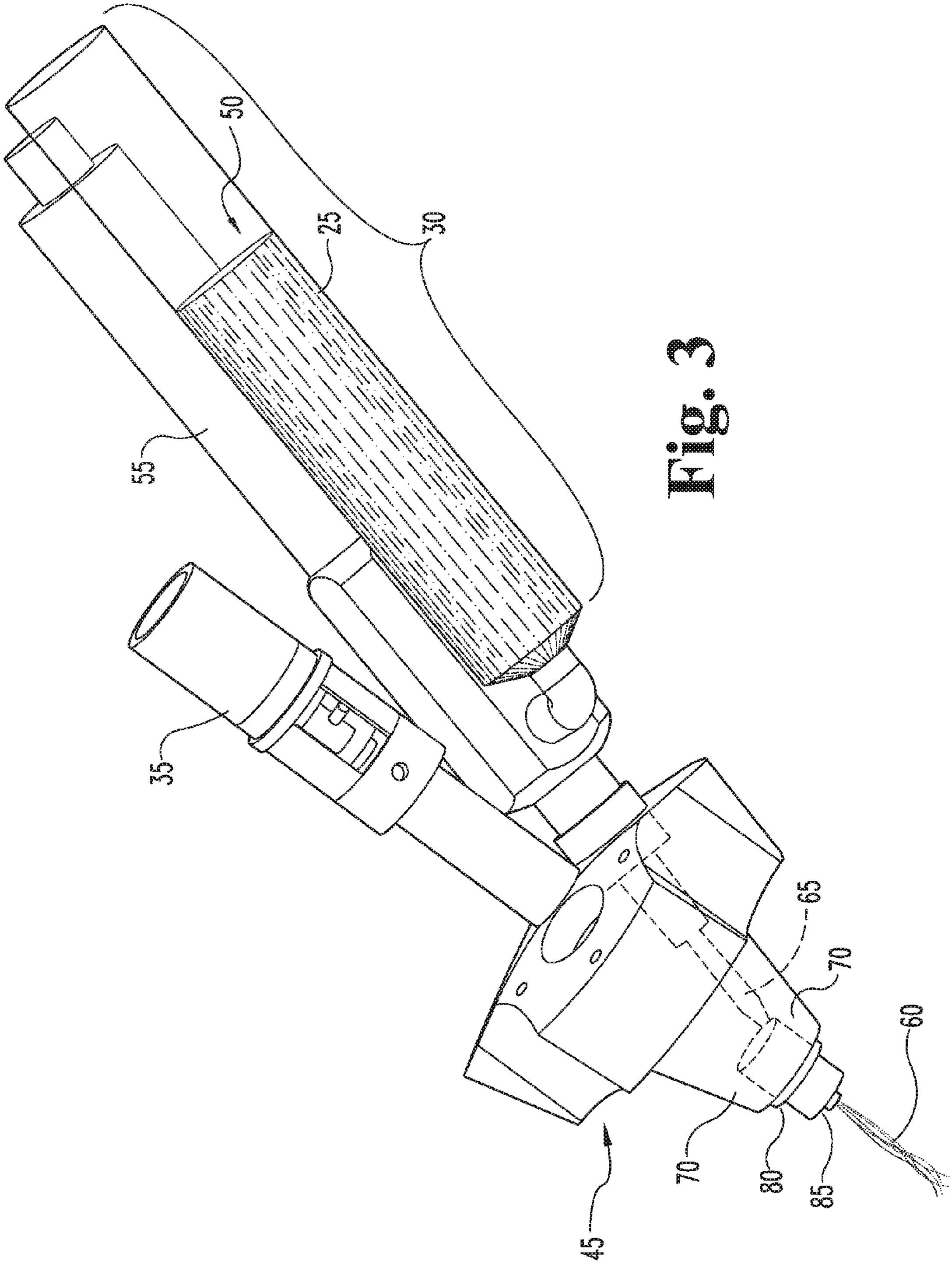


Fig. 3

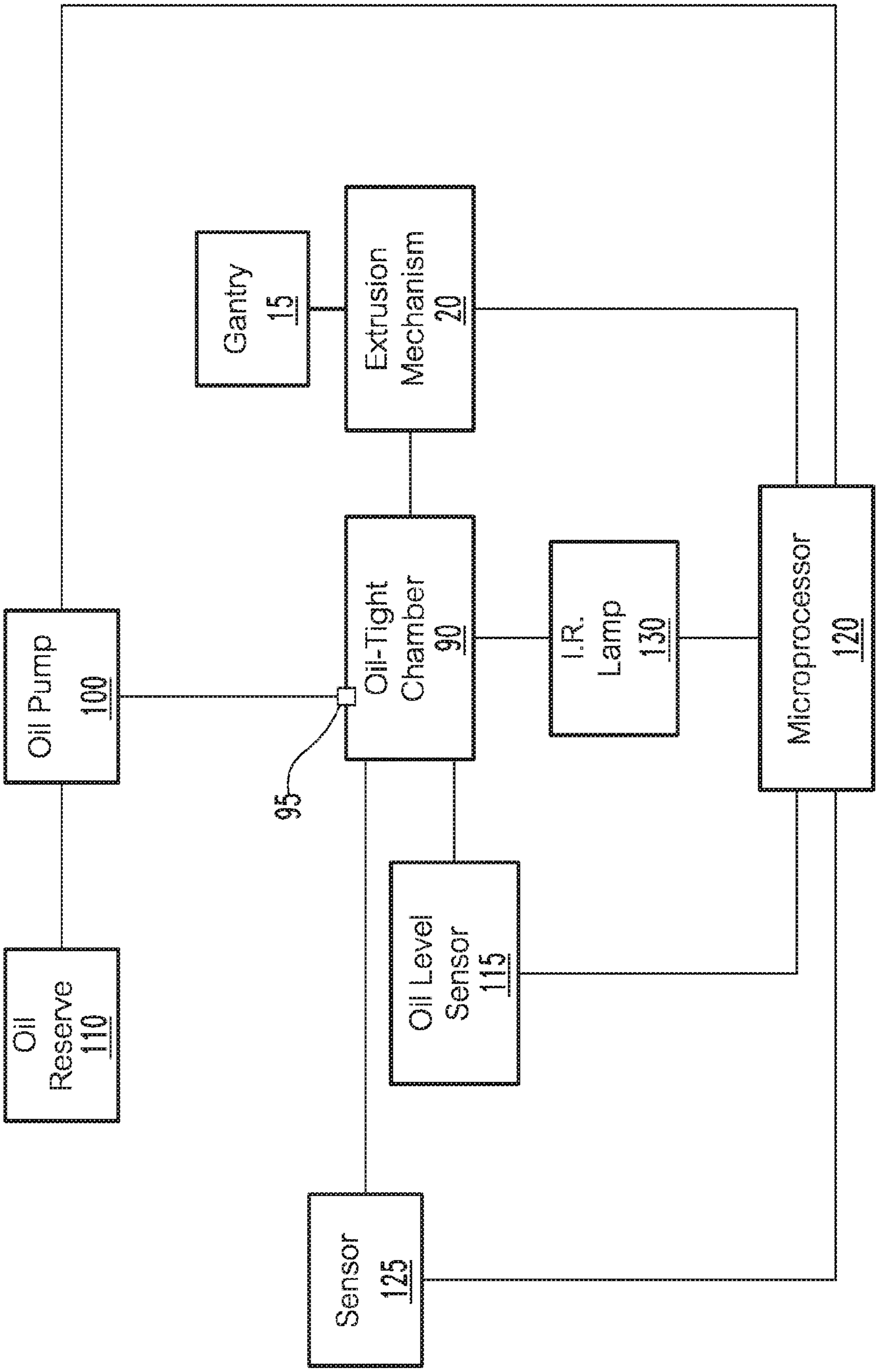

Oil Reserve
110
Oil Pump
100
Gantry
15
Extrusion Mechanism
20
Oil-Tight Chamber
90
95
I.R. Lamp
130
Microprocessor
120
Oil Level Sensor
115
Sensor
125

Fig. 4

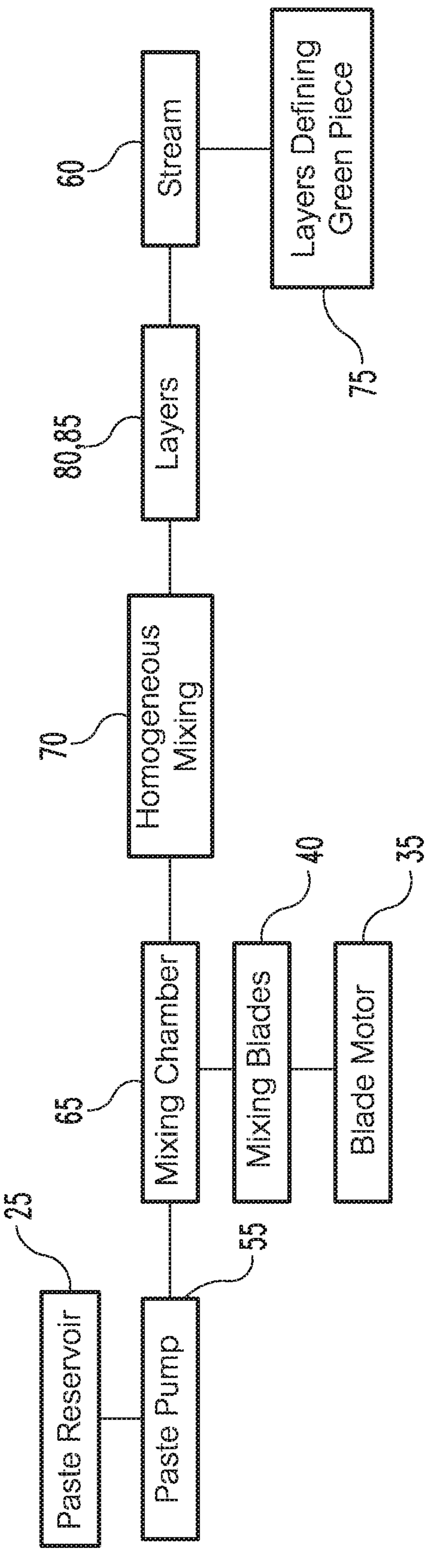

Paste Reservoir
25
Paste Pump
55
Mixing Chamber
65
Mixing Blades
40
Blade Motor
35
Homogeneous Mixing
70
Layers
80,85
Stream
60
Layers Defining Green Piece
75

Fig. 5

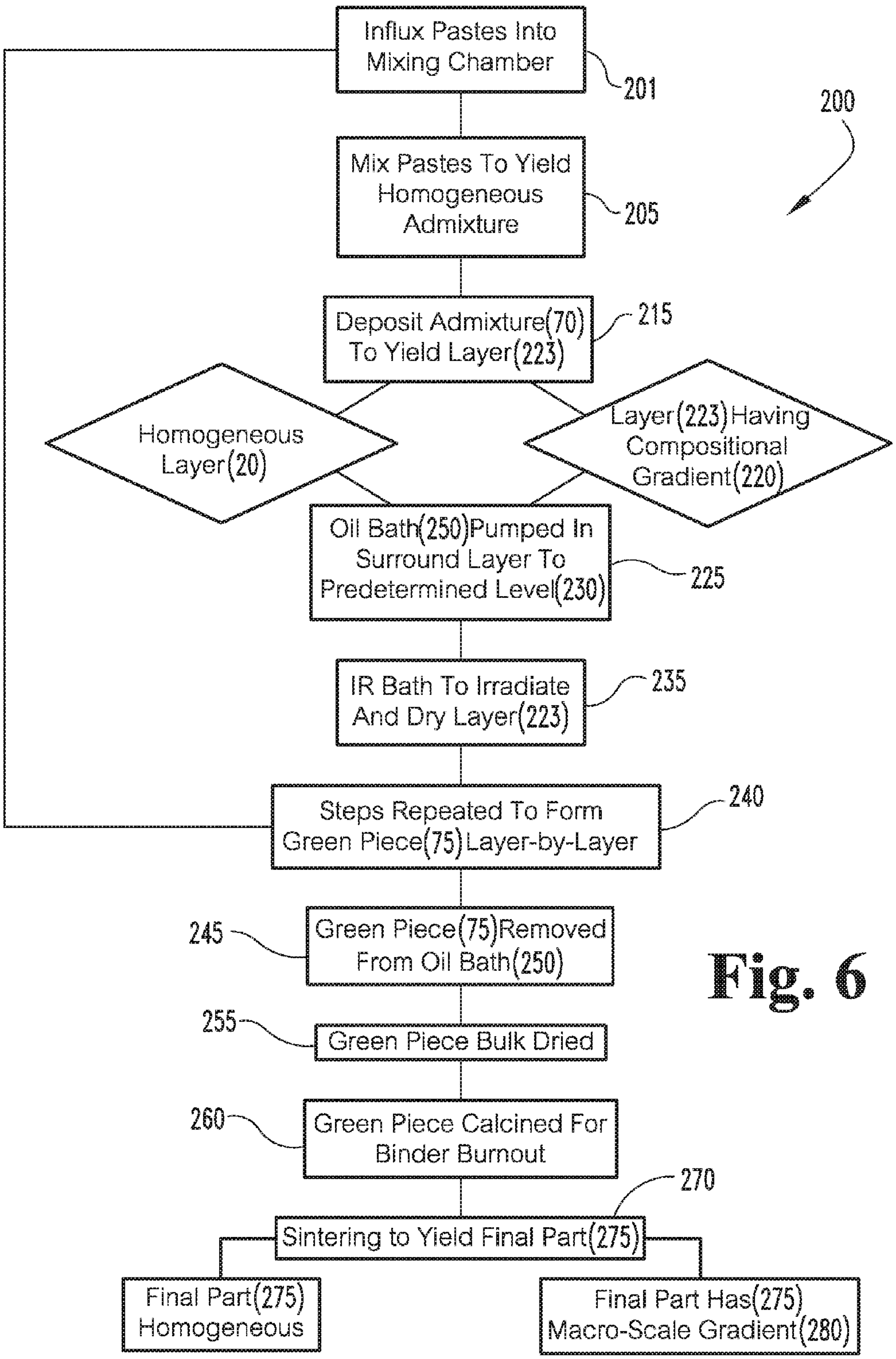

Influx Pastes Into Mixing Chamber
201
200
Mix Pastes To Yield Homogeneous Admixture
205
Deposit Admixture(70) To Yield Layer(223)
215
Homogeneous Layer(20)
Layer(223) Having Compositional Gradient(220)
Oil Bath(250) Pumped In Surround Layer To Predetermined Level(230)
225
IR Bath To Irradiate And Dry Layer(223)
235
Steps Repeated To Form Green Piece(75) Layer-by-Layer
240
245
Green Piece(75) Removed From Oil Bath(250)
255
Green Piece Bulk Dried
260
Green Piece Calcined For Binder Burnout
270
Sintering to Yield Final Part(275)
Final Part(275) Homogeneous
Final Part Has(275) Macro-Scale Gradient(280)

Fig. 6

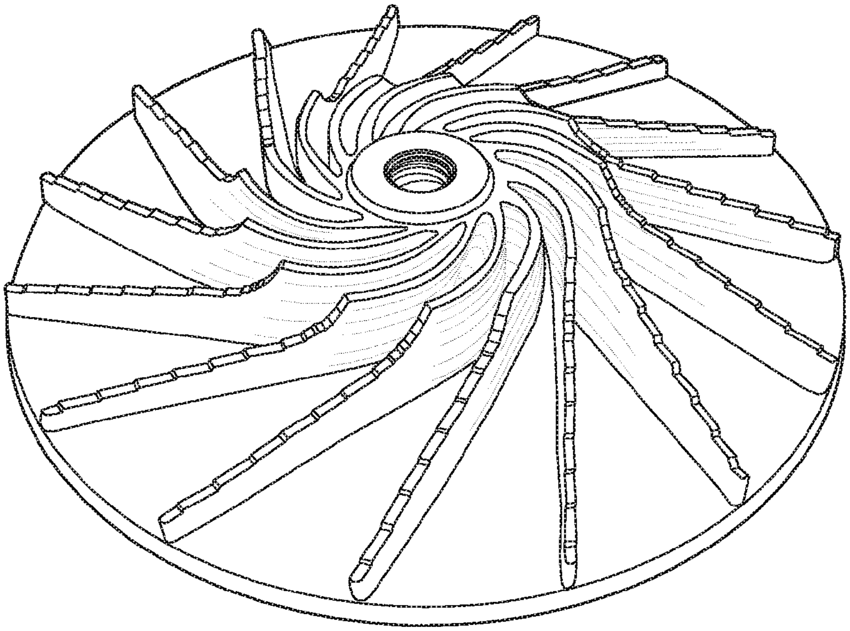


Fig. 7

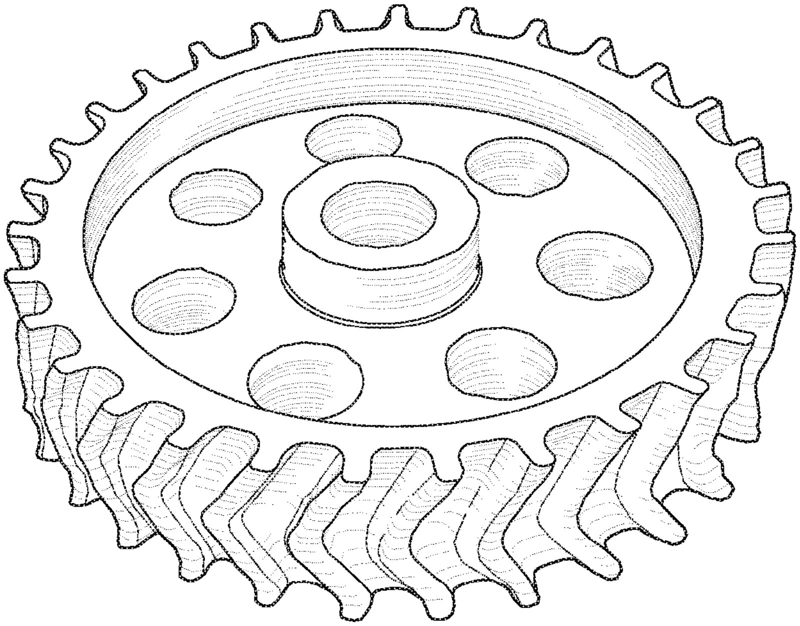


Fig. 8

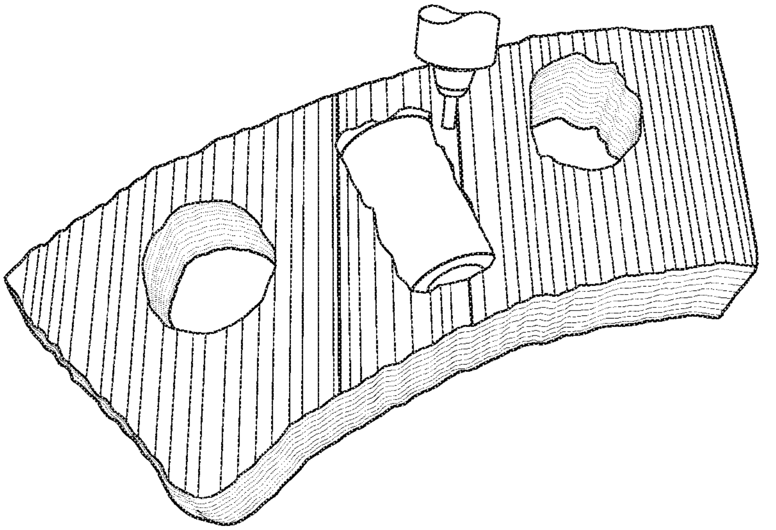


Fig. 9A

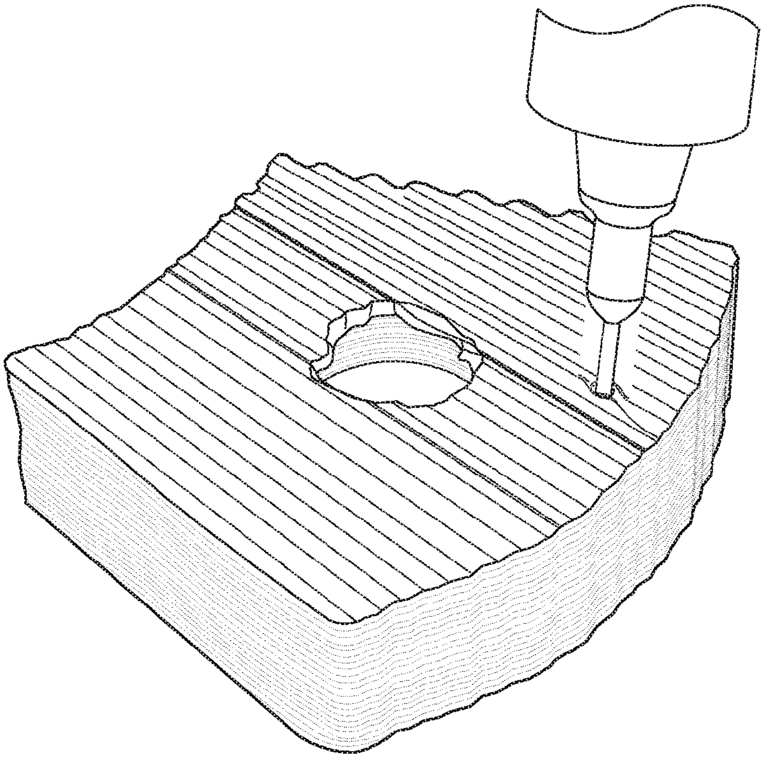


Fig. 9B

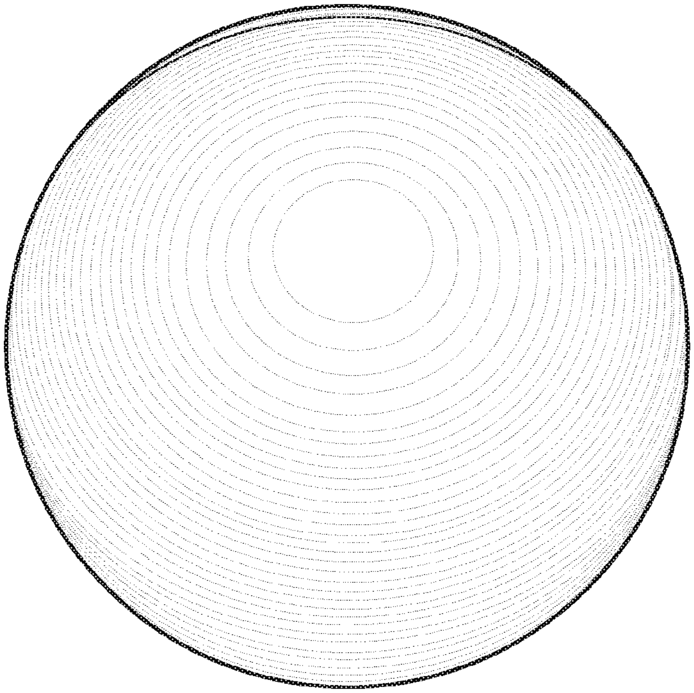


Fig. 10A

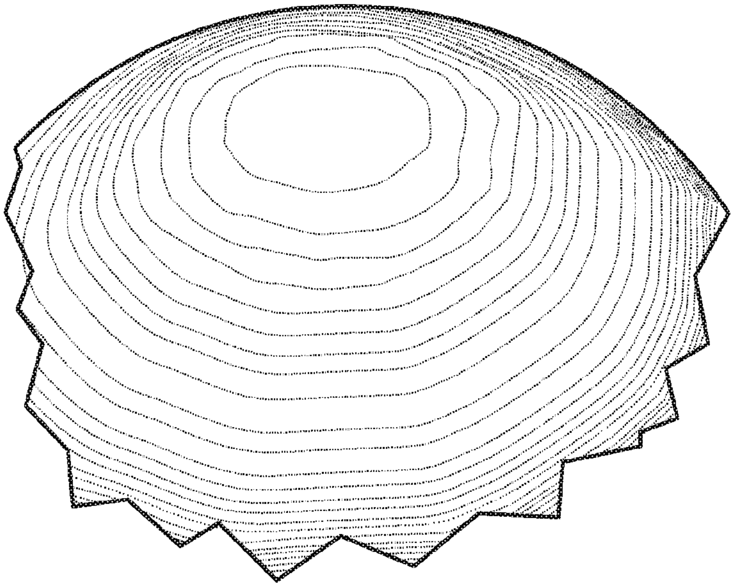


Fig. 10B

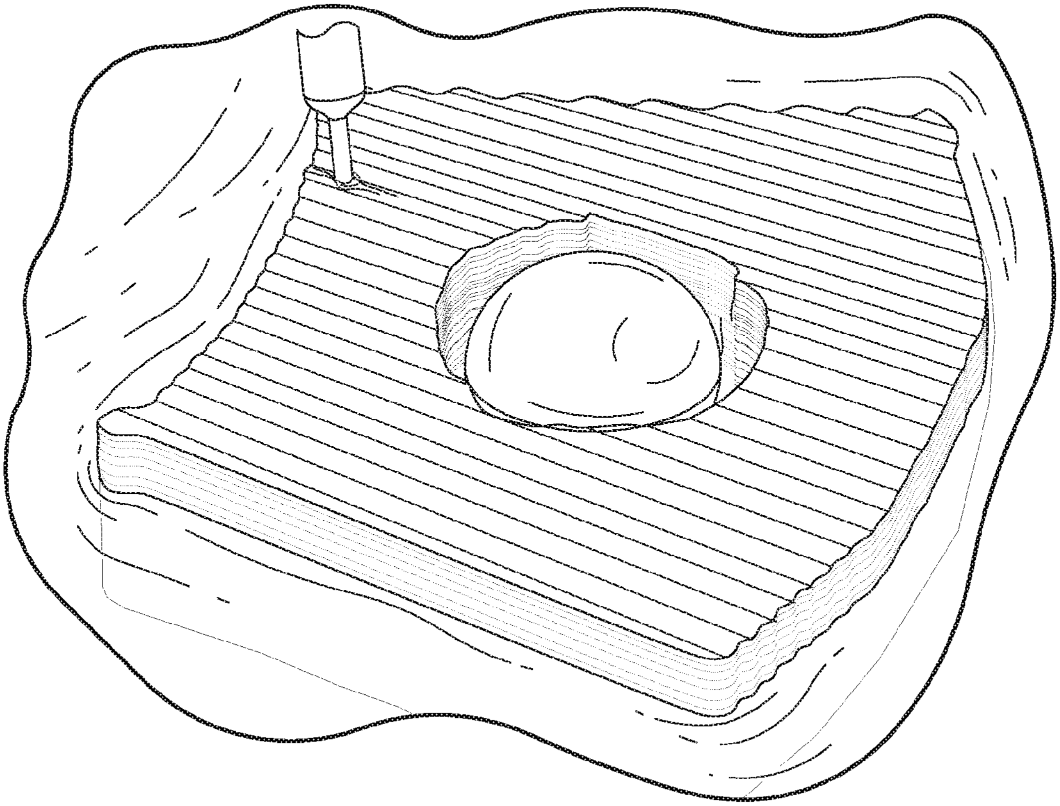


Fig. 9C

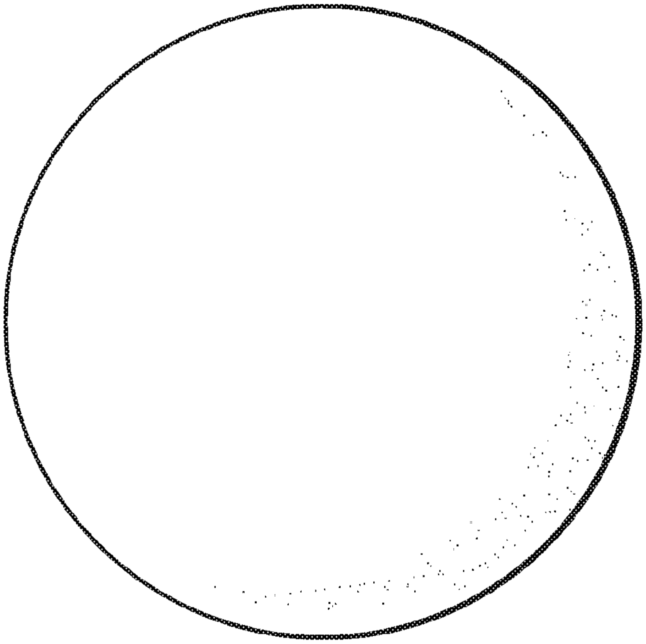


Fig. 11A

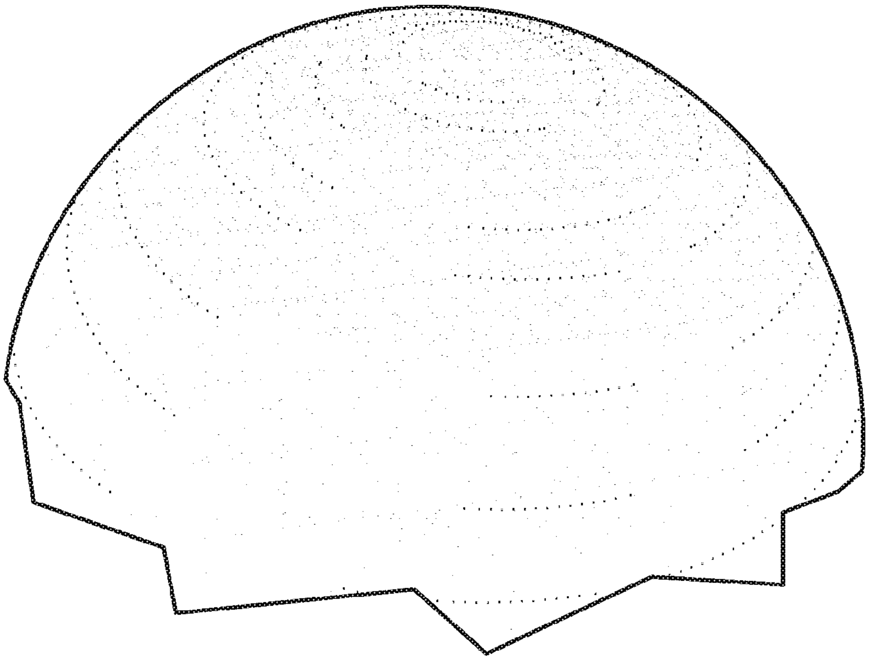


Fig. 11B

# METHOD AND APPARATUS FOR FABRICATING CERAMIC AND METAL COMPONENTS VIA ADDITIVE MANUFACTURING WITH UNIFORM LAYERED RADIATION DRYING

## TECHNICAL FIELD

**[0001]** The present novel technology relates generally to the field of material science and engineering, and, more particularly, to an extrusion-based additive fabrication for producing ceramic, metal and composite parts from multiple aqueous suspension precursors, paste precursors, or the like.

## BACKGROUND

**[0002]** There is an increasing need for complex three-dimensional (3D) parts having high-performance mechanical and thermal properties. One attempt at meeting this need has been to combine unique properties of different materials to yield 3D parts of functionally gradient properties. Because some materials have desirable properties in some aspects (such as resistance to high temperatures) but less desirable properties in other aspects (such as toughness and/or shock absorption), attempts have been made to combine and grade different materials to make parts for use under critical or extreme service conditions. These attempts have met with limited success.

**[0003]** Several additive manufacturing techniques have been developed or modified to fabricate three-dimensional ceramic components, including 3D Printing, Ink-jet Printing, Selective Laser Sintering (SLS), Stereolithography (SLA), Laminated Object Manufacturing (LOM), and extrusion-based techniques. All of these techniques involve adding materials layer by layer.

**[0004]** Extrusion-based methods are among the most popular approaches due to the simplicity and low cost of their fabrication system, high density of their products, their capability of producing parts with multiple materials and functionally graded materials, and low amount of material wastage during pre-processing and processing. Major extrusion-based processes that have been developed include Extrusion Freeform Fabrication (EFF), Fused Deposition of Ceramics (FDC), Robocasting (RC), and Freeze-form Extrusion Fabrication (FEF).

**[0005]** EFF is the first technique developed to utilize extrusion of ceramic slurries to produce three-dimensional components. In this process, slurries of ceramic powders (such as alumina, silicon nitride, and the like) are prepared in liquid acrylic monomers and other organic-based media, and then deposited onto a (sometimes preheated) platen. This process is also the first extrusion-based process to produce ceramic-based functionally graded materials such as ceramic oxides graded to Inconel or stainless steel.

**[0006]** FDC uses a modified Fused Deposition Modeling (FDM) system to extrude ceramic-loaded thermoplastic filaments. The filament is liquefied, extruded, and re-solidified to retain its shape.

**[0007]** In RC, typically an aqueous suspension is prepared from ceramic materials (e.g. alumina, silica, lead zirconate titanate, hydroxyapatite, silicon carbide, and silicon nitride) and extruded onto a hot plate to dry and maintain its shape. The main advantage of RC over EFF and FDC is using low amount of binder in the feedstock, which facilitates pre-processing and post-processing.

**[0008]** In the FEF process, an aqueous paste is extruded in a freezing environment to solidify the paste after its deposition. Freeze-drying is then used to remove the water content before sintering. This process is also capable of producing complex and functionally graded parts made of different materials such as alumina, zirconium diboride, boron carbide, zirconium carbide, and bio-active glasses.

**[0009]** The above processes each have their own limitations. The binder removal stage for the EFF and FDC processes is difficult and time-consuming, and sometimes causes severe warpage or other defects. Also, it might require multiple cycles with different atmospheres. For the FDC process, the feedstock preparation is also burdensome and requires several steps. The filament must maintain a high dimensional tolerance to ensure consistent flowrates. Although components of multiple materials could be produced, an FDC system is not capable of mixing these materials to fabricate functionally graded parts. RC is not capable of building large solid parts due to its non-uniform drying, which often causes warpage and cracks in the parts. Furthermore, due to inconsistency in extrudate flowrate and inevitable presence of air bubbles in the suspension, the products are not fully dense and their mechanical strength cannot match that produced by the EFF and FDC processes. These challenges add to ice crystal formation and weak layer bonding in FEF, further decreasing the density and mechanical properties. Furthermore, all of the above processes suffer from nozzle clogging resulted from paste agglomerates in the feedstock and freezing or drying inside the nozzle. Thus, there remain needs for an improved method of manufacturing a complex three-dimensional part. The present novel technology addresses this need.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]** FIG. **1** is a schematic view showing one embodiment freeform extrusion fabrication system for making three-dimensional functionally gradient composite parts according to the present novel technology.

**[0011]** FIG. **2** is a perspective view of the embodiment of FIG. **1**.

**[0012]** FIG. **3** is an enlarged cutaway view of the paste extruder and mixing system of the embodiment of FIG. **1**.

**[0013]** FIG. **4** is a schematic diagram of the system of FIG. **1**

**[0014]** FIG. **5** is a schematic diagram of FIG. **3**.

**[0015]** FIG. **6** is a process flow diagram of the operation of the system of FIG. **1**.

**[0016]** FIG. **7** is a perspective view of an impeller in the green state formed according to the present novel technology.

**[0017]** FIG. **8** is a perspective view of a sintered gear formed according to the present novel technology.

**[0018]** FIGS. **9**A-**9**C are perspective views of refractory lining blocks with embedded sensors formed according to the present novel technology.

**[0019]** FIGS. **10**A-B are perspective views of a solid spherical part resembling a prosthetic hip joint in the green state formed according to the present novel technology.

**[0020]** FIGS. **11**A-B are perspective views of the sphere of FIGS. **10**A-B after manual grinding in the green state.

## DETAILED DESCRIPTION

**[0021]** For the purposes of promoting an understanding of the principles of the novel technology, 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 novel technology is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the novel technology as illustrated therein being contemplated as would normally occur to one skilled in the art to which the novel technology relates.

**[0022]** The present novel technology relates to a system, method and apparatus for extruding aqueous pastes or slurries of one or more compositions and depositing them, layer by layer, to yield a three-dimensional (3D) part. In some embodiments, the pastes are homogeneous and yield a part having a homogeneous composition, while in other embodiments, multiple aqueous pastes of different materials are extruded and may or may not be mixed during extrusion at predetermined proportions, and are subsequently deposited layer-by-layer under automatic control inside an oil-tight chamber partially filled with oil. The paste layers are extruded and an oil environment is introduced to surround the sides of the part during deposition to fabricate 3D composite parts having functionally graded properties. The oil level is increased along with the height of the growing fabricated part so that the sides of the part are always immersed in oil. This technique allows for building 3D parts of complex geometry from multiple source materials that can be graded as desired. The novel technique addresses the issue of parts deforming due to uneven drying from the sides and edges by maintaining an oil bath around the growing, as-deposited part. This is done by extruding aqueous-based pastes into an oil-tight chamber, and introducing oil during and/or after the deposition of each layer to keep the sides in physical contact and in thermal communication with the resultant oil bath. This technique has been successfully demonstrated for fabrication of parts using monolithic material such as $Al_2O_3$ and $ZrO_2$.

**[0023]** The present novel technology relates to both a process and tool for fabricating 3D composite parts that may be homogeneous, may have discrete portions having different material compositions, and/or may be functionally graded materials, as deposited in a layer-by-layer fashion such as by using a computer controlled apparatus with a single or multiple extruders to fabricate 3D ceramic and/or metallic parts from a single or multiple aqueous pastes to fabricate 3D composite parts. When using multiple, typically aqueous, pastes, each paste respectively typically incorporates different raw or source materials. Simultaneous with deposition, an oil bath is typically maintained at the level of the last extruded layer to maintain an oil barrier in physical and thermal contact with the sides of the forming green piece. This novel technology enables producing 3D components from a single material, multiple materials, or functionally graded materials with desired electrical, chemical, mechanical, thermal and other like properties.

**[0024]** Several ceramic materials, including $Al_2O_3$, $ZrO_2$, 13-93 bioactive glass, and the like, have successfully lent themselves to the manufacture of complex three-dimensional bodies according to this technique. Example applications include leading edges for hypersonic vehicles, missile nose cones, nozzle throat inserts for spacecraft propulsion systems, prosthetic hip and knee joints, dental implants, hydraulic pump parts, extrusion dies, and mechanical bearings.

**[0025]** In one example, advanced aerospace systems such as hypersonic air vehicles are required to operate at extremely high flight speeds and under extremely high temperatures. The desired hypersonic speed will result in high heat fluxes at the leading and trailing edges, requiring thermal protection systems that can withstand very high temperatures. In another example, the desire for increased propulsion leads to extremely high temperature environments in which components such as combustors and propulsion nozzles must survive. Ultra-High Temperature Ceramics (UHTCs) such as HfC, ZrC, TaC, $ZrB_2$, $HfB_2$, and HfN exhibit very good refractory properties, high melting points, reasonable oxidation and thermal shock resistance, low coefficient of thermal expansion, and good creep and fatigue properties. However, the use of monolithic UHTCs in the extreme environments has some disadvantages. Monolithic UHTCs typically do not possess the thermal shock resistance needed to survive the high temperature gradients due to the extreme heating cycles required for high-performance propulsion systems. Further, UHTCs typically are difficult to attach to the typically metallic underlying substructure. A functionally graded material architecture of UHTC-refractory metal composite can minimize thermal stresses in applications that involve extremely high temperatures and high heat flux and allow for attachment to an underlying metal substructure.

**[0026]** One potential biomedical application relates to the fabrication of a functionally graded prosthetic hip joint. There are mechanical stresses and impacts inherent at the junction of the prosthetic joint with the surrounding bone, thus a material with high toughness and flexural strength (such as $ZrO_2$) is desired for the prosthetic piece. However, due to movements of the joint, there is a continuous wear at the surface, recommending a material with high hardness (such as $Al_2O_3$) for the contact surface. A grading from a tough material to a hard material can result in a prosthetic hip joint that is both tougher and more durable.

**[0027]** The present novel technology relates to the process and apparatus for fabricating 3D composite parts, typically having functionally gradient properties, by providing materials prepared in the form of aqueous pastes and depositing the pastes layer by layer. In some embodiments, these respective pastes have different respective compositions and may be mixed to yield a part having a predetermined compositional gradient. The novel process typically uses aqueous pastes, typically with very low organic binder content (typically less than four volume percent, more typically less than one volume percent). Unlike the robocasting process, the novel process builds a green part in an oil bath environment to retard or prevent an evaporative moisture gradient from developing in the drying paste during the "green" part fabrication process. The green part is fabricated, such as by using a single-extruder, a triple-extruder, or the like, in a layer-by-layer manner. The fabricated part is then maintained in an oil bath with the oil level provided high enough to cover the otherwise exposed sides of the growing green body. After each layer is deposited, the green piece is subjected to a thermal radiation treatment, such as an IR bath, to uniformly and at least partially dry the deposited layer. Once the piece is completely formed, the oil bath is drained and the piece is bulk dried to remove remaining water. The binder is then removed through a burnout process. The calcined or “brown” part is then sintered to obtain a final part.

**[0028]** Drawing FIGS. **1-6** illustrate a first embodiment multi-extruder system **10** of the present novel technology. FIG. **1** illustrates a schematic view of the multi-extruder apparatus **10** for making three-dimensional functionally gradient composite parts. Gantry system **15** supports and positions extrusion assembly **20**, which is operationally connected to one or more paste reservoirs **25**. The extrusion assembly **20** may include a single paste receptacle or extruder **30** or, more typically, multiple paste extruders **30** and one or more (typically servo) motors **35** for driving mixing blades **40** operationally connected thereto for mixing the extrudate output of the extruders **30** as fed into mixing station **45** to yield a homogeneous extrudate mixture therefrom. In some embodiments, the paste receptacles **30** and paste reservoirs **25** are unitary, such as syringes feeding into the mixing station **45**, while in other embodiments, the receptacles **30** are holding tanks for receiving paste pumped from a paste reservoir **25**.

**[0029]** In the multi-extruder embodiment, the extrusion assembly **20** typically includes a dynamic mixer **45** for mixing multiple pastes **50** from multiple paste sources **25**, such as syringe extruders **30** or fluidically connected reservoirs or the like. Paste sources **25** are typically connected in fluidic communication to paste urging mechanisms **55**, such as pumps, plungers, pressurizers, or the like. Mixing is first done by merging pastes **50** into a homogeneous stream **60** as the different pastes **50** pass into the mixing chamber **65** where mixing blades **40** blend respective pastes **50** into a homogeneous mixture **70**, so that a nearly homogeneous uniformity of the green part **75** may be obtained. The mixer **40** is typically low shear, such as a series of continuous in-line units which mix pastes **50** that can be extruded or pumped to the required consistency. Materials to be mixed into pastes **50** include combinations of fluids, powders, granules, and gases. The mixer **40** typically requires no external power source, although a dynamic mixer **40** may also be used instead as required.

**[0030]** Mixing chamber **65** also includes a nozzle **80** operationally connected thereto, which may terminate in a high-pressure needle nozzle **85** to more precisely control the deposition of the extrudate, such as the positioning and/or thickness of the deposition layer. Gantry **15** is operationally connected to motor **87** for moving and positioning nozzle **80**, **85** in the Cartesian X, Y, and Z directions.

**[0031]** Nozzle **80** is positioned over an open-topped oil tank **90**. Oil tank **90** includes an oil inlet port **95** fluidically connected to an oil pump **100**, which is fluidically connected to an oil reserve **110**. Oil level sensor **115** is operationally connected to oil tank **90**.

**[0032]** Microprocessor **120** is operationally connected to mixing motor **45**, paste pump **55**, gantry motors **87**, oil pump **110**, oil level sensor **115**, and any other sensors **125**, such as positioning sensors operationally connected to the nozzle and/or gantry, green body height sensors, moisture sensors, or the like.

**[0033]** A (typically) infrared heating lamp **130** is positioned to shine into the oil tank **90** and evenly onto the green body **75** as it is constructed by layer by layer deposition. Microprocessor **120** is operationally connected to infrared lamp **130**. A water sink **135** is typically provided within which to rest the nozzle **80**, **85** when not in use to arrest or retard drying out and clogging.

**[0034]** FIG. **6** shows the operation of fabricating **200** a part **75** with gradient materials **50**A, **50**B, **50**C using the freeform extrusion system **10**. The process **200** extrudes one or a plurality of different aqueous pastes **50** to yield a finished green body **75**. For example, three compositionally different pastes **50**A, **50**B, **50**C are continuously fed **201** into the mixing chamber **65** at different respective rates, typically via automatic computer control **120** and are mixed **205** to yield a homogeneous admixture **70** which is then deposited **215** in sequential layers to build a green part **75** with continuous compositional gradients **220** as the composition of the admixture **70** is varied.

**[0035]** After each layer **223** of predetermined (and potentially variable) thickness **225** (typically between about 150 microns and 400 microns, although thinner or thicker layers, up to 2 mm or more, may be deposited as desired) is deposited **215**, oil is pumped **225** into the chamber **90** to a predetermined level **230** sufficient to envelop the sides of the newly deposited layer **223**. Then, the layer **223** is irradiated **235** to at least partially dry the layer **223**, after which another layer **223** is deposited **215**, more oil is pumped **225** into the chamber **90**, and the new layer **223** is irradiated **235**. These steps are repeated until the green piece **75** is built. It should be noted that each layer **223** may have its own unique compositional gradient topography **240**. Once completed, the green piece **75** is removed **245** from the oil bath **250**, bulk dried **255** (such as in a drying oven at about no degrees Fahrenheit or the like), and then undergoes binder burnout **260**.

**[0036]** After binder burnout **260** and subsequent sintering **270** of the green part **75** built **200** by the triple-extruder system **10**, the final part **275** typically has a compositional gradient **280** as predetermined, having dimensions and compositions that are predetermined.

**[0037]** To fabricate a functionally graded composite part **75** using system **10**, three compositionally different pastes **50**A, **50**B, **50**C are typically used, although in alternate systems, two, four or more pastes **50** may be combined. The respective pastes **50**A, **50**B, **50**C typically each have an engineered composition and a predetermined rheological behavior in order for the mixed paste **70** to pass through a fine nozzle **85** to yield a 3D geometry as deposited layer-by-layer. Typically, pastes **50** have high solids loading, exhibit little or no phase separation under pressure, and behave like pseudoplastics with high yield stresses. For example, methocell is an efficient binder for transforming the rheological behavior of many pastes **50** to exhibit pseudoplastic behavior with high yield stress. A controllable yield stress is helpful for the extrudate **223** to maintain its shape under pressure during the paste extrusion process for fabricating the 3D part.

## Examples

**[0038]** To examine the performance of the above-described novel technology, complex parts with numerous starts and stops have been fabricated. FIG. **7** shows one example of such a complex part, an impeller body in the green state having no visible printing flaws.

**[0039]** To investigate the capabilities of the novel technology to fabricate solid parts with complex geometries, a solid gear was chosen and successfully built. As shown in FIG. **8**, the sintered wear gear part is free of pores between contours and lines.

**[0040]** In yet another practical application of the novel technology, smart refractory lining blocks were fabricated with sensors embedded during the fabrication process. The sensors are for monitoring temperature, pressure, and spalling of walls in the integrated gasification combined cycle of coal and other carbon-containing fuels. FIGS. **9**A-**9**C illustrate several lining blocks in which sensors were successfully embedded during the fabrication process.

**[0041]** Alumina is a common material used to produce prosthetic hip joints due to its hardness and biocompatibility. As another example, a spherical solid part resembling a prosthetic hip joint has been fabricated with alumina using the novel technology (see FIGS. **10**A-**10**B). An advantage of this process is producing a relatively strong green part that may easily be ground to improve the surface quality. FIGS. **11**A-**11**B show the same part after manual grinding, which has significantly improved the surface quality.

**[0042]** While the novel technology has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character. It is understood that the embodiments have been shown and described in the foregoing specification in satisfaction of the best mode and enablement requirements. It is understood that one of ordinary skill in the art could readily make a nigh-infinite number of insubstantial changes and modifications to the above-described embodiments and that it would be impractical to attempt to describe all such embodiment variations in the present specification. Accordingly, it is understood that all changes and modifications that come within the spirit of the novel technology are desired to be protected.

**1**. A multilayered extrusion fabrication process for producing three-dimensional ceramic and metal objects, comprising:
- a) preparing an aqueous paste;
- b) extruding aqueous paste onto a target surface in an oil-tight chamber to define an extruded layer;
- c) filling the oil-tight chamber with sufficient oil to submerge the sides of the extruded layer in oil;
- d) drying the extruded layer sufficiently to at least partially remove moisture contained therein; and
- e) repeating steps b) through d) to define a green body made of a plurality of stacked, partially dried layers.

**2**. A multilayered extrusion fabrication process for producing three-dimensional functionally gradient composite objects, comprising:
- a) preparing a plurality of volumes of aqueous pastes, each respective paste having a very low binder content;
- b) connecting at least two respective volumes of respective aqueous paste compositions in hydraulic communication with a mixing chamber;
- c) extruding aqueous paste into the mixing chamber;
- d) blending disparate aqueous pastes in the mixing chamber to yield a homogenous admixture;
- e) extruding the homogeneous admixture from the mixing chamber onto a target surface in an oil-tight chamber to define an extruded layer;
- f) filling the oil-tight chamber with sufficient oil to submerge the sides of the extruded layer in oil;
- g) drying the extruded layer sufficiently to at least partially remove moisture contained therein; and
- h) stacking a plurality of extruded, dried layers to define a green body.

**3**. The process of claim **2** wherein each respective volume contains a different respective aqueous paste composition.

**4**. The process of claim **2** wherein steps c) through e) further comprising the operation of continuously filling the mixing chamber with aqueous pastes of different compositions at varying, predetermined rates to yield a substantially homogeneous admixture of changing composition that is extruded to define layers having predetermined composition gradients.

**5**. The process of claim **2** wherein the green body has predetermined compositional gradients.

**6**. The process of claim **2** and further comprising:
- i) automatically mixing aqueous pastes of different compositions in the mixing chamber to yield a substantially homogeneous admixture by controlling the extrusion rates of the aqueous pastes;
- wherein each respective volume is operationally connected to a respective plunger;
- wherein each respective plunger is operationally connected to a respective servomotor;
- wherein a microprocessor is operationally connected to each respective servomotor; and
- wherein the microprocessor is programmed to control each respective servomotor to control the speed of each respective plunger to yield an admixture of predetermined composition.

**7**. The process of claim **2** wherein the mixing chamber further comprises:
- a first portion operationally connected to each respective volume for receiving paste from each respective volume; and
- a second portion operationally connected to the first portion for receiving and mixing paste from the first portion.

**8**. The process of claim **2** and further comprising:
- i) generating a deposition path according to a predetermined geometric model of a desired object shape;
- j) mixing pastes to define a first generally homogeneous paste admixture having a first composition;
- k) automatically depositing the first paste admixture along the deposition path to define a first layer;
- l) mixing pastes to define a second generally homogeneous paste admixture having a second composition different from the first composition; and
- m) automatically depositing the second paste admixture along the deposition path to define a second layer.

**9**. The process of claim **2** wherein mixed paste in the mixing chamber has a compositional gradient and wherein the compositional gradient is generated by varying paste extrusion rates from the respective volumes.

**10**. The process of claim **2** and further comprising:
- n) generating a deposition path according to a predetermined geometric model of a desired object shape;
- o) mixing pastes to define a generally homogeneous paste admixture having a first composition;
- p) automatically depositing the paste admixture having the first composition along the deposition path;
- q) varying the composition of the paste generally homogeneous admixture over time; and
- r) automatically depositing the admixture along the deposition path to define an extrudate having a composition that varies along the deposition path.

**11**. An extrusion fabrication process for producing three-dimensional functionally gradient composite objects, comprising:

a) filling a plurality of syringes with a respective plurality of aqueous paste compositions;

b) operationally connecting respective syringes containing respective aqueous paste compositions to a mixing chamber;

c) moving a first aqueous paste composition from a first respective syringe into the mixing chamber;

d) moving a second aqueous paste composition from a second respective syringe into the mixing chamber;

e) mixing the first and second aqueous paste compositions to define a first admixture having a first admixture composition;

f) extruding the first admixture onto a surface to define an extruded layer having a first admixture composition;

g) surrounding the sides of the extruded layer with an oil bath; and

h) radiatively drying the extruded layer.

**12**. The process of claim **11** and further comprising:

i) mixing aqueous pastes to define a second admixture having a second admixture composition;

j) extruding the second admixture to define a second extruded layer having a second admixture composition, wherein the second extruded layer is contiguous with the first extruded layer;

k) surrounding the sides of the second extruded layer with oil;

l) radiatively drying the second extruded layer;

m) extruding a plurality of respective layers, wherein each respective extruded portion is contiguous with at least one other respective extruded layer, to define an object;

wherein each respective layer is surrounded with oil;

wherein each respective layer is radiatively dried before the next layer is extruded.

**13**. The process of claim **11** wherein at least one layer has a compositional gradient.

**14**. The process of claim **12** and further comprising:

n) removing the object from the oil bath;

o) bulk drying the object;

p) calcining the object; and

q) sintering the object.

**15**. An extrusion fabrication process for producing three-dimensional functionally gradient composite objects, comprising:

a) engaging a microprocessor to generate a deposition path according to a predetermined compositional model of a desired object shape;

b) filling a plurality of syringes with a respective plurality of aqueous paste compositions with low organic binder content, wherein each respective syringe includes a respective servomotor-actuated plunger to urge paste therefrom;

c) operationally connecting at least two respective syringes of respective aqueous paste compositions to a mixing chamber;

d) automatically extruding a first combination of respective aqueous paste compositions from respective syringes into the mixing chamber, wherein each respective paste composition is extruded into the mixing chamber at a respective extrusion rate;

e) mixing the first combination of respective aqueous paste compositions in the mixing chamber to define a first admixture having an admixture composition;

f) automatically varying the admixture composition by varying the respective extrusion rates of the respective aqueous paste compositions from respective syringes into the mixing chamber;

g) automatically extruding the admixture along the deposition path to define an extruded layer having a compositional gradient;

h) surrounding the extruded layer with an oil bath;

i) radiatively drying the extruded layer;

j) repeating steps g through i a predetermined number of times to yield a three-dimensional composite object having a compositional gradient.

**16**. An extrusion fabrication system for producing three-dimensional functionally gradient composite objects, comprising:

an oil-tight chamber;

an oil pulp fluidically connected to the oil-tight chamber;

an oil reservoir fluidically connected to the oil pump;

an extrusion assembly positioned to extrude layers of paste into the oil-tight chamber; the extrusion assembly further comprising:

a mixing chamber;

a mixer operationally connected in the mixing chamber;

a plurality of paste sources operationally connected to the mixing chamber;

a plurality of paste pumps, each respective paste pump operationally connected to a respective paste source;

an extrusion nozzle fluidically connected to the mixing chamber; and

a movable gantry operationally connected to the mixing chamber for moving and positioning the nozzle;

a microprocessor operationally connected to the extrusion assembly and to the oil pump;

an infrared lamp positioned to shine into the oil-tight chamber and operationally connected to the microprocessor;

wherein the microprocessor is operable to initiate moving a first combination of respective aqueous paste compositions from respective paste sources into the mixing chamber, wherein each respective paste composition is extruded into the mixing chamber at a respective extrusion rate;

wherein the microprocessor is operable to engage the mixer;

wherein the microprocessor is operable to automatically vary the admixture composition by varying the respective extrusion rates of the respective aqueous paste compositions from respective paste sources into the mixing chamber;

wherein the microprocessor is operable to automatically control extrusion of the admixture along a predetermined deposition path to define an extruded layer having a compositional gradient;

wherein the microprocessor is operable to surround the extruded layer with an oil bath; and

wherein the microprocessor is operable to initiate radiative drying of the extruded layer.

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