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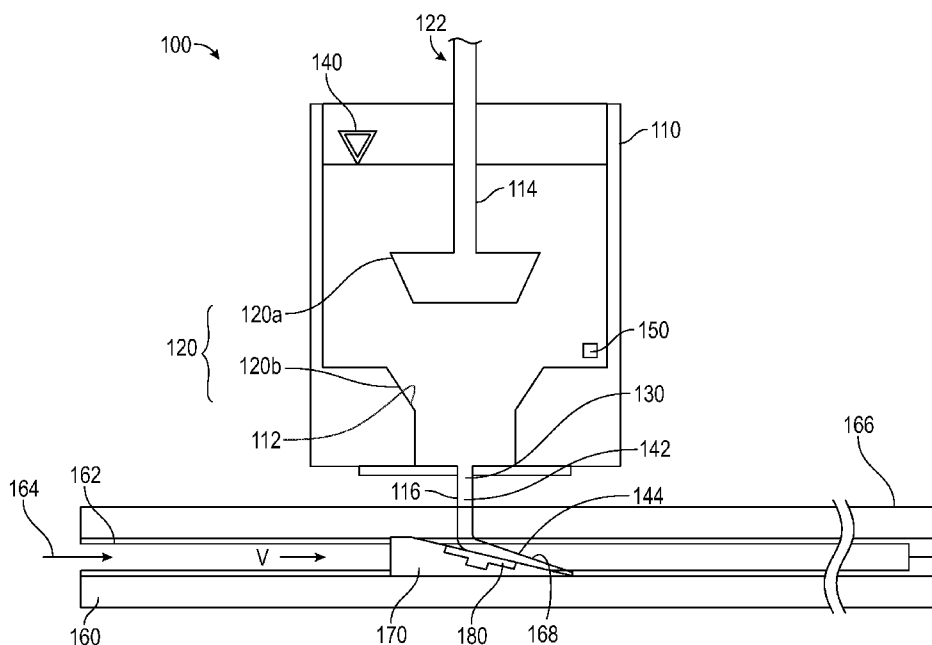


FIG. 1

(57) Abstract: Provided herein are systems and methods for applying materials to articles or projectiles in order to coat at least a portion of the projectile. An embodiment of disclosure provides launching the a projectile into a stream of fluid. The fluid may be a molten metal, powder suspension or slip to be later sintered, molten polymer, monomers to be later polymerized or gaseous species that can locally react with the projectile to produce coatings such as oxides, nitrides, carbides, etc. The passage of the projectile through the fluid results in a coating on the projectile.



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## METHODS AND SYSTEMS FOR BALLISTIC MANUFACTURING OF MICRO/NANO COATINGS AND ARTIFACTS

### CROSS-REFERENCES TO RELATED APPLICATIONS

**[001]** The present disclosure claims priority to U.S. Provisional App. No. 62/337,868 entitled “Method, System and Device for Micro/Nano Coatings for Ballistics”, filed May 18, 2016, which is incorporated herein by reference in its entirety.

### FIELD

**[002]** The disclosure relates generally to the field of ultra rapid manufacturing and products produced therefrom.

### BACKGROUND

**[003]** The automation revolution of vehicles, manufacturing equipment and the increasing demand for more interactive personal technology is bound to increase the demand of miniaturized sensors, electronic components and micro-electro-mechanical systems (MEMS). Additive manufacturing of thick and thin films plays a main role in the manufacturing of devices for these technologies. This disclosure presents Ballistic Manufacturing (BM) technology, a novel rapid manufacturing process with potential applications in, and not restricted to, the fields of thin-film, thick-film, MEMS, rapid solidification, micro- and nano-scale stand-alone and integrated artifact/parts manufacturing, additive manufacturing and impact manufacturing.

**[004]** As the miniaturization of these technologies continues, demand for new materials and processes capable of producing more reliable components grows. In the manufacturing of miniaturized interconnects for instance, the trend is to change aluminum for better conducting copper as the main material, although the current processing techniques have made that difficult. Explosive compaction and rapid solidification processes have provided options for the processing of materials with unique characteristics and features. BM, being a unique processing technique, should be able to combine components of rapid solidification, miniaturized additive manufacturing, and extreme compacting to produce new materials and components.

## SUMMARY

**[005]** There are provided herein systems and methods for applying materials to articles or projectiles in order to coat at least a portion of the projectile. An embodiment of disclosure provides launching a projectile into a stream of fluid. The fluid may be a molten or semi-molten metal or metal composite, powder suspension or slip to be later sintered, molten polymer, monomers to be later polymerized or gaseous species that can locally react with the projectile to produce coatings such as oxides, nitrides, carbides, or provide quenching or heating conditions, etc. The passage of the projectile through the fluid primarily results in a coating on the projectile.

**[006]** In a first aspect, a method of applying a material to an article is disclosed. The method includes: flowing a stream comprising a material in a first direction; and passing an article through the stream such that the material is applied to at least a portion of the article, wherein the article travels in a second direction at a speed of at least 1 m/s when passing through the flowing material.

**[007]** In a second aspect, a method of coating an article is disclosed. The method includes: flowing a molten metal in a first direction; passing an article through the flowing molten metal such that the molten metal is applied to at least a portion of the article, wherein the article travels in a second direction at a speed of at least 1 m/s when passing through the flowing molten metal; and solidifying the molten metal to form a coating .

**[008]** In a third aspect, a system for applying a material to an article is disclosed. The system includes: a reservoir for receiving a material; a conduit fluidly coupled to the reservoir and configured to flow a stream comprising the material in a first direction; a channel configured to provide a path for moving an article in a second direction, wherein the conduit is fluidly coupled to the channel and configured such that the article passes through the stream when moving through the channel; and means for forcing the article through the channel.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[009]** The details of the present disclosure, both as to its structure and operation, may be understood in part by study of the accompanying drawings, in which like reference numerals refer to like parts. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the disclosure.

**[010]** FIG. 1 illustrates a schematic of one example of a ballistic manufacturing system for low temperature lead free solder in accordance with an embodiment of the present disclosure.

[011] FIG. 2 illustrates an example flow chart of a ballistic manufacturing process in accordance with an embodiment of the disclosure.

[012] FIG. 3a illustrates an example model of an approaching projectile with wax substrate in accordance with an embodiment of the disclosure.

[013] FIG. 3b illustrates an example model of an impinging projectile in accordance with an embodiment of the disclosure.

[014] FIG. 3c illustrates an example cross-section of coated wax projectile in accordance with an embodiment of the disclosure.

[015] FIG. 3d illustrates an example final component after projectile disintegration in accordance with an embodiment of the disclosure.

[016] FIG. 4 illustrates a side view of an example carrier with wax substrate inclined at 15° in accordance with an embodiment of the disclosure.

[017] FIG. 5 illustrates an example mold or substrate with surface depressions of shapes than can be filled during deposition in accordance with an embodiment of the disclosure.

[018] FIG. 6 illustrates an example continuous thick film of Sn-0.7Cu produced in accordance with an embodiment of the disclosure.

[019] FIG. 7a illustrates an example relationship between accelerating air pressure and casting velocity in accordance with an embodiment of the disclosure.

[020] FIG. 7b illustrates snapshots of high-speed videos taken during BM at 24.9 m/s and 36.1 m/s in accordance with an embodiment of the disclosure.

[021] FIG. 8a illustrates a SEM cross-section of a thick film in accordance with an embodiment of the disclosure.

[022] FIG. 8b illustrates a low magnification SEM micrograph showing multiple 2D Sn cells surrounded by a eutectic phase in accordance with an embodiment of the disclosure.

[023] FIG. 8c illustrates a higher magnification image showing possible initiation of secondary arms in accordance with an embodiment of the disclosure.

[024] FIG. 8d illustrates a higher magnification electron micrograph of the interface between two cells showing different orientation of the eutectic phase in accordance with an embodiment of the disclosure.

[025] FIG. 9a illustrates average primary dendrite spacing in accordance with an embodiment of the disclosure.

[026] FIG. 9b illustrates average film thickness as functions of the casting velocity in accordance with an embodiment of the disclosure.

[027] FIG. 10a illustrates a side view low magnification SEM micrograph showing textured surface without using textured substrate in accordance with an embodiment of the disclosure.

[028] FIG. 10b illustrates a side view high magnification SEM micrograph showing textured surface without using textured substrate in accordance with an embodiment of the disclosure.

[029] FIG. 10c illustrates a top view low magnification SEM micrograph showing textured surface without using textured substrate in accordance with an embodiment of the disclosure.

[030] FIG. 10d illustrates a top view high magnification SEM micrograph showing textured surface without using textured substrate in accordance with an embodiment of the disclosure.

#### DETAILED DESCRIPTION

[031] The behavior and structure of materials subjected to ultra-rapid (extreme) processing techniques are expected to be different than during conventional processing. Processes such as explosive compaction and rapid solidification have provided options for the processing of materials with unique characteristics and features. Thick films have been defined as those having thicknesses between 2 $\mu$ m and 100 $\mu$ m, whereas less than 2 $\mu$ m they are considered thin films. Processing approaches for films include plasma physical vapor deposition (PVD), flash evaporation, sputtering, electroplating and sol-gel coating. These are complex processes involving high vacuum, chemicals or multiple processing steps. For thick films, screen printing is fundamentally a cost-effective processing technique, involving the use of bonding materials like glass or metallic oxides that usually reduce the conductivity of the film, or an active metal (that can increase the processing cost). Amorphous films have also received a great deal of attention because of their promising applications in micro-electro-mechanical (MEMS) devices and biomedicine.

[032] Within the area of melt processing, planar flow melt spinning (PFMS) is a common and effective process for manufacturing long ribbons of metallic glasses. The process consists of flowing molten metal through a nozzle onto a rotating chilled (with water or other fluids) wheel, to increase the temperature gradients at the casting surface, which allows for undercooling of the material into an amorphous state. Wheel speed has strong effects on both cooling rate and ribbon

thickness. Typical speeds investigated in the planar-flow melt spinning process for metals can range from 5 to 80ms<sup>-1</sup> with typical thicknesses between 8 μm and a few hundred micrometers depending on material and process conditions. The present disclosure discusses ballistic manufacturing (BM), a novel ultra-rapid processing technique with possibilities in thin, thick, and amorphous film processing, additive manufacturing in addition to micro- and nano-scale standalone or integrated devices

**[033]** As used herein, ballistic manufacturing (BM) is a process that involves the launching of a projectile or carrier, in the form of, or carrying, a substrate or mold (hereafter called a “projectile”) at high speed (e.g., below/at or above 343 m/s) into a stream of fluid of certain thickness and width (or radius if cylindrical). The fluid may be a molten metal, powder suspension or slip to be later sintered, molten polymer, monomers to be later polymerized or gaseous species that can locally react with the projectile to produce coatings such as oxides, nitrides, and carbides for example. The passage of the projectile through the fluid leaves a metallic coating on the projectile that can have thicknesses down to the nanoscale.

**[034]** Using BM, essentially thousands and potentially millions of nano-scale or micro-scale stand-alone or integrated components can be shaped at speeds below, at or above the speed of sound (342 m/s), e.g., instantaneously. Microstructures and nanostructures developed are unique due to the extreme and complex processing conditions applied. Likewise, BM can produce thick and thin films as stand-alone or as coatings ultra-rapidly.

**[035]** In some embodiments, the projectile is made out of a removable, dissolvable or decomposable material (e.g., ice or wax), which may be separated from the projectile leaving behind microscale and/or nanoscale standalone metallic layers or shapes after removal of the projectile material. Alternatively the projectile may include a permanent mold or substrate on to which the e.g., fluid, is deposited, thereby becoming a coating after solidification, sintering or freezing, or may be lifted off if poor bonding conditions between the coating and substrate/mold prevail. As described in more detail below, the mold may be masked or unmasked, textured or untextured, containing intruding or extruding features.

**[036]** In some embodiments, the fluid stream includes any existing molten metal such as aluminum, titanium, nickel, steel, or it can include any intermetallic material such as NiAl, TiAl, MoSi<sub>2</sub>, and FeAl. Alternatively, the fluid stream may include any metal or intermetallic composite material, such as Ti-TiB, Al-SiC, Al-CNT, Ni<sub>3</sub>Al-CNT. It may include polymer melt, solution or

monomer solution including composites, powder suspension (with or without dispersant, binder and plasticizers)

**[037]** The fluid stream is usually between 20°C and 2000°C, although the fluid stream may be between -200°C and 3000°C. The temperature range may vary depending on the type of fluid. A fluid is defined herein as a molten or semi-molten solid material, powder suspension/slip, liquid, gas, or combination thereof. For example, fluids may include molten or semi-molten metal (including mercury) (e.g., 25-2000°C), molten or semi-molten intermetallic (e.g., 300-2500°C), molten or semi-molten metal including composite particles (e.g., 25-2000°C), a molten or semi-molten intermetallic including composite particles (e.g., 300-2500°C), a molten or semi-molten polymer with or without composite particle or fibers (e.g., 100-600°C), powder suspended in a solvent such as water, e.g., ethyl alcohol (e.g., -30-80°C), powder suspended in solvent with dispersant and/or binder and/or plasticizer (e.g., -30-80°C), any liquid (e.g., liquid nitrogen) or gas (reacting or non-reacting) (e.g., -210-500°C). As defined herein, for molten metals, the fluid stream is at a temperature hot enough that at least a portion of the fluid stream is in liquid phase (e.g., molten or semi-molten).

**[038]** In some embodiments, the fluid stream is moving at a velocity of between about 0 m/s and 600 m/s. The velocity may be achieved by applying a pressure to the fluid stream. For example, a pressure of between about 1 psi and 100 kpsi may be applied to the fluid stream (typically between 14.7 and 1 k psi), as will be explained below with reference to Figure 1. At 14.7 psi, the fluid may be stationary for example when a heated projectile goes through a reactive gas at atmospheric pressure. Also the fluid stream maybe under vacuum and flow under its own weight.

**[039]** Figure 1 shows a schematic of one example of a ballistic manufacturing system 100 for low temperature lead-free solder. BM system 100 includes a crucible 110, a plunger valve 120, a carrier chamber 160, and a carrier 170. As shown, crucible 110 is a reservoir or chamber for receiving a plunger 122 having a shaft 114 and a head 120a. Crucible 110 includes an inlet 140 for receiving a molten material and an outlet or slit 130 for the molten material to exit out of crucible 110.

**[040]** Crucible 110 also includes a funnel-shaped surface 112 that makes up the female portion 120b of plunger valve 120. Plunger head 120a makes up the male portion of the plunger valve 120. Crucible 110 may also include a thermocouple 150 and/or any other electronics for monitoring the process conditions of BM system 100.

**[041]** In communication with slit 130 is a channel 116 that connects the crucible 110 with carrier chamber 160. Carrier chamber 160 includes one or more guide rails 162, an inlet 164 for receiving carrier 170, and a capped end 166.

**[042]** In some embodiments, the inlet 164 may be used as a pressure input, such that pressure is applied to carrier 170, making it move toward and receive molten material 144 from channel 116.

**[043]** As shown, carrier 170 includes a wax substrate 180. Wax substrate 180 and carrier 170 are exposed to the molten material 142 as it exits crucible 110 through slit and into channel 116. The molten material 142 received on carrier 170 is depicted as deposited material 144.

**[044]** In order to use BM system 100, the crucible 110 is filled with a coating material via e.g., inlet 140. The material is brought to a desired melt temperature with the plunger valve 120 closed (e.g., male portion 120a in contact with female portion 120b) such that the molten material is blocked from flowing out of the crucible 110. The material inserted into crucible 110 can be introduced as solid or liquid, and then heated to a desired temperature. The temperature of the molten coating material may be monitored by thermocouple 150 in crucible 110.

**[045]** To initiate molten material flow, the plunger 122 is lifted e.g., via lifting shaft 114, disengaging the plunger valve 120 to allow the coating material to flow down and out slit 130, forming a molten curtain of molten material 142. The molten material 142 projects downwards from the bottom of the crucible 110 through channel 116 and into a coating zone 168 of carrier chamber 160. As shown, BM system 100 uses slit 130 to govern the molten material's 142 geometry, but other systems could utilize an atomized curtain or other methods for forming the curtain/coating supply.

**[046]** Once the molten curtain/stream has formed and stabilized in the coating zone 168, the carrier 170 and/or substrate 180 is launched down the guide rail 162 by accelerating pressure, bringing the carrier 170 into contact with the molten curtain. The carrier 170 and/or substrate 180 goes through the molten metal stream/curtain, leaving a deposited coating 144 on the projectile (e.g., carrier 170 and/or substrate 180).

**[047]** Once the projectile leaves the curtain, it may be decelerated to allow for processing. BM system 100 uses compressive air braking to accomplish this deceleration, allowing the projectile to slow down to a stop without applying any physical pressure that could compromise the integrity of the coating on the projectile. Other methods for accomplishing deceleration may alternatively be used and are within the scope of the present teachings.

**[048]** Still referring to Figure 1, multiple fluid streams (of same or different materials) resulting in sequential layering of the projectile may be used, thus enabling additive manufacturing type processing with reactive or nonreactive layers. Alternately the stream or environment could be a medium that allows quenching or heating of the substrate/projectile. The layers can be macro, micro- or nano-scale. This layering is discussed in further detail below.

**[049]** In some embodiments, the fluid stream may include particles (e.g., nano, micro, macro) to produce micro/nanocomposites. For example, molten aluminum mixed with SiC particles, when applied will solidify as Al-SiC composite.

**[050]** In some embodiments, the fluid stream includes a slip (e.g., a solvent in which are suspended micro sized or nanosized particle (ceramic, polymer, metallic or intermetallic) to be used as is or later processed to produce consolidated features). Suitable slips include alumina nano powder suspended in water to which is added a dispersant and/or binder and/or plasticizer (e.g. polyethylene glycol, polyvinyl alcohol).

**[051]** In some embodiments, the fluid stream includes a gas, or gas emitting entities (including particles) to produce porous layers or artifacts. For example particles of  $TiH_2$  (foaming agents) suspended in aluminum melt, so that before/during or after coating the  $TiH_2$  dissociates giving off hydrogen, which can generate porosity in the coating. Alternatively the substrate/mold or substrate may contain the foaming agent or dissolvable micro or nanofeatures, which leave behind porosity after dissolution or reaction (if reacts with the coatings).

**[052]** In some embodiments, the environment includes a vacuum or a gas that reacts or does not react with any of the materials during the process. For example an oxidizing environment such as air in which a heated substrate such as aluminum can go through atmosphere and react to form a nano-oxide layer. Otherwise the projectile/mold/substrate can accelerate in air/vacuum/inert gas for reactive gas with or without the fluid stream.

**[053]** In some embodiments, the fluid stream may include various shapes and dimensions. For example, the molten stream may take the shape of solid or hollow cylinder, or a square or rectangular cross-section and/or have exemplary dimensions of 10cm length, 5mm thickness and 30mm width. It should be appreciated that many other shapes and/or dimensions are contemplated within the scope of this disclosure.

**[054]** In some embodiments, the fluid stream is electrically charged. In other embodiments, the fluid stream is not electrically charged. Suitable charges may be in the range of approximately 0 to 100kV. Electrically charging may be achieved via a suitable power supply.

**[055]** In some embodiments, the fluid stream is magnetic. In other embodiments, the molten stream is not magnetic. A combination of magnetic fluid with a suitable magnetic substrate or projectile may provide better coverage on the projectile by fluid attraction, e.g., in intricately small and complex features.

**[056]** In some embodiments, the fluid stream is generated under pressure. For example, suitable pressures include approximately 1 psi to 100 kpsi (typically between 14.7 and 1 kpsi). The pressures may be introduced to the molten stream via gas or piston or other approaches. In other embodiments, the fluid stream is not generated under pressure. For example the projectile is accelerated through the guide chamber filled with a fluid.

**[057]** While thus far referred to as a fluid stream, in some embodiments, the stream is an atomized spray instead of molten material. For example, molten stream is met by inert gas jets, which break it up into droplets that coat and solidify on the substrate/mold/projectile. In some embodiments, the stream is spray dried powder.

**[058]** Figure 2 shows an example flow chart of a ballistic manufacturing process 200. In a first step 210, the material is melted to produce a fluid. In some embodiments, the material is exposed to temperatures between about  $-50^{\circ}\text{C}$  to about  $4,000^{\circ}\text{C}$ . In a second step 220, the molten material flows through an opening in the crucible to produce a falling fluid stream. In some embodiments, the fluid stream cross-section shape varies such as cylindrical, square or rectangular and may be produced by the shape of the opening in the crucible. For example, the thickness or radius may be in the range of about 1 micron to 12 inches, and the width may be in the range of about 1 micron to 100 feet.

**[059]** In a third step 230, the projectile is launched into the molten stream. The projectile may be launched at speeds, for example, ranging from about 0.01 m/s to 1000 m/s (typically e.g., 1-400m/s). Also the projectile may enter the molten fluid stream at an incidence angle in the range of about  $-180^{\circ}$  to about  $+180^{\circ}$ .

**[060]** In a fourth step 240, the fluid material, such as molten metal, coats the projectile. In a fifth step 250, the resultant product is produced. As shown, various resultant products may include: stand alone products where the coating or shapes are removed from the projectile 252; integral products where the coating is left on the projectile 254; functionally graded and/or multilayer coatings or shapes 256; and coatings subsequently reacted within or with the projectile or fluid to form a new material 258.

[061] In some embodiments, if molten metal is allowed to flow as a vertical stream (e.g., as is the case in the process of atomization), the molten metal stream can be met by ultra-rapidly traveling projectiles of controlled small shape and size. These projectiles may be of two types.

[062] The first type of projectile/mold or substrate may be made of a material that would survive the impact with the molten metal and provide conditions for its subsequent coating with the metal. Hence ultra-rapid micro-and nano- coating can be enabled. Depending on surface conditions, these coatings may be removed or left as is. Depending on the projectile/substrate or mold thermal properties (e.g., thermal conductivity) enhanced rapid cooling or slower cooling maybe achieved.

[063] The second type of projectile may involve the use of a disintegrable projectile. In this case, the projectile would initially have the shape and cavities to be coated or filled respectively by metal from the molten metal stream. However following the ultra- rapid solidification of the metal, the initial disintegrable projectile can then be either melted away, burned off or in other instances the projectile would exothermically react with the molten metal (or simply inter-diffuse) and form a totally new compound or alloy.

[064] Examples of materials that can be used for the disintegrable projectile are, but not limited to, ice, wax, polymer, or metal. For example, the molten metal rapidly coats and rapidly solidifies (e.g., due to the high convective heat loss enabled by the high speed projectile) on the wax and then the wax is later dissolved leaving a micro-scale product of controlled shape and size. This would turn powder atomization from a process that could produce powders of shapes ranging from spherical to irregular, into a process that can produce powder of precise meaningful micro-scale shapes. Figure 1 and 2 show a models of the disclosed process.

[065] Figure 3 shows models of (a) approaching wax projectile (b) impinging projectile (c) cross-section of coated wax projectile and (d) final component after projectile disintegration. The projectile speeds can be sub-sonic, and supersonic. As described below, devices may be in place to stop the projectile without damaging the artifact.

[066] Another alternative for very small molds and hence artifacts, is that molds can be placed on “carrier” projectiles that allow the successful entrance and exit of the molten metal stream, e.g., maintains an appropriate kinetic energy. Here dense material such as tungsten (e.g. density  $19.3 \text{ g/cm}^3$ ) may be an example of projectiles for small projectiles.

[067] As can be appreciated, a variety of shapes of projectiles and surface features on the substrates/molds may be produced using BM. The various product shapes that can result include

stand-alone 0D, 1D, 2D, 3D microscale and nanoscale structures. These shapes may be accomplished producing a mold or substrate that contains numerous micro and/or nanofeatures as templates. Such features can be simple or complex (e.g., dots, lines, 2D, 3D shapes, extruding or intruding (e.g., male or female)). Areas of the substrate can be masked or treated prior to processing, such that standalone microscale and nanoscale parts can be produced on the unmasked or untreated areas once released.

**[068]** In some embodiments, the projectile pulls any extended/long substrate or mold, so that large areas may be coated. In such embodiments, the projectile may be rotating or non-rotating.

**[069]** In some embodiments, the mold is masked or unmasked, textured or un-textured, containing intruding or extruding features. For example, by masking or treating areas of the substrate/mold or projectile so that fluid does not adhere to it, this leaves other attached or unattached micro and nano shapes on which the fluid stream may be deposited and later released if need be resulting in stand-alone shapes or devices such as microgears or nanogears. Extruding features on the substrate can be coated to increase surface area, for surface area dependent applications such as solar energy and batteries etc. For example, in some embodiments, mask may be used to produce patterns (e.g., macro/micro/nano) of various shapes.

**[070]** Alternatively, under certain conditions textured surfaces may be produced without the use of textured projectile/mold/substrate. This is due to the complex coating interactions with substrate and atmosphere, thermal properties of substrate/mold and speed of projectile. An example is seen in Figure 10, showing a side view of film (Figure 10a at lower resolution and Figure 10b at higher resolution) with extruding texture and top view (Figure 10c at lower resolution and Figure 10d at higher resolution) with microstructure, in cases hierarchal structures have been observed.

**[071]** Figure 4 shows a side view of carrier 410 with wax substrate 420 inclined at 15° and Figure 5 shows an example mold or substrate 510, 550 with surface depressions of shapes than can be filled during deposition. In Figure 4, the resultant projectile would take the shape of wax substrate 420. In Figure 5, the resultant projectile, mold or substrate would take the shape of a single or multiple macro, micro or nano gears 520, 560, depending on if the substrate has multiple depressions with the gear shapes at macro-micro and nano-scales.

**[072]** Figure 6 shows a continuous thick film 610 of Sn-0.7Cu. As can be appreciated, such films were produced at projectile speeds as high as 36m/s in the present example. In some embodiments, increasing the projectile speed to extreme levels such as below and above the speed

of sound in air (e.g., 343 m/s) could result in nano-thick coating being produced virtually instantaneously.

**[073]** In some embodiments, the projectile or substrate includes an integrated surface coating. In such embodiments, continuous or isolated areas of components and shapes (e.g., using masking/treatment) can be coated rapidly. For example, below, at or above the speed of sound in air, e.g., 343m/s. These surface coatings are an integral part of the component to be coated. Multiple coatings may also be applied by having a sequence of fluid streams through which the projectile/substrate travels.

**[074]** In some embodiments, the projectile or substrate includes a surface reactive coating. In such embodiments, continuous or isolated areas and shapes using masking followed by a reaction of the substrate to produce a new material product. In some embodiments, a reaction on the substrate may be achieved with a gaseous and/or liquid phase to produce a new material product. Examples of surface reactive coating include deposition of multiple layers in sequence during ballistic manufacturing such that a first metal is deposited followed by second metal (e.g., using 2 or more molten metal streams in succession).

**[075]** In some embodiments, the projectile or substrate includes functionally graded composites and multi-layered products. In such embodiments, the projectile goes through multiple consecutive melt streams to deposit metal composite multilayers of varying reinforcement volume fraction/and or particle sizes (e.g., functionally graded). Similarly different materials can be deposited to produce multi-layered coatings or multi-layered stand alone shapes. Alternatively, the graded composites or multi-layered products may further subsequently be reacted to produce new coating materials (e.g., surface reactive coatings). Alternatively powders suspended in a fluid is used to make the fluid stream and coat the substrate while another powder suspension follows, and so on to produce composite nanolayered composites or functionally graded coatings following sintering or high temperature consolidation.

**[076]** In some embodiments, the layered features may be stand-alone or coatings on other materials (e.g., reactive or non-reactive). For example, a nickel substrate material coated with molten aluminum followed by heat treatment either by electrically heating the projectile or subsequent to convert aluminum and the nearest nickel into nickel aluminide coatings by reactive synthesis. In some embodiments, the layers are made out of multifunctional materials or functionally graded, as provided above.

**[077]** In some embodiments, the projectile and/or mold may include a textured negative or positive mold or flat surface or curved surface. For example, for the production of nano gears or springs.

**[078]** In some embodiments, the projectile and/or mold may include artifacts to be coated. For example, the projectile could be the intended final component that needs to be coated. Or it could simply act as a carrier that carries the mold or substrate that may or may not include pre-machined or imprinted or formed nano or micro features, which the fluid subsequently coats.

**[079]** In some embodiments, the projectile may be guided. In other embodiments, the projectile is not guided. As an example, a projectile may be guided by rails to control the trajectory and stability of the projectile. Alternatively the projectile may be guided by magnetic forces without physical contact. In another example the projectile may achieve flight in air, vacuum or other gasses or liquids.

**[080]** In some embodiments, the projectile is heated. Suitable temperatures are in the range of approximately 50°C to 2000°C, depending on various factors such as the composition of the projectile, the composition of the fluid stream, etc. In alternative embodiments, the projectile is not heated. For example the projectile would be used at room temperature or cooled to cryogenic temperatures, e.g., -260°C.

**[081]** In some embodiments, the projectile is electrically charged. In other embodiments, the projectile is not electrically charged. Suitable charges may be in the range of approximately 0 kV to 100 kV. Electrically charging may be achieved via a suitable power supply.

**[082]** In some embodiments, the projectile is magnetic. In other embodiments, the projectile is not magnetic. Suitable magnetic strength may be in the range of approximately  $10^{-18}$  Tesla to 100 Tesla. Magnetically charging may be achieved via a suitable magneto or generator.

**[083]** In some embodiments, the projectile may include multiple sub projectiles (and/or molds) with dimensions that may be controlled laterally and length-wise. For example, the projectile may itself project other smaller projectiles at yet higher speeds than the primary projectile. In some embodiments, the substrate or mold and carrier (which carries the mold or substrate) may be separate pieces or components. Alternatively, the substrate or mold and carrier may be a single piece or integral components.

**[084]** In some embodiments, the projectile may have spin motion on one or more axes. For example, axial rotation, such as the flight of a bullet in air.

[085] In some embodiments, the projectile, or mold/substrate may be disintegrable, dissolvable, meltable, etc. In such embodiments, the projectile is generally constructed from a wax type of material. In other embodiments, the projectile is generally constructed from a polymeric type of material, such that the projectile is a polymer that can later be burned off or dissolved.

[086] In some embodiments, the projectile, material and/or mold surface may be partially or fully bondable (through controlling surface chemistry for example) to the fluid stream. In other embodiments, the projectile, material and/or mold surface is not bondable to the fluid stream (e.g., by controlling again surface chemistry of substrate/mold or projectile or other masking techniques)

[087] In some embodiments, the projectile may be accelerated or decelerated when introduced into or within the fluid stream. The acceleration/deceleration may be achieved by pushing or pulling using, for example: gas pressure, electromagnetic forces, ballistically/explosively/reactively, and/or mechanically. For example speed may be halved or doubled, or projectile speed variation controlled by varying e.g., electromagnetic parameters.

[088] In some embodiments, the projectile may also be texturized in the fluid stream. By charging the stream and projectile/substrate/mold atomized particles may preferentially be deposited on certain regions by design.

### **Example**

[089] A tin-copper (Sn-0.7Cu) alloy was used as a model material due to its low melting point, however obviously results are applicable to many other material systems. Although the present disclosure investigates processing velocities up to 36.1 m/s, higher ballistic velocities even above the speed of sound are possible with Ballistic Manufacturing. The present example provides an initial insight into the capabilities of BM and the developed microstructures in the lower velocity regime.

### **Materials and Methods**

[090] The experimental equipment for this investigation was all custom built at San Diego State University's Advanced Materials Processing Lab (AMPL). The casting material used was a low melting point Kester K100LD lead free solder alloy (Sn-0.7Cu), USA.

[091] A schematic of the BM process and setup is shown in Figure 1. An aluminum carrier (projectile) holds a flat wax substrate. The wax is machinable and purchased from MachinableWax.com, Inc., USA. The wax was initially melted, and cast into the carriers using a

glass microscope slide at the bottom to ensure a flat casting surface with very good surface finish. The projectile/substrate was designed having an inclined surface of  $15^\circ$ .

**[092]** For each experiment, the solid Sn-0.7Cu solder alloy was melted in a stainless steel crucible heated by a tape heater to a temperature of  $375^\circ\text{C}$  (648 K) prior to casting. A plunger valve at the bottom of the crucible is opened after the desired temperature is reached. The molten solder was then allowed to flow through a rectangular slit 0.9mm in thickness and 31.75mm in width and a curtain of molten alloy was formed as seen in Figure 1. The carrier/substrate were then accelerated pneumatically inside the barrel, using air pressures of 200, 700, 1000, and 1500 psi. The end of the barrel was capped allowing projectile deceleration through backpressure buildup after the projectile had gone through the molten metal stream.

**[093]** Casting velocity (e.g. projectile velocity at point of melt contact) was determined by analyzing the video frames from a high-speed camera (Photron SA.1 high speed camera, USA, capability up to 180,000 frames per second (fps)). For the 200psi and 700psi velocity measurement experiments, the camera was set to record at 5400fps and for the higher pressures of 1000psi and 1500psi the camera was set to record at 40000fps. The actual casting experiments were also recorded using the high-speed camera. This time, 90000fps were used and the video was shot at an angle of approximately  $60^\circ$  to the projectile path in order to capture rapid events.

**[094]** A Cryostat Microm HM550 microtome was used to cross-section the films attached to the wax substrate. Microstructural characterization and thickness were conducted using a Quanta 400 field emission scanning electron microscope (FESEM), USA. The average cell size was measured using the line intercept method. Images were taken from the front, middle, and back of each film, and an average calculated.

### Results and discussion

**[095]** Figure 7a shows the relationship between accelerating air pressure and casting velocity (e.g. projectile velocity at the point of casting). Figure 7a shows limited gain in velocity at the higher pressures. Although factors such as projectile design and weight optimization may help to exceed the maximum velocity of 36.1 m/s, other means of acceleration and deceleration are required to achieve significantly higher processing velocities (even above the speed of sound).

**[096]** Although the crucible was maintained at a temperature of  $375^\circ\text{C}$  (648 K) prior to casting, pre-calibration tests have shown that the melt exits the crucible at an average temperature of  $352.1^\circ\text{C}$  (625.1K). (e.g.  $\sim 125^\circ\text{C}$  (398 K) above the material's melting point of  $227^\circ\text{C}$  (500K), at

which the viscosity of the Sn-0.7Cu melt has been reported to be still low with a value of ~1.9 mPa.s.

**[097]** The high-speed videos (Figure 7b) were helpful in revealing the nature of the thick film casting process, which was fairly chaotic. As can be seen, the casting/coating process is complete within a few milliseconds at the investigated projectile speeds. The initial contact between the projectile/wax surface and the molten Sn-0.7Cu stream initiates melt splashing, which is somewhat reduced at the slowest investigated velocity of 14.7m/s. Additionally, at the highest speeds of 34.6 m/s and 36.1m/s, the melt droplets formed from the initial projectile/substrate-melt contact typically re-contact the back substrate surface. Substrates had good coverage of thick film. Although most films appeared continuous, pockets of uncoated regions were still observed (possibly due to un-optimized substrate surface condition).

**[098]** Figure 8 shows an example for films processed at 14.7 m/s. These structures are characterized by primary Sn cells surrounded by eutectic lamellar microstructures (a microstructure typical of this off-eutectic alloy). Some interesting microstructural features were however evident. First the microstructures generated in our study are 2-D in nature with aspect ratios of at least ~9-13:1. It is also clear that there is no preferred orientation for the eutectic phase, as can be seen in Figure 8d, showing the interface between two eutectic regions of different orientation.

**[099]** The average primary dendrite spacing ( $d$ ) was found to significantly decrease with an increase in projectile velocity (Figure 9a), reaching around 70  $\mu\text{m}$  at the highest velocity investigated. As can be seen in Figure 9b as the projectile velocity is increased, the thickness of the films also decreases (a similar trend to that observed in PFMS), such that an average thickness of 6.06  $\mu\text{m}$  was obtained at the highest projectile velocity of 36.1 m/s. Eutectic cellular structures were observed in all of the processed films. The relation between solidification kinetics and resulting microstructure of Sn-0.7Cu has been studied by Ventura et al., *Acta Mater.* **59**, 1651 (2011) who found that when Sn-0.7Cu is directionally solidified, it forms aligned off-eutectic cellular or dendritic structures, with a primary  $\beta$ -Sn phase surrounded by eutectic phase  $\beta$ -Sn+Cu<sub>6</sub>Sn<sub>5</sub>. The dendrite arm spacing is known to decrease with the increase in solidification rate. Flemings, *Metall. Trans.* **5**, 2121 (1974) arrived at the following simple relation:

$$\mathbf{[0100]} \quad d = at_f^n \quad (1)$$

**[0101]** Where  $d$  is the spacing between primary dendrites,  $a$  is an alloy-specific constant,  $t_f$  is the local solidification time and  $n$  is close to  $\frac{1}{2}$  for primary dendrites. Solidification time  $t_f$  can be expressed as,

$$[0102] \quad t_f = \frac{\Delta T}{Q} \quad (2)$$

[0103] Where  $\Delta T$  is the solidus-liquidus temperature range and  $Q$  is the cooling rate. In order to compare the relative cooling rates for the Sn-0.7Cu alloy processed at our different speeds, Eq. (2) can be substituted into Eq. (1) yielding:

$$[0104] \quad d = a \left( \frac{\Delta T}{Q} \right)^n \quad (3)$$

[0105] Taking the dendrite arm spacing of the specimen shot at the slowest velocity,  $d_s$ , as a reference with  $Q_s$  being its corresponding cooling rate, the ratio of  $d_s$  to the other dendrite arm spacings is:

$$[0106] \quad \left( \frac{d_s}{d} \right)^{1/n} = \frac{Q}{Q_s} \quad (4)$$

[0107] This same relationship was applied by Byrne et al., Materials Science and Engineering A 459 (2007) 172–181 to compare the cooling rates of PFMS ribbons whose cooling rate were modified by laser heating. The relative cooling rates for the 24.9m/s, 34.6m/s, and 36.1m/s projectile velocities are 2.71, 3.88, and 5.62 respectively, showing significant changes in the relative cooling rates within our investigated projectile velocities.

[0108] It should be noted that although the minimum average thickness of 6.06  $\mu\text{m}$  was obtained at only a velocity of 36.1m/s, we expect considerably thinner films with an increase in casting temperature, projectile velocity and projectile/melt contact angle which are the subject of on-going work. In fact, extrapolation of our current data (using simple data fitting models) for the effects of projectile velocity on dendrite arm spacings and film thickness, to projectile velocities around the speed of sound (340m/s) results in dendrite arm spacings on the order of a nanometer and a film thickness of  $\sim 0.4\text{nm}$ . More research is however needed to experimentally confirm these expectations.

## Conclusions

[0109] A number of conclusions can be deduced from the present work.

[0110] Ballistic manufacturing has been successfully implemented for the first time to produce thick film of Sn-0.7Cu alloy.

[0111] A 2-D hypo-eutectic microstructure was obtained at all speeds investigated.

[0112] Increase in projectile velocity was found to decrease both dendrite arm spacing and thickness, with the lowest dendrite arm spacing being 70  $\mu\text{m}$  and a film thickness of 6.06  $\mu\text{m}$  at the maximum investigated velocity of 36.1m/s.

[0113] Although described specifically throughout the entirety of the instant disclosure, representative embodiments have utility over a wide range of applications, and the above discussion is not intended and should not be construed to be limiting, but is offered as an illustrative discussion of aspects of the disclosure. What has been described and illustrated herein are embodiments of the disclosure along with some of their variations. The terms, descriptions and figures used herein are set forth by way of illustration only and are not meant as limitations. Those skilled in the art will recognize that many variations are possible within the spirit and scope of the disclosure, wherein the disclosure is intended to be defined by the following claims—and their equivalents—in which all terms are mean in their broadest reasonable sense unless otherwise indicated.

## CLAIMS

What is claimed is:

1. A method of applying a material to an article, the method comprising:  
    flowing a stream comprising a material in a first direction; and  
    passing an article through the stream such that the material is applied to at least a portion of the article, wherein the article travels in a second direction at a speed of at least 1 m/s when passing through the flowing material.
2. The method of Claim 1, wherein the material is a molten metal.
3. The method of Claim 2, where the molten metal is an alloy, an intermetallic material, or intermetallic composite material
4. The method of Claim 1, wherein the material comprises a polymer, a ceramic, an inorganic material, an organic material, a metal, an alloy, water, or combinations thereof.
5. The method of Claim 1, wherein the material comprises a powder, suspension, a gas, a liquid, or combinations thereof.
6. The method of Claim 1, wherein the material comprises NiAl, TiAl, FeAl, Ti-TiB, Al-SiC, Al-carbon nanotube (CNT), Ni<sub>3</sub>Al-CNT, or combinations thereof.
7. The method of Claim 1, wherein the material has a temperature of at least 270° F.
8. The method of Claim 1, wherein the material has a temperature of at least 350° F.
9. The method of Claim 1, wherein the material has a temperature of no more than 4000° F.
10. The method of Claim 1, wherein the material has a temperature of no more than 2000° F.
11. The method of Claim 1, wherein the article travels in the second direction through a channel, wherein the stream flows in the first direction through an opening into the channel such that the material is applied to the article within the channel.
12. The method of Claim 1, the method further comprising solidifying the material applied to the article to form a coating.
13. The method of Claim 12, wherein solidifying the material comprises cooling, applying radiation, curing, heating, applying solidifying reagents, or combinations thereof.

14. The method of Claim 1, the method further comprising sintering the material applied to the article.
15. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 10 m/s.
16. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 50 m/s.
17. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 100 m/s.
18. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 300 m/s.
19. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 330 m/s.
20. The method of Claim 1, wherein the article travels in the second direction at a speed of at least 400 m/s.
21. The method of any one of Claims 15-20, wherein the article travels in the second direction at a speed of no more than 900 m/s.
22. The method of any one of Claims 15-20, wherein the article travels in the second direction at a speed of no more than 600 m/s.
23. The method of any one of Claims 15-20, wherein the article travels in the second direction at a speed of no more than 400 m/s.
24. The method of any one of Claims 15-20, wherein the article travels in the second direction at a speed of no more than 100 m/s.
25. The method of any one of Claims 15-20, wherein the article travels in the second direction at a speed of no more than 50 m/s.
26. The method of Claim 1, the method further comprising separating at least a portion of the article from the material applied to the article.
27. The method of Claim 26, wherein separating at least a portion of the article comprising melting, dissolving, degrading, or volatilizing at least a portion of the article.

28. The method of Claim 26, wherein the article is a composite comprising a first material and a second material, and wherein separating at least a portion of the article comprises removing the first material while the second material remains.
29. The method of Claim 1, wherein the method does not include separating the material applied to the article from the article.
30. The method of Claim 1, wherein the article comprises a patterned mask on the surface of the article, and wherein the material is selectively applied to exposed portions of the article uncovered by the mask.
31. The method of Claim 30, where in the mask is a photolithographic mask.
32. The method of Claim 1, wherein the article comprises a beveled edge.
33. The method of Claim 32, where the beveled edge has an angle of at least  $5^{\circ}$ .
34. The method of Claim 32, where the beveled edge has an angle of at least  $10^{\circ}$ .
35. The method of Claim 32, where the beveled edge has an angle of at least  $25^{\circ}$ .
36. The method of any one of Claims 32-35, wherein the beveled edge has an angle of no more than  $60^{\circ}$ .
37. The method of any one of Claims 32-35, wherein the beveled edge has an angle of no more than  $45^{\circ}$ .
38. The method of any one of Claims 32-35, wherein the beveled edge has an angle of no more than  $30^{\circ}$ .
39. The method of Claim 1, wherein the first direction forms an angle with the second direction that is at least  $0^{\circ}$ .
40. The method of Claim 1, wherein the first direction forms an angle with the second direction that is at least  $30^{\circ}$ .
41. The method of Claim 1, wherein the first direction forms an angle with the second direction that is at least  $45^{\circ}$ .
42. The method of Claim 1, wherein the first direction forms an angle with the second direction that is at least  $60^{\circ}$ .

43. The method of Claim 1, wherein the first direction forms an angle with the second direction that is at least 80°.
44. The method of any one of Claims 39-43, wherein the first direction forms an angle with the second direction that is no more than 180°.
45. The method of any one of Claims 39-43, wherein the first direction forms an angle with the second direction that is no more than 150°.
46. The method of any one of Claims 39-43, wherein the first direction forms an angle with the second direction that is no more than 135°.
47. The method of any one of Claims 39-43, wherein the first direction forms an angle with the second direction that is no more than 120°.
48. The method of any one of Claims 39-43, wherein the first direction forms an angle with the second direction that is no more than 100°.
49. The method of Claim 1, wherein the first direction is perpendicular to the second direction.
50. The method of Claim 1, the method further comprising applying a decelerating force to the article after the article passes through the flowing material.
51. The method of Claim 50, wherein applying the decelerating force comprises applying a fluid pressure to the article.
52. The method of Claim 1, wherein a vacuum is applied to the article before, during, or after the article passes through the flowing material.
53. The method of Claim 1, wherein a gas is applied to the article before, during, or after the article passes through the flowing material.
54. The method of Claim 53, wherein the gas is configured to react with the material or the article.
55. The method of Claim 53, wherein the gas is an inert gas.
56. The method of Claim 1, wherein the article comprises one or more cavities, and wherein the material enters the one or more cavities when the article passes through the flowing material.

57. The method of Claim 56, the method further comprising solidifying the material and separating the solidified article from the cavity, wherein the shape of the solidified material corresponds to the shape of the cavity.
58. The method of Claim 56, the method further comprising solidifying the material and not separating the solidified article from the cavity.
59. The method of Claim 1, a surface of the article comprises one or more features with at least one dimension less than 1 mm.
60. The method of Claim 1, a surface of the article comprises one or more features with at least one dimension less than 500 microns.
61. The method of Claim 1, a surface of the article comprises one or more features with at least one dimension less than 100 microns.
62. The method of Claim 1, a surface of the article comprises a feature with at least one dimension less than 10 microns.
63. The method of Claim 1, wherein a surface of the article comprises a feature with at least one dimension less than 1 micron.
64. The method of Claim 1, wherein a surface of the article comprises a feature with at least one dimension less than 100nm.
65. The method of any one of Claims 59-63, wherein the feature is a groove, a channel, a cavity, dots, or a pedestal.
66. The method of Claim 1, wherein the article has an extended shape to provide large surface area for coating
67. The method of Claim 1, wherein the article is rotating while passing through the flowing of material.
68. The method of Claim 67, wherein the article rotates about an axis that is parallel to the first direction.
69. The method of Claim 67, wherein the article rotates about an axis that is perpendicular to the first direction.

70. The method of Claim 67, wherein the article rotates about an axis that is parallel to the second direction.
71. The method of Claim 67, wherein the article rotates about an axis that is perpendicular to the second direction.
72. The method of Claim 1, the method further comprising reacting the material with the article after the article passes through the flowing material.
73. The method of Claim 72, wherein reacting the material with the article comprises heating the article.
74. The method of Claim 1, the method further comprising:
  - flowing a second material; and
  - passing the article through the second material, wherein the second material is applied to the article after the material is applied to the article.
75. The method of Claim 74, wherein the material and second material are different.
76. The method of Claim 75, wherein the material is a molten metal, and the second material is a molten metal.
77. The method of Claim 1, the method further comprising heating the article before passing the article through the flowing material.
78. The method of Claim 1, wherein the article is electrically charged.
79. The method of Claim 1, wherein the stream has at least one dimension less than 1 mm.
80. The method of Claim 1, wherein the stream has at least one dimension less than 100 microns.
81. The method of Claim 1, wherein the stream has at least one dimension less than 12 inches.
82. The method of Claim 1, wherein the stream has a circular, rectangular, polygonal, irregular, or square cross-section.
83. The method of Claim 1, wherein the article is passed through the flowing material by applying gas pressure, electromagnetic force, combustion force, or explosion force.
84. The method of Claim 1, wherein the material applied to the article has a thickness of less than 100 microns.

85. The method of Claim 1, wherein the material applied to the article has a thickness of less 50 microns.
86. The method of Claim 1, wherein the material applied to the article has a thickness of less 25 microns.
87. The method of Claim 1, wherein the material applied to the article has a thickness of less 1 micron.
88. A method of coating an article, the method comprising:  
    flowing a molten metal in a first direction;  
    passing an article through the flowing molten metal such that the molten metal is applied to at least a portion of the article, wherein the article travels in a second direction at a speed of at least 1 m/s when passing through the flowing molten metal; and  
    solidifying the molten metal to form a coating .
89. The article obtained by the method of any one of Claims 1-88.
90. A system for applying a material to an article, the system comprising:  
    a reservoir for receiving a material;  
    a conduit fluidly coupled to the reservoir and configured to flow a stream comprising the material in a first direction;  
    a channel configured to provide a path for moving an article in a second direction, wherein the conduit is fluidly coupled to the channel and configured such that the article passes through the stream when moving through the channel; and  
    means for forcing the article through the channel.
91. The system of Claim 90, where the means for forcing the article through the channel is a pressure source.
92. The system of Claim 91, wherein the pressure source is pneumatic.
93. The system of Claim 90, where the means for forcing the article is configured to move the article through the channel at a speed of at least about 1 m/s.
94. The system of Claim 90, the system further comprising heater configured to heat the material in the reservoir.

95. The system of Claim 94, wherein the material is a metal, and where the heater is configured to maintain the material in a molten state.
96. The system of Claim 90, wherein the conduit is configured such that the stream has at least one dimension less than 1 cm.
97. The system of Claim 90, wherein the conduit is configured such that the stream has at least one dimension less than 1 mm.
98. The system of Claim 90, wherein the reservoir and conduit are configured such that the stream flows using gravitational force.
99. The system of Claim 90, the system further comprising a valve for controlling a rate of flow for the stream.
100. The system of Claim 90, the system further comprising a piston for applying pressure and increasing rate of flow for the stream.
101. The system of Claim 90, the system further comprising a second conduit fluidly coupled to the reservoir and configured to flow a second stream comprising a second material into the channel, and wherein the channel is configured such that the article passes through the second stream when moving through the channel.



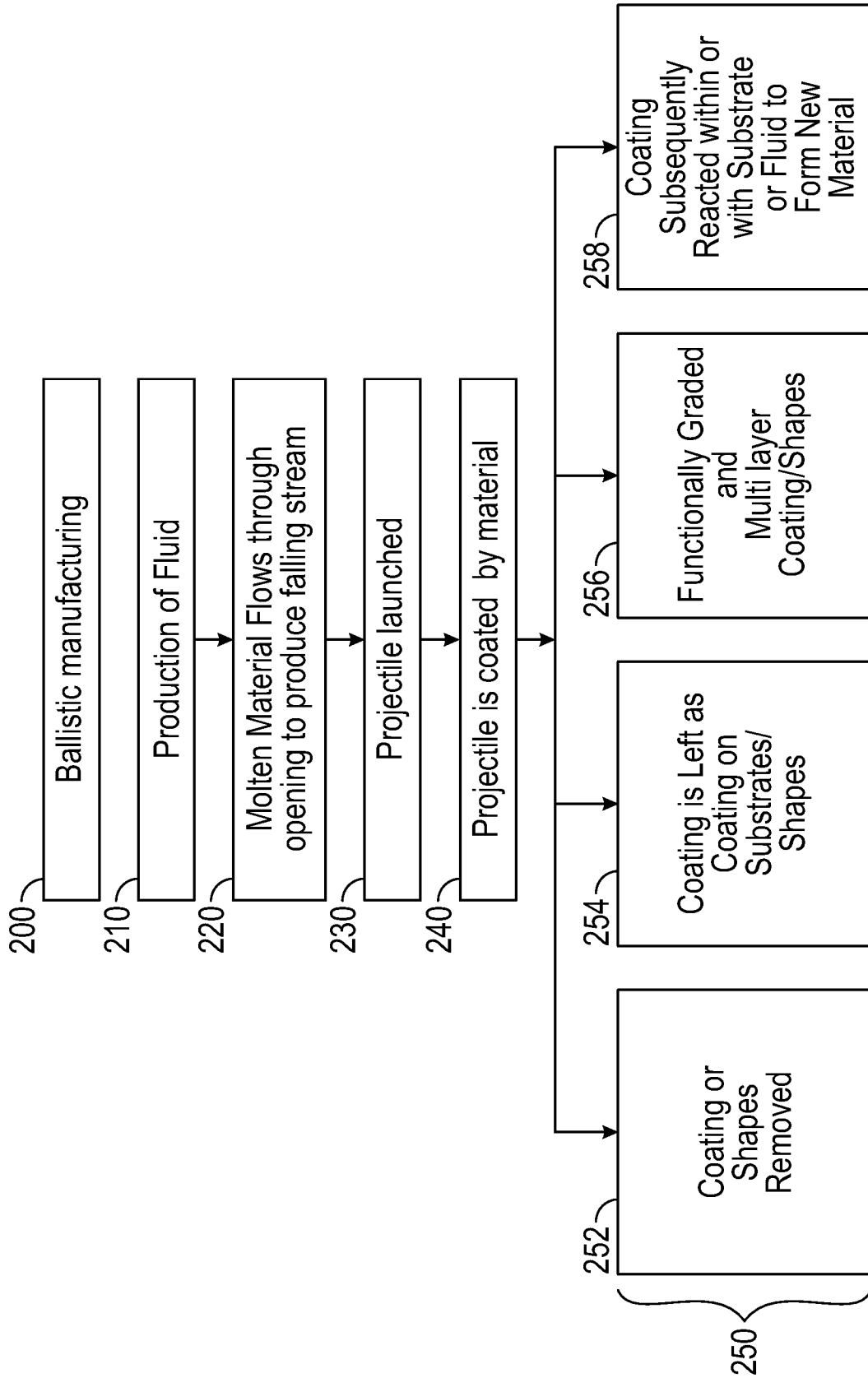


FIG. 2

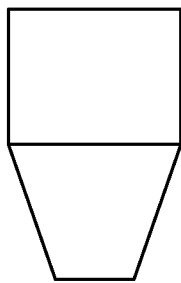


FIG. 3(a)

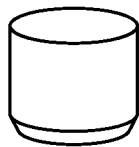


FIG. 3(b)

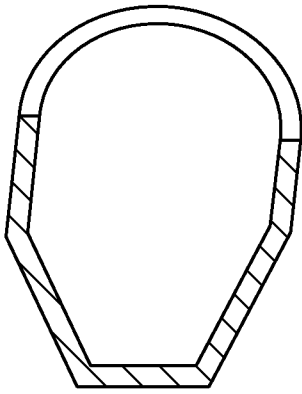


FIG. 3(c)

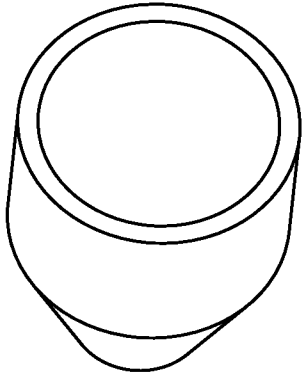


FIG. 3(d)

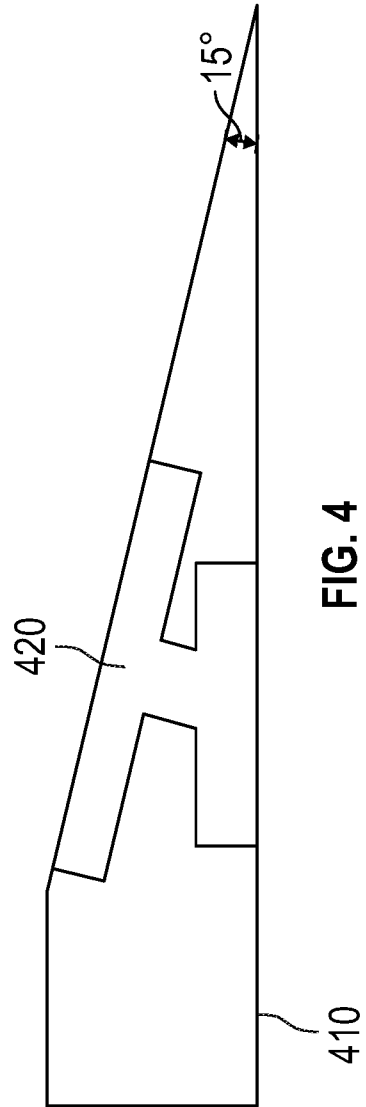


FIG. 4

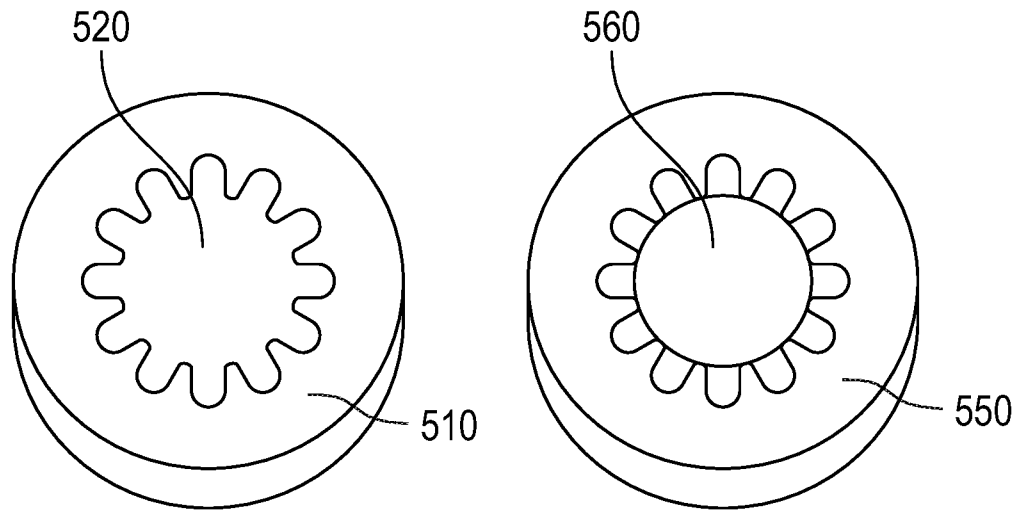


FIG. 5

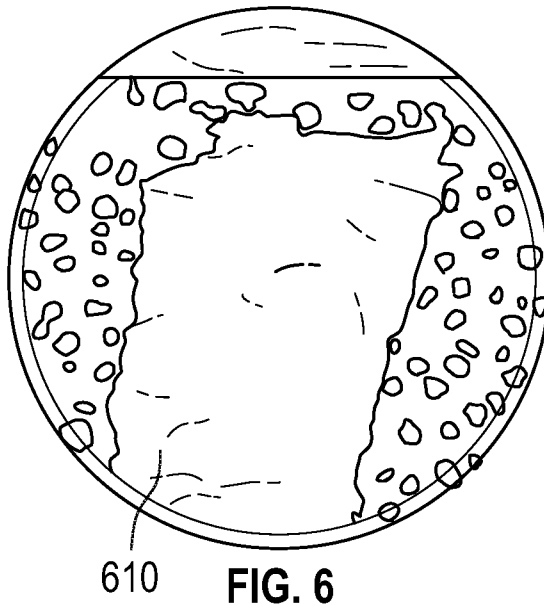
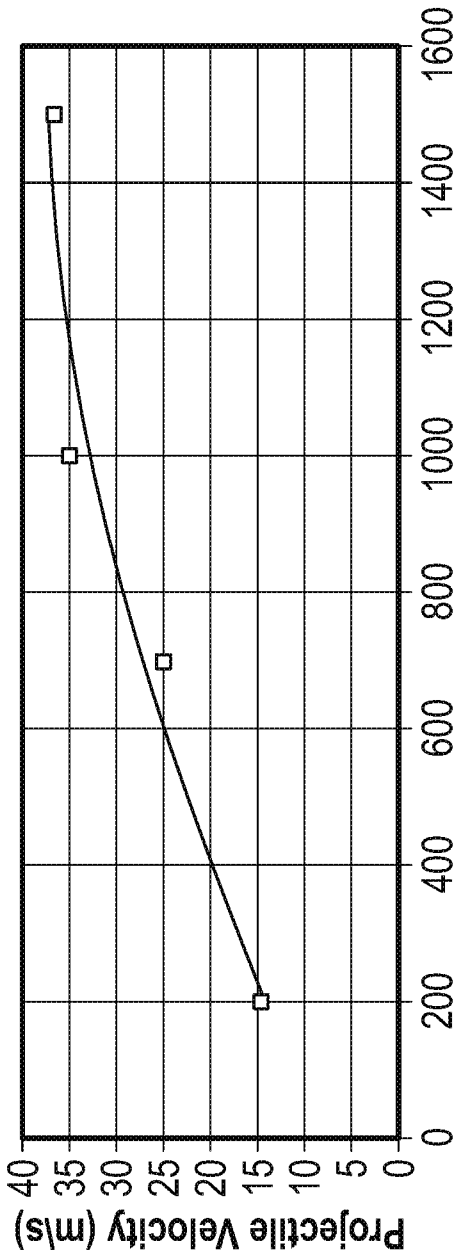


FIG. 6



Gas Pressure (psi)

FIG. 7(a)

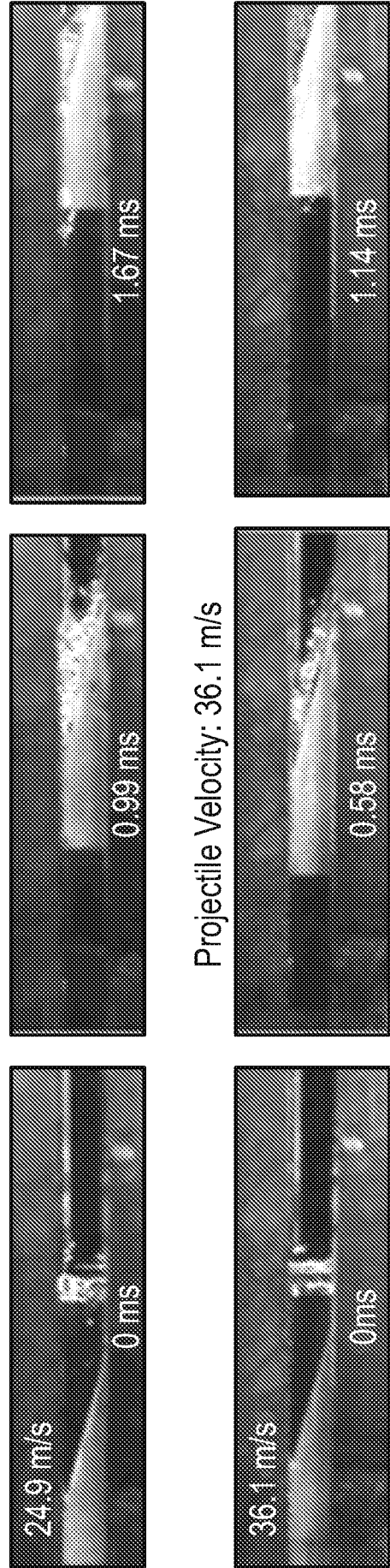


FIG. 7(b)

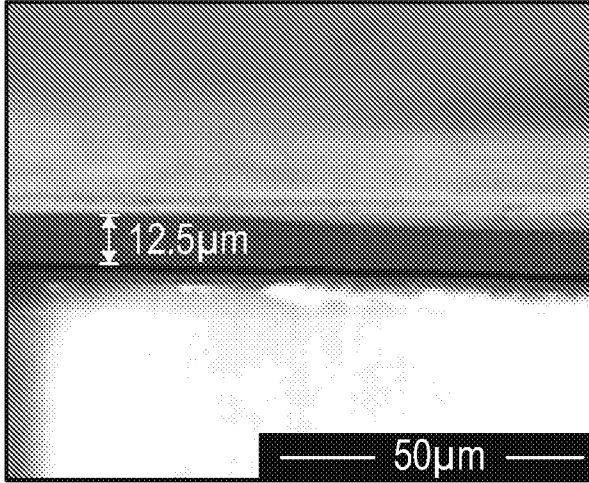


FIG. 8(a)

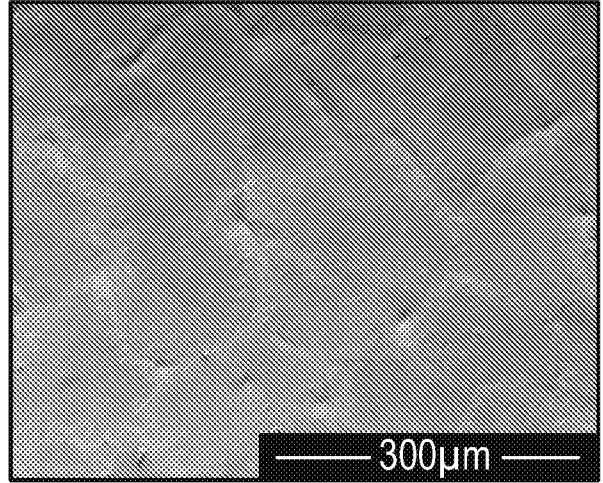


FIG. 8(b)

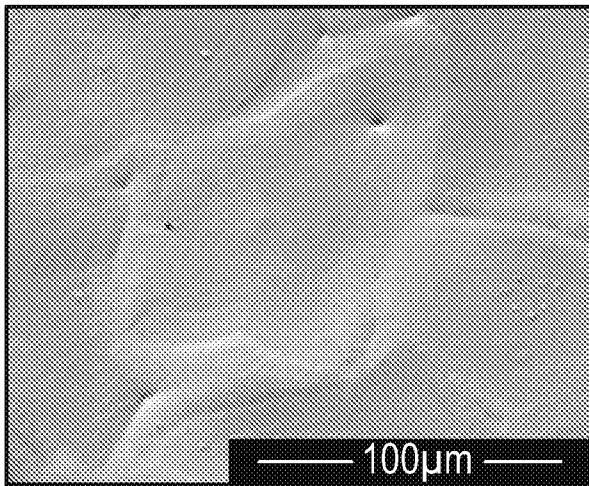


FIG. 8(c)

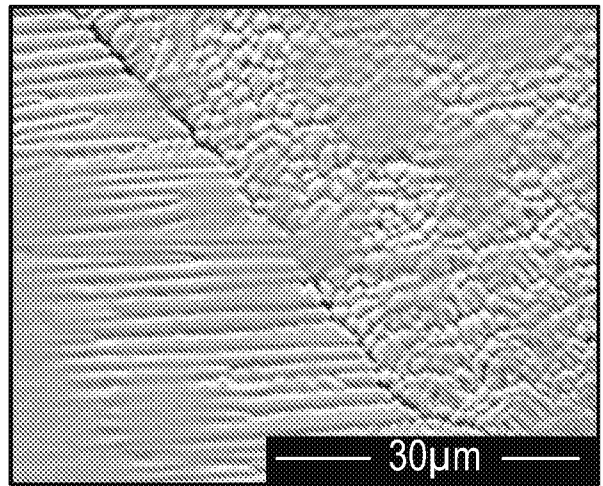


FIG. 8(d)

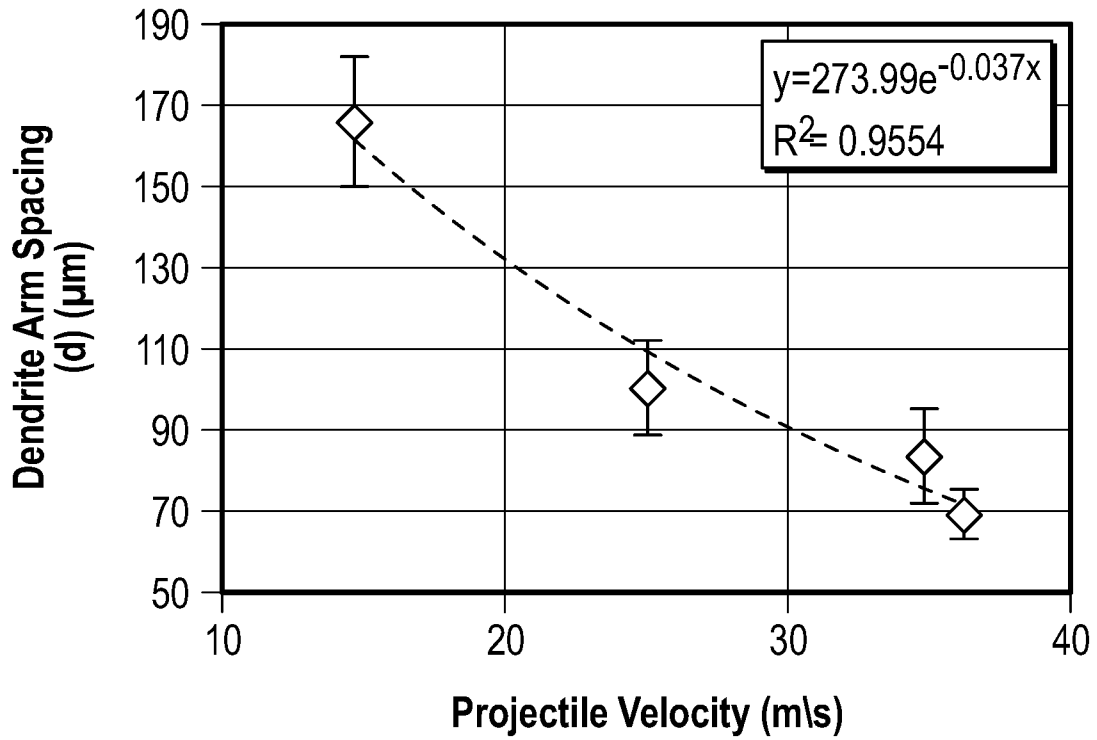


FIG. 9(a)

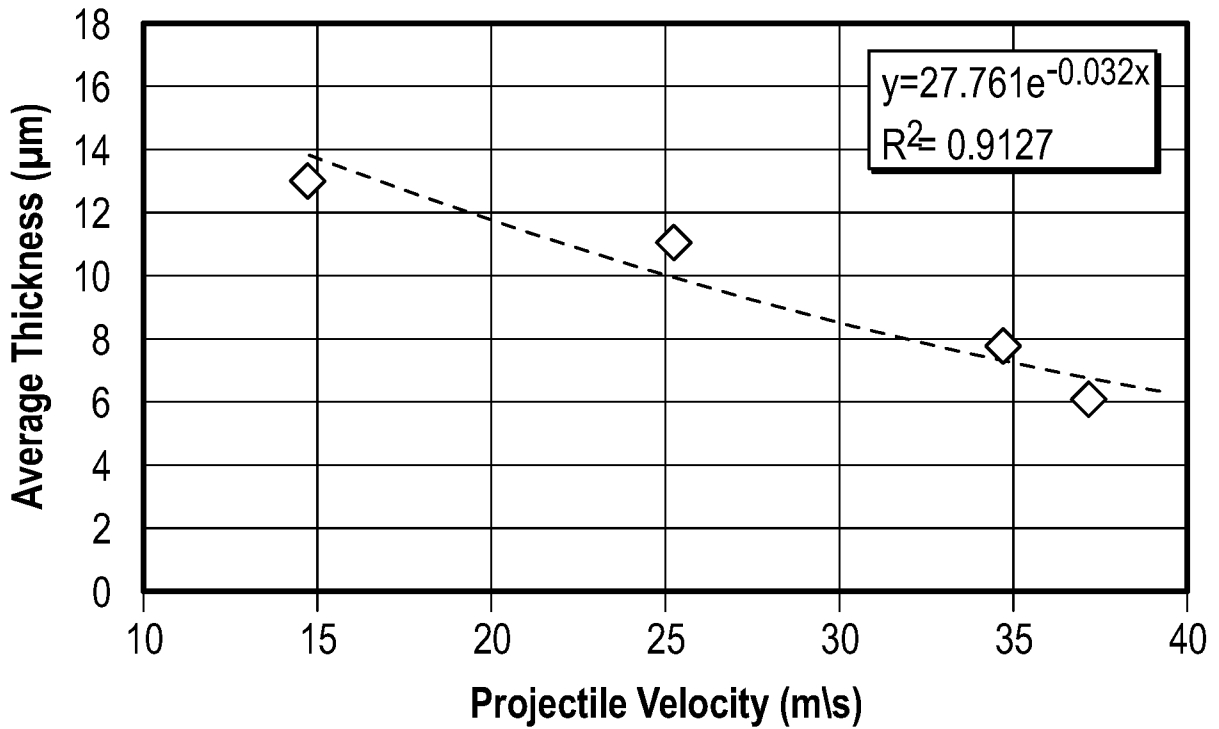


FIG. 9(b)

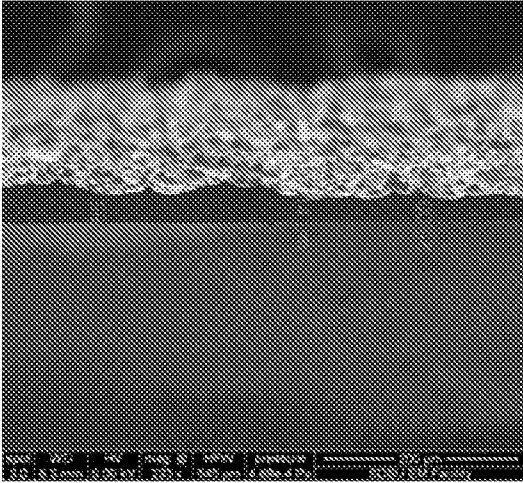


FIG. 10(a)

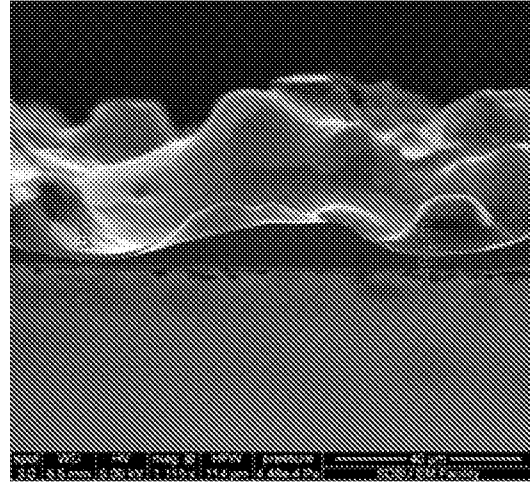


FIG. 10(b)

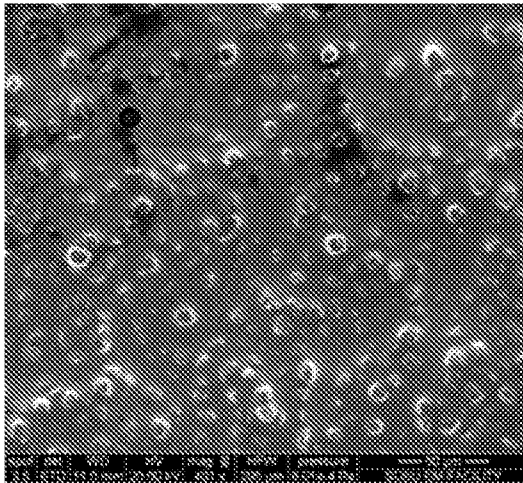


FIG. 10(c)

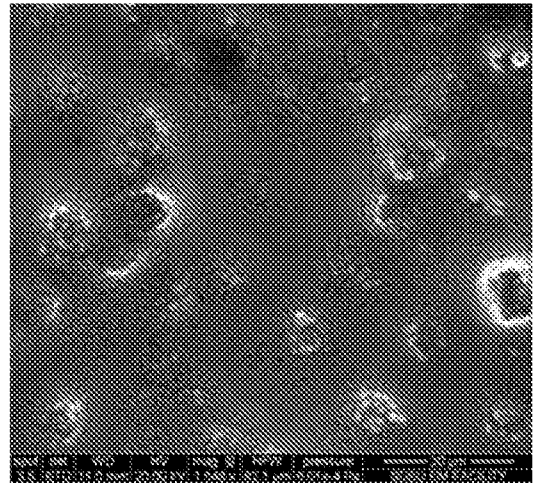


FIG. 10(d)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/032988

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B05D 1/40; B05D 1/02; B05D 1/06; B05D 1/32 (2017.01)

CPC - B05D 1/40; B05D 1/02; B05D 1/06; B05D 1/32 (2017.05)

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 - 118/300; 118/301; 118/302; 118/303; 118/314 (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	Morsi. Ballistic Manufacturing. YouTube.com 15 September 2014 (15.09.2014); retrieved from the Internet on 11 July 2017 (11.07.2017). <URL: https://www.youtube.com/watch?v=Ci0MPyTusr4> entire document	1-11, 15-25, 29, 39-50, 53, 55, 66, 74-76, 79-87, 90-99, 101
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Y		12-14, 30, 32-35, 52, 54, 56, 58-63, 65, 67, 69, 70, 72, 73, 77, 78, 88, 100
Y	US 4,657,787 A (SINGER et al) 14 April 1987 (14.04.1987) entire document	12, 13, 88
Y	US 5,194,295 A (IACOVANGELO) 16 March 1993 (16.03.1993) entire document	14, 54, 72, 73
Y	US 2010/0055295 A1 (HOSSAINY et al) 04 March 2010 (04.03.2010) entire document	30, 67, 69, 70
Y	US 2005/0089673 A1 (FLEMING et al) 28 April 2005 (28.04.2005) entire document	32-35, 56, 58-63, 65
Y	US 2012/0070928 A1 (KIM et al) 22 March 2012 (22.03.2012) entire document	52
Y	US 2015/0017325 A1 (DHILLON) 15 January 2015 (15.01.2015) entire document	77
Y	US 4,169,903 A (SCHOLES) 02 October 1979 (02.10.1979) entire document	78
Y	US 2005/0150449 A1 (MATSUNAGA et al) 14 July 2005 (14.07.2005) entire document	100
A	US 6,273,308 B1 (CHOSHI) 14 August 2001 (14.08.2001) entire document	1-88, 90-101

 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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 July 2017

Date of mailing of the international search report

10 AUG 2017

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Authorized officer

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PCT Helpdesk: 571-272-4300  
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/032988

**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.: 89  
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/US2017/032988

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/0052819 A1 (EBISAWA) 03 March 2011 (03.03.2011) entire document	1-88, 90-101
A	US 3,016,876 A (SEDLACSIK JR) 16 January 1962 (16.01.1962) entire document	1-88, 90-101