Systems and methods in accordance with embodiments of the invention fabricate objects including amorphous metals using techniques akin to additive manufacturing. In one embodiment, a method of fabricating an object that includes an amorphous metal includes: applying a first layer of molten metallic alloy to a surface; cooling the first layer of molten metallic alloy such that it solidifies and thereby forms a first layer including amorphous metal; subsequently applying at least one layer of molten metallic alloy onto a layer including amorphous metal; cooling each subsequently applied layer of molten metallic alloy such that it solidifies and thereby forms a layer including amorphous metal prior to the application of any adjacent layer of molten metallic alloy; where the aggregate of the solidified layers including amorphous metal forms a desired shape in the object to be fabricated; and removing at least the first layer including amorphous metal from the surface.
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Start

100

Apply first layer of molten metallic alloy to a surface

102

Cool first layer of molten metallic layer so as to form first layer including amorphous metal

104

Apply layer of molten metallic alloy onto a layer including amorphous metal

106

Cool applied layer of molten metallic alloy so that it forms layer including amorphous metal

108

Remove at least the first layer including amorphous metal

112

End

Repeat as desired until desired shape is formed

110

FIG. 1
Relationship between cooling rate and properties for Metallic Glasses

Cooling Rate (K/s)

Shear Modulus (arbitrary)

Arc Melting

Metal Mold Casting

Ribbon or Splat Quenching

Thermal Spraying

Atomic Deposition

Increasing Toughness

FIG. 2
Each layer has \( G = Z \) and \( Z \ll X < Y \).
Apply first layer of molten metallic alloy to a surface

Cool first layer of molten metallic alloy so as to form first layer including amorphous metal

Apply layer of molten metallic alloy onto a layer including amorphous metal

Cool applied layer of molten metallic alloy so that it forms layer including amorphous metal

Repeat as desired until desired shape is formed

End

FIG. 22
SYSTEMS AND METHODS FOR FABRICATING OBJECTS INCLUDING AMORPHOUS METAL USING TECHNIQUES AKIN TO ADDITIVE MANUFACTURING

CROSS-REFERENCE TO RELATED APPLICATIONS

The current application claims priority to U.S. Provisional Application No. 61/756,157, filed Jan. 24, 2013, the disclosure of which is incorporated herein by reference.

STATEMENT OF FEDERAL FUNDING

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. §202) in which the Contractor has elected to retain title.

FIELD OF THE INVENTION

The present invention generally regards techniques for fabricating objects including amorphous metal.

BACKGROUND

Metallic glasses, also known as amorphous metals, have generated much interest for their potential as robust engineering materials. Metallic glasses are characterized by their disordered atomic-scale structure in spite of their metallic constituent elements—i.e., whereas conventional metallic materials typically possess a highly ordered atomic structure, metallic glasses are characterized by their disordered atomic structure. Notably, metallic glasses typically possess a number of useful material properties that can allow them to be implemented as highly effective engineering materials. For example, metallic glasses are generally much harder than conventional metals, and are generally tougher than ceramic materials. They are also relatively corrosion resistant, and, unlike conventional glass, they can have good electrical conductivity.

Nonetheless, the manufacture and implementation of metallic glasses present challenges that limit their viability as engineering materials. In particular, metallic glasses are typically formed by raising a metallic glass above its melting temperature, and rapidly cooling the melt to solidify it in a way such that its crystallization is avoided, thereby forming the metallic glass. The first metallic glasses required extraordinary cooling rates, e.g. on the order of $10^6$ K/s, to avoid crystallization, and were thereby limited in the thickness with which they could be formed because thicker parts could not be cooled as quickly. Indeed, because of this limitation in thickness, metallic glasses were initially largely limited to applications that involved coatings. Since then, however, metallic glass compositions that have lower critical cooling rates have been developed, which can thereby form metallic glasses at much lower cooling rates, and can therefore be made to be much thicker (e.g. greater than 1 mm), for example via die casting. These thicker metallic glasses are known as ‘bulk metallic glasses’ (‘BMGs’).

SUMMARY OF THE INVENTION

Systems and methods in accordance with embodiments of the invention fabricate objects including amorphous metals using techniques akin to additive manufacturing. In one embodiment, a method of fabricating an object that includes an amorphous metal includes: applying a first layer of molten metallic alloy to a surface; cooling the first layer of molten metallic alloy such that it solidifies and thereby forms a first layer including amorphous metal; subsequently applying at least one layer of molten metallic alloy onto a layer including amorphous metal; cooling each subsequently applied layer of molten metallic alloy such that it solidifies and thereby forms a layer including amorphous metal prior to the application of any adjacent layer of molten metallic alloy; where the aggregate of the solidified layers including amorphous metal forms a desired shape in the object to be fabricated; and removing at least the first layer including amorphous metal from the surface.

In another embodiment, a plurality of layers including amorphous metal is removed from the surface.

In yet another embodiment, all of the applied layers of molten metallic alloy that have solidified into layers including amorphous metal are removed from the surface.

In still another embodiment, at least one layer of molten metallic alloy is applied using a spraying technique.

In still yet another embodiment, at least one layer of molten metallic alloy is applied using a thermal spraying technique.

In a further embodiment, at least one layer of molten metallic alloy is applied using a technique that is one of: high velocity oxy-fuel spraying, plasma spraying, wire arc spraying, and mixtures thereof.

In a yet further embodiment, the feedstock for the spraying technique uses feedstock that is one of: wire, powder, a molten pool of the metallic alloy composition being applied, a molten pool of the constituent elements of the metallic alloy composition being applied, and mixtures thereof.

In still further embodiment, the spraying technique utilizes a computer-controlled apparatus.

In a still yet further embodiment, multiple spraying apparatuses are used to apply layers of molten metallic alloy.

In another embodiment, at least one layer of molten metallic alloy has a composition that has a critical casting thickness of greater than approximately 1 mm.

In yet another embodiment, at least one layer of molten metallic alloy has a composition that has a critical casting thickness of less than approximately 100 µm.

In still another embodiment, at least one layer of applied molten metallic alloy has a different composition than at least one other layer of applied molten metallic alloy.

In still yet another embodiment, at least one layer of applied molten metallic alloy has a thickness of between approximately 10 nanometers and approximately 100 micrometers.

In a further embodiment, at least one layer of molten metallic alloy includes a composition that is one of: a zirconium based composition, a nickel based composition, a palladium based composition, an iron based composition, a platinum based composition, a gold based composition, a copper based composition, a tungsten based composition, a niobium based composition, a hafnium based composition, an aluminum based composition, a composition that includes at least 50% (atomic) of a mixture of Zr—Ti—Be, a composition that includes at least 50% (atomic) of a mixture of Zr—Be, a composition that includes at least 50% (atomic) of a mixture of Cu—Zr, a composition that includes at least 50% (atomic) of a mixture of Cu—Zr—Al, a composition that includes at least 50% (atomic) of a mixture of Fe—Ni, a composition that includes at least 50% (atomic) of a mixture of Ni—P, a composition that includes at least 50% (atomic) of a mixture of Fe—Ni—B, a composition that includes at least 50%
(atomic) of a mixture of Fe—P, a composition that includes at least 50% (atomic) of a mixture of Pd—P, a composition that includes at least 50% (atomic) of a mixture of Cu—P, a composition that includes at least 50% (atomic) of a mixture of Al—Y, and a composition that includes at least 50% (atomic) of a mixture of Ni—Nb.

In a yet further embodiment, the layers of molten metallic alloy are cooled such that the fabricated object includes 25% amorphous metal by volume.

In a still further embodiment, the layers of molten metallic alloy are cooled such that the shear modulus of the fabricated object is at least approximately 5% lower than it would be of the part had been fabricated using a casting technique.

In a still yet further embodiment, the layers of molten metallic alloy are cooled such that the fracture toughness of the fabricated object is at least approximately 10% higher than if the object were fabricating using a casting technique.

In another embodiment, the surface is one of: a flat surface, a curved surface, and a surface having a periodic cellular structure.

In yet another embodiment, the surface has axial symmetry and the layer of molten metallic alloy is applied to the surface while it is being rotated about its axis of symmetry.

In still another embodiment, the surface includes one of: metal, carbide, graphite, ceramic, glass, plastic, and mixtures thereof.

In still yet another embodiment, the surface includes a coating of graphite powder.

In a further embodiment, the solidified layers including amorphous metal are removed from the surface by one of: mechanically removing the solidified layers including amorphous metal from the surface, dissolving the surface, melting the surface, and mixtures thereof.

In a yet further embodiment, the fabricated object has a thickness of between approximately 0.1 mm and approximately 25 mm.

In a still further embodiment, the fabricated object has a thickness that is greater than the critical casting thickness of any of the compositions of the applied layers of molten metallic alloy.

In a still yet further embodiment, the fabricated object is sheet metal.

In another embodiment, the sheet metal has a thickness of between approximately 0.1 mm and approximately 2 mm.

In yet another embodiment, the method further includes subjecting the solidified layers including amorphous metal to one of: a rolling process; an embossing process; a stamping process; a heating process; a chemical etching process; and mixtures thereof.

In still another embodiment, the solidified layers including amorphous metal are subjected to a rolling process that removes undesired imperfections in the solidified layers including amorphous metal.

In still yet another embodiment: an additional surface is used to define the shape of the fabricated object; the fabricated object has extrusion symmetry; and the fabricated object is removed from the additional surface using a pressing technique.

In a further embodiment, a method of fabricating an object that includes an amorphous metal includes: applying a first layer of molten metallic alloy to a surface; cooling the first layer of molten metallic alloy such that it solidifies and thereby forms a first layer including amorphous metal; subsequently applying at least one layer of molten metallic alloy onto a layer including amorphous metal; and cooling each subsequently applied layer of molten metallic alloy such that it solidifies and thereby forms a layer including amorphous metal prior to the application of any adjacent layer of molten metallic alloy; where at least two applied layers of molten metallic alloy are not coextensive in shape; and where the aggregate of the solidified layers including amorphous metal forms a desired shape in the object to be fabricated.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a process for fabricating an object that includes amorphous metal in accordance with embodiments of the invention.

FIG. 2 illustrates a chart comparing the impact of various techniques for forming amorphous metal.

FIGS. 3A-3C illustrate how a spray nozzle may be incorporated in the fabrication of an object including amorphous metal to control the application of layers of molten metallic alloy in accordance with embodiments of the invention.

FIG. 4 illustrates using a cooling jet to facilitate the cooling of molten metallic alloy in accordance with embodiments of the invention.

FIGS. 5A-5B illustrate the implementation of a coating layer that facilitates the removal of a formed object from the surface upon which it was formed in accordance with embodiments of the invention.

FIGS. 6A-6C illustrate fabricating an object that includes amorphous metal in accordance with embodiments of the invention.

FIGS. 7A-7C illustrate fabricating an object that includes amorphous metal in accordance with embodiments of the invention.

FIGS. 8A-8C illustrate using a supporting structure in forming an object including amorphous metal in accordance with embodiments of the invention.

FIGS. 9A-9D illustrate the beneficial impact of fabrication processes in accordance with embodiments of the invention.

FIGS. 10A-10C illustrate the fabrication of an object including amorphous metal using a curved surface in accordance with embodiments of the invention.

FIGS. 11A-11B illustrate the fabrication of an object including amorphous metal using a surface having a periodic cellular structure in accordance with embodiments of the invention.

FIGS. 12A-12C illustrate fabricating an object including amorphous metal using a surface including a mold cavity in accordance with embodiments of the invention.

FIGS. 13A-13C illustrate fabricating an object having extrusion symmetry and removing the object from an adjacent surface using a pressing technique in accordance with embodiments of the invention.

FIG. 14 illustrates fabricating a plurality of objects using a plurality of additional surfaces that can define the shape of the formed object in accordance with embodiments of the invention.

FIGS. 15A-15B illustrate moving a surface relative to a fixed spraying apparatus in fabricating an object including amorphous metal in accordance with embodiments of the invention.

FIGS. 16A-16D illustrate the fabrication of a tube-like structure using a rotating cylindrical surface in accordance with embodiments of the invention.

FIGS. 17A-17C illustrate incorporating multiple spraying apparatuses and/or cooling jets in fabricating objects in accordance with embodiments of the invention.
Anelastic to Plastic Transition in Metallic Glass - Forming
increasing the cooling rate used in the formation of the
to the fabrication of an object in accordance
with embodiments of the invention.
FIG. 20 illustrates using heating elements in conjunction
with a press in the fabrication of an object in accordance
with embodiments of the invention.
FIG. 21A-21C illustrate using a computer numerically
controlled milling machine in fabricating an object in accord-
ance with embodiments of the invention.
FIG. 22 illustrates fabricating an object including amor-
phous metal onto a surface in accordance with embodiments
of the invention.

DETAILED DESCRIPTION

Turning now to the drawings, systems and methods for
fabricating objects including amorphous metal are illus-
trated. In many embodiments, a method of fabricating an
object that includes amorphous metal involves applying
successive layers of molten metallic alloy into the shape of
an object to be formed, allowing each applied layer to
solidify into a layer including amorphous metal prior to the
application of a subsequent adjacent layer of molten metallic
alloy. In numerous embodiments, cooling mechanisms are
used to facilitate the cooling of the molten metallic layers so
that they form amorphous metal. In a number of embodi-
ments molten metallic alloy is sprayed into mold cavities
which help define the shape of the object to be formed.

While amorphous metal compositions have been discov-
ered that can allow the alloys to be cast into parts having a
thickness greater than 1 mm (bulk metallic glasses), casting
these particular compositions generally cannot be used to
create an arbitrarily thick object. Instead, the geometries of
cast objects are generally limited by the composition’s
critical cooling rate, i.e. the cooling rate above which the
melt must be cooled in order for it to form amorphous metal.
As can be appreciated, thicker geometries have lower cool-
ing rates. Accordingly, the geometries of cast bulk metallic
glass objects are generally limited to several centimeters
based upon the particular metallic alloy’s critical cooling
rate. The maximum thickness that a given metallic alloy
composition can be cast using conventional casting tech-
niques and still form amorphous metal across its width is
known as the critical casting thickness.

Importantly, the toughness of the cast amorphous metal is
also a function of the cooling rate by which it was formed.
Demetriou et al. demonstrate this phenomenon in Applied
Physics Letters 95, 041907 (2009), “Glassy steel optimized
for glass-forming ability and toughness.” The disclosure of
Applied Physics Letters 95, 041907 (2009) is hereby incor-
porated by reference. In general, Demetriou et al. demon-
strate that the toughness of a cast part will tend to linearly
decrease as a function of its thickness.

Harmon et al. explain the underlying mechanisms for this
“Anelastic to Plastic Transition in Metallic Glass-Forming
 Liquids”; generally, Harmon et al. explain that the toughness
of an amorphous metal is related to its internal energy, and
increasing the cooling rate used in the formation of the
amorphous metal can increase its internal energy. Thus, as
thicker castings have lower cooling rates, parts that are cast
thicker will tend to have a correspondingly lower toughness.
And it follows that increasing the cooling rate in forming an
amorphous metal can increase its toughness. By extension,
the fracture toughness can also increase with an increased
cooling rate. Note also that when parts are cast, the cooling
rate of the casting can vary throughout the casting (e.g. the
cooling rate in the middle of the casting can be noticeably
lower than that at the surface of the casting) and thereby
cause the toughness to vary throughout the casting. In many
instances, this can be an undesirable outcome.

Bear in mind that the toughness of a material can corre-
spond with any of a variety of its material properties. For
example, that the toughness is correlated with its shear
modulus is touched on in Garret et al., in Applied Physics
toughness of metallic glasses.” The disclosure of Applied
Physics Letters 101, 241913 (2012) is hereby incorpo-
rated by reference. Generally, lower shear moduli correspond
with higher toughness values.

Thus, in many embodiments, manufacturing techniques
that resemble additive manufacturing techniques are imple-
mented that can allow the fabrication of an object that
includes amorphous metal and is not limited by a critical
casting thickness. Moreover, these fabrication techniques

Processes for Fabricating Objects Including Amorphous
Metal Using Techniques Akin to Additive Manufacturing

In many embodiments, a method of fabricating an object
that includes amorphous metal involves applying successive
layers of molten metallic alloy into the shape of an object to
be formed, allowing each applied layer to solidify into a
layer including amorphous metal prior to the application of
a subsequent adjacent layer of molten metallic alloy. In
many embodiments the layers of molten metallic alloy are
applied using a spraying technique. In a number of embodi-
ments, a distinct cooling mechanism is used to facilitate
the cooling of the applied layers of molten metallic alloy.
In several embodiments, the layers are sprayed onto a surface,
and subsequently removed from the surface in aggregate. In
some embodiments, the surface is configured to facilitate the
removal of layers including amorphous metal from it.

FIG. 1 illustrates a process for fabricating an object that
includes amorphous metal by applying successive layers
of molten metallic alloy onto a surface, and subsequently
removing the solidified layers that include amorphous metal
in accordance with embodiments of the invention. In par-

In particular, the process 100 includes applying 102 a first layer
of molten metallic alloy to a surface. The layer of molten
metallic alloy can be applied using any suitable technique,
including via thermal spraying. The layers can be of any
appropriate thickness. In many embodiments, the applied
layers have a thickness of between approximately 10 nm and
approximately 100 μm. Of course, the layers can be applied
in any suitable thickness. Moreover, the layer can be applied
using a computer-controlled apparatus. In this way, the layer
can be applied in a precise and/or accurate pattern. Further,
in many embodiments, a layer of molten metallic alloy is
applied under conditions designed to reduce occurrences of
unwanted oxidation. Note that metallic alloy compositions
that include titanium and/or zirconium may be particularly susceptible to unwanted oxidation. Thus, in some embodiments, a layer of molten metallic alloy is applied in at least a partial vacuum. In many embodiments, layers of molten metallic alloy are applied in an atmosphere of inert gas. In this way, the chances of unwanted oxidation can be reduced.

Note that any molten metallic alloy that is capable of forming amorphous metal may be used. For example, in many embodiments, the molten metallic alloy has a composition based on one of: zirconium, titanium, nickel, cobalt, iron, palladium, platinum, gold, copper, tungsten, niobium, hafnium, aluminum, and mixtures thereof. The term ‘based on’ can be understood as follows: when a composition is ‘based on’ an element, that element is the most abundant within the given composition. In a number of embodiments, the molten metallic alloy composition includes at least 50% (atomic) of one of the following combinations: Zr—Ti—Be, Zr—Be, Cu—Zr, Cu—Zr—Al, Fe—Ni, Ni—P, Fe—Ni—B, Fe—P, Pd—P, Cu—P, Al—Y, and Ni—Nb (note that the relative atomic ratios of the elements are not listed—they can be present in any relative amount in accordance with embodiments of the invention). Although several examples are given, it should be clear that any suitable metallic alloy composition that can be made to form an amorphous metal can be used in accordance with embodiments of the invention. Note that the metallic alloy compositions that are used do not have to be bulk metallic glass compositions because the techniques described herein largely rely on cooling thinly deposited layers of molten metallic alloys—thinly formed geometries cool much more rapidly than thick ones, and can thereby form amorphous metal much more easily. In other words, the metallic alloys used do not have to have relatively high critical cooling rates. As a result, whereas conventional techniques (e.g. casting) for forming relatively large objects were largely limited to implementing bulk metallic glass compositions, the techniques described herein are generally not so limited.

FIG. 2 depicts how using thermal spraying in forming amorphous metal can allow for a comparatively high cooling rate relative to other processes for forming amorphous metal. From FIG. 2, it is seen that thermal spraying techniques can allow for cooling rates on the order of 10⁹ K/s. As discussed above and illustrated in FIG. 2, the high cooling rate can result in a relatively lower shear modulus, which is indicative of increased toughness. Note that thermal spraying techniques are further advantageous insofar as they can be used to create objects having a broad range of thicknesses in accordance with the techniques described herein. By contrast: arc melting and metal mold casting are typically limited to creating objects having thicknesses on the order of a several nanometers.

Accordingly, in many embodiments, thermal spraying techniques are utilized to apply layers of molten metallic alloy. Any suitable spraying technique can be incorporated in accordance with embodiments of the invention. In many embodiments, spraying techniques that involve heating, atomizing, and spraying are used. Generally, spraying techniques involve melting a feedstock metallic alloy composition, and thereafter spraying the melt onto an applied surface. The feedstock can be in the form of wire or it can be in the form of powder, for instance. In some embodiments, the feedstock is a molten pool of the final desired composition for the applied molten metallic alloy; or a molten pool of individual elements that make up the molten metallic alloy.

TABLE 1

<table>
<thead>
<tr>
<th>Thermal Spray Techniques and Characteristics</th>
<th>Gas Flow (m³/h)</th>
<th>Flame or exit plasma temperature (°C)</th>
<th>Particle Impact Velocity (m/s)</th>
<th>Relative Adhesive Strength (a)</th>
<th>Corrosive Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame Wire Powder</td>
<td>11</td>
<td>2200</td>
<td>30</td>
<td>3</td>
<td>Low</td>
</tr>
<tr>
<td>Flame Wire</td>
<td>71</td>
<td>2800</td>
<td>180</td>
<td>4</td>
<td>Medium</td>
</tr>
<tr>
<td>High Velocity Oxy-fuel (HVOF)</td>
<td>28-57</td>
<td>3100</td>
<td>610-1060</td>
<td>8</td>
<td>Very High</td>
</tr>
<tr>
<td>Deformation Gun</td>
<td>11</td>
<td>3900</td>
<td>910</td>
<td>8</td>
<td>Very High</td>
</tr>
<tr>
<td>Wire Arc</td>
<td>71</td>
<td>5500</td>
<td>240</td>
<td>6</td>
<td>High</td>
</tr>
<tr>
<td>Conventional Plasma</td>
<td>4.2</td>
<td>5500</td>
<td>240</td>
<td>6</td>
<td>High</td>
</tr>
<tr>
<td>High-energy Plasma</td>
<td>17-28</td>
<td>8300</td>
<td>240-1220</td>
<td>8</td>
<td>Very High</td>
</tr>
<tr>
<td>Vacuum plasma</td>
<td>8.4</td>
<td>8300</td>
<td>240-610</td>
<td>9</td>
<td>Very High</td>
</tr>
</tbody>
</table>

TABLE 2

<table>
<thead>
<tr>
<th>Thermal Spray Techniques and Characteristics (Continued)</th>
<th>Oxide Content (%)</th>
<th>Relative Process Cost (a)</th>
<th>Maximum Spray Rate (kg/hr)</th>
<th>Power (kW)</th>
<th>Energy Required (kW/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame Powder</td>
<td>6</td>
<td>3</td>
<td>7</td>
<td>25-75</td>
<td>11-22</td>
</tr>
<tr>
<td>Flame Wire</td>
<td>4</td>
<td>3</td>
<td>9</td>
<td>50-100</td>
<td>11-22</td>
</tr>
<tr>
<td>High Velocity Oxy-fuel (HVOF)</td>
<td>0.2</td>
<td>5</td>
<td>14</td>
<td>100-270</td>
<td>22-200</td>
</tr>
<tr>
<td>Deformation Gun</td>
<td>0.1</td>
<td>10</td>
<td>1</td>
<td>100-270</td>
<td>220</td>
</tr>
<tr>
<td>Wire Arc</td>
<td>0.5-3</td>
<td>1</td>
<td>16</td>
<td>4-6</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Conventional Plasma</td>
<td>0.5-1</td>
<td>5</td>
<td>5</td>
<td>30-80</td>
<td>13-22</td>
</tr>
<tr>
<td>High-energy Plasma</td>
<td>0.1</td>
<td>4</td>
<td>23</td>
<td>100-250</td>
<td>9-13</td>
</tr>
<tr>
<td>Vacuum plasma (ppm levels)</td>
<td>10</td>
<td>10</td>
<td>50-100</td>
<td>11-22</td>
<td></td>
</tr>
</tbody>
</table>

The data in table 1 is obtained from Handbook of Thermal Spray Technology (#06994G), "Introduction to Thermal Spray Processing," published by ASM International. The disclosure of Handbook of Thermal Spray Technology (#06994G), "Introduction to Thermal Spray Processing," is incorporated by reference herein. In many embodiments, HVOF is used to apply layers of molten metallic glass, as HVOF techniques can be particularly beneficial in this application. For example, HVOF techniques are capable of delivering molten metallic alloy at relatively high rates; this
can enable objects to be fabricated much more quickly. Although not listed in Tables 1 or 2, cold-spraying techniques may also be used in accordance with embodiments of the invention. Indeed, any suitable spray technique may be used to apply a layer of molten metallic alloy in accordance with embodiments of the invention. More generally, any suitable spray technique for applying a layer of molten metallic alloy may be incorporated.

In many embodiments, where spraying is used to apply layers of molten metallic glass, a spray nozzle is utilized that can adjust the surface area by which the molten metallic alloy is deposited. For example, FIGS. 3A-3C illustrate the adjustment of the nozzle of a spraying mechanism to control the distribution of the molten metallic alloy. In particular, FIG. 3A depicts a nozzle 300 that is spraying molten metallic alloy such that a layer of molten metallic alloy is applied having a baseline surface area. FIG. 3B illustrates that the nozzle 300 has been adjusted to broaden the spraying distribution thereby causing the application of a layer of molten metallic alloy having a relatively larger surface area. Conversely, FIG. 3C illustrates that the nozzle 300 has been adjusted to narrow the spraying distribution thereby causing the application of a layer of molten metallic alloy having a smaller surface area. In other words, FIGS. 3A-3C illustrate that the ‘spot size’ of the spraying can be controlled in accordance with embodiments of the invention. In many embodiments the spot size has a diameter between approximately 1 mm and approximately 100 mm. In this way, the pattern of the layer of the applied molten layer can be better controlled.

Referring back to FIG. 1, the process of fabricating an object 100 further includes cooling 104 the first layer of molten metallic alloy so that it forms a first layer including amorphous metal. Thus, in many embodiments, the first layer of molten metallic alloy is cooled at a rate that is above its critical cooling rate so that it forms a layer including amorphous metal. In many embodiments, the layer solidifies and thereby forms a layer including amorphous metal. In some embodiments, the layer of molten metallic alloy is cooled so that it forms amorphous metal throughout. In a number of embodiments, the only part of the cooled layer forms amorphous metal. In some embodiments, the solidified layer includes 25% by volume of amorphous metal. Although it should be clear that amorphous metal can be present in any amount in accordance with embodiments of the invention. The remainder of the cooled solidified layer can be in any phase—for example it can be in a crystalline phase.

The cooling 104 of the layer can be achieved by any suitable means. In a number of embodiments, the first layer of molten metallic alloy is allowed to cool by conduction. In some embodiments, the first layer of molten metallic alloy is cooled by convection. In several embodiments, the first layer of molten metallic alloy is subjected to an airflow that has a temperature lower than that of the first layer, and thereby cooled. In many embodiments, a separate cooling mechanism is employed to cool 104 the first layer of molten metallic alloy. For example, in some embodiments, cooling jets are implemented. FIG. 4 illustrates the cooling of a molten metallic alloy layer using a cooling jet. In particular, FIG. 4 illustrates a spraying mechanism 402 that is applying a layer of molten metallic alloy 404, and using a cooling jet 406 to facilitate the cooling of the molten metallic alloy layer 404. Using a cooling jet can expedite the cooling of the molten metallic alloy, and can additionally allow the cooling rate of the metallic alloy to be controlled with greater accuracy. Thus, in many embodiments, a cooling rate is imposed onto a molten metallic alloy layer in order to establish a desired toughness value for the resulting layer of amorphous metal. Note that in many embodiments, it is desirable to form an object that does not have a uniform toughness throughout it. Accordingly, in many embodiments, when subsequent layers of molten metallic alloy are applied, they are each not necessarily cooled at the same rate, bearing in mind that the cooling rate of a particular layer can help determine its toughness.

Referring back to FIG. 1, the process for fabricating an object 100 further includes applying 106 a layer of molten metallic alloy onto a layer including amorphous metal. The layer including amorphous metal can be the above-mentioned first layer including amorphous metal. The applying 106 can be achieved using any suitable technique including those discussed above with respect to applying 102 a first layer of molten metallic alloy. Additionally, it should be noted that the layer of molten metallic alloy applied 106 can be of a different composition than a layer previously applied. In this way the object being fabricated can include amorphous metal of a plurality of compositions. The process 100 further includes cooling 108 this applied layer so that it forms a layer including amorphous metal. In many embodiments, the layer solidifies and thereby forms a layer including amorphous metal. As before, the amorphous metal can be present in any suitable amount in accordance with embodiments of the invention. Again, any suitable cooling technique may be implemented including any of the previously mentioned cooling methods discussed above with respect to cooling 108 the first layer of molten metallic alloy. Also, as mentioned previously, subsequently applied layers of molten metallic alloy do not have to be cooled at the same cooling rate. The application 106 and cooling 108 of layers of molten metallic alloy is repeated 110 so as to form a desired shape. For instance, the layers can be deposited in particular patterns so as to form the desired shape. In other words, the applied layers can be thought of as cross-sections of the desired shape (within tolerance). In many embodiments, the layers are deposited so as to form substantially the desired shape; to the extent that the formed layers including amorphous metal deviate from the desired shape, they can be post-processed to remove any undesired imperfections. As can be appreciated, these iterative processes resemble conventional additive manufacturing techniques. Accordingly, techniques that are conventionally used in additive manufacturing may be incorporated in accordance with embodiments of the invention. Thus, for example, where a spraying mechanism is used in applying a layer of molten metallic alloy, the spraying mechanism can be moved relative to the surface (and any previously deposited and cooled layers) so as to control the shape of the deposited layer. In some embodiments, the direction of the spraying is controlled so as to form the shape of the layer to be deposited. Also, as can be appreciated, where a spray nozzle that can control the spraying distribution of the molten metallic alloy is used, this too can help control the shape of the deposited layer. In this way, the shape of the object can be controlled and made to develop as desired. Additionally, supporting structures may be deposited in conjunction with molten metallic layers to facilitate the development of a desired shape. The solidified layers can later be removed from any supporting structures. Of course, any of a variety of techniques conventionally used in additive manufacturing may be implemented in accordance with embodiments of the invention.

The process for fabricating an object 100 further includes removing 112 at least the first solidified layer including amorphous metal. In a number of embodiments, a plurality
of solidified layers including amorphous metal is removed. In many embodiments, all of the solidified layers including amorphous metal that were applied as molten metallic alloy and cooled are removed from the surface. Any suitable technique for removing the layers can be used. For example, in many embodiments solidified layers are removed mechanically (e.g., by excising) from the surface. In a number of embodiments, the surface is made to dissolve, and solidified layers are thereby removed from the surface. In a number of embodiments, the surface is melted and solidified layers are thereby removed from it. As can be appreciated, any suitable technique for removing layers including amorphous metal from the surface can be implemented.

In many embodiments, a surface is used that is configured to facilitate the removal of solidified layers including amorphous metal. For example, in many embodiments, the surface includes a ‘non-stick coating’ that is a layer that does not adhere well to layers including amorphous metal. For example, in many embodiments, the surface includes graphite powder that can promote the removal of layers including amorphous metal. FIGS. 5A and 5B illustrate the inclusion of a layer that is meant to facilitate the removal of layers including amorphous metal from the surface. In particular, FIG. 5A illustrates the application of molten metallic alloy onto a surface including a ‘non-stick coating’ 502, and FIG. 5B illustrates how the non-stick coating 502 facilitates the removal of the solidified layers. Of course, it should be understood that the surface can incorporate any of a variety of materials that facilitate the removal of layers including amorphous metal, and not just graphite powder, in accordance with embodiments of the invention.

In many embodiments, the surface inherently weakly adheres to the layers including amorphous metal, and thereby facilitates the removal of solidified layers including amorphous metal from it. For example, in many embodiments, the surface constitutes copper which is known to have poor adhesion. It should of course be understood that any of a variety of materials inherently having poor adhesive properties can be used that promote the removal of the aggregate of solidified layers in accordance with embodiments of the invention. In many embodiments, the surface includes one of: metal, carbide, graphite, ceramic, glass, plastic, and mixtures thereof. More generally, any suitable techniques can be implemented that promote the removal of layers including amorphous metal from the surface can be implemented.

FIGS. 6A-6C illustrate the fabrication of an object according to the process described in FIG. 1 in accordance with embodiments of the invention. In particular, FIG. 6A illustrates the application of a first layer of molten metallic alloy 604 to a surface (not shown) using a spraying apparatus 602. The spraying apparatus 602 is shown as moving relative to the surface in applying the layer 604. In this way, the layer 604 can be applied in a desired pattern. FIG. 6B illustrates that an object having a desired shape 608 has been developed from the applied layers of molten metallic alloy. In the illustrated embodiment, the object 608 is in the shape of a rectangular prism. FIG. 6C illustrates the removal of the object 608 including amorphous metal from the surface from the surface 600. In this way, an object including amorphous metal is removed.

FIGS. 7A-7C illustrate the fabrication of an object having more nuanced features according to the process illustrated in FIG. 1 in accordance with embodiments of the invention. FIG. 7A illustrates the application of a first layer of molten metallic alloy 704 to a surface (not shown). Again, the spraying apparatus 702 is shown as moving relative to the surface in applying the layer 704. FIG. 7B illustrates that the desired object 708 having more nuanced features has been developed from the layers including amorphous metal. FIG. 7C illustrates the removal of the object 708 from the surface 700. Thus, an object including amorphous metal is achieved.

FIGS. 8A-8C illustrate the fabrication of an object having a nuanced object, that incorporates the use of a supporting structure in accordance with embodiments of the invention. FIG. 8A illustrates the deposition of layers of molten metallic alloy 804 so as to form an object onto a surface 800 as well as the deposition of a supporting structure 809 onto the surface 800. The supporting structure 809 can be applied in any suitable way, and the material of the supporting structure 809 can be any suitable material, including those materials that are typically used as supporting structures in conventional additive manufacturing processes in accordance with embodiments of the invention. Materials that can withstand high temperatures are best suited for the described techniques. FIG. 8B illustrates that supporting structure 809 is used to support the deposition of the subsequent layers of the object 808. FIG. 8C illustrates that the object 808 is thereafter removed from the surface 800 as well as the supporting structure 809. As can be appreciated, the described techniques that resemble additive manufacturing processes can be used to create geometries that are more nuanced than those seen in FIGS. 6A-8C. The objects illustrated in FIGS. 6A-8C are simply meant to be illustrative of the principles of the described techniques, and should not be interpreted as being comprehensive of them.

FIGS. 9A-9D illustrate the advantages in materials properties that can result from fabricating objects in accordance with the techniques described herein as opposed to fabricating objects by casting. In particular, FIG. 9A illustrates an object cast from a bulk metallic glass composition having a shear modulus X. FIG. 9B illustrates a thinner object cast from the same metallic alloy having a shear modulus Y. As the object cast in FIG. 9B is thinner, it has a higher cooling rate, and therefore forms an object having a lower shear modulus (higher toughness). FIG. 9C depicts an object having a varying thickness. As a result, the portion of the object that is thinner has a lower shear modulus, while the portion of the cast object that is thicker has a higher shear modulus. Accordingly, the part’s toughness varies throughout its cross-section. FIG. 9D illustrates a part formed from the same metallic alloy in accordance with techniques described herein. Because each layer is cooled individually and rapidly, each layer develops a shear modulus that is much lower than those seen in FIGS. 9A-9C. Moreover, the object can be made to have a relatively homogenous toughness throughout its cross section, irrespective of any variation in geometry. However, as mentioned above, the toughness of the object can be made to vary throughout its geometry if desired by varying the cooling rate of the corresponding applied layer.

As can be appreciated from the above discussion, the described processes can be varied in any number of ways in...
accordance with embodiments of the invention. In several embodiments, the surface that is used is non-planar, and this aspect is now discussed below.

**Fabricating Objects Including Amorphous Alloys Using Non-Planar Surfaces**

In many embodiments, layers of molten metallic alloy are deposited onto non-planar surfaces in fabricating objects. In this way, the surfaces can help define the geometry of the fabricated objects. In many embodiments, the surface includes mold cavities that help define the shape of the fabricated object.

**FIGS. 10A-10C** illustrate the fabrication of a curved object whereby layers of molten metallic alloy are applied to a curved surface. In particular, **FIG. 10A** illustrates the application of a first layer of molten metallic alloy to a curved surface **1000** using a spraying apparatus **1002**. **FIG. 10B** illustrates that the object to be formed **1008** traces the shape of curved surface **1000**. **FIG. 10C** illustrates that the object to be formed **1008** is removed from the curved surface **1000**. According to this, it is seen that a curved surface can be used to help define the shape of a desired object. Indeed, as can be appreciated, a surface having any geometry can be used in accordance with embodiments of the invention. As can be appreciated, the illustrated process is similar to that seen in **FIGS. 6A-6C**. Accordingly, it should be clear many of the above-described variations are compatible with the processes illustrated in **FIGS. 10A-10C**, and can be implemented in accordance with embodiments of the invention.

**FIGS. 11A-11B** illustrate the use of a surface that has a periodic cellular geometry in fabricating an object in accordance with embodiments of the invention. **FIGS. 11A-11B** are similar to **FIGS. 10A-10C**, except that a surface having a periodic cellular structure **1100** is used. In this way, an object **1108** can be fabricated that has a geometry that conforms to the periodic cellular geometry of the surface **1100**. Again, it should be clear that a surface having any geometry can be incorporated in accordance with embodiments of the invention, and it should be clear that any of the variations described above may also be implemented in accordance with embodiments of the invention.

In many embodiments, a surface that includes mold cavities is used in the fabrication of an object in accordance with embodiments of the invention. **FIGS. 12A-12C** illustrate the fabrication of an object including amorphous metal using a surface that includes a mold cavity in accordance with embodiments of the invention. In particular, **FIGS. 12A-12C** are similar to those seen with respect to **FIGS. 10A-10C**, except that the surface **1200** includes a mold cavity portion **1201** that is in the shape of a hemisphere. The mold cavity portion helps define the shape of the object to be formed. Thus, **FIG. 12A** illustrates the application of layers of molten metallic alloy into the mold cavity portion **1201** of the surface **1200** using a spraying apparatus **1202**. **FIG. 12B** illustrates that the object has been formed within, and conforms to, the mold cavity portion of the **1201** of the surface **1200**. And **FIG. 12C** illustrates the removal of the formed object **1206** from the surface **1200**. It should of course be clear that a surface including a mold cavity having any suitable geometry can be used in accordance with embodiments of the invention.

In many embodiments, an additional surface is used to form an object to be fabricated in accordance with embodiments of the invention. **FIGS. 13A-13C** depict the use of an additional surface that is in the shape of a tube to help define the shape of the object to be formed. In particular, **FIG. 13A** depicts an additional surface **1310** is used to help shape the object to be formed **1308** while a spray mechanism **1302** is applying layers of molten metallic alloy **1304** onto a surface **1300**. **FIG. 13B** depicts that the object has been formed, bounded by the surface (not shown) and the additional surface **1310**. **FIG. 13C** depicts that the object **1308**, having first been removed from the initial surface, is removed from the additional surface **1310** using a pressing technique. Note that in the illustrated embodiment, the object to be formed has “extrusion symmetry”—its cross-section is constant throughout its height; as a result, the object **1308** can be removed from the additional surface by a pressing technique. Thus, as can be appreciated, similar techniques can be used in forming objects having extrusion symmetry, i.e. having a constant cross-section. For example, in many embodiments gears having extrusion symmetry can be fabricated using techniques similar to those seen in **FIGS. 13A-13C**.

In many embodiments a plurality of mold cavities and/or a plurality of additional surfaces are incorporated so that a plurality of objects can be formed. **FIG. 14** illustrates a surface that includes a plurality of additional surfaces that can allow multiple objects to be formed in accordance with embodiments of the invention. In particular, it is illustrated that a plurality of additional surfaces **1410** are incorporated and used to define the shape of objects to be formed. A spraying mechanism **1402** is moved relative to the surfaces **1410**, and applies layers of molten metallic glass within them so that the objects can be formed. The additional surfaces **1410** are shown as being tubular in shape and therefore can facilitate the formation of cylindrically shaped objects including amorphous metal. However, it should be understood that the additional surfaces can be of any shape in accordance with embodiments of the invention.

While the techniques described above may have suggested that the layers of molten metallic glass are applied by holding the surface constant and moving a spraying apparatus relative to the fixed surface, the application of molten layers of metallic alloy can occur in any variety of ways. In many embodiments, a spraying mechanism is fixed spatially, and a surface is moved relative to the fixed spraying apparatus during the application of layers of molten metallic alloy. Moreover, while the above-discussion and accompanying figures may have suggested a single spraying apparatus in the fabrication of objects, it should be clear that any number of spraying apparatuses can be utilized in accordance with embodiments of the invention. These variations are now discussed.

**Process Variations in the Fabrication of Objects Including Amorphous Metal**

In many embodiments, during the application of layers of molten metallic alloy, a spraying apparatus is held fixed in space, and a surface is moved relative to the fixed spraying apparatus; in this way a layer of molten metallic alloy can be applied in a desired pattern. In a number of embodiments, a plurality of spraying apparatuses is used to apply layers of molten metallic alloy. In several embodiments, a plurality of cooling mechanisms is used to cool applied layers of molten metallic alloy.

**FIGS. 15A-15B** illustrate a process for fabricating an object whereby an underlying surface is moved relative to a fixed spraying mechanism during the application of layers of molten metallic alloy in accordance with embodiments of the invention. In particular, **FIG. 15A** illustrates that an underlying surface **1500** is moved relative to a fixed spraying apparatus **1502** while it is applying a layer of molten metallic alloy. The underlying surface **1500** can be moved so as to cause the layer of molten metallic alloy to be applied in a desired pattern. **FIG. 15B** illustrates how a conveyor belt
can be used to move the underlying surface. In particular, the surface 1500 is depicted as being located on the conveyor belt 1512, such that movement of the conveyor belt will cause movement of the surface 1500. Of course, it should be understood that the underlying substrate can be moved relative to a fixed spraying apparatus in any suitable way in accordance with embodiments of the invention.

Additionally, as can be appreciated, the surface can be of any shape in accordance with embodiments of the invention. For example, in some embodiments, the surface is cylindrical. FIGS. 16A-16D illustrate the fabrication of a tube-shaped object using a cylindrical surface. In particular, FIG. 16A illustrates a spraying apparatus 1602 being used to deposit a layer of molten metallic alloy 1604 onto a surface 1600 that is in the shape of a cylinder. The surface 1600 is rotating about its central axis, while the spraying apparatus is used to cool the applied layers of molten metallic alloy. FIG. 16B illustrates that a tube-like shape that includes amorphous metal 1608 has been formed onto the surface 1600. FIG. 16C illustrates that as the formed object 1608 has extrusion symmetry, it can be removed from the surface 1600 by a pressing technique. FIG. 16D illustrates the formed object having a tube-like shape 1608. Thus, it is seen that surfaces having any of a variety of shapes can be used in the fabrication of objects including amorphous metal in accordance with embodiments of the invention.

In many embodiments, multiple spraying mechanisms are utilized in applying layers of molten metallic alloy. In a number of embodiments, multiple cooling mechanisms are utilized in cooling applied layers of molten metallic alloy. FIGS. 17A-17C illustrate processes for fabricating objects that include amorphous metal using multiple spraying mechanisms and/or multiple cooling mechanisms in accordance with embodiments of the invention. In particular, FIG. 17A depicts a plurality of spraying apparatuses 1702 that are applying layers of molten metallic alloy onto a surface that is disposed on a conveyor belt. However, it should be understood that a plurality of spraying apparatuses can also apply layers of molten metallic alloy onto a surface that is fixed, and the spraying apparatuses may move relative the fixed layer in order to apply a desired pattern onto the surface in accordance with embodiments of the invention. FIG. 17B illustrates incorporating multiple cooling jets in cooling applied layers of molten metallic alloy in accordance with embodiments of the invention. In particular, FIG. 17B illustrates a similar setup as that seen in FIG. 17A, except that multiple cooling jets 1706 are illustrated that can cool the applied layers of molten metallic alloy. Of course, it should be understood that although cooling jets 1706 are depicted, any of a variety of cooling mechanisms can be applied to the applied layers of molten metallic alloy. FIG. 17C illustrates that multiple spraying mechanisms can be used in applying molten metallic alloy to a surface including a plurality of mold cavities. In particular, the setup is similar to that seen in FIG. 17A, except that a surface 1700 including multiple mold cavities 1701 is used. Of course, it should be understood that the discussed techniques can be utilized in conjunction with one another in any of a variety of ways in accordance with embodiments of the invention. The illustrated examples are only meant to be illustrative and should not be construed as limiting the scope of the invention.

In general, as can be inferred, the above-described techniques are versatile and can be used to create any of a variety of different objects. For example, the above-described processes are particularly well suited in the fabrication of sheet metal, the fabrication of sheet metal is now described.

Fabricating Sheet Metal That Includes Amorphous Metal

In many embodiments of the invention, molten metallic alloy is iteratively applied and cooled onto a surface to form sheet metal. FIGS. 18A and 18B illustrate the fabrication of sheet metal in accordance with embodiment of the invention. In particular, FIG. 18A illustrates the application of a layer molten metallic alloy 1804 onto a surface (not shown) using a spraying apparatus 1802. FIG. 18B illustrates that the application of the layers of molten metallic alloy is controlled so that the resulting object 1808 is in the shape of sheet metal. The object 1808 can then be removed from the underlying mechanisms. In the illustrated embodiment, the sheet metal is shown to be in the shape of a rectangular prism (having a small thickness); although, it should be understood that the sheet metal can be fabricated in any planar shape in accordance with embodiments of the invention. Additionally, the sheet metal can fabricated to be any suitable thickness in accordance with embodiments of the invention. As can be appreciated, where sheet metal of thicker dimensions is desired, more layers of molten metallic alloy may be applied. In many embodiments, the thickness of the formed sheet metal is between approximately 0.1 mm and approximately 2 mm. Note that sheet metal of these dimensions typically cannot be formed using traditional casting techniques or ribbon quenching techniques. The sheet metal can have any suitable lateral dimensions. In some embodiments the fabricated sheet metal has a lateral surface area of 10 cm²; in several embodiments the fabricated sheet metal has a lateral surface area of 1 m². Though it should be clear that the lateral surface area can be of any suitable dimension in accordance with embodiments of the invention. As can be appreciated, the sheet metal can then be further formed and thereby used to create any of a variety of apparatuses. Of course, it should be clear that the fabrication of the sheet metal can be accomplished using any of the described techniques and variations; the above discussion with respect to FIGS. 18A and 18B is merely meant to be illustrative. In many embodiments, where sheet metal is being fabricated, the applied layers of molten metallic alloy is of a composition known to form amorphous metal that is relatively more pliable. For example, in many embodiments, layers of one of the following molten compositions are applied to form the sheet metal: Ti—Zr—Cu—Be, Cu—Zr—Ni—Al, Zr—Nb—Ni—Cu—Al, and Zr—Ti—Cu—Ni—Al (note that the relative atomic ratios of the elements are not listed—they can be present in any suitable relative amount in accordance with embodiments of the invention). In general, amorphous alloys that exhibit large supercooled liquid regions and are thus robust to plastic processing techniques are well-suited to the fabrication of sheet metal. In many embodiments, the applied molten metallic alloy is based on one of: zirconium, titanium, copper, nickel, iron, and mixtures thereof. Note that amorphous metals that can be reheated and formed thermoplastically in their supercooled liquid regions above their glass transition temperature and can be cooled into a glass without crystallizing thereafter can allow the formed sheet metal to be used more practically. To be clear though, the sheet metal can be formed to include any amorphous metal in accordance with embodiments of the invention.

In many embodiments, the solidified layers including amorphous metal are post-processed, and this aspect is now discussed.

Post-Processing of Objects Including Amorphous Metal

In many embodiments, after the layers of molten metallic alloy have been applied and have formed layers including amorphous metal, they are processed to refine their shape.
many embodiments, where sheet metal is formed, the formed sheet metal is subjected to a roller to smoothen the formed sheet metal and thereby mitigate surface imperfections. In several embodiments, a pressing mechanism is used to impose a surface geometry onto solidified layers including amorphous metal. In a number of embodiments, a computer numerically controlled milling procedure is used in post-processing the solidified layers including amorphous metal. Indeed, any of a variety of post-processing techniques can be incorporated in the fabrication of an object in accordance with embodiments of the invention including, but not limited to: rolling, embossing, forging, stamping, heating, or chemically etching.

FIGS. 19A-19B illustrate subjecting solidified layers in the shape of sheet metal to rollers to smoothen out any imperfections in the sheet metal in accordance with embodiments of the invention. In particular, FIG. 19A illustrates that the fabricated sheet metal 1908 is subjected to rollers 1920 that help refine the shape of the solidified layers 1908. FIG. 19B illustrates how the rollers 1920 can be used to eliminate imperfections in the shape of the sheet metal in accordance with embodiments of the invention. In this way, the sheet metal can be made to be of higher quality.

FIG. 20 illustrates using a press to post-process solidified layers including amorphous metal in accordance with embodiments of the invention. In particular, solidified layers that are in the shape of sheet metal are heated using heating elements 2018, and then subjected to a press. The heating elements 2018 can be used to soften the formed sheet metal so that it is pliable and can readily be formed by the press. The press 2020 can be used to impose a particular geometry onto the formed sheet metal.

FIGS. 21A-21C illustrate the post-processing of solidified layers including amorphous alloy by using a computer numerically controlled milling apparatus. In particular, FIG. 21A illustrates the application of a first layer of molten metallic alloy 2104 to a surface (not shown) using a spraying apparatus 2102. FIG. 21B illustrates that an object 2108 in the shape of a rectangular prism is formed by the application of the layers of molten metallic alloy. FIG. 21C illustrates that a computer numerically controlled milling apparatus 2120 is thereafter used to obtain the desired shape. In general, it can be seen that solidified layers including amorphous metal can be post-processed in any suitable way to obtain a desired shape in accordance with embodiments of the invention. For example, in many embodiments, the solidified layers including amorphous metal are subjected to one of: a rolling process, an embossing process, a forging process, a stamping process, a heating process, a chemical etching process, and mixtures thereof.

Note that in many embodiments of the invention, the solidified layers including amorphous metal are not removed from the surface. In this way, an object containing amorphous metal can be built onto a surface, and this technique is now discussed below.

Fabricating Objects Including Amorphous Metal onto a Surface

In many embodiments, an object including amorphous metal is fabricated onto a surface. In many embodiments, a process similar to that seen in FIG. 1 is used to fabricate an object including amorphous metal onto a surface, except that the solidified layers including amorphous metal are not removed from the surface.

FIG. 22 illustrates the fabrication of an object onto a surface in accordance with embodiments of the invention. In particular, FIG. 22 is similar to that seen with respect to FIG. 1, except that solidified layers including amorphous metal are not removed from the surface. In particular, the process 2200 includes: applying 2202 a first layer of molten metallic alloy to a surface; cooling 2204 the first applied layer of molten metallic alloy so as to form a layer including amorphous metal; applying 2206 a layer of molten metallic alloy onto a layer including amorphous metal; cooling the applied layer of molten metallic alloy so that it forms a layer including amorphous metal; and repeating 2210 the application 2206 and cooling 2208 of layers of molten metallic alloy, where the layers are applied so as to form an object of the desired shape (within tolerance). As can be appreciated, the above discussion with respect to FIG. 1 is largely applicable in this context as well. Accordingly, the variations that are discussed above may also be implemented in the process illustrated in FIG. 22 in accordance with embodiments of the invention. Note that in many embodiments, the object that is formed onto a surface includes nuanced features. Thus, in many embodiments, the object includes cross-sections having different shapes. As a result, in many embodiments, at least two layers are applied having different shapes. In other words, at least two applied layers of molten metallic alloy are not coextensive in shape. In this way nuanced features that include amorphous metal can be fabricated onto a surface.

As can be appreciated from the above discussion, the above description is meant to be illustrative and not meant to be a comprehensive definition of the scope of invention. In general, as can be inferred from the above discussion, the above-mentioned concepts can be implemented in a variety of arrangements, including in conjunction with one-another, in accordance with embodiments of the invention. Accordingly, although the present invention has been described in certain specific aspects, many additional modifications and variations would be apparent to those skilled in the art. It is therefore to be understood that the present invention may be practiced otherwise than specifically described. Thus, embodiments of the present invention should be considered in all respects as illustrative and not restrictive.

What claimed is:

1. A method of fabricating a free-standing object comprising an amorphous metal, the method comprising:
   applying a first layer of molten metallic alloy to a surface using a thermal spraying technique and a spot size having a diameter of about 1 to 100 mm, wherein the molten metallic alloy comprises one or more of Ti, Zr, and Cu, wherein the surface comprises a removal promoting material, and wherein the thermal spraying technique is selected from the group consisting of: high velocity oxy-fuel spraying, plasma spraying, wire arc spraying, and mixtures thereof;
   cooling the first layer of molten metallic alloy such that it solidifies and thereby forms a first cooled and solidified layer comprising the amorphous metal, wherein the amorphous metal comprises one or more of Ti, Zr, and Cu, and wherein the removal promoting material facilitates separation of the amorphous metal from the surface;
   applying a second layer of molten metallic alloy onto the first cooled and solidified layer comprising the amorphous metal using the thermal spraying technique and the spot size having a diameter of about 1 to 100 mm; cooling the second layer of molten metallic alloy such that it solidifies and thereby forms a second cooled and solidified layer comprising the amorphous metal on the first cooled and solidified layer comprising the amorphous metal;
wherein an aggregate of the cooled and solidified layers comprising the amorphous metal forms a desired shape of the free-standing object to be fabricated; and separating the aggregate of the cooled and solidified layers comprising the amorphous metal from the surface, thereby fabricating the free-standing object comprising the amorphous metal.

2. The method of claim 1, further comprising applying and cooling one or more additional layers of molten metallic alloy to form one or more additional cooled and solidified layers comprising the amorphous metal that are each formed on a previously formed cooled and solidified layer comprising the amorphous metal.

3. The method of claim 1, wherein the feedstock for the thermal spraying technique is selected from the group consisting of: wire, powder, a molten pool of the metallic alloy composition being applied, a molten pool of the constituent elements of the metallic alloy composition being applied, and mixtures thereof.

4. The method of claim 1, wherein the thermal spraying technique utilizes a computer-controlled apparatus.

5. The method of claim 1, wherein multiple thermal spraying apparatuses are used to apply the layers of molten metallic alloy.

6. The method of claim 1, wherein at least one of the layers of molten metallic alloy has a composition that has a critical casting thickness of greater than approximately 1 mm.

7. The method of claim 1, wherein at least one of the layers of molten metallic alloy has a composition that has a critical casting thickness of less than approximately 100 µm.

8. The method of claim 1, wherein at least one of the layers of molten metallic alloy has a different composition than at least one other of the layers of molten metallic alloy.

9. The method of claim 1, wherein at least one of the layers of molten metallic alloy has a thickness of between approximately 10 nanometers and approximately 100 micrometers.

10. The method of claim 1, wherein the amorphous metal comprising one or more of Ti, Zr, and Cu further comprises a composition selected from the group consisting of: a zirconium based composition, a nickel based composition, a cobalt based composition, an iron based composition, a palladium based composition, a platinum based composition, a gold based composition, a copper based composition, a tungsten based composition, a niobium based composition, a hafnium based composition, an aluminum based composition, a composition that includes at least 50% (atomic) of a mixture of Zr—Ti—Be, a composition that includes at least 50% (atomic) of a mixture of Zr—Be, a composition that includes at least 50% (atomic) of a mixture of Cu—Zr, a composition that includes at least 50% (atomic) of a mixture of Cu—Zr—Al, a composition that includes at least 50% (atomic) of a mixture of Fe—Ni, a composition that includes at least 50% (atomic) of a mixture of Fe—Ni—P, a composition that includes at least 50% (atomic) of a mixture of Fe—Ni—B, a composition that includes at least 50% (atomic) of a mixture of Fe—P, a composition that includes at least 50% (atomic) of a mixture of Pd—P, a composition that includes at least 50% (atomic) of a mixture of Al—Y, and a composition that includes at least 50% (atomic) of a mixture of Ni—Nb.

11. The method of claim 1, wherein the free-standing object comprises 25% amorphous metal by volume.

12. The method of claim 1, wherein a shear modulus of the free-standing object is at least 5% lower than if the free-standing object were fabricated using a casting technique.

13. The method of claim 1, wherein a fracture toughness of the free-standing object is at least 10% higher than if the free-standing object were fabricated using a casting technique.

14. The method of claim 1, wherein the surface is one of: a flat surface, a curved surface, or a surface having a periodic cellular structure.

15. The method of claim 1, wherein the surface has axial symmetry, and wherein the first layer of molten metallic alloy is applied to the surface while the surface is being rotated about its axis of symmetry.

16. The method of claim 1, wherein the surface comprises a material selected from the group consisting of: metal, carbide, graphite, ceramic, glass, plastic, and mixtures thereof.

17. The method of claim 1, wherein the removal promoting material comprises a coating of graphite powder.

18. The method of claim 1, wherein the aggregate of the cooled and solidified layers comprising the amorphous metal is separated from the surface by mechanically separating the aggregate of the cooled and solidified layers comprising the amorphous metal from the surface.

19. The method of claim 1, wherein the free-standing object has a thickness of between approximately 0.1 mm and approximately 25 mm.

20. The method of claim 1, wherein the free-standing object has a thickness that is greater than a critical casting thickness of any composition of the applied layers of molten metallic alloy.

21. The method of claim 1, wherein the free-standing object is sheet metal.

22. The method of claim 1, wherein the free-standing object is separated from the additional surface by an embossing process, a stamping process, a heating process, a chemical etching process, or mixtures thereof.

23. The method of claim 1, further comprising subjecting the aggregate of the cooled and solidified layers including the amorphous metal to one of: a rolling process, an embossing process, a stamping process, a heating process, a chemical etching process, or mixtures thereof.

24. The method of claim 1, wherein the aggregate of the cooled and solidified layers including the amorphous metal is subjected to a rolling process that removes undesired imperfections in the aggregate of the solidified layers including the amorphous metal.

25. The method of claim 1, wherein: an additional surface is used to define a shape of the free-standing object; the free-standing object has extrusion symmetry; and the free-standing object is separated from the additional surface using a pressing technique.

26. A method of fabricating a free-standing object comprising an amorphous metal, the method comprising: applying a first layer of molten metallic alloy to a surface using a thermal spraying technique and a spot size having a diameter of about 1 to 100 mm, wherein the molten metallic alloy comprises one or more of Ti, Zr, and Cu, wherein the surface comprises a removal promoting material, and wherein the thermal spraying technique is selected from the group consisting of: high velocity oxy-fuel spraying, plasma spraying, wire arc spraying, and mixtures thereof; cooling the first layer of molten metallic alloy such that it solidifies and thereby forms a first cooled and solidified
applying a second layer of molten metallic alloy onto the first cooled and solidified layer comprising the amorphous metal using the thermal spraying technique and the spot size having a diameter of about 1 to 100 mm; and

cooling the second layer of molten metallic alloy such that it solidifies and thereby forms a second cooled and solidified layer comprising the amorphous metal on the first cooled and solidified layer comprising the amorphous metal;

applying and cooling one or more additional layers of molten metallic alloy to form one or more additional cooled and solidified layers comprising the amorphous metal that are each formed on a previously formed cooled and solidified layer comprising the amorphous metal;

wherein at least two of the applied layers of molten metallic alloy are not coextensive in shape; and

wherein an aggregate of the cooled and solidified layers comprising the amorphous metal forms a desired shape of the free-standing object to be fabricated.