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(54) Title: PROCESS FOR ADDITIVE MANUFACTURING

(57) **Abstract**: Disclosed here is a method of making an article, the method including forming a plurality of layers of a material in a preset pattern, wherein at least one of the formed layers is an expandable layer that increases in volume during or prior to forming the next layer on the expandable layer; and fusing the plurality of formed layers to provide the article.

PROCESS FOR ADDITIVE MANUFACTURING

BACKGROUND

[0001] Additive manufacturing (also known in the art as "three-dimensional or "3D" printing) is a process for the manufacture of three-dimensional objects by formation of multiple fused layers. Because multiple layers, for example greater than fifty (or more), are formed, production speeds can be slower than desired. This can result in small build volumes over a given increment of time. Accordingly, there remains a need in the art for methods that allow faster production of large build volumes.

SUMMARY

[0002] One embodiment is a method of making an article, the method including forming a plurality of layers of a material in a preset pattern, wherein at least one of the formed layers is an expandable layer that increases in volume during or prior to forming the next layer on the expandable layer; and fusing the plurality of formed layers to provide the article.

[0003] Also described herein are the articles produced by the method described above.

[0004] The above described and other features are exemplified by the following detailed description, examples, and claims.

DETAILED DESCRIPTION

[0005] Disclosed herein are additive manufacturing methods wherein at least one layer formed during the additive manufacturing process comprises an expandable material. The layer including the expandable material increases in volume before or during formation of the next layer. The methods can have one or more of the following advantages. For example, due to the expansion of the at least one layer, a larger build volume can be achieved with deposition of fewer layers. The method can produce the parts with the same volume faster than methods that do not use an expandable layer. Since fewer deposited layers, and thus less material, can be used to form the same volume, use of an expandable material can also be cost effective and environmentally friendly. Use of an expandable layer can also decrease the presence or size of voids between layers in the finished articles, because the expanding material fills spaces present at the time of material deposition.

[0006] In some embodiments of the methods, a plurality of layers is formed in a preset pattern by an additive manufacturing process. "Plurality" as used in the context of additive manufacturing includes 20 or more layers. The maximum number of layers can vary greatly, determined, for example, by considerations such as the size of the article being manufactured, the technique used, the capabilities of the equipment used, and the level of detail desired in the final article. For example, 20 to 100,000 layers can be formed, or 50 to 50,000 layers can be formed.

[0007] As used herein, "layer" is a term of convenience that includes any shape, regular or irregular, having at least a predetermined thickness. In some embodiments, the size and configuration two dimensions are predetermined, and on some embodiments, the size and shape of all three dimensions of the layer is predetermined. The thickness of each layer can vary widely depending on the additive manufacturing method. In some embodiments the thickness of each layer as formed differs from a previous or subsequent layer. In some embodiments, the thickness of each layer is the same. In some embodiments the thickness of each layer as formed is 0.5 millimeters (mm) to 5 mm.

[0008] The preset pattern can be determined from a three-dimensional digital representation of the desired article as is known in the art and described in further detail below.

[0009] Any additive manufacturing process can be used, provided that the process allows formation of at least one layer of a thermoplastic material that is expandable. In some embodiments, more than one of the formed layers is expandable. In some embodiments all of the formed layers are expandable. The expandable layer is capable of increasing in volume. The volume increase can be during formation of the layer or after formation of the layer. In some embodiments the volume increase is after formation of the layer. Expansion of the layer provides increased build volume. Thus, the same or larger volume can be achieved with deposition of fewer layers. Similarly, the same or larger volume can be obtained with use of less material. In some embodiments, more than one layer is expanded, providing even greater volume.

[0010] The volume increase can be in response to a stimulus, such as a change in pressure or temperature. In some embodiments the volume increase is due to the presence of a blowing agent that expands the layer to provide a foam as described in further detail below. The increase can be 1% to 300% of the unexpanded volume of the layer. In some embodiments the increase is 5% to 200% of the unexpanded volume of the layer. In other embodiments the increase is 10% to 100% of the unexpanded volume of the layer. The degree of increase in volume can be tailored to the design of the article, the desired manufacturing time, the desired material usage, and similar considerations.

[0011] The volume increase can be completed prior to formation of the next layer or during formation of the next layer. In some embodiments, the volume increase is completed prior to formation of the next layer. The volume increase can be during the formation of the next layer in a coextrusion process as described in further detail below.

[0012] The plurality of layers in the predetermined pattern are fused to provide the article. Any method effective to fuse the plurality of layers during additive manufacturing can be used. In some embodiments, the fusing occurs during formation of each of the layers. In some embodiments the fusing occurs while subsequent layers are formed, or after all layers are formed.

[0013] In some embodiments, an additive manufacturing technique known generally as material extrusion can be used. In material extrusion, an article can be formed by dispensing a flowable material ("the build material") in a layer-by-layer manner and fusing the layers. "Fusing" as used herein includes the chemical or physical interlocking of the individual layers, and provides a "build structure". The flowable build material can be rendered flowable by dissolving or suspending the material in a solvent. In other embodiments, the flowable material can be rendered flowable by melting. In other embodiments, a flowable prepolymer composition that can be crosslinked or otherwise reacted to form a solid can be used. Fusing can be by removal of the solvent, cooling of the melted material, or reaction of the prepolymer composition.

[0014] In particular, an article can be formed from a three-dimensional digital representation of the article by depositing the flowable material as one or more roads on a substrate in an x-y plane to form the layer. The position of the dispenser (e.g., a nozzle) relative to the substrate is then incremented along a z-axis (perpendicular to the x-y plane), and the process is then repeated to form an article from the digital representation. The dispensed material is thus also referred to as a "modeling material" as well as a "build material." In some embodiments a support material as is known in the art can optionally be used to form a support structure. In these embodiments, the build material and the support material can be selectively dispensed during manufacture of the article to provide the article and a support structure. The support material can be present in the form of a support structure, for example a scaffolding, that can be mechanically removed or washed away when the layering process is completed to the desired degree.

[0015] Systems for material extrusion are known. An exemplary material extrusion additive manufacturing system includes a build chamber and a supply source for the thermoplastic material. The build chamber includes a build platform, a gantry, and a dispenser for dispensing the thermoplastic material, for example an extrusion head. The build platform is a platform on which the article is built, and desirably moves along a vertical z-axis based on signals provided from a computer-operated controller. The gantry is a guide rail system that can be configured to move the dispenser in a horizontal x-y plane within the build chamber, for example based on signals provided from a controller. The horizontal x-y plane is a plane defined by an x-axis and a y-axis where the x-axis, the y-axis, and the z-axis are orthogonal to each other. Alternatively the platform can be configured to move in the horizontal x-y plane and the extrusion head can be configured to move along the z-axis. Other similar arrangements can also be used such that one or both of the platform and extrusion head are moveable relative to each other. The build platform can be isolated or exposed to atmospheric conditions.

[0016] For some embodiments, both the build structure and the support structure of the article formed can include a fused expandable layer. In other embodiments , the build structured includes a fused expandable layer and the support material does not include an expandable layer. In still other embodiments, the build structure does not include an expandable layer and the support structure does include a fused expandable layer. In those embodiments where the support structure includes an expandable layer, the lower density of the expanded layer can allow for the support material to be easily or more easily broken off than the non-expanded layer, and re-used or discarded.

[0017] In some embodiments, the support structure can be made purposely breakable, to facilitate breakage where desired. For example, the support material can have an inherently lower tensile or impact strength than the build material. In other embodiments, the shape of the support structure can be designed to increase the breakability of the support structure relative to the build structure.

[0018] For example, in some embodiments, the build material can be made from a round print nozzle or round extrusion head. A round shape as used herein means means any cross-sectional shape that is a enclosed by one or more curved lines. A round shape includes circles, ovals, ellipses, and the like, as well as shapes having an irregular cross-sectional shape. Three dimensional articles formed from round shaped layers of build material can possess strong structural strength. In other embodiments, the support material for the articles can be can made from a non-round print nozzle or non-round extrusion head. A non-round shape means any cross-sectional shape enclosed by at least one straight line, optionally together with one or more curved lines. A non-round shape can include squares, rectangles, ribbons, horseshoes, stars, T head shapes, X shapes, chevrons, and the like. These nonround shapes can render the support material weaker, bittle and with lower strength than round shaped build material.

[0019] In some embodiments, the lower density support materials that include an expanded layer can be made from a non-round print nozzle or round extrusion head. These non-round shaped lower density support materials can be easily removed from build materials, particularly higher density round shaped build materials that do not include a expandable layer.

[0020] In some embodiments the flowable material includes a blowing agent to expand the layer and provide a foam. The blowing agent can be a physical blowing agent, a chemical blowing agent, or a combination thereof. The type of blowing agent can be chosen based on the type of expandable material used and the desired properties of the expanded layer, for example cell shape, cell size, and percent volume increase.

[0021] Exemplary physical blowing agents include water, super critical carbon dioxide, liquids such as pentane and butane, paraffins such as isobutene or isopentane, and gases such as air, nitrogen, carbon dioxide, 1,2-dichloroethylene, and the like. Physical blowing agents can be selected based on the compatibility with the thermoplastic material and ability to be distributed in the material. Physical blowing agents can provide greater expansion than chemical blowing agents. Physical blowing agents are incorporated in amounts effective to provide the desired increase in volume as is known in the art.

[0022] Chemical blowing agents can be chosen based on factors such as the decomposition mechanism. For example, a blowing agent that thermally decomposes is selected to be compatible with the temperatures of the additive manufacturing process. Chemical blowing agents can further be selected based on compatibility with the expandable material, and degradation products of the chemical blowing agent. Preferably, any degradation products have little or no impact on any desired property of the expandable material. Exemplary chemical blowing agents include azodicarbonamide, hydrazine, and other nitrogen compounds such as bitetrazole, sodium carbonate, and citric acid. Chemical blowing agents are generally used in amounts from 0.05 to 5 weight percent (wt%) of the expandable material.

[0023] The foams produced by the blowing agent are cellular materials, preferably closed-cell materials. The size and distribution of the cells can be varied by appropriate selection of the thermoplastic material and its melt strength, the blowing agent, the amount of blowing agent, and the expansion conditions. For example, higher melt strength materials tend to form closed cell foams. The sizes of the cells can be 0.01 mm to 4 mm, depending on the thickness of the layer. In some embodiments the sizes of the cells can be 0.05 mm to 0.5 mm. The foams can have a density of 5 to 800 kilograms per cubic meter (kg/m^3). In some embodiments the foams can have a density of 20 to 500 kg/m^3. Varying densities can be achieved by adjusting one or more of the amount of blowing agent, the type of blowing agent, the type of thermoplastic material, and the expansion conditions.

[0024] The above material extrusion techniques include techniques such as fused deposition modeling and fused filament fabrication as well as others as described in ASTM F2792-12a. In fused material extrusion techniques, an article can be produced by heating a thermoplastic material to a flowable state that can be deposited to form a layer. The layer can have a predetermined shape in the x-y axis and a predetermined thickness in the z-axis. The flowable material can be deposited as roads as described above, or through a die to provide a specific profile. The layer cools and solidifies as it is deposited. A subsequent layer of melted thermoplastic material fuses to the previously deposited layer, and solidifies upon a drop in temperature. Extrusion of multiple subsequent layers builds the desired shape. In some embodiments at least one layer of an article is formed by melt deposition, and in other embodiments, more than 10, or more than 20, or more than 50 of the layers of an article are formed by melt deposition, up to and including all of the layers of an article being formed by melt deposition.

[0025] In some embodiments the thermoplastic material is supplied in a melted form to the dispenser. The dispenser can be configured as an extrusion head. The extrusion head can deposit the thermoplastic composition as an extruded material strand to build the article. Examples of average diameters for the extruded material strands can be from 1.27 millimeters (0.050 inches) to 3.0 millimeters (0.120 inches). Depending on the type of thermoplastic material, the thermoplastic material can be extruded at a temperature of 200 to 450 °C. In some embodiments the thermoplastic material can be extruded at a temperature of 300 to 415 °C. The layers can be deposited at a build temperature (the temperature of deposition of the thermoplastic extruded material) that is 50 to 200 °C lower than the extrusion temperature. For example, the build temperature can be 15 to 250 °C. In some embodiments the thermoplastic material is extruded at a temperature of 200 to 450 °C, or 300 to 415 °C, and the build temperature is maintained at ambient temperature.

[0026] In some embodiments the expandable thermoplastic material includes a blowing agent to expand the layer and provide a foam. The blowing agent can be a physical blowing agent, a chemical blowing agent, or a combination thereof as described above.

[0027] The blowing agent, for example a chemical blowing agent, can be added directly to a melt of the thermoplastic material before depositing or extruding the thermoplastic material to form the layer. In other embodiments, the blowing agent can be pre-incorporated into the thermoplastic material, which then is formed to provide a shape suitable for use in an additive manufacturing process. Such shapes include pellets or filaments. The filaments being used in the additive manufacturing process (e.g., fed into the nozzle) can have a diameter that varies.

[0028] Methods are known for pre-incorporating a physical or chemical blowing agent into a thermoplastic material, then forming the thermoplastic material into a desired shape. For example, a physical or chemical blowing agent can be incorporated into a melt of the thermoplastic material, then the melt formed into the desired shape and rapidly cooled, for example using underwater pelletization. This prevents or reduces escape or expansion of the blowing agent in the shaped material. When a chemical blowing agent is used, the temperature of the melt is maintained below the activation temperature of the blowing agent. In other embodiments, the blowing agent can be pre-encapsulated and then added to the thermoplastic material. Pre-encapsulated blowing agents can be added directly to the melt used in the additive manufacturing process, or pre-incorporated into the thermoplastic material.

[0029] Examples of thermoplastic polymers that can be used include polyacetals, polyacrylates, polyacrylics, polyamideimides, polyamides, polyanhydrides, polyaramides, polyarylates, polyarylene ethers (e.g., polyphenylene ethers), polyarylene sulfides (e.g., polyphenylene sulfides), polyarylsulfones, polycarbonates (including polycarbonate copolymers such as polycarbonate-siloxanes, polycarbonate-esters, and polycarbonate-ester-siloxanes), polyesters (e.g., polyethylene terephthalates and polybutylene terephthalates), polyetheretherketones, polyetherimides (including copolymers such as polyetherimide-siloxane copolymers), polyetherketoneketones, polyetherketones, polyethersulfones, polyimides (including copolymers such as polyimide-siloxane copolymers), polyolefins (e.g., polyethylenes, polypropylenes, polytetrafluoroethylenes, and their copolymers), polyphthalides, polysilazanes, polysiloxanes, polystyrenes (including copolymers such as acrylonitrile-butadiene-styrene (ABS) and methyl methacrylate-butadiene-styrene (MBS)), polysulfides, polysulfonamides, polysulfonates, polysulfones, polythioesters, polytriazines, polyureas, polyvinyl alcohols, polyvinyl esters, polyvinyl ethers, polyvinyl halides, polyvinyl ketones, polyvinylidene fluorides, silicones, or the like, or a combination comprising at least one of the foregoing thermoplastic polymers. In some embodiments, polyacetals, polyamides (nylons), polycarbonates, polyesters, polyetherimides, polyolefins, and polystyrene copolymers such as ABS, are especially useful in a wide variety of articles, have good processability, and are recyclable.

[0030] In some embodiments, the thermoplastic elastomer is a polycarbonate (including homopolymers and copolymers that include carbonate units, elastomer-modified graft copolymer, polyester, polyolefin, polyetherimide, polyetherimide sulfone, polyphenylene sulfide, polysulfone, polyketone, polyphenylene ether, polystyrene, polyacrylate ester, polymethacrylate ester, or a combination comprising at least one of the foregoing.

[0031] Exemplary polycarbonates are described, for example, in WO 2013/175448 A1, US 2014/0295363, and WO 2014/072923. Polycarbonates are generally manufactured from bisphenol compounds such as 2,2-bis(4-hydroxyphenyl) propane (“bisphenol-A” or “BPA”), 3,3-bis(4-hydroxyphenyl) phthalimidine, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane, or 1,1-bis(4-hydroxy-3-methylphenyl)-3,3,5-trimethylcyclohexane, or a combination comprising at least one of the foregoing bisphenol compounds can also be used. In a specific embodiment, the polycarbonate is a homopolymer derived from BPA or a copolymer derived from BPA and another bisphenol or dihydroxy aromatic compound such as resorcinol. Other polycarbonate copolymers include poly(aliphatic ester-carbonate) poly(siloxane-carbonate), and polycarbonate-ester-siloxanes),

[0032] Specific elastomer-modified graft copolymers include those formed from styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), styrene-ethylene-butadiene-styrene (SEBS), ABS (acrylonitrile-butadiene-styrene), acrylonitrile-ethylene-propylene-diene-styrene (AES), styrene-isoprene-styrene (SIS), methyl methacrylate-butadiene-styrene (MBS), and styrene-acrylonitrile (SAN). In some embodiments the elastomer-modified graft copolymers include acrylonitrile butadiene styrene (ABS).

[0033] The thermoplastic material can include various additives ordinarily incorporated into polymer compositions of this type, with the proviso that any additives is selected so as to not significantly adversely affect the desired properties of the thermoplastic composition, in particular the melt flow index. Such additives can be mixed at a suitable time during the mixing of the components for forming the composition. Additives include nucleating agents, fillers, reinforcing agents, antioxidants, heat stabilizers, light stabilizers, ultraviolet (UV) light stabilizers, plasticizers, lubricants, mold release agents, surfactants, antistatic agents, colorants such as titanium dioxide, carbon black, and organic dyes, surface effect additives, radiation stabilizers, flame retardants, and anti-drip agents. A combination of additives can be used, for example a combination of a heat stabilizer and ultraviolet light stabilizer. In general, the additives are used in the amounts generally known to be effective. For example, the total amount of the additives (other than any impact modifier, filler, or reinforcing agents) can be 0.01 to 5 wt.%, based on the total weight of the thermoplastic material.

[0034] In some embodiments, the expandable thermoplastic material can be used in conjunction with non-expandable thermoplastic materials in an additive manufacturing process. Thus, at least one expandable layer can be formed and the layer expanded; and at least one non-expandable layer can be deposited on the expanded layer. Alternatively, a non-expandable layer can be formed; and at least one expandable layer can be formed on the expandable layer. Each of the layers can be fused before, during, or after deposition or expansion.

[0035] In still other embodiments an expandable and non-expandable material can be co-deposited to form the expandable layer and the non-expandable layer essentially simultaneously. For example, the expandable material and the non-expandable material can be formed as side-by-side filaments, or co-axially. In co-axial formation, an exterior of a filament can include a non-expandable material and an interior of the filament can include an expandable material. Alternatively, an exterior of a filament can include an expandable material and an interior of the filament can include a non-expandable material. Expansion of the expandable materials ensures good physical contact of each filament.

[0036] In other embodiments, an exterior shell (or other component) can be formed from non-expandable thermoplastic materials and then used as a substrate for the additive manufacturing process. In other embodiments, a non-expandable shell can be partially or completely filled by forming a core at least in part by additive manufacturing as described herein. The core accordingly includes at least one layer of the expandable thermoplastic material. It is also contemplated that the core of an article can be formed first by additive manufacturing as described herein, and a nonexpandable exterior shell (or other component) can then be formed or attached. The nonexpendable exterior shell or other component can also be formed by additive manufacturing, for example using material extrusion methods.

[0037] Once formed, in some embodiments a surface of the article, in particular an expanded thermoplastic layer, can be shaped, smoothed, or otherwise manipulated using a heated tool such as a knife, paddle, or molding tool. The surface can be an intermediate layer or a final layer. In other embodiments, a surface of the article, in particular an expanded thermoplastic layer, can be smoothed or manipulated by applying a solvent for the layer or a varnish. Application of the solvent or the varnish can occur by dipping, spraying, brushing, or other appropriate method. Varnish, as used herein, describes a polymer precursor or combination of polymer precursors that can be applied and then polymerized.

[0038] Use of a combination of expandable and non-expandable materials allows for the use of different materials having different properties, for example different stiffnesses, different wear, different impact, colors, and the like, based on a desired application. For example, the exterior can be formed from a solvent resistant thermoplastic material while the interior can be formed from a less solvent resistant (and less expensive) thermoplastic material. As another example, the combination of materials can be chosen to achieve a desired tactile experience such as “soft touch” or “warm touch.” A non-expandable material can be used as an interior component to achieve desired physical properties in the final article. For example, one or more non-expandable layers can be used to provide structural support in combination with the at least one expanded layer. The interior non-expandable material can be manufactured by additive manufacturing.

[0039] The present invention is further illustrated by the following Embodiments.

[0040] Embodiment 1. A method of making an article, the method comprising forming a plurality of layers of a material in a preset pattern, wherein at least one of the formed layers is an expandable layer that increases in volume during or prior to forming the next layer on the expandable layer; and fusing the plurality of formed layers to provide the article.

[0041] Embodiment 2. The method of Embodiment 1, comprising simultaneously forming and increasing volume of the expandable layer.

[0042] Embodiment 3. The method of Embodiment 1, comprising forming the expandable layer, then increasing volume of the expandable layer.

[0043] Embodiment 4. The method of any of Embodiment 1 to 3, further comprising forming a non-expandable layer on the increased volume layer.

[0044] Embodiment 5. The method of method of Embodiment 4, comprising forming an expandable layer and a non-expandable layer simultaneously.

[0045] Embodiment 6. The method of any of the preceding Embodiments, comprising forming at least one of the plurality of layers in an exterior shell.

[0046] Embodiment 7. The method of Embodiment 6, wherein the exterior shell and the expandable material each comprise different materials.

[0047] Embodiment 8. The method of any of the preceding Embodiments, further comprising applying a solvent or a varnish to an exterior surface of a layer of the article.

[0048] Embodiment 9. The method of any of the preceding Embodiments, wherein the plurality of layers comprises at least twenty layers.

[0049] Embodiment 10. The method of any of the preceding Embodiments, wherein the expandable layer comprises a blowing agent.

[0050] Embodiment 11. The method of any of the preceding Embodiments, wherein forming the expandable layer comprises depositing a flowable expandable material.

[0051] Embodiment 12. The method of any of the preceding Embodiments, wherein forming the expandable layer comprises melt-extruding a thermoplastic material.

[0052] Embodiment 13. The method of Embodiment 12, further comprising manipulating a surface of an expandable layer comprising the thermoplastic material with a heated tool.

[0053] Embodiment 14. The method of any of Embodiments 1 to 13, wherein the forming of a plurality of layers comprises forming a plurality of layers comprising the build material and forming a plurality of layers comprising a support material.

[0054] Embodiment 15. The method of Embodiment 14 wherein the support material, build material or both comprises the expandable layer.

[0055] Embodiment 16. An article made by any of the methods of the preceding claims.

[0056] Embodiment 17. An article comprising a plurality of fused layers, wherein at least one of the layers is an expanded layer and wherein the article comprises at least 20 layers.

[0057] Embodiment 18. The article of Embodiment 17, wherein the article comprises a build structure and a support structure, and at least one of the layers of the support material making up the support structure is an expanded layer.

[0058] Embodiment 19. The article of Embodiment 18, wherein the support structure comprises a cross-section effective to provide the support structure with a breakability greater than the breakability of the build structure.

[0059] Embodiment 20. The article of Embodiment 19, wherein the cross-section of the support structure is a non-round shape.

[0060] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “less than or equal to 25 wt%, or 5 wt% to 20 wt%,” is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. The suffix “(s)” is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0061] This application claims priority to U.S. Provisional Application No. 62/183,343, filed on June 23, 2015, the entire disclosure of which is incorporated herein by reference.

[0062] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0063] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

[0064] What is claimed is:

CLAIMS

1. A method of making an article, the method comprising

forming a plurality of layers of a material in a preset pattern, wherein at least one of the formed layers is an expandable layer that increases in volume during or prior to forming the next layer on the expandable layer; and

fusing the plurality of formed layers to provide the article.

2. The method of Claim 1, comprising simultaneously forming and increasing volume of the expandable layer.

3. The method of Claim 1, comprising forming the expandable layer, then increasing volume of the expandable layer.

4. The method of any of Claims 1 to 3, further comprising forming a non-expandable layer on the increased volume layer.

5. The method of method of Claim 4, comprising forming anexpandable layer and a non-expandable layer simultaneously.

6. The method of any of the preceding claims, comprising forming at least one of the plurality of layers in an exterior shell.

7. The method of Claim 6, wherein the exterior shell and the expandable material each comprise different materials.

8. The method of any of the preceding claims, further comprising applying a solvent or a varnish to an exterior surface of a layer of the article.

9. The method of any of the preceding claims, wherein the plurality of layers comprises at least twenty layers.

10. The method of any of the preceding claims, wherein the expandable layer comprises a blowing agent.

11. The method of any of the preceding claims, wherein forming the expandable layer comprises depositing a flowable expandable material.

12. The method of any of the preceding claims, wherein forming the expandable layer comprises melt-extruding a thermoplastic material.

13. The method of Claim 12, further comprising manipulating a surface of an expandable layer comprising the thermoplastic material with a heated tool.

14. The method of any of Claims 1 to 13, wherein the forming of a plurality of layers comprises forming a plurality of layers comprising the build material and forming a plurality of layers comprising a support material.

15. The method of Claim 14, wherein the support material, build material or both comprises the expandable layer.

16. An article made by any of the methods of the preceding claims.

17. An article comprising

a plurality of fused layers, wherein at least one of the layers is an expanded layer and wherein the article comprises at least 20 layers.

18. The article of Claim 17, wherein the article comprises a build structure and a support structure, and at least one of the layers of the support material making up the support structure is an expanded layer.

19. The article of Claim 18, wherein the support structure comprises a cross-section effective to provide the support structure with a breakability greater than the breakability of the build structure.

20. The article of Claim 19, wherein the cross-section of the support structure is a non-round shape.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/038633

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C67/00 B33Y70/00 B33Y10/00 B29C44/56 B32B5/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C B33Y B32B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 494 484 A (2K MFG LTD [GB]) 13 March 2013 (2013-03-13) page 12, line 23 - page 14, line 7	1-7,10, 11,14-20
X	JP H06 226869 A (NISSAN MOTOR) 16 August 1994 (1994-08-16) abstract; figures paragraphs [0014] - [0015], [0050]	1,2, 9-12, 14-20
X	US 2007/184258 A1 (STOCKHEIM UWE [DE]) 9 August 2007 (2007-08-09) paragraphs [0027], [0028], [0031]; claim 2	1-3, 10-12, 14-16

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 September 2016	12/10/2016

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 695 908 A2 (YETOO CO LTD [KR]; CLIFE CO LTD [KR]) 12 February 2014 (2014-02-12) paragraphs [0069], [0070], [0074] - [0076], [0080]; figures -----	1,2,4, 6-8,10, 11,15,16

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/038633

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			JP	5727089	B2	03-06-2015
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			US	2014030457	A1	30-01-2014
			WO	2012138081	A2	11-10-2012