



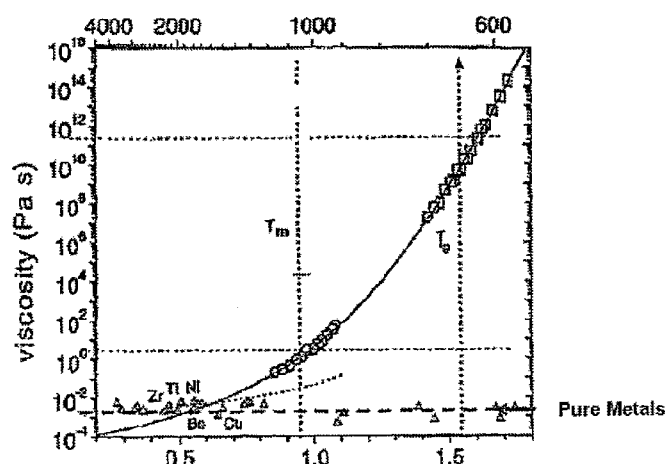
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- (71) **Applicant** (for all designated States except US): **CRUCIBLE INTELLECTUAL PROPERTY LLC** [US/US]; 30452 Esperanza, Rancho Santa Margarita, California 92688 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants** (for US only): **PHAM, Tran Quoc** [US/US]; 2568 W. Rome Ave., Anaheim, California 92804 (US). **O'KEEFE, Sean** [US/US]; 23211 Pradera Road, Coto de Caza, California 92679 (US). **WANIUK, Theodore Andrew** [US/US]; 1 Infinite Loop, M/S 36-2 PAT, Cupertino, California 95014 (US). **KANG, John** [US/US]; 23211 Pradera Road, Coto de Caza, California 92679 (US).
- (74) **Agents:** **DAVE, Raj S.** et al.; Pillsbury Winthrop Shaw Pittman LLP, P.O. Box 10500, McLean, Virginia 22102 (US).

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- Title:**
- ARTICLES CONTAINING SHAPE RETAINING WIRE THEREIN

**FIG. 1**

- (57) **Abstract:** Various embodiments of an article of manufacture include a first material arranged in contact with a desired object or objects in a selected configuration; and a shape memory component arranged in or adjacent to the first material. The shape memory component includes a bulk amorphous alloy (BAA) in a memorized shape, and which is designed and adapted to return to the memorized shape and maintain the selected configuration of the first material after experiencing a deformation. Embodiments of a shape memory structure of this disclosure are valuable in the manufacture of clothing, e.g., in brassieres, as a shape retaining wire or loop. In addition, embodiments of a shape memory structure of this disclosure can also be valuable in the manufacture of other consumer items, e.g., retainer rings, eye glass frame, live hinges, dome switches, and keyboard springs that utilize a shape retaining wire described herein.

ARTICLES CONTAINING SHAPE RETAINING WIRE THEREIN

BACKGROUND

[0001] This disclosure relates to articles containing one or more shape-memory alloy (SMA) structures of bulk amorphous alloy (BAA) and/or bulk metallic glass (BMG) materials, including SMA fibers and/or wires with improved material strength, stress resistance, corrosion resistance, cost effectiveness, high elasticity and shape retention, among other properties.

[0002] An amorphous metal is a metallic material with a disordered atomic-scale structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous alloys are non-crystalline. Materials in which such a disordered structure is produced directly from the liquid state during cooling are called "glasses", and so amorphous metals are commonly referred to as "metallic glasses" or "glassy metals". The term glass is usually defined in a wide sense, to include every solid that possesses a non-crystalline (i.e., amorphous) structure and that exhibits a glass transition when heated towards the liquid state. In this wider sense, glasses can be made of quite different classes of materials: metallic alloys, ionic melts, aqueous solutions, molecular liquids, and polymers.

[0003] There are several ways besides extremely rapid cooling in which amorphous metals can be produced, including physical vapor deposition, solid-state reaction, ion irradiation, and mechanical alloying. Conventionally, small batches of amorphous metals have been produced through a variety of small-scale quick-cooling methods. For instance, amorphous metal wires have been produced by sputtering molten metal onto a spinning metal disk (melt spinning). The rapid cooling, on the order of millions of degrees a second, is too fast for crystals to form and the material is "locked in" a glassy state. More recently a number of alloys with critical cooling rates low enough to allow formation of amorphous structure in thick layers (over 1 mm) have been produced; these are known as bulk metallic glasses (BMG) or, alternatively, bulk amorphous alloys (BAA).

[0004] Amorphous alloys have a variety of potentially useful properties. In particular, they tend to be stronger than crystalline alloys of similar chemical composition, and they can

sustain larger reversible ("elastic") deformations than crystalline alloys. Amorphous metals derive their strength directly from their non-crystalline structure, which does not have any of the defects (such as dislocations) that limit the strength of crystalline alloys. However, metallic glasses at room temperature are not ductile and tend to fail suddenly when loaded in tension beyond about 1.0-1.5% strain-to-failure-without-yield, which can limit the material applicability in reliability-critical applications, as the impending failure is not evident.

[0005] Therefore, while amorphous alloy materials can provide acceptable material properties while under that influence of compressive forces, these materials are generally brittle, resulting in unacceptable tensile strength for some applications.

[0006] What is needed is a BAA composite structure with improved tensile strength that uses a BAA material as either a matrix material and/or a reinforcing material, and a method for making such a structure.

SUMMARY

[0007] A proposed solution according to embodiments herein is applicable in or the fabrication of electronic devices, circuits, components, and/or protective cases for such devices using a BMG. Embodiments of a shape memory structure of this disclosure can also be valuable in the manufacture of clothing, e.g., in brassieres, as a shape retaining wire or loop. In addition, embodiments of a shape memory structure of this disclosure can also be valuable in the manufacture of other consumer items, e.g., retainer rings, eye glass frame, live hinges, dome switches, and keyboard springs that utilize a shape retaining wire of this disclosure.

[0008] In one embodiment, an article of manufacture includes, *inter alia*, a first material arranged in contact with a desired object or objects in a selected configuration; and a shape memory component arranged in or adjacent to the first material, said shape memory component comprising a bulk amorphous alloy (BAA) in a memorized shape, said shape memory component being designed and adapted to return to the memorized shape and maintain the selected configuration of the first material after experiencing a deformation therefrom. In one aspect of this embodiment, the first material may be arranged to at least partially envelope the shape memory component. In another aspect of this embodiment, the shape memory component is arranged to at least partially surround the first material and/or the desired object.

[0009] In an embodiment, the first material comprises a casing containing an electronic device therein, said shape memory component comprising a loop arranged to fit around the casing and thereby maintain closure of the casing and protect the electronic device from an environment external to the casing.

[0010] In one aspect of this embodiment, the first material comprises an eyeglass frame arrangement that holds an optical element therein, said shape memory component comprising a BAA wire arranged to hold the optical glass in the eyeglass frame.

[0011] In another aspect of this embodiment, the first material comprises a fabric shaped as a brassiere, and wherein the shape memory component comprises a BAA wire arranged as an underwire attached to the brassiere.

[0012] In another aspect, the first material may be a leather, plastic or nylon material, and the shape memory component may be operatively connected to the leather, plastic or nylon material to provide a desired shape.

[0013] In another embodiment, the first material comprises retaining assembly operatively coupled to a rotating shaft, and the shape memory component comprises a retaining ring that maintains the assembly in a relatively fixed longitudinal position with respect to the shaft.

[0014] In another embodiment, the first material comprises a clam-shaped material, and the shape memory component is arranged between two sections of the clam-shaped material as a live hinge that allows opening and closing of the clam-shaped material. In an aspect of this embodiment, the clam-shape material comprises a BAA material and the shape memory component is integral with the clam-shape material.

[0015] In an embodiment, the article of manufacture comprises a keyboard and the first material comprises a key for the keyboard, wherein the shape memory component comprises a switching component for the keyboard. In an aspect of this embodiment, the switching component comprises a dome switch mechanically coupled to the key. In another aspect of this embodiment, the switching component comprises a buckling spring mechanism mechanically coupled to the key. In another aspect of this embodiment, a mechanical switch is mechanically coupled to and is in registration with the key, wherein the switching component comprises a spring mechanism coupled to the key.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 provides a temperature-viscosity diagram of an exemplary bulk solidifying amorphous alloy;

[0017] FIG. 2 provides a schematic of a time-temperature-transformation (TTT) diagram for an exemplary bulk solidifying amorphous alloy;

[0018] FIG. 3A illustrates an embodiment of a casing in an unassembled condition, e.g., a casing for enclosing an electronic device therein;

[0019] FIG. 3B illustrates an embodiment of the casing of FIG. 3A in an assembled configuration;

[0020] FIG. 4A provides a cross-sectional view of the casing of FIG. 3A along sectional line 4-4';

[0021] FIG. 5A illustrates an alternative embodiment of a casing in an unassembled condition, e.g., a casing for enclosing an electronic device therein;

[0022] FIG. 5B provides an end-view of the casing of FIG. 5A in an assembled configuration;

[0023] FIG. 6 illustrates an exemplary embodiment of a live hinge;

[0024] FIG. 7 illustrates an alternative embodiment of a live hinge that augments a conventional hinge arrangement;

[0025] FIG. 8 illustrates an exemplary embodiment of an article of clothing, e.g., a brassiere;

[0026] FIG. 9 illustrates an exemplary embodiment of an eyeglass arrangement;

[0027] FIG. 10 provides a cross-sectional view of the eyeglass arrangement of FIG. 9 along sectional line 10-10';

[0028] FIG. 11A illustrates an embodiment of a shaft retaining mechanism in an unassembled configuration;

[0029] FIG. 11B illustrates the embodiment of FIG. 11A in an assembled configuration;

[0030] FIG. 12 illustrates an embodiment of a buckling spring switch arrangement; and

[0031] FIG. 13 illustrates an embodiment of a dome switch arrangement.

DETAILED DESCRIPTION

[0032] All publications, patents, and patent applications cited in this Specification are hereby incorporated by reference in their entirety.

[0033] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "a polymer resin" means one polymer resin or more than one polymer resin. Any ranges cited herein are inclusive. The terms "substantially" and "about" used throughout this Specification are used to describe and account for small fluctuations. For example, they can refer to less than or equal to $\pm 5\%$, such as less than or equal to $\pm 2\%$, such as less than or equal to $\pm 1\%$, such as less than or equal to $\pm 0.5\%$, such as less than or equal to $\pm 0.2\%$, such as less than or equal to $\pm 0.1\%$, such as less than or equal to $\pm 0.05\%$.

[0034] Bulk-solidifying amorphous alloys, or bulk metallic glasses ("BMG"), are a recently developed class of metallic materials. These alloys may be solidified and cooled at relatively slow rates, and they retain the amorphous, non-crystalline (i.e., glassy) state at room temperature. Amorphous alloys have many superior properties than their crystalline counterparts. However, if the cooling rate is not sufficiently high, crystals may form inside the alloy during cooling, so that the benefits of the amorphous state can be lost. For example, one challenge with the fabrication of bulk amorphous alloy parts is partial crystallization of the parts due to either slow cooling or impurities in the raw alloy material. As a high degree of amorphicity (and, conversely, a low degree of crystallinity) is desirable in BMG parts, there is a need to develop methods for casting BMG parts having controlled amount of amorphicity.

[0035] Figure 1 (obtained from U.S. Pat. No. 7,575,040) shows a viscosity-temperature graph of an exemplary bulk solidifying amorphous alloy, from the VIT-001 series of Zr--Ti--Ni--Cu--Be family manufactured by Liquidmetal Technology. It should be noted that there is no clear liquid/solid transformation for a bulk solidifying amorphous metal during the formation of an amorphous solid. The molten alloy becomes more and more viscous with increasing undercooling until it approaches solid form around the glass transition temperature. Accordingly, the temperature of solidification front for bulk solidifying

amorphous alloys can be around glass transition temperature, where the alloy will practically act as a solid for the purposes of pulling out the quenched amorphous sheet product.

[0036] Figure 2 (obtained from U.S. Pat. No. 7,575,040) shows the time-temperature-transformation (TTT) cooling curve of an exemplary bulk solidifying amorphous alloy, or TTT diagram. Bulk-solidifying amorphous metals do not experience a liquid/solid crystallization transformation upon cooling, as with conventional metals. Instead, the highly fluid, non crystalline form of the metal found at high temperatures (near a "melting temperature" T_m) becomes more viscous as the temperature is reduced (near to the glass transition temperature T_g), eventually taking on the outward physical properties of a conventional solid.

[0037] Even though there is no liquid/crystallization transformation for a bulk solidifying amorphous metal, a "melting temperature" T_m may be defined as the thermodynamic liquidus temperature of the corresponding crystalline phase. Under this regime, the viscosity of bulk-solidifying amorphous alloys at the melting temperature could lie in the range of about 0.1 poise to about 10,000 poise, and even sometimes under 0.01 poise. A lower viscosity at the "melting temperature" would provide faster and complete filling of intricate portions of the shell/mold with a bulk solidifying amorphous metal for forming the BMG parts. Furthermore, the cooling rate of the molten metal to form a BMG part has to such that the time-temperature profile during cooling does not traverse through the nose-shaped region bounding the crystallized region in the TTT diagram of Figure 2. In Figure 2, T_{nose} is the critical crystallization temperature T_x where crystallization is most rapid and occurs in the shortest time scale.

[0038] The supercooled liquid region, the temperature region between T_g and T_x is a manifestation of the extraordinary stability against crystallization of bulk solidification alloys. In this temperature region the bulk solidifying alloy can exist as a high viscous liquid. The viscosity of the bulk solidifying alloy in the supercooled liquid region can vary between 10^{12} Pa s at the glass transition temperature down to 10^5 Pa s at the crystallization temperature, the high temperature limit of the supercooled liquid region. Liquids with such viscosities can undergo substantial plastic strain under an applied pressure. The embodiments herein make use of the large plastic formability in the supercooled liquid region as a forming and separating method.

[0039] One needs to clarify something about Tx. Technically, the nose-shaped curve shown in the TTT diagram describes Tx as a function of temperature and time. Thus, regardless of the trajectory that one takes while heating or cooling a metal alloy, when one hits the TTT curve, one has reached Tx. In Figure 2, Tx is shown as a dashed line as Tx can vary from close to Tm to close to Tg.

[0040] The schematic TTT diagram of Figure 2 shows processing methods of die casting from at or above Tm to below Tg without the time-temperature trajectory (shown as (1) as an example trajectory) hitting the TTT curve. During die casting, the forming takes place substantially simultaneously with fast cooling to avoid the trajectory hitting the TTT curve. The processing methods for superplastic forming (SPF) from at or below Tg to below Tm without the time-temperature trajectory (shown as (2), (3) and (4) as example trajectories) hitting the TTT curve. In SPF, the amorphous BMG is reheated into the supercooled liquid region where the available processing window could be much larger than die casting, resulting in better controllability of the process. The SPF process does not require fast cooling to avoid crystallization during cooling. Also, as shown by example trajectories (2), (3) and (4), the SPF can be carried out with the highest temperature during SPF being above Tnose or below Tnose, up to about Tm. If one heats up a piece of amorphous alloy but manages to avoid hitting the TTT curve, you have heated "between Tg and Tm", but one would have not reached Tx.

[0041] Typical differential scanning calorimeter (DSC) heating curves of bulk-solidifying amorphous alloys taken at a heating rate of 20 C/min describe, for the most part, a particular trajectory across the TTT data where one would likely see a Tg at a certain temperature, a Tx when the DSC heating ramp crosses the TTT crystallization onset, and eventually melting peaks when the same trajectory crosses the temperature range for melting. If one heats a bulk-solidifying amorphous alloy at a rapid heating rate as shown by the ramp up portion of trajectories (2), (3) and (4) in Figure 2, then one could avoid the TTT curve entirely, and the DSC data would show a glass transition but no Tx upon heating. Another way to think about it is trajectories (2), (3) and (4) can fall anywhere in temperature between the nose of the TTT curve (and even above it) and the Tg line, as long as it does not hit the crystallization curve. That just means that the horizontal plateau in trajectories might get much shorter as one increases the processing temperature.

Phase

[0042] The term “phase” herein can refer to one that can be found in a thermodynamic phase diagram. A phase is a region of space (e.g., a thermodynamic system) throughout which all physical properties of a material are essentially uniform. Examples of physical properties include density, index of refraction, chemical composition and lattice periodicity. A simple description of a phase is a region of material that is chemically uniform, physically distinct, and/or mechanically separable. For example, in a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air over the water is a third phase. The glass of the jar is another separate phase. A phase can refer to a solid solution, which can be a binary, tertiary, quaternary, or more, solution, or a compound, such as an intermetallic compound. As another example, an amorphous phase is distinct from a crystalline phase.

Metal, Transition Metal, and Non-metal

[0043] The term “metal” refers to an electropositive chemical element. The term “element” in this Specification refers generally to an element that can be found in a Periodic Table. Physically, a metal atom in the ground state contains a partially filled band with an empty state close to an occupied state. The term “transition metal” is any of the metallic elements within Groups 3 to 12 in the Periodic Table that have an incomplete inner electron shell and that serve as transitional links between the most and the least electropositive in a series of elements. Transition metals are characterized by multiple valences, colored compounds, and the ability to form stable complex ions. The term “nonmetal” refers to a chemical element that does not have the capacity to lose electrons and form a positive ion.

[0044] Depending on the application, any suitable nonmetal elements, or their combinations, can be used. The alloy (or “alloy composition”) can comprise multiple nonmetal elements, such as at least two, at least three, at least four, or more, nonmetal elements. A nonmetal element can be any element that is found in Groups 13-17 in the Periodic Table. For example, a nonmetal element can be any one of F, Cl, Br, I, At, O, S, Se, Te, Po, N, P, As, Sb, Bi, C, Si, Ge, Sn, Pb, and B. Occasionally, a nonmetal element can also refer to certain metalloids (e.g., B, Si, Ge, As, Sb, Te, and Po) in Groups 13-17. In one embodiment, the nonmetal elements can include B, Si, C, P, or combinations thereof. Accordingly, for example, the alloy can comprise a boride, a carbide, or both.

[0045] A transition metal element can be any of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, rutherfordium, dubnium, seaborgium, bohrium, hassium, meitnerium, ununnilium, ununium, and ununbium. In one embodiment, a BMG containing a transition metal element can have at least one of Sc, Y, La, Ac, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, and Hg. Depending on the application, any suitable transitional metal elements, or their combinations, can be used. The alloy composition can comprise multiple transitional metal elements, such as at least two, at least three, at least four, or more, transitional metal elements.

[0046] The presently described alloy or alloy “sample” or “specimen” alloy can have any shape or size. For example, the alloy can have a shape of a particulate, which can have a shape such as spherical, ellipsoid, wire-like, rod-like, sheet-like, flake-like, or an irregular shape. The particulate can have any size. For example, it can have an average diameter of between about 1 micron and about 100 microns, such as between about 5 microns and about 80 microns, such as between about 10 microns and about 60 microns, such as between about 15 microns and about 50 microns, such as between about 15 microns and about 45 microns, such as between about 20 microns and about 40 microns, such as between about 25 microns and about 35 microns. For example, in one embodiment, the average diameter of the particulate is between about 25 microns and about 44 microns. In some embodiments, smaller particulates, such as those in the nanometer range, or larger particulates, such as those bigger than 100 microns, can be used.

[0047] The alloy sample or specimen can also be of a much larger dimension. For example, it can be a bulk structural component, such as an ingot, housing/casing of an electronic device or even a portion of a structural component that has dimensions in the millimeter, centimeter, or meter range.

Solid solution

[0048] The term “solid solution” refers to a solid form of a solution. The term “solution” refers to a mixture of two or more substances, which may be solids, liquids, gases, or a combination of these. The mixture can be homogeneous or heterogeneous. The term

“mixture” is a composition of two or more substances that are combined with each other and are generally capable of being separated. Generally, the two or more substances are not chemically combined with each other.

Alloy

[0049] In some embodiments, the alloy composition described herein can be fully alloyed. In one embodiment, an “alloy” refers to a homogeneous mixture or solid solution of two or more metals, the atoms of one replacing or occupying interstitial positions between the atoms of the other; for example, brass is an alloy of zinc and copper. An alloy, in contrast to a composite, can refer to a partial or complete solid solution of one or more elements in a metal matrix, such as one or more compounds in a metallic matrix. The term alloy herein can refer to both a complete solid solution alloy that can give single solid phase microstructure and a partial solution that can give two or more phases. An alloy composition described herein can refer to one comprising an alloy or one comprising an alloy-containing composite.

[0050] Thus, a fully alloyed alloy can have a homogenous distribution of the constituents, be it a solid solution phase, a compound phase, or both. The term “fully alloyed” used herein can account for minor variations within the error tolerance. For example, it can refer to at least 90% alloyed, such as at least 95% alloyed, such as at least 99% alloyed, such as at least 99.5% alloyed, such as at least 99.9% alloyed. The percentage herein can refer to either volume percent or weight percentage, depending on the context. These percentages can be balanced by impurities, which can be in terms of composition or phases that are not a part of the alloy.

Amorphous or non-crystalline solid

[0051] An “amorphous” or “non-crystalline solid” is a solid that lacks lattice periodicity, which is characteristic of a crystal. As used herein, an “amorphous solid” includes “glass” which is an amorphous solid that softens and transforms into a liquid-like state upon heating through the glass transition. Generally, amorphous materials lack the long-range order characteristic of a crystal, though they can possess some short-range order at the atomic length scale due to the nature of chemical bonding. The distinction between amorphous solids and crystalline solids can be made based on lattice periodicity as determined by

structural characterization techniques such as x-ray diffraction and transmission electron microscopy.

[0052] The terms “order” and “disorder” designate the presence or absence of some symmetry or correlation in a many-particle system. The terms “long-range order” and “short-range order” distinguish order in materials based on length scales.

[0053] The strictest form of order in a solid is lattice periodicity: a certain pattern (the arrangement of atoms in a unit cell) is repeated again and again to form a translationally invariant tiling of space. This is the defining property of a crystal. Possible symmetries have been classified in 14 Bravais lattices and 230 space groups.

[0054] Lattice periodicity implies long-range order. If only one unit cell is known, then by virtue of the translational symmetry it is possible to accurately predict all atomic positions at arbitrary distances. The converse is generally true, except, for example, in quasi-crystals that have perfectly deterministic tilings but do not possess lattice periodicity.

[0055] Long-range order characterizes physical systems in which remote portions of the same sample exhibit correlated behavior. This can be expressed as a correlation function, namely the spin-spin correlation function: $G(x, x') = \langle s(x), s(x') \rangle$.

[0056] In the above function, s is the spin quantum number and x is the distance function within the particular system. This function is equal to unity when $x = x'$ and decreases as the distance $|x - x'|$ increases. Typically, it decays exponentially to zero at large distances, and the system is considered to be disordered. If, however, the correlation function decays to a constant value at large $|x - x'|$, then the system can be said to possess long-range order. If it decays to zero as a power of the distance, then it can be called quasi-long-range order. Note that what constitutes a large value of $|x - x'|$ is relative.

[0057] A system can be said to present quenched disorder when some parameters defining its behavior are random variables that do not evolve with time (i.e., they are quenched or frozen) – e.g., spin glasses. It is opposite to annealed disorder, where the random variables are allowed to evolve themselves. Embodiments herein include systems comprising quenched disorder.

[0058] The alloy described herein can be crystalline, partially crystalline, amorphous, or substantially amorphous. For example, the alloy sample/specimen can include at least some crystallinity, with grains/crystals having sizes in the nanometer and/or micrometer ranges. Alternatively, the alloy can be substantially amorphous, such as fully amorphous. In one embodiment, the alloy composition is at least substantially not amorphous, such as being substantially crystalline, such as being entirely crystalline.

[0059] In one embodiment, the presence of a crystal or a plurality of crystals in an otherwise amorphous alloy can be construed as a “crystalline phase” therein. The degree of crystallinity (or “crystallinity” for short in some embodiments) of an alloy can refer to the amount of the crystalline phase present in the alloy. The degree can refer to, for example, a fraction of crystals present in the alloy. The fraction can refer to volume fraction or weight fraction, depending on the context. A measure of how “amorphous” an amorphous alloy is can be amorphicity. Amorphicity can be measured in terms of a degree of crystallinity. For example, in one embodiment, an alloy having a low degree of crystallinity can be said to have a high degree of amorphicity. In one embodiment, for example, an alloy having 60 vol% crystalline phase can have a 40 vol% amorphous phase.

Amorphous alloy or amorphous metal

[0060] An “amorphous alloy” is an alloy having an amorphous content of more than 50% by volume, preferably more than 90% by volume of amorphous content, more preferably more than 95% by volume of amorphous content, and most preferably more than 99% to almost 100% by volume of amorphous content. Note that, as described above, an alloy high in amorphicity is equivalently low in degree of crystallinity. An “amorphous metal” is an amorphous metal material with a disordered atomic-scale structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous alloys are non-crystalline. Materials in which such a disordered structure is produced directly from the liquid state during cooling are sometimes referred to as “glasses.” Accordingly, amorphous metals are commonly referred to as “metallic glasses” or “glassy metals.” In one embodiment, a bulk metallic glass (“BMG”) can refer to an alloy, of which the microstructure is at least partially amorphous. However, there are several ways besides extremely rapid cooling to produce amorphous metals, including physical vapor deposition, solid-state reaction, ion irradiation, melt spinning, and mechanical alloying. Amorphous alloys can be a single class of materials, regardless of how they are prepared.

[0061] Amorphous metals can be produced through a variety of quick-cooling methods. For instance, amorphous metals can be produced by sputtering molten metal onto a spinning metal disk. The rapid cooling, on the order of millions of degrees a second, can be too fast for crystals to form, and the material is thus “locked in” a glassy state. Also, amorphous metals/alloys can be produced with critical cooling rates low enough to allow formation of amorphous structures in thick layers – e.g., bulk metallic glasses.

[0062] The terms “bulk metallic glass” (“BMG”), bulk amorphous alloy (“BAA”), and bulk solidifying amorphous alloy are used interchangeably herein. They refer to amorphous alloys having the smallest dimension at least in the millimeter range. For example, the dimension can be at least about 0.5 mm, such as at least about 1 mm, such as at least about 2 mm, such as at least about 4 mm, such as at least about 5 mm, such as at least about 6 mm, such as at least about 8 mm, such as at least about 10 mm, such as at least about 12 mm. Depending on the geometry, the dimension can refer to the diameter, radius, thickness, width, length, etc. A BMG can also be a metallic glass having at least one dimension in the centimeter range, such as at least about 1.0 cm, such as at least about 2.0 cm, such as at least about 5.0 cm, such as at least about 10.0 cm. In some embodiments, a BMG can have at least one dimension at least in the meter range. A BMG can take any of the shapes or forms described above, as related to a metallic glass. Accordingly, a BMG described herein in some embodiments can be different from a thin film made by a conventional deposition technique in one important aspect – the former can be of a much larger dimension than the latter.

[0063] Amorphous metals can be an alloy rather than a pure metal. The alloys may contain atoms of significantly different sizes, leading to low free volume (and therefore having viscosity up to orders of magnitude higher than other metals and alloys) in a molten state. The viscosity prevents the atoms from moving enough to form an ordered lattice. The material structure may result in low shrinkage during cooling and resistance to plastic deformation. The absence of grain boundaries, the weak spots of crystalline materials in some cases, may, for example, lead to better resistance to wear and corrosion. In one embodiment, amorphous metals, while technically glasses, may also be much tougher and less brittle than oxide glasses and ceramics.

[0064] Thermal conductivity of amorphous materials may be lower than that of their crystalline counterparts. To achieve formation of an amorphous structure even during slower cooling, the alloy may be made of three or more components, leading to complex crystal

units with higher potential energy and lower probability of formation. The formation of amorphous alloy can depend on several factors: the composition of the components of the alloy; the atomic radius of the components (preferably with a significant difference of over 12% to achieve high packing density and low free volume); and the negative heat of mixing the combination of components, inhibiting crystal nucleation and prolonging the time the molten metal stays in a supercooled state. However, as the formation of an amorphous alloy is based on many different variables, it can be difficult to make a prior determination of whether an alloy composition would form an amorphous alloy.

[0065] Amorphous alloys, for example, of boron, silicon, phosphorus, and other glass formers with magnetic metals (iron, cobalt, nickel) may be magnetic, with low coercivity and high electrical resistance. The high resistance leads to low losses by eddy currents when subjected to alternating magnetic fields, a property useful, for example, as transformer magnetic cores.

[0066] Amorphous alloys may have a variety of potentially useful properties. In particular, they tend to be stronger than crystalline alloys of similar chemical composition, and they can sustain larger reversible (“elastic”) deformations than crystalline alloys. Amorphous metals derive their strength directly from their non-crystalline structure, which can have none of the defects (such as dislocations) that limit the strength of crystalline alloys. For example, one modern amorphous metal, known as Vitreloy™, has a tensile strength that is almost twice that of high-grade titanium. In some embodiments, metallic glasses at room temperature are not ductile and tend to fail suddenly when loaded in tension, which limits the material applicability in reliability-critical applications, as the impending failure is not evident. Therefore, to overcome this challenge, metal matrix composite materials having a metallic glass matrix containing dendritic particles or fibers of a ductile crystalline metal can be used. Alternatively, a BMG low in element(s) that tend to cause embitterment (e.g., Ni) can be used. For example, a Ni-free BMG can be used to improve the ductility of the BMG.

[0067] Another useful property of bulk amorphous alloys is that they can be true glasses; in other words, they can soften and flow upon heating. This can allow for easy processing, such as by injection molding, in much the same way as polymers. As a result, amorphous alloys can be used for making sports equipment, medical devices, electronic components and equipment, and thin films. Thin films of amorphous metals can be deposited as protective coatings via a high velocity oxygen fuel technique.

[0068] A material can have an amorphous phase, a crystalline phase, or both. The amorphous and crystalline phases can have the same chemical composition and differ only in the microstructure – i.e., one amorphous and the other crystalline. Microstructure in one embodiment refers to the structure of a material as revealed by a microscope at 25X magnification or higher. Alternatively, the two phases can have different chemical compositions and microstructures. For example, a composition can be partially amorphous, substantially amorphous, or completely amorphous.

[0069] As described above, the degree of amorphicity (and conversely the degree of crystallinity) can be measured by fraction of crystals present in the alloy. The degree can refer to volume fraction or weight fraction of the crystalline phase present in the alloy. A partially amorphous composition can refer to a composition of at least about 5 vol% of which is of an amorphous phase, such as at least about 10 vol%, such as at least about 20 vol%, such as at least about 40 vol%, such as at least about 60 vol%, such as at least about 80 vol%, such as at least about 90 vol%. The terms “substantially” and “about” have been defined elsewhere in this application. Accordingly, a composition that is at least substantially amorphous can refer to one of which at least about 90 vol% is amorphous, such as at least about 95 vol%, such as at least about 98 vol%, such as at least about 99 vol%, such as at least about 99.5 vol%, such as at least about 99.8 vol%, such as at least about 99.9 vol%. In one embodiment, a substantially amorphous composition can have some incidental, insignificant amount of crystalline phase present therein.

[0070] In one embodiment, an amorphous alloy composition can be homogeneous with respect to the amorphous phase. A substance that is uniform in composition is homogeneous. This is in contrast to a substance that is heterogeneous. The term “composition” refers to the chemical composition and/or microstructure in the substance. A substance is homogeneous when a volume of the substance is divided in half and both halves have substantially the same composition. For example, a particulate suspension is homogeneous when a volume of the particulate suspension is divided in half and both halves have substantially the same volume of particles. However, it might be possible to see the individual particles under a microscope. Another example of a homogeneous substance is air where different ingredients therein are equally suspended, though the particles, gases and liquids in air can be analyzed separately or separated from air.

[0071] A composition that is homogeneous with respect to an amorphous alloy can refer to one having an amorphous phase substantially uniformly distributed throughout its microstructure. In other words, the composition macroscopically comprises a substantially uniformly distributed amorphous alloy throughout the composition. In an alternative embodiment, the composition can be of a composite, having an amorphous phase having therein a non-amorphous phase. The non-amorphous phase can be a crystal or a plurality of crystals. The crystals can be in the form of particulates of any shape, such as spherical, ellipsoid, wire-like, rod-like, sheet-like, flake-like, or an irregular shape. In one embodiment, it can have a dendritic form. For example, an at least partially amorphous composite composition can have a crystalline phase in the shape of dendrites dispersed in an amorphous phase matrix; the dispersion can be uniform or non-uniform, and the amorphous phase and the crystalline phase can have the same or a different chemical composition. In one embodiment, they have substantially the same chemical composition. In another embodiment, the crystalline phase can be more ductile than the BMG phase.

[0072] The methods described herein can be applicable to any type of amorphous alloy. Similarly, the amorphous alloy described herein as a constituent of a composition or article can be of any type. The amorphous alloy can comprise the element Zr, Hf, Ti, Cu, Ni, Pt, Pd, Fe, Mg, Au, La, Ag, Al, Mo, Nb, Be, or combinations thereof. Namely, the alloy can include any combination of these elements in its chemical formula or chemical composition. The elements can be present at different weight or volume percentages. For example, an iron “based” alloy can refer to an alloy having a non-insignificant weight percentage of iron present therein, the weight percent can be, for example, at least about 20 wt%, such as at least about 40 wt%, such as at least about 50 wt%, such as at least about 60 wt%, such as at least about 80 wt%. Alternatively, in one embodiment, the above-described percentages can be volume percentages, instead of weight percentages. Accordingly, an amorphous alloy can be zirconium-based, titanium-based, platinum-based, palladium-based, gold-based, silver-based, copper-based, iron-based, nickel-based, aluminum-based, molybdenum-based, and the like. The alloy can also be free of any of the aforementioned elements to suit a particular purpose. For example, in some embodiments, the alloy, or the composition including the alloy, can be substantially free of nickel, aluminum, titanium, beryllium, or combinations thereof. In one embodiment, the alloy or the composite is completely free of nickel, aluminum, titanium, beryllium, or combinations thereof.

[0073] For example, the amorphous alloy can have the formula $(\text{Zr}, \text{Ti})_a(\text{Ni}, \text{Cu}, \text{Fe})_b(\text{Be}, \text{Al}, \text{Si}, \text{B})_c$, wherein a, b, and c each represents a weight or atomic percentage. In one embodiment, a is in the range of from 30 to 75, b is in the range of from 5 to 60, and c is in the range of from 0 to 50 in atomic percentages. Alternatively, the amorphous alloy can have the formula $(\text{Zr}, \text{Ti})_a(\text{Ni}, \text{Cu})_b(\text{Be})_c$, wherein a, b, and c each represents a weight or atomic percentage. In one embodiment, a is in the range of from 40 to 75, b is in the range of from 5 to 50, and c is in the range of from 5 to 50 in atomic percentages. The alloy can also have the formula $(\text{Zr}, \text{Ti})_a(\text{Ni}, \text{Cu})_b(\text{Be})_c$, wherein a, b, and c each represents a weight or atomic percentage. In one embodiment, a is in the range of from 45 to 65, b is in the range of from 7.5 to 35, and c is in the range of from 10 to 37.5 in atomic percentages. Alternatively, the alloy can have the formula $(\text{Zr})_a(\text{Nb}, \text{Ti})_b(\text{Ni}, \text{Cu})_c(\text{Al})_d$, wherein a, b, c, and d each represents a weight or atomic percentage. In one embodiment, a is in the range of from 45 to 65, b is in the range of from 0 to 10, c is in the range of from 20 to 40 and d is in the range of from 7.5 to 15 in atomic percentages. One exemplary embodiment of the aforescribed alloy system is a Zr-Ti-Ni-Cu-Be based amorphous alloy under the trade name Vitreloy™, such as Vitreloy-1 and Vitreloy-101, as fabricated by Liquidmetal Technologies, CA, USA. Some examples of amorphous alloys of the different systems are provided in Table 1 and Table 2.

Table 1. Exemplary amorphous alloy compositions

Alloy	Atm %	Atm %	Atm %	Atm %	Atm %	Atm %	Atm%	Atm%
1	Fe	Mo	Ni	Cr	P	C	B	
	68.00%	5.00%	5.00%	2.00%	12.50%	5.00%	2.50%	
2	Fe	Mo	Ni	Cr	P	C	B	Si
	68.00%	5.00%	5.00%	2.00%	11.00%	5.00%	2.50%	1.50%
3	Pd	Cu	Co	P				
	44.48%	32.35%	4.05%	19.11%				
4	Pd	Ag	Si	P				
	77.50%	6.00%	9.00%	7.50%				
5	Pd	Ag	Si	P	Ge			
	79.00%	3.50%	9.50%	6.00%	2.00%			
6	Pt	Cu	Ag	P	B	Si		
	74.70%	1.50%	0.30%	18.0%	4.00%	1.50%		

Table 2. Additional Exemplary amorphous alloy compositions (atomic %)

Alloy	Atm %	Atm %	Atm %	Atm %	Atm %	Atm %
1	Zr	Ti	Cu	Ni	Be	
	41.20%	13.80%	12.50%	10.00%	22.50%	
2	Zr	Ti	Cu	Ni	Be	
	44.00%	11.00%	10.00%	10.00%	25.00%	
3	Zr	Ti	Cu	Ni	Nb	Be
	56.25%	11.25%	6.88%	5.63%	7.50%	12.50%
4	Zr	Ti	Cu	Ni	Al	Be
	64.75%	5.60%	14.90%	11.15%	2.60%	1.00%
5	Zr	Ti	Cu	Ni	Al	
	52.50%	5.00%	17.90%	14.60%	10.00%	
6	Zr	Nb	Cu	Ni	Al	
	57.00%	5.00%	15.40%	12.60%	10.00%	
7	Zr	Cu	Ni	Al		
	50.75%	36.23%	4.03%	9.00%		
8	Zr	Ti	Cu	Ni	Be	
	46.75%	8.25%	7.50%	10.00%	27.50%	
9	Zr	Ti	Ni	Be		
	21.67%	43.33%	7.50%	27.50%		
10	Zr	Ti	Cu	Be		
	35.00%	30.00%	7.50%	27.50%		
11	Zr	Ti	Co	Be		
	35.00%	30.00%	6.00%	29.00%		
12	Zr	Ti	Fe	Be		
	35.00%	30.00%	2.00%	33.00%		
13	Au	Ag	Pd	Cu	Si	
	49.00%	5.50%	2.30%	26.90%	16.30%	
14	Au	Ag	Pd	Cu	Si	
	50.90%	3.00%	2.30%	27.80%	16.00%	
15	Pt	Cu	Ni	P		
	57.50%	14.70%	5.30%	22.50%		
16	Zr	Ti	Nb	Cu	Be	
	36.60%	31.40%	7.00%	5.90%	19.10%	
17	Zr	Ti	Nb	Cu	Be	
	38.30%	32.90%	7.30%	6.20%	15.30%	
18	Zr	Ti	Nb	Cu	Be	
	39.60%	33.90%	7.60%	6.40%	12.50%	
19	Cu	Ti	Zr	Ni		
	47.00%	34.00%	11.00%	8.00%		
20	Zr	Co	Al			
	55.00%	25.00%	20.00%			

[0074] Other exemplary ferrous metal-based alloys include compositions such as those disclosed in U.S. Patent Application Publication Nos. 2007/0079907 and 2008/0118387. These compositions include the Fe(Mn, Co, Ni, Cu) (C, Si, B, P, Al) system, wherein the Fe content is from 60 to 75 atomic percentage, the total of (Mn, Co, Ni, Cu) is in the range of

from 5 to 25 atomic percentage, and the total of (C, Si, B, P, Al) is in the range of from 8 to 20 atomic percentage, as well as the exemplary composition Fe₄₈Cr₁₅Mo₁₄Y₂C₁₅B₆. They also include the alloy systems described by Fe-Cr-Mo-(Y,Ln)-C-B, Co-Cr-Mo-Ln-C-B, Fe-Mn-Cr-Mo-(Y,Ln)-C-B, (Fe, Cr, Co)-(Mo,Mn)-(C,B)-Y, Fe-(Co,Ni)-(Zr,Nb,Ta)-(Mo,W)-B, Fe-(Al,Ga)-(P,C,B,Si,Ge), Fe-(Co, Cr,Mo,Ga,Sb)-P-B-C, (Fe, Co)-B-Si-Nb alloys, and Fe-(Cr-Mo)-(C,B)-Tm, where Ln denotes a lanthanide element and Tm denotes a transition metal element. Furthermore, the amorphous alloy can also be one of the exemplary compositions Fe₈₀P_{12.5}C₅B_{2.5}, Fe₈₀P₁₁C₅B_{2.5}Si_{1.5}, Fe_{74.5}Mo_{5.5}P_{12.5}C₅B_{2.5}, Fe_{74.5}Mo_{5.5}P₁₁C₅B_{2.5}Si_{1.5}, Fe₇₀Mo₅Ni₅P_{12.5}C₅B_{2.5}, Fe₇₀Mo₅Ni₅P₁₁C₅B_{2.5}Si_{1.5}, Fe₆₈Mo₅Ni₅Cr₂P_{12.5}C₅B_{2.5}, and Fe₆₈Mo₅Ni₅Cr₂P₁₁C₅B_{2.5}Si_{1.5}, described in U.S. Patent Application Publication No. 2010/0300148.

[0075] The amorphous alloys can also be ferrous alloys, such as (Fe, Ni, Co) based alloys. Examples of such compositions are disclosed in U.S. Patent Nos. 6,325,868; 5,288,344; 5,368,659; 5,618,359; and 5,735,975, Inoue *et al.*, Appl. Phys. Lett., Volume 71, p 464 (1997), Shen *et al.*, Mater. Trans., JIM, Volume 42, p 2136 (2001), and Japanese Patent Application No. 200126277 (Pub. No. 2001303218 A). One exemplary composition is Fe₇₂Al₅Ga₂P₁₁C₆B₄. Another example is Fe₇₂Al₇Zr₁₀Mo₅W₂B₁₅. Another iron-based alloy system that can be used in the coating herein is disclosed in U.S. Patent Application Publication No. 2010/0084052, wherein the amorphous metal contains, for example, manganese (1 to 3 atomic %), yttrium (0.1 to 10 atomic %), and silicon (0.3 to 3.1 atomic %) in the range of composition given in parentheses; and that contains the following elements in the specified range of composition given in parentheses: chromium (15 to 20 atomic %), molybdenum (2 to 15 atomic %), tungsten (1 to 3 atomic %), boron (5 to 16 atomic %), carbon (3 to 16 atomic %), and the balance iron.

[0076] The amorphous alloy can also be one of the Pt- or Pd- based alloys described by U.S. Patent Application Publication Nos. 2008/0135136, 2009/0162629, and 2010/0230012. Exemplary compositions include Pd_{44.48}Cu_{32.35}Co_{4.05}P_{19.11}, Pd_{77.5}Ag₆Si₉P_{7.5}, and Pt_{74.7}Cu_{1.5}Ag_{0.3}P₁₈B₄Si_{1.5}.

[0077] The aforescribed amorphous alloy systems can further include additional elements, such as additional transition metal elements, including Nb, Cr, V, and Co. The additional elements can be present at less than or equal to about 30 wt%, such as less than or equal to about 20 wt%, such as less than or equal to about 10 wt%, such as less than or equal

to about 5 wt%. In one embodiment, the additional, optional element is at least one of cobalt, manganese, zirconium, tantalum, niobium, tungsten, yttrium, titanium, vanadium and hafnium to form carbides and further improve wear and corrosion resistance. Further optional elements may include phosphorous, germanium and arsenic, totaling up to about 2%, and preferably less than 1%, to reduce melting point. Otherwise incidental impurities should be less than about 2% and preferably 0.5%.

[0078] In some embodiments, a composition having an amorphous alloy can include a small amount of impurities. The impurity elements can be intentionally added to modify the properties of the composition, such as improving the mechanical properties (e.g., hardness, strength, fracture mechanism, etc.) and/or improving the corrosion resistance. Alternatively, the impurities can be present as inevitable, incidental impurities, such as those obtained as a byproduct of processing and manufacturing. The impurities can be less than or equal to about 10 wt%, such as about 5 wt%, such as about 2 wt%, such as about 1 wt%, such as about 0.5 wt%, such as about 0.1 wt%. In some embodiments, these percentages can be volume percentages instead of weight percentages. In one embodiment, the alloy sample/composition consists essentially of the amorphous alloy (with only a small incidental amount of impurities). In another embodiment, the composition includes the amorphous alloy (with no observable trace of impurities).

[0079] In one embodiment, the final parts exceeded the critical casting thickness of the bulk solidifying amorphous alloys.

[0080] In embodiments herein, the existence of a supercooled liquid region in which the bulk-solidifying amorphous alloy can exist as a high viscous liquid allows for superplastic forming. Large plastic deformations can be obtained. The ability to undergo large plastic deformation in the supercooled liquid region is used for the forming and/or cutting process. As oppose to solids, the liquid bulk solidifying alloy deforms locally which drastically lowers the required energy for cutting and forming. The ease of cutting and forming depends on the temperature of the alloy, the mold, and the cutting tool. As higher is the temperature, the lower is the viscosity, and consequently easier is the cutting and forming.

[0081] Embodiments herein can utilize a thermoplastic-forming process with amorphous alloys carried out between T_g and T_x , for example. Herein, T_x and T_g are determined from

standard DSC measurements at typical heating rates (e.g. 20 °C/min) as the onset of crystallization temperature and the onset of glass transition temperature.

[0082] The amorphous alloy components can have the critical casting thickness and the final part can have thickness that is thicker than the critical casting thickness. Moreover, the time and temperature of the heating and shaping operation is selected such that the elastic strain limit of the amorphous alloy could be substantially preserved to be not less than 1.0 %, and preferably not being less than 1.5 %. In the context of the embodiments herein, temperatures around glass transition means the forming temperatures can be below glass transition, at or around glass transition, and above glass transition temperature, but preferably at temperatures below the crystallization temperature T_X . The cooling step is carried out at rates similar to the heating rates at the heating step, and preferably at rates greater than the heating rates at the heating step. The cooling step is also achieved preferably while the forming and shaping loads are still maintained.

Electronic Devices

[0083] The embodiments herein can be valuable in the fabrication of electronic devices using a BMG. An electronic device herein can refer to any electronic device known in the art. For example, it can be a telephone, such as a cell phone, and a land-line phone, or any communication device, such as a smart phone, including, for example an iPhone™, and an electronic email sending/receiving device. It can be a part of a display, such as a digital display, a TV monitor, an electronic-book reader, a portable web-browser (e.g., iPad™), and a computer monitor. It can also be an entertainment device, including a portable DVD player, conventional DVD player, Blue-Ray disk player, video game console, music player, such as a portable music player (e.g., iPod™), etc. It can also be a part of a device that provides control, such as controlling the streaming of images, videos, sounds (e.g., Apple TV™), or it can be a remote control for an electronic device. It can be a part of a computer or its accessories, such as the hard drive tower housing or casing, laptop housing, laptop keyboard, laptop track pad, desktop keyboard, mouse, and speaker. The article can also be applied to a device such as a watch or a clock.

Illustrative Embodiments

[0084] Turning now to FIG. 3A, an embodiment of a casing is illustrated, e.g., a casing for enclosing an electronic device therein (not shown). The electronic device may be a portable

electronic device such as an electronic game, tablet or laptop computer, or mobile phone or smartphone. Casing 300 includes upper shell 310 and lower shell 320. Shells 310 and 320 may include groove 330 extending into edge portions of the shells. Loop-shape memory element 340 may be made of, for example, a bulk amorphous alloy (BAA) which is elastic, and which provides stretch 360 under tension force 350 so as to fit around the exterior of shells 310 and 320 over groove 330. Figure 3B illustrates casing 300 in an assembled configuration where memory element 340 is engaged with groove 330 when tension force 350 has been removed.

[0085] Figure 4 is a cross-sectional view along section line 4-4' of casing 300 when in an assembled condition showing memory element 340 held within groove 330.

[0086] Figure 5A illustrates an alternative embodiment of casing 300', e.g., an alternative casing for enclosing an electronic device therein (not shown). Instead of engaging in a groove around an edge as in FIG. 3A, groove 330' in casing 300' is located on faces of upper shell 310' and lower shell 320'. Loop-shape memory element 340' may also be made of, for example, a BAA which is elastic, and which is stretched under tension so as to fit around the exterior faces of shells 310' and 320' over groove 330'. Figure 5B illustrates casing 300' in an assembled configuration where memory element 340' is engaged with groove 330' after memory element 340' is detensioned.

[0087] In another embodiment, FIG. 6 illustrates clamshell enclosure 600 which may be an electronic device such as an electronic game, tablet or laptop computer, or mobile phone or smartphone. Clamshell enclosure 600 includes upper clamshell 610 and lower clamshell 620 connected to upper clamshell 610 by connecting portion 630 which may be, for example, a flexible electrical conductor arrangement. Live hinge memory element 640 may be a BAA material that is flexible and which avoids the need for conventional mechanical hinge arrangements. Live hinge memory element 640 may be suitably attached at ends thereof to upper clamshell 610 and lower clamshell 620.

[0088] A living hinge or "live hinge" is a thin flexible web of material that joints two bodies together, e.g., rigid bodies, and which, if made of the correct material, will never fail. Conventional long-life living hinges are made of polypropylene or polyethylene, or shorter life living hinges may be made of resins such as nylon and acetyl. Live hinge memory element 640 may provide various advantages when constructed of a BMG/BAA material, as discussed above.

[0089] In an alternative embodiment of FIG. 6, FIG. 7 illustrates alternative clamshell enclosure 700 which may also be a portable electronic device. Clamshell enclosure 700 includes upper clamshell 710 and lower clamshell 720 connected to upper clamshell 710 by connecting portion 730 which may be, for example, a flexible electrical conductor arrangement. Live hinge memory element 740 may be a BAA material that is flexible and which works in conjunction with conventional mechanical hinge arrangement 750. Live hinge memory element 740 may be suitably attached at ends thereof to upper clamshell 710 and lower clamshell 720.

[0090] In another embodiment, FIG. 8 illustrates brassiere 800 which includes underwire-shape memory component 810 which is sewn or other wise connected in a known manner to brassiere fabric 820 to maintain the shape of fabric 820 and provide support to the wearer. Underwire-shape memory component 810 is a BMG/BAA material which provides light weight, sufficient support, and which does not rust or otherwise stain fabric 820. Other articles of clothing may be manufactured using something similar to memory component 810.

[0091] In yet another embodiment, FIG. 9 illustrates eyeglass arrangement 900 that includes optical element 910 arranged in contact with upper frame arrangement 920 in a groove in upper frame arrangement 920 (not shown). Ear piece 930 connects to upper frame arrangement 920 via hinge 960. Nose piece 970 is attached to upper frame arrangement 920. Eyeglass arrangement 900 also includes another optical element, frame, and ear piece on the opposite side, but is omitted for simplicity. Loop-shape memory component 940 may be of a BAA material which is elastic under a tensioning force 950 so as to loop around optical element 910 and upper frame arrangement 920 and thereby hold optical element 910 securely in upper frame arrangement 920. In various aspects of this embodiment, eyeglass arrangement 900 may include a lower frame arrangement (not shown).

[0092] Figure 10 is a cross-sectional view of eyeglass arrangement 900 in FIG. 9 along sectional line **10-10'** and which illustrates loop-shape memory component 940 in its retaining position after detensioning. Other structural arrangements may be determined that utilize loop-shape memory component 940 in similar configurations.

[0093] In another embodiment that may be utilized with rotating machinery (not shown), e.g., pumps and/or motors, retainer arrangement 1100 in FIG. 11A may be used in conjunction with bearing assemblies. Retainer arrangement 1100 is depicted in an unassembled condition which includes cylindrical shaft 1110 with groove 1120 centered

around groove centerline 1130. Circular-shaped retainer memory component 1140 may be slidably arranged over groove 1120 when subjected to tension force 1150. Figure 11B illustrates retainer arrangement 1100 in an assembled condition, which also depicts illustrates an exemplary direction of shaft rotation 1160 associated with the rotating machinery. Circular-shaped retainer memory component 1140 is shown in its detensioned position centered in groove 1120 along groove centerline 1130.

[0094] Figure 12 illustrates an embodiment that includes buckling spring switch arrangement 1200. A buckling spring is a type of keyswitch mechanism that refers to the fact that a coil spring arranged between the keycap and a pivoting hammer "buckles", i.e., kinks or collapses, at a certain point in its downward motion to provide auditory and tactile feedback to the keyboard operator. Upon buckling, the hammer is pivoted forward by the spring and strikes an electrical contact which registers the key depression. The electrical contact may be a membrane sheet or capacitive contact, for example. In an embodiment, buckling spring switch arrangement 1200 may include keycap 1210 arranged over lower key portion 1220 so as to contain buckling spring-shape memory component 1240 therebetween. Buckling spring-shape memory component 1240 is, contrary to conventional approaches, made of a BMG/BAA material. One end of buckling spring-shape memory component 1240 may be in mechanical contact with an interior portion of keycap 1210, and an opposite end of buckling spring-shape memory component 1240 may be mechanically coupled to electrical contact arrangement 1230 contained in lower key portion 1220. Upon depression of keycap 1210, buckling spring-shape memory component 1240 compresses until the point that it kinks or collapses and causes electrical contact arrangement 1230 to complete the electrical connection and thereby register the keystroke or key depression, as depicted in FIG. 12.

[0095] In another embodiment, dome switch arrangement 1300 is illustrated in FIG. 13. A dome switch is a hybrid of a flat-panel membrane switch and mechanical keyswitch. Dome switches bring two circuit board traces together under a rubber or silicone keypad using metal "dome" switches which typically are stainless steel domes that, when compressed, give the user a crisp, positive tactile feedback. Dome switch arrangement 1300 includes upper switch portion 1310 that may be in two parts with dome-shape memory component 1340 interposed between the two parts. Dome-shape memory component 1340 is a BMG/BAA material. Under the force of switch depression 1350, dome-shape memory component 1340 will move/deform in direction of movement 1360 to make electrical contact with lower switch portion 1320, thus registering a keystroke, for example. Dome switches may be used in other

applications other than keyboards. A rubber or silicone layer (not shown) may be provided on top of dome-shape memory component 1340 for electrical and/or environmental insulation.

LIST OF REFERENCE NUMBERS

[0096] Table 2 below lists reference numbers utilized in the specification and drawings:

Table 2			
Ref. No.	Description	Ref. No.	Description
300	casing	900	eyeglass arrangement
300'	alternative casing	910	optical element
310	upper shell	920	upper frame arrangement
310'	alternative upper shell	930	ear piece
320	lower shell	940	loop-shape memory component
320'	alternative lower shell	950	tension force
330	groove	960	hinge
330'	alternative groove	970	nose piece
340	loop-shape memory component	1100	retainer arrangement
340'	alternative loop-shape memory component	1110	cylindrical shaft
350	tension force	1120	groove
360	loop stretch	1130	groove centerline
600	clamshell enclosure	1140	circular-shaped retainer memory component
610	upper clamshell	1150	tension force
620	lower clamshell	1160	direction of shaft rotation
630	connecting portion	1200	buckling spring switch arrangement
640	live hinge memory element	1210	keycap
700	alternative clamshell enclosure	1220	lower key portion
710	upper clamshell	1230	electrical contact arrangement
720	lower clamshell	1240	buckling spring-shape memory component
730	connecting portion	1300	dome switch arrangement
740	live hinge	1310	upper switch portion
750	conventional mechanical hinge arrangement	1320	lower switch portion
800	brassiere	1340	dome-shape memory component
810	underwire-shape memory component	1350	switch depression
820	fabric	1360	dome direction of movement

[0097] The above-discussed embodiments and aspects of this disclosure are not intended to be limiting, but have been shown and described for the purposes of illustrating the functional and structural principles of the inventive concept, and are intended to encompass various modifications that would be within the spirit and scope of the following claims.

STATEMENT OF INDUSTRIAL APPLICABILITY

[0098] This disclosure finds utility in the manufacture of various articles, including electronic devices, clothing, and electro-mechanical switching devices.

CLAIMS

What is claimed is:

1. An article of manufacture, comprising:

a first material arranged in contact with a desired object or objects in a selected configuration; and

a shape memory component arranged in or adjacent to the first material, said shape memory component comprising a bulk amorphous alloy (BAA) in a memorized shape, said shape memory component being designed and adapted to return to the memorized shape and maintain the selected configuration of the first material after experiencing a deformation therefrom.
2. The article of manufacture of claim 1, wherein the first material is arranged to at least partially envelope the shape memory component.
3. The article of manufacture of claim 1, wherein the shape memory component is arranged to at least partially surround the first material and/or the desired object.
4. The article of manufacture of claim 3, wherein the first material comprises a casing containing an electronic device therein, said shape memory component comprising a loop arranged to fit around the casing and thereby maintain closure of the casing and protect the electronic device from an environment external to the casing.
5. The article of manufacture of claim 1, wherein the first material comprises an eyeglass frame arrangement that holds an optical element therein, said shape memory component comprising a BAA wire arranged to hold the optical glass in the eyeglass frame.
6. The article of manufacture of claim 1, wherein the first material comprises a fabric shaped as a brassiere, and wherein the shape memory component comprises a BAA wire arranged as an underwire attached to the brassiere.
7. The article of manufacture of claim 1, wherein the first material comprises a leather, plastic or nylon material, and wherein the shape memory component is operatively connected to the leather or nylon material to provide a desired shape thereto.

8. The article of manufacture of claim 1, wherein the first material comprises an assembly operatively coupled to a shaft, and wherein the shape memory component comprises a retaining ring that maintains the assembly in a relatively fixed longitudinal position with respect to the shaft.

9. The article of manufacture of claim 1, wherein the first material comprises a clam-shaped material, and wherein the shape memory component is arranged between two sections of the clam-shaped material as a live hinge that allows opening and closing of the clam-shaped material.

10. The article of manufacture of claim 9, wherein the clam-shape material comprises a BAA material and the shape memory component is integral with the clam-shape material.

11. The article of manufacture of claim 1, wherein the article of manufacture comprises a keyboard and the first material comprises a key for the keyboard, wherein the shape memory component comprises a switching component for the keyboard.

12. The article of manufacture of claim 11, wherein the switching component comprises a dome switch mechanically coupled to the key.

13. The article of manufacture of claim 11, wherein the switching component comprises a buckling spring mechanism mechanically coupled to the key.

14. The article of manufacture of claim 11, further comprising a mechanical switch mechanically coupled to and in registration with the key, wherein the switching component comprises a spring mechanism coupled to the key.

15. The article of claim 1, wherein the shape memory component comprises two or more pieces comprising the BAA in one or more memorized shape.

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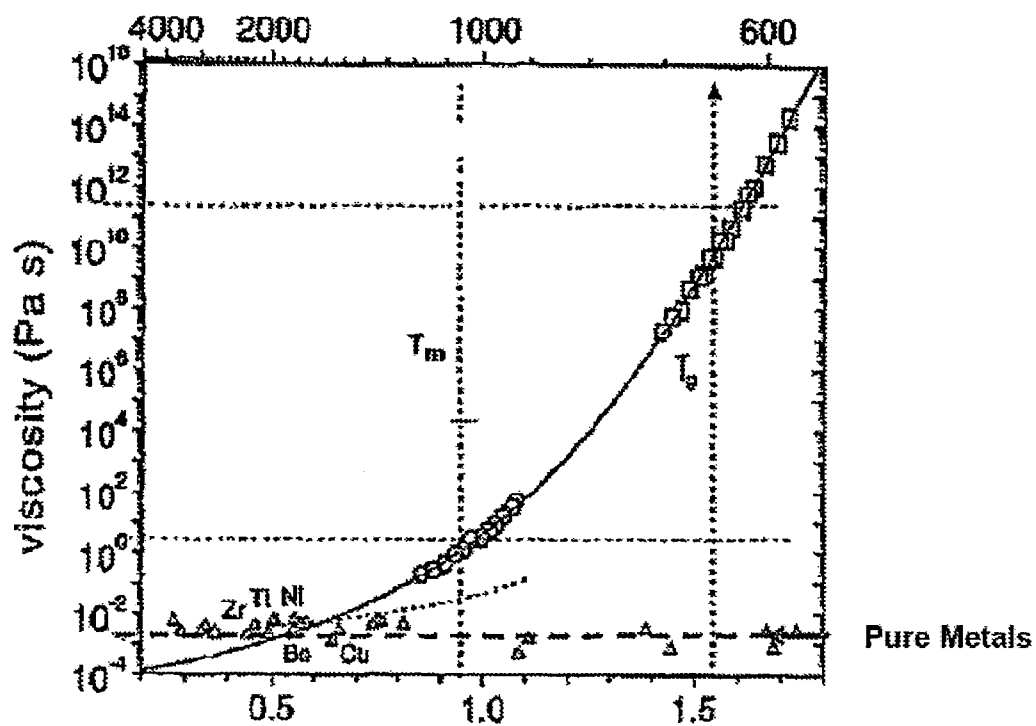


FIG. 1

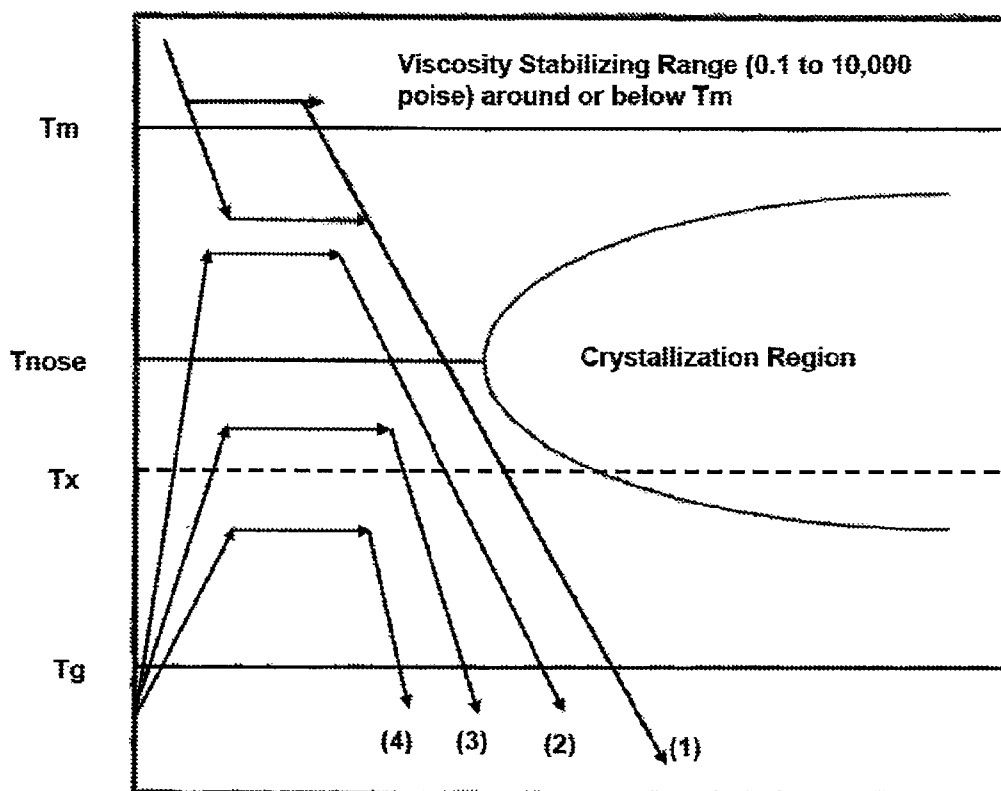


FIG. 2

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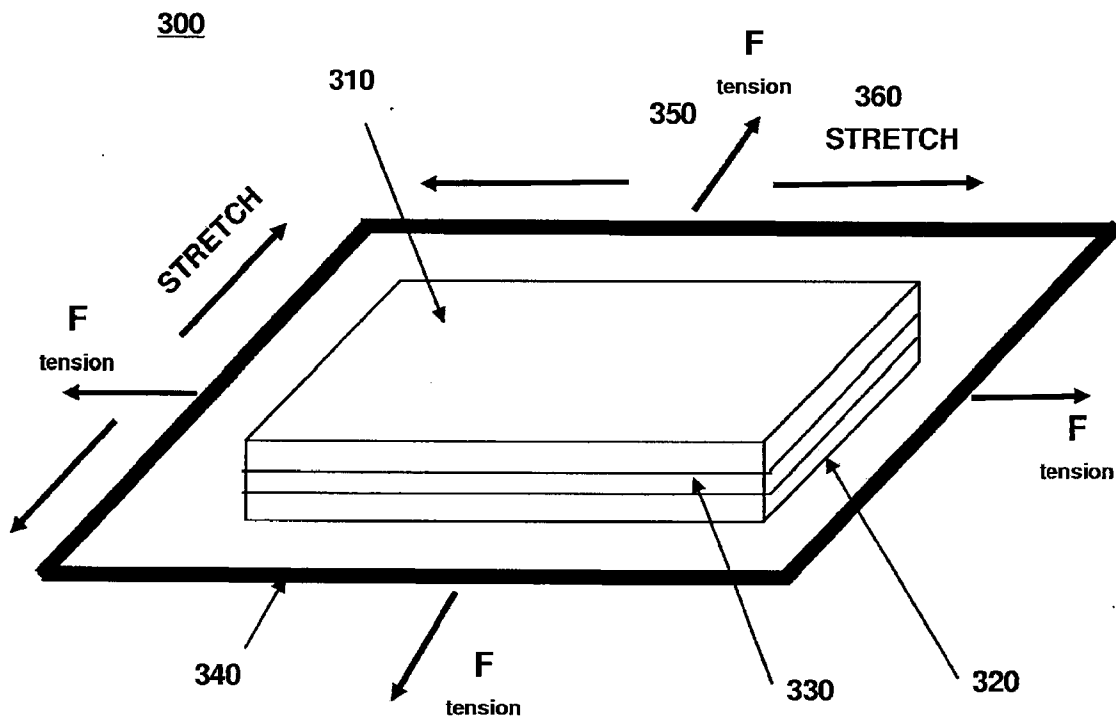


FIG. 3A

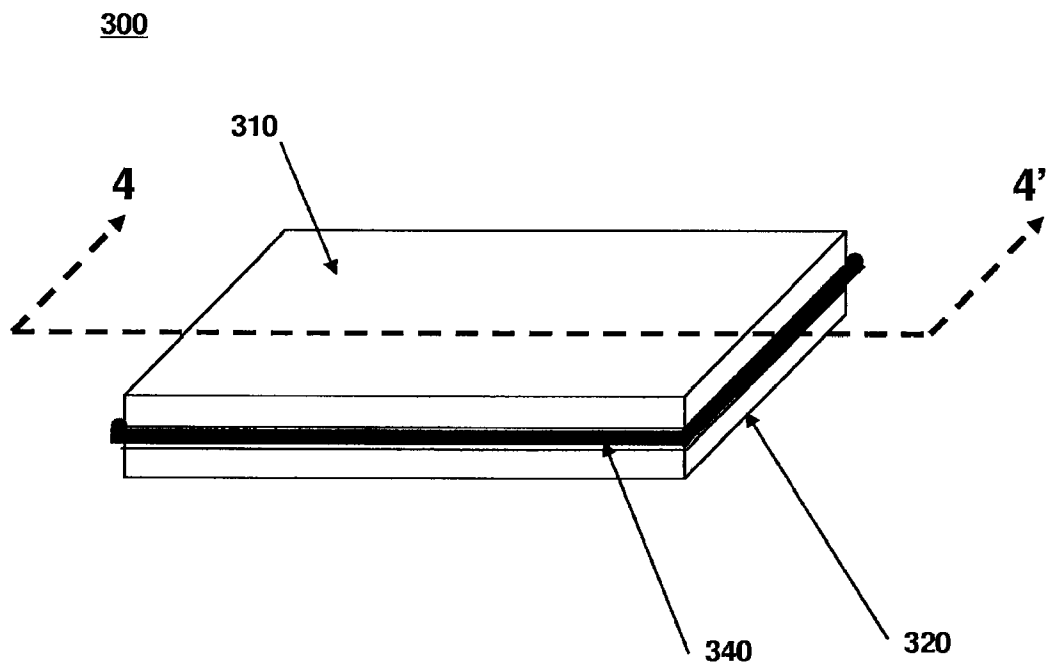
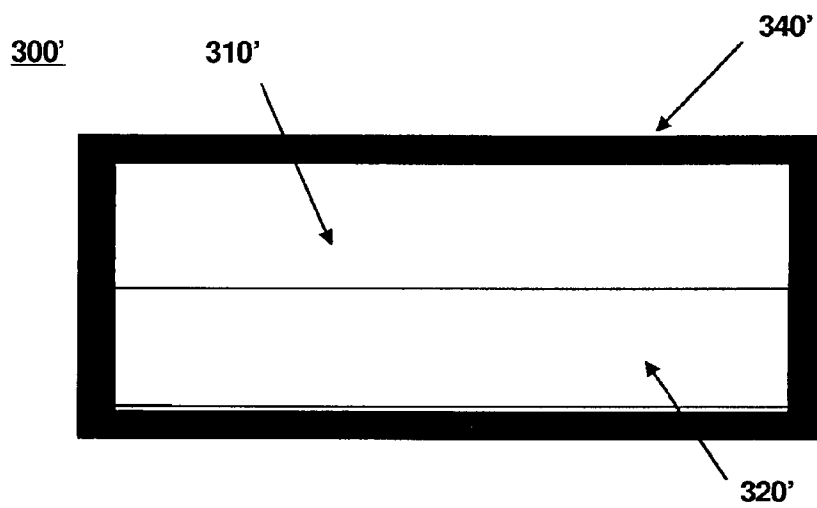
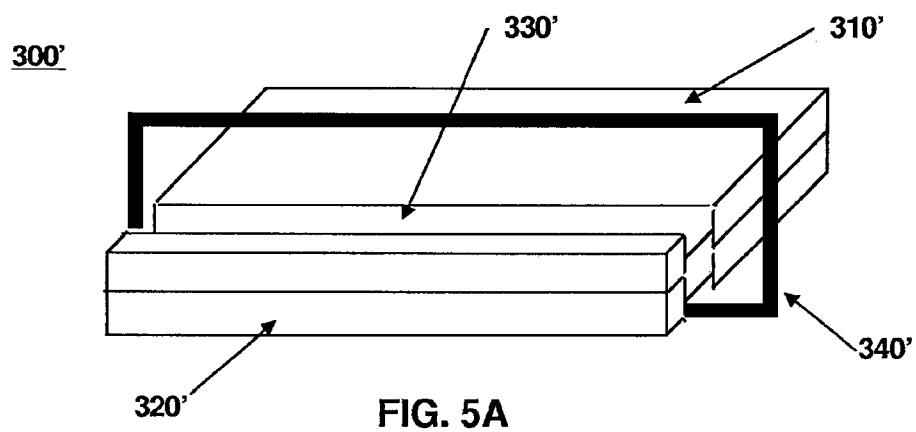
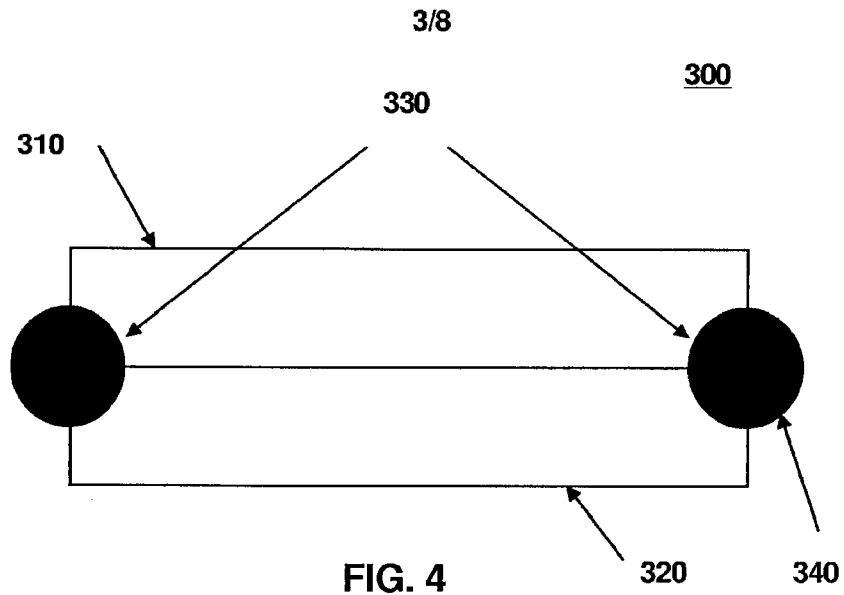


FIG. 3B



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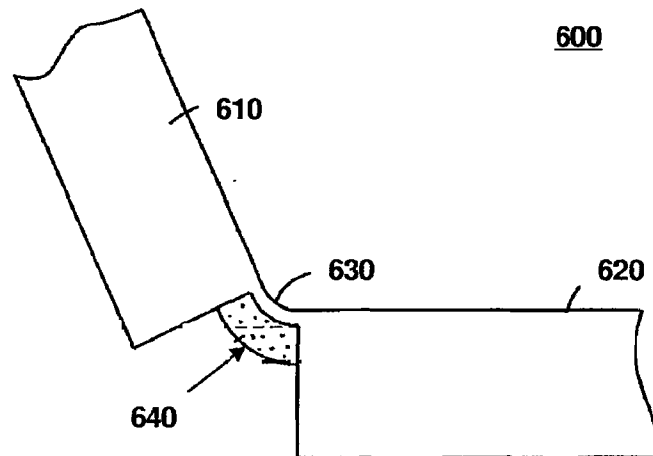


FIG. 6

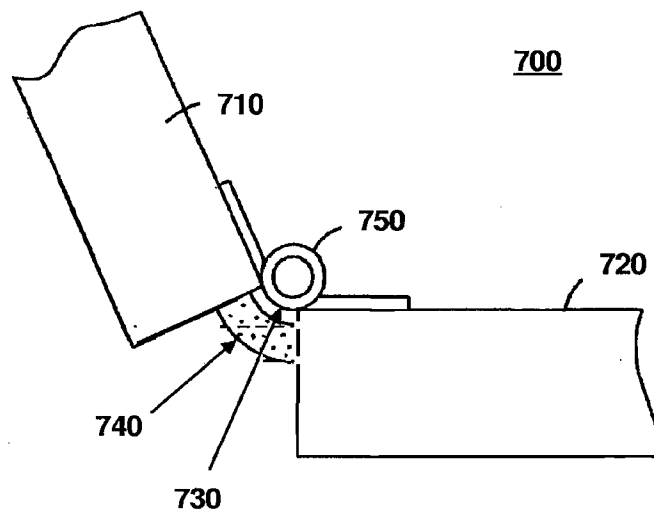


FIG. 7

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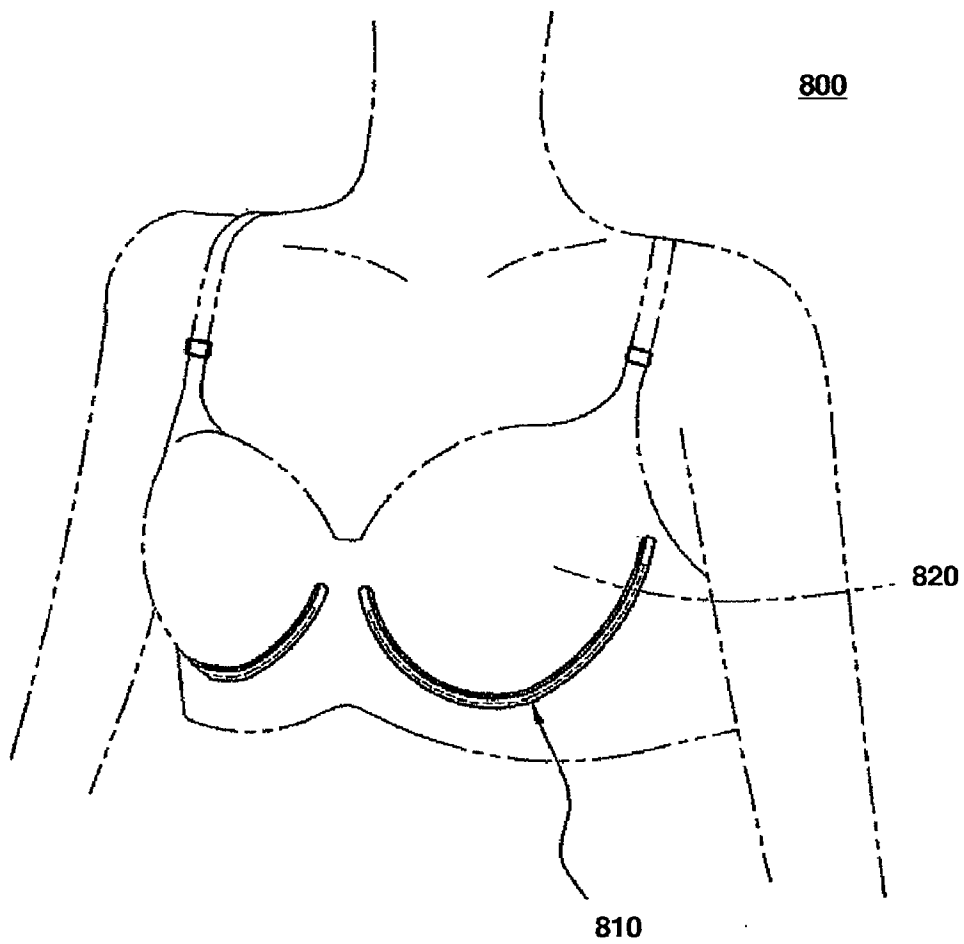
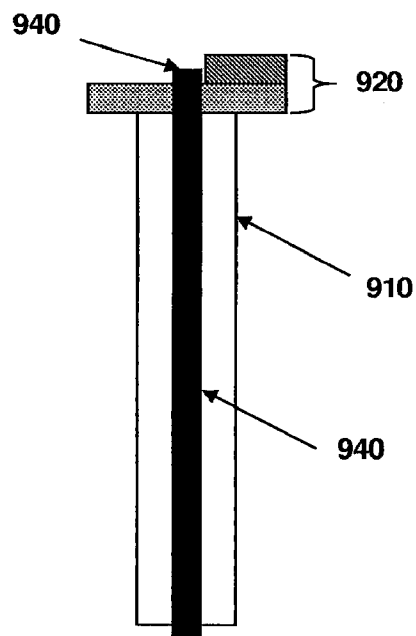
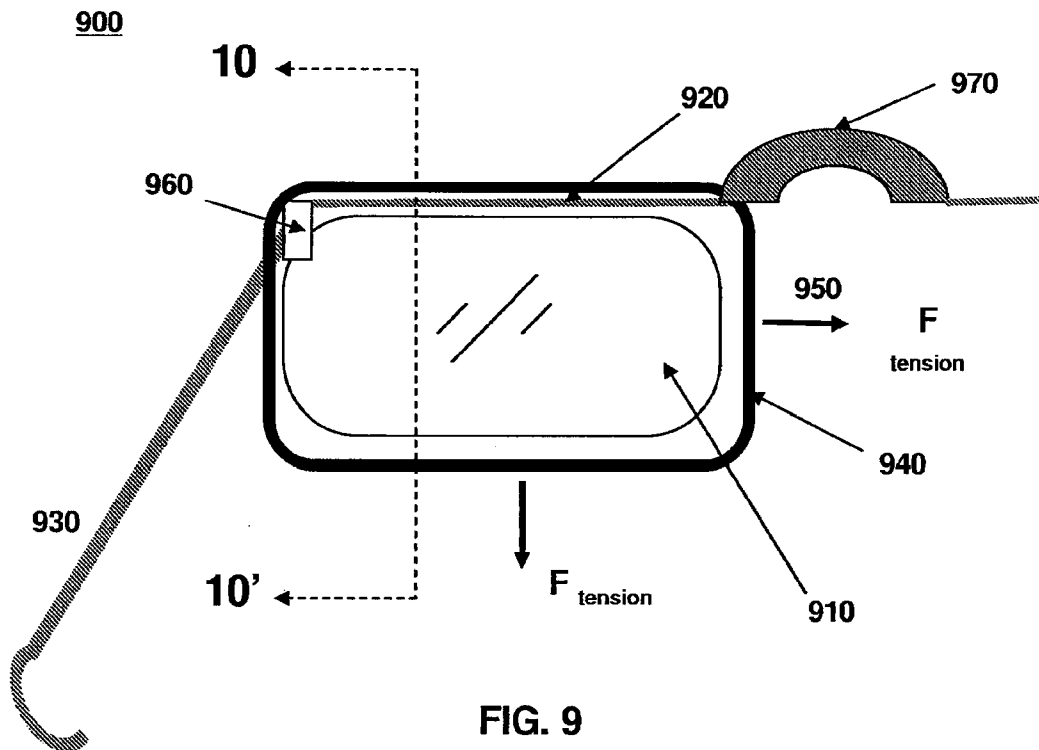


FIG. 8

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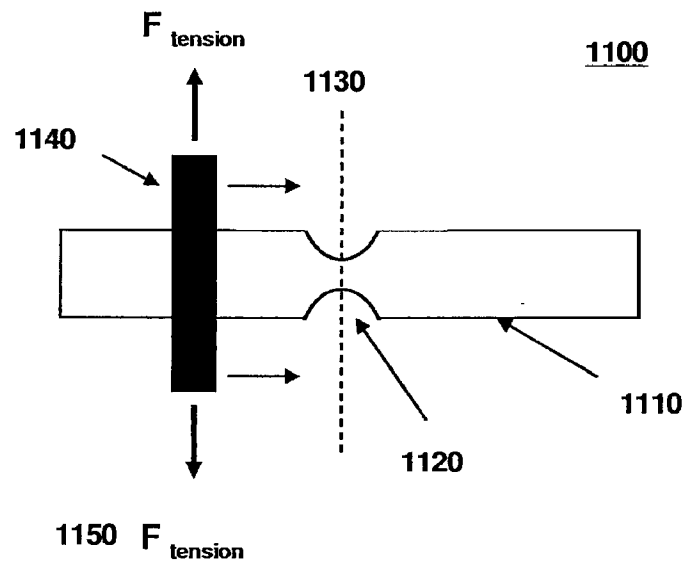


FIG. 11A

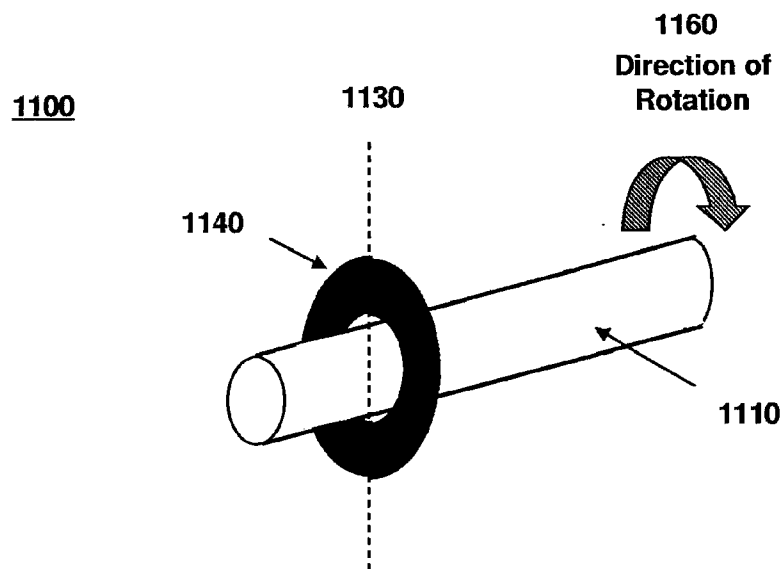


FIG. 11B

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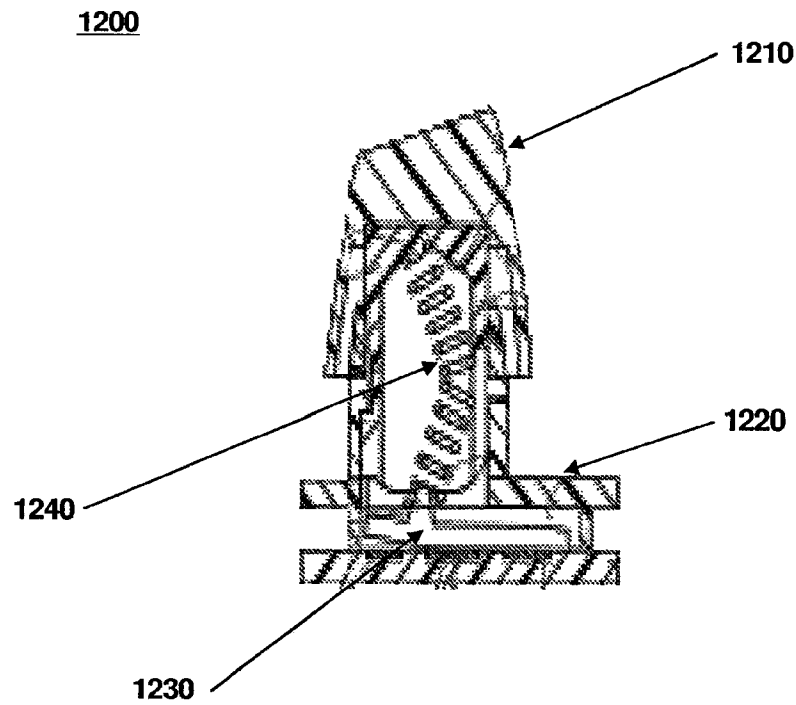


FIG. 12

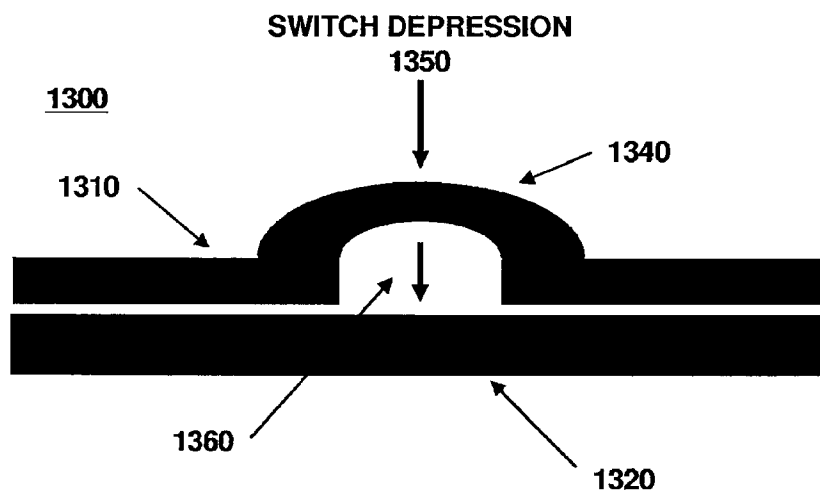


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/034897

A. CLASSIFICATION OF SUBJECT MATTER

INV. F03G7/06 C22C45/02
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)

F03G C22C

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 149 704 A1 (NAT INST FOR MATERIALS SCIENCE [JP]) 3 February 2010 (2010-02-03) the whole document	1-15
A	----- WO 2010/135415 A2 (CALIFORNIA INST OF TECHN [US]; DEMETRIOU MARIOS D [US]; JOHNSON WILLIA) 25 November 2010 (2010-11-25) the whole document	1-15
A	----- US 2008/135136 A1 (DEMETRIOU MARIOS D [US] ET AL) 12 June 2008 (2008-06-12) cited in the application the whole document	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

20 February 2013

Date of mailing of the international search report

28/02/2013

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Giorgini, Gabriele

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/034897

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