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(54) Amorphous alloys on the base of Zr and their use

(57) An alloy is disclosed which contains at least four components. Optionally, a small proportion of a fifth component may be present. The alloy has a bulk structure containing at least one amorphous phase. The alloy composition follows an "80:20 scheme", i.e., the alloy composition is $[(A_x D_{100-x})_a (E_y G_{100-y})_{100-a}]_{100-b} Z_b$ with the number "a" being approximately 80. Component A is Zr,

Hf, Ti, Nb, La, Pd and/or Pt. The other components D, E, G and, optionally, Z are all different from each other and different from component A. Component A is the main component of the alloy. Importantly, the alloy is substantially free of nickel. This makes the alloy especially suitable for medical applications. Methods of preparing such an alloy, uses of the alloy and articles manufactured from the alloy are also disclosed.

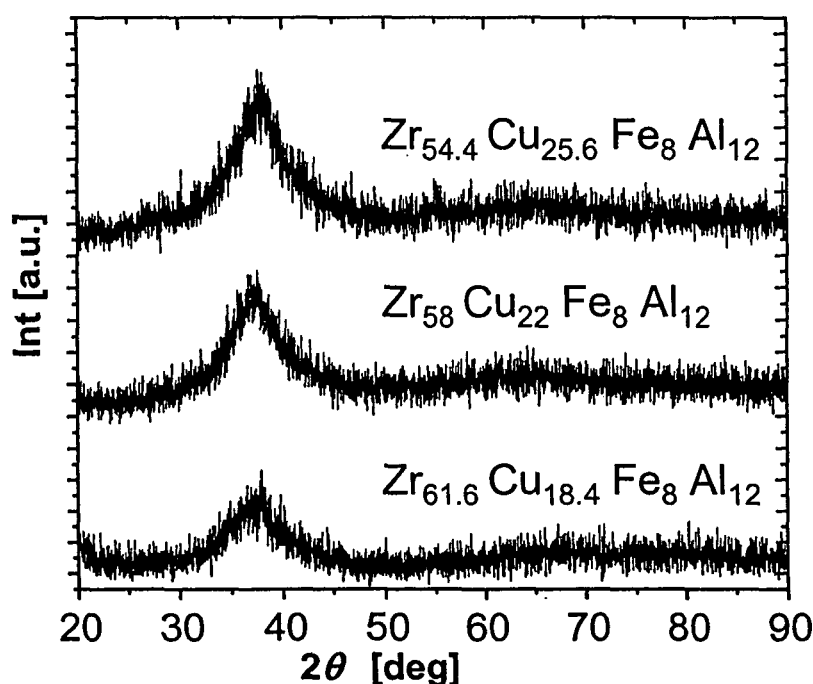


FIG. 4

Description**Field of the invention**

- 5 **[0001]** The present invention relates to an alloy with the features of the preamble of claim 1, to the use of such an alloy, and to articles manufactured from such an alloy, in particular implants such as endoprostheses.

Background of the invention

- 10 **[0002]** A number of alloys may be brought into a glassy state, i.e., an amorphous, non-crystalline structure, by splat cooling at very high cooling rates, e.g., 10^6 K/s. However, most of these alloys cannot be cast into a bulk glassy structure at much lower cooling rates achievable with casting.

- [0003]** In recent years, many bulk metallic glass-forming liquids have been discovered for which cooling rates of less than 1000 K/s are sufficient for vitrification. For the purposes of this document, a "bulk metallic glass" is to be understood as an alloy which develops an at least partially amorphous structure when cooled from a temperature above the melting point to a temperature below the glass-transition temperature of the amorphous phase with a cooling rate of 1000 K/s or less, preferably with a cooling rate of 100 K/s or less. Cooling rates in this range are typically experienced in bulk casting operations.

- [0004]** Bulk metallic glasses generally have mechanical properties that are superior to their crystalline counterparts. Due to the absence of a dislocation mechanism for plastic deformation, they often have a high yield strength and elastic limit. Furthermore, many bulk metallic glasses show good fracture toughness, corrosion resistance, and fatigue characteristics. For an overview of the properties and areas of application of such materials see, for example, Johnson WL, MRS Bull. **24**, 42 (1999) and Löffler JF, Intermetallics **11**, 529 (2003). Reference is made explicitly to the disclosure of these documents and the references cited therein for teaching properties of glass-forming metallic alloys and methods for the determination of such properties. Commercial applications of bulk metallic glasses are described, e.g., in Buchanan O, MRS Bull. **27**, 850 (2002).

[0005] Currently, only Zr-based bulk metallic glasses (and some Pt-based glasses for jewelry) have found their way into applications. The following documents of the prior art deal with Zr-based glass-forming alloys:

- 30 - US Patent No. 5,740,854 discloses an alloy of composition $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$.
- US Patent No. 5,288,344 discloses alloys of general composition Zr-Ti-Cu-Ni-Be. Specifically, the alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, which has become known under the trade name Vitreloy 1™ or Vit1™, and $Zr_{46.75}Ti_{8.8}Ni_{10}Cu_{7.5}Be_{27.5}$, which is known under the trade name Vitreloy 4™ or Vit4™, are disclosed in that document.
- 35 - US Patent No. 5,737,975 discloses alloys of the general composition Zr-Cu-Ni-Al-Nb. Specifically, an alloy of composition $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$, which is known under the trade name Vitreloy 106™ or as Vit106™, is disclosed in this document.
- Lin X H, Johnson W L, Rhim W K, *Mater. Trans. JIM* **38**, 473 (1997) discloses the alloy $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$, also known as Vit105™.
- 40 - Löffler JF, Bossuyt S, Glade SC, Johnson WL, Wagner W, Thiyagarajan P, *Appl. Phys. Lett.* **77**, 525 (2000) and Löffler JF, Johnson WL, *Appl. Phys. Lett.* **76**, 3394 (2000) describe comparative investigations of Vit1™, Vit105™ and Vit106™.
- Kundig AA, Löffler JF, Johnson WL, Uggowitzer PJ, Thiyagarajan P, *Scr. mater.* **44**, 1269 (2001) describes alloys of the general formula $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10-x}Ti_{5+x}$, i.e., alloy compositions which have been varied in the vicinity of the composition of Vit105™.
- 45 - Inoue A, Shibata T. and Zhang T., *Mater. Trans. JIM* **36**, 1426 (1995) discloses alloys of composition $Zr_{65-x}Ti_xAl_{10}Cu_{15}Ni_{10}$.
- Zhang T, Inoue A, *Mater. Trans. JIM* **39**, 1230 (1998) discloses alloys of composition $Zr_{70-x-y}Ti_xAl_yCu_{20}Ni_{10}$.
- Xing LQ, Ochin P, Harmelin M *et al*, *Mat. Sci. Eng.* **A220**, 155 (1996) discloses, inter alia, an alloy of composition $Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$, as well as other Zr-Cu-Al-Ni-Ti alloys.
- 50 - Löffler JF, Thiyagarajan P, Johnson WL, *J. Appl. Cryst.* **33**, 500 (2000) describes Zr-Ti-Cu-Ni-Be alloys whose (Zr, Ti) and (Cu, Be) contents were varied between the compositions of Vit1™ and Vit4™.
- Inoue A, Zhang T, Nishiyama N, Ohba K, Masumoto T, *Mater. Trans. JIM* **34**, 1234 (1993) discloses an alloy of composition $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$.

55 **[0006]** According to the following documents, the addition of Fe to an Zr-Al-Ni-Cu alloy was believed not to improve or to even decrease the glass-forming ability:

- Inoue A, Shibata T, Zhang T, *Mater. Trans. JIM* 36, 1420 (1995).
- Eckert J, Kubler A, Reger-Leonhard A *et al*, *Mater. Trans. JIM* 41, 1415 (2000).
- Mattern N, Roth S, Kuhn U *et al*, *Mater. Trans. JIM* 42, 1509 (2001).

[0007] Due to their favorable mechanical properties, bulk metallic glasses are interesting candidate materials for biomedical applications. However, most known glass-forming alloys, especially Zr-based alloys, contain a considerable proportion of nickel (Ni). Exposure to nickel is known to possibly cause allergies. Therefore these alloys are not well suited for medical applications, in which the alloy can come into contact with body fluids, with the skin, with tissue or other body parts. Specifically, these alloys may cause allergic reactions because they tend to release small amounts of nickel when they come into a prolonged contact with the body.

[0008] Fan C, Inoue A, *Mater. Trans. JIM* 38, 1040 (1997) describes the improvement of mechanical properties by precipitation of nanoscale compound particles in Zr-Cu-Pd-Al amorphous alloys. However, these alloys are not bulk metallic glasses; they are only amorphous when using melt spinning or splat quenching.

Summary of the invention

[0009] It is therefore an object of the present invention to provide an alloy which has good glass-forming ability while not releasing nickel in contact with body liquids.

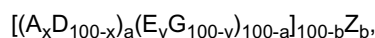
[0010] This object is achieved by an alloy with the features of claim 1.

[0011] Thus, an alloy is provided which contains at least four components A, D, E and G. Optionally, a fifth component Z may be present. The alloy has a bulk structure containing at least one amorphous phase, i.e., a volume fraction of at least 10%, preferably at least 50% of the alloy is amorphous. In the context of this document, a structure is considered to be fully amorphous if the material having this structure does not exhibit significant Bragg peaks in an X-ray diffraction pattern. Accordingly, the volume fraction of the amorphous phase in a mixed-phase material may be estimated by integrating the intensity of Bragg peaks and comparing with the intensity of non-Bragg features.

[0012] Preferably, the amorphous phase can be obtained by cooling from a temperature above the melting point to a temperature below the glass-transition temperature of the amorphous phase with a cooling rate of 1000 K/s or less, i.e., preferably the alloy is a bulk metallic glass. More preferably, the amorphous phase can be obtained by cooling with a cooling rate of 100 K/s or less. This enables the material to be formed by casting, in particular copper-mold casting. In other words, preferably the alloy with at least one amorphous phase can be obtained in a shape with dimensions of at least 0.1 mm, preferably at least 0.5 mm, more preferred at least 1 mm in any spatial direction. This is not possible for alloys which adopt an amorphous structure only at cooling rates as achievable by splat cooling or melt spinning.

[0013] Component A consists of at least one element selected from the group consisting of Zr (zirconium), Hf (hafnium), Ti (titanium), Nb (niobium), La (lanthanum), Pd (palladium) and Pt (platinum). The other components D, E, G and, optionally, Z are all different from each other and from component A. Each of these components may consist of more than one element, as long as all elements of all components are different. Preferably, however, components D, E and G each consist of a single element. The alloy composition follows an "80:20 scheme", i.e., the ratio of the combined atomic content of components A and D to the combined atomic content of components E and G is approximately 80 to 20, within a band of plus or minus 10, preferably a band of plus or minus 5, in particular a band of plus or minus 2.

[0014] Expressed as a chemical formula, the alloy composition is



where x, y, a and b are independent numbers selected from zero and the positive real numbers and denote atomic percentages, with $70 \leq a \leq 90$, preferably $75 \leq a \leq 85$, more preferred $78 \leq a \leq 82$. The following example is meant to illustrate the meaning of the term "atomic percentage": Before multiplying indices outside and inside of brackets, the indices inside the brackets should be divided by 100, e.g., $(Zr_{72.5}Cu_{27.5})_{80}(Fe_{40}Al_{60})_{20} = Zr_{58}Cu_{22}Fe_8Al_{12}$. After all brackets have been removed, each index indicates the number of atoms contributing to a formula unit of the alloy. In the present example, 58 atoms of Zr would be combined with 22 atoms of Cu, 8 atoms of Fe and 12 atoms of Al in order to arrive at one formula unit. In other words, if a number is an "atomic percentage", this means that the number, when divided by 100, indicates the stoichiometry in the sense as it is usually understood in chemistry.

[0015] Component A is the main component of the alloy, in the sense that $x \geq 50$. In order to have a significant content of component D, preferably $x \leq 95$ and more preferably $x \leq 90$. Advantageously, the content of component G relative to component E is not too small, preferably $y \geq 5$, more preferred $y \geq 10$. On the other hand, the content should not be too large. Preferably $y \leq 95$, more preferred $y \leq 90$. If a fifth component Z is present at all, then it is present in a comparatively small proportion only. In numbers, $0 \leq b \leq 6$, preferably $0 \leq b \leq 4$, more preferably $0 \leq b \leq 2$. The numbers x, y, a and b are generally independent of each other.

[0016] Importantly, the alloy is substantially free of nickel. In the context of this document, "substantially free of nickel"

means that the total nickel content of the alloy is less than 1 atomic percent, preferably less than 0.1 atomic percent. It may even be required that the nickel content is below 10 atomic ppm, e.g., in medical applications. In particular, none of the components A, D, E, G or Z should comprise nickel.

[0017] Preferably, components A and E are miscible in a wide composition and temperature range. The term "wide composition and temperature range" is to be understood as a range extending over a temperature range of at least 600 K and over a range of compositions spanning at least 60 at.% of either component in the liquid state and below the liquidus temperature in the A-E phase diagram. In the present example, a wide composition range would, e.g., be the range from 20 at.% to 80 at.% of component A in the binary mixture A-E.

[0018] More preferably, components A and E are capable of forming a deep eutectic composition in the absence of other components. The term "capable of forming a deep eutectic composition" is to be understood as meaning that, if A and E are mixed in the melt in the absence of other components, there is a composition for which A and E are miscible down to the liquidus temperature, and the liquidus temperature of the mixture for that composition has a local minimum as a function of composition. In other words, when varying the composition in a small vicinity of a deep eutectic, the liquidus temperature is higher than at the composition of the deep eutectic itself. Often, the liquidus temperature of the binary mixture at the deep eutectic will additionally be lower than the melting point of each of the components taken alone. As an example for a very deep eutectic, for A = Zr, the melting temperature is $T_m(\text{Zr}) = 2128 \text{ K}$, for E = Fe, it is $T_m(\text{Fe}) = 1811 \text{ K}$; an eutectic occurs at $1201 \text{ K} = 0.66 T_m(\text{Fe})$; likewise, for $T_m(\text{Au}) = 1337 \text{ K}$, $T_m(\text{Si}) = 1687 \text{ K}$, and an eutectic is at $636 \text{ K} = 0.47 T_m(\text{Au})$.

[0019] Preferably, the components are chosen such that a deep eutectic composition of the A-E mixture occurs at a composition A_aE_{100-a} , with $70 \leq a' \leq 90$, preferably $75 \leq a' \leq 85$. Then the number a is preferably chosen such that the absolute value of the difference between a and a' is smaller or equal to 10 (i.e., $|a - a'| \leq 10$), preferably $|a - a'| \leq 5$.

[0020] Preferably, also components A and D are miscible over a wide temperature and composition range. More preferably, they are capable of forming a deep eutectic composition when mixed in a binary mixture. If components A and D form a deep eutectic composition at A_xD_{100-x} , then x is preferably chosen such that $|x - x'| \leq 10$, more preferably $|x - x'| \leq 5$.

[0021] Preferably, component G is miscible with component E over a wide temperature and composition range, in particular if E is at least one element selected from the group consisting of the transition metals, in particular the group consisting of Fe and Co. It is then preferred that G is capable of forming a deep eutectic composition with component A.

[0022] More preferably, components G and E are capable of forming a deep eutectic composition at E_yG_{100-y} . Then y is preferably chosen such that $|y - y'| \leq 10$, more preferably $|y - y'| \leq 5$. Alternatively or additionally, A and G are preferably capable of forming a deep eutectic composition.

[0023] Preferably, the atomic Goldschmidt radius of each element in component A is relatively large, at least 0.137 nm, preferably at least 0.147 nm, more preferred at least 0.159 nm. In particular, if the atomic Goldschmidt radius of each element in component A is at least 0.159 nm, then preferably $70 \leq a \leq 90$, if this radius is at least 0.147 nm, then preferably $75 \leq a \leq 85$, and if this radius is at least 0.137 nm, then preferably $78 \leq a \leq 82$. In particular, this means that for Zr-, Hf-, and La-based alloys, preferably $70 \leq a \leq 90$; for Ti- and Nb-based alloys, preferably $75 \leq a \leq 85$; and for Pt- and Pd-based alloys, preferably $78 \leq a \leq 82$.

[0024] The components A, D, E and G may have similar atomic radii and atomic properties. However, it is preferred that the atomic radius of each element in component E is smaller than the atomic radius of each element in component A.

[0025] The atomic (Goldschmidt) radii of the elements can be found tabulated in standard textbooks or in the 2004 Goodfellow Catalog, available from Goodfellow Inc., Huntingdon, U.K. In particular, for selected elements, reference is made to Table 1 below.

Table 1: Atomic Goldschmidt radii of selected elements

Element	Ag	Al	As	Au	B	Be	C	Ca
Atomic radius [nm]	0.144	0.143	0.125	0.144	0.097	0.113	0.077	0.197

Element	Cd	Ce	Co	Cr	Cu	Fe	Ga	Ge
Atomic radius [nm]	0.152	0.182	0.125	0.128	0.128	0.128	0.135	0.139

Element	In	Ir	Hf	La	Mo	Mg	Mn	Nb
Atomic radius [nm]	0.157	0.135	0.159	0.187	0.140	0.160	0.112	0.147

Element	Nd	Ni	P	Pb	Pd	Pt	Rh	Rb
Atomic radius [nm]	0.182	0.125	0.109	0.175	0.137	0.138	0.134	0.251

Element	Se	Si	Ta	Ti	Sb	Sn	W	V
Atomic radius [nm]	0.116	0.117	0.147	0.147	0.161	0.158	0.141	0.136

Element	Y	Yb	Zn	Zr
Atomic radius [nm]	0.181	0.193	0.137	0.160

[0026] In general terms, component D is preferably at least one element selected from the group consisting of Cu (copper), Be (beryllium), Ag (silver) and Au (gold). Specifically, if component A is at least one element selected from the group consisting of La (lanthanum), Pd (palladium) and Pt (platinum), component D is preferably Cu (copper). If A is at least one element selected from the group consisting of Zr (zirconium), Hf (hafnium) and Ti (titanium), then D is preferably Cu (copper) or Be (beryllium). Both copper and beryllium have deep eutectics with Zr, Hf and Ti.

[0027] In general terms, component E is preferably at least one metal selected from the group consisting of the transition metals except Ni (nickel); particularly Sc (scandium), Ti (titanium), V (vanadium), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Zn (zinc), Y (yttrium), Mo (molybdenum), Ta (tantalum), and W (tungsten). A transition metal is defined as any of the thirty chemical elements with atomic number 21 through 30, 39 through 48, and 71 through 80. These metals are preferred because of their tendency to form deep eutectics with component A and because of their specific electronic properties. In particular, component E is preferably at least one metal selected from Fe (iron) and Co (cobalt). These metals have empirically been found to be preferred.

[0028] Component G is preferably at least one element selected from the group consisting of Al (aluminum), Zr (zirconium), P (phosphorus), C (carbon), Ga (gallium), In (indium) and the metalloids, particularly B (boron), Si (silicon), and Ge (germanium). The known metalloids are B (boron), Si (silicon), Ge (germanium), As (arsenic), Sb (antimony), Te (tellurium), and Po (polonium). It is believed that the specific electronic properties of these elements favorably influence the glass-forming ability. Furthermore, the elements B, P, C, and Si have particularly small atomic sizes (≤ 0.117 nm), which contributes to a large size difference between the components A and G. In particular, if component E is Fe (iron),

component G is preferably selected from the group consisting of Al (aluminum), Zr (zirconium), P (phosphorus), B (boron), Si (silicon) and C (carbon). More preferred, if component E is Fe (iron), then component G is Al (aluminum). Then y is advantageously chosen to be in the range from about 30 to about 50, in particular approximately 40. Alternatively, if component E is Co (cobalt), component G is preferably at least one element selected from the group consisting of Zr (zirconium), Al (aluminum), B (boron), Si (silicon), Ge (germanium), Ga (gallium) and In (indium).

[0029] In a preferred embodiment, component A is Zr (zirconium) or a mixture of Zr (zirconium) with either Hf (hafnium) or Ti (titanium) or both wherein at least 80 atomic percent of component A is Zr (zirconium). It is then preferred that component D is Cu (copper). It has been found empirically that this combination leads to alloys with superior glass-forming ability.

[0030] If component A is Zr and component D is Cu, it is preferred that x is chosen between 62 and 83 (i.e., $62 \leq x \leq 83$), preferably $68 \leq x \leq 77$, in particular that x is approximately 72.5. If component A is Zr and component D is Cu, it is further preferred that component E is Fe (iron) and component G is Al (aluminum). Then y is advantageously chosen to be in the range from about 30 to about 50, in particular approximately 40. Alloys of this composition, specifically, the alloy compositions in the vicinity of $Zr_{58}Cu_{22}Fe_8Al_{12}$, have been found by the inventors to belong to the best glass formers known to date.

[0031] If a fifth component Z is present, this component is preferably at least one element selected from the group consisting of Ti, Nb, Hf. Alternatively, component Z may preferably be at least one element selected from the group consisting of the transition metals, or component Z may preferably be at least one element selected from the group consisting of Be (beryllium), Y (yttrium), Pd (palladium), Ag (silver), Pt (platinum), and Sn (tin). In general terms, component Z is preferably capable of forming a deep eutectic composition with component A.

[0032] The alloy may have a structure comprising at least one amorphous phase and at least one crystalline phase. The volume fraction of the amorphous phase preferably is at least 10%. The amorphous and crystalline phases should not be macroscopically separated. Such a structure can be generated by different means. In one approach, a composite comprising crystals embedded in an amorphous matrix is produced by subjecting the alloy to heat treatment at a temperature above the glass transition temperature. For details, see the description of the preferred embodiments below. In another approach, the alloy is subjected to electric currents, as described, e.g., in (Holland TB, Löffler JF, Mu-nir ZA, *J. Appl. Phys.* 95, 2896 (2004)), who describe the crystallization of metallic glasses under the influence of high density DC currents. In still another approach, the alloy composition in the melt is chosen to be initially outside the glass-forming region. During cooling, crystals start forming in the melt. This alters the composition of the mixture remaining in the melt, which is shifted into the glass-forming region. Upon further cooling, a glassy matrix with embedded crystals is formed. For details, see (Hays CC, Kim CP, Johnson WL, *Phys Rev. Lett.* **84**, 2901 (2000)). In yet another approach, development of crystals in the amorphous matrix is fostered by a suitable choice of the fifth component Z. Suitable components Z are preferably at least one element selected from the group consisting of Ti, Nb, Ta, or at least one element selected from the group consisting of the transition metals, or at least one element selected from the group consisting of Be and Pd. For details, see, e.g., (He G, Eckert J, Löser W, Schultz L, *Nature Materials* **2**, 33 (2003)).

[0033] The present invention is further directed at a method of manufacture of the inventive alloys. The method comprises

- preparing a melt of aliquots of A, D, E, G, and optionally Z, and
- cooling the melt from a temperature above the melting point to a temperature below the glass-transition temperature of the amorphous phase with a cooling rate of 1000 K/s or less to obtain a solidified material. Preferably, the method comprises casting of the melt into a mold, in particular, a copper mold.

[0034] Alternatively, the inventive alloys may be produced by mechanical alloying, as described, e.g., in (Eckert J, Mater. Sci. Eng. A **226-228**, 364 (1997): Mechanical alloying of highly processable glassy alloys). Mechanical alloying means mechanical processing of the alloy or its constituents in the solid state, without passing through the liquid state. In particular, by mechanical alloying of, e.g., a crystalline powder, an amorphous metallic alloy may be obtained. Suitable mechanical alloying methods include, but are not restricted to, ball milling. For details, explicit reference is made to the teachings of the above-mentioned Eckert paper.

[0035] The method may additionally comprise a step of processing the alloy above the glass transition temperature, e.g., for obtaining a mixed-phase material. In particular, the method may comprise a step of heat-treating the solidified material for a few minutes up to 15 hours at a temperature below the first crystallization temperature or for a few seconds up to 2 hours at a temperature above the first crystallization temperature. The first crystallization temperature is the temperature of the first exothermic feature in a DTA scan of the amorphous alloy when the temperature is raised from the glass transition temperature. Heat treatment at relatively low temperatures results in slow kinetics, which is believed to lead to the formation of small crystals. For details, see the description of the preferred embodiments below.

[0036] For obtaining material with specific surface properties, the alloy may be subjected to a microstructuring process as described, e.g., in (Kundig AA, Cucinelli M, Uggowitzer PJ, Dommann A, *Microelectr. Eng.* **67**, 405 (2003): Preparation

of high aspect ratio surface microstructures out of a Zr-based bulk metallic glass) or in the patent application PCT/CH 2004/000401. The content of these documents is incorporated herein by reference in its entirety. Microstructuring may be achieved by casting the liquid alloy into a mold having itself a microstructured surface. For details, reference is made to the teachings of the above-mentioned Kundig et al. paper and to PCT/CH 2004/000401. In a different embodiment, an already solidified alloy is brought into a superplastic state, i.e., into a state in which it can be easily shaped, by heating the alloy to a temperature above the glass-transition temperature, and is pressed onto a microstructured matrix. For details, reference is made to PCT/CH 2004/000401. In an advantageous embodiment, the microstructured mold resp. matrix is a silicon wafer which has been structured by etching, as it is well known in the art. In yet another embodiment, the liquid alloy is drawn into a system of capillaries by the capillary effect and rapidly solidified within the capillaries. For details, reference is made to the teachings of the application PCT/CH 2004/000401.

[0037] The invention is also directed at the use of an inventive alloy for the manufacture of an article destined to be brought into contact with the human or animal body. In particular, the invention is directed at the use of such an alloy for the manufacture of a surgical instrument, a jewelry item, in particular a watch case, or a prosthesis, in particular an endoprosthesis, specifically, a so-called stent. A stent is an endoprosthesis for insertion into a blood vessel, lining the inner surface of the vessel. Stents are used in particular for ensuring sufficient blood flow through the vessel, or for stabilizing the blood vessel to prevent aneurisms. Other implants for which the inventive alloys can be used are in the field of os-teosynthesis, e.g., hip implants, artificial knees, etc. The present invention is also directed at an endoprosthesis, in particular a stent, manufactured from an inventive alloy.

[0038] The inventive alloys are particularly suited for such biomedical applications due to their good biocompatibility, high strength and high elasticity. In particular, the inventive alloys of general composition Zr-Cu-Fe-Al are well suited for these purposes.

Brief description of the drawings

[0039] The invention will be described in more detail in connection with an exemplary embodiment illustrated in the drawings, in which

- Fig. 1 shows a strongly simplified, schematic phase diagram of a binary Zr-Fe alloy;
- Fig. 2 shows a strongly simplified, schematic phase diagram of a binary Cu-Zr alloy;
- Fig. 3 shows a strongly simplified, schematic phase diagram of a binary Fe-Al alloy together with the ϵ -phase;
- Fig. 4 shows XRD patterns of as-cast $1\text{ mm} \times 1\text{ cm}^2$ alloys of composition $\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$, $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$, and $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$;
- Fig. 5 shows SANS intensity data of as-cast $1\text{ mm} \times 1\text{ cm}^2$ alloys of composition $\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$, $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$, and $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$ (wave number $Q = 4\pi \sin\theta/\lambda$, with θ = half the scattering angle and λ = wavelength of neutrons);
- Fig. 6 shows DTA scans on samples of composition $\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$, $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$, $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$, and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$, performed with a heating rate of 20 K/min (T_g = glass transition, T_{x1} = first crystallization temperature);
- Fig. 7 shows a DTA scan of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$, performed with a heating rate of 20 K/min;
- Fig. 8 shows a photograph of cast samples of composition $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ together with a ruler illustrating their actual size;
- Fig. 9 shows XRD patterns of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ cast to cylindrical rods of diameters 5, 7 and 8 mm, and to a plate of 1 mm thickness (inset);
- Fig. 10 shows DTA scans of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ cast to cylindrical rods of diameters 5, 7 and 8 mm (heating rate 20 K/min);
- Fig. 11 shows XRD patterns of $\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$ cast to a cone with outer diameter 6 mm;
- Fig. 12 shows a DTA scan of $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$, performed with a heating rate of 20 K/min;
- Fig. 13 shows a SEM image showing the fracture surface of glassy $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$;
- Fig. 14 shows a room-temperature tensile stress-strain curve of an ascast cylindrical $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ sample with a diameter of 5 mm;
- Fig. 15 shows XRD patterns of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ in the as-prepared state and after annealing for several hours at different temperatures;
- Fig. 16 shows an XRD pattern (72 hours scan) of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ after annealing at 708 K for 12 h. The indexing shows an icosahedral phase with a lattice constant of 4.76 Å;
- Fig. 17 shows DTA scans of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ in the as-prepared state and after annealing for several hours at different temperatures, as indicated in the figure (heating rate 20 K/min);
- Fig. 18 shows SANS intensity data of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ obtained from *in-situ* SANS measurements performed at a temperature of 708 K at different times, as indicated in the figure; and
- Fig. 19 shows the time evolution of the particle size, Φ , of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ using the Guinier approximation.

Detailed description of the invention

[0040] Before describing specific examples of inventive alloys and their characterization, the concept which led to the development of the inventive alloys shall be described and exemplified.

[0041] Many binary alloys which form metallic glasses when splat-cooled have the composition $A_{80}X_{20}$, where the atomic radius of A is significantly larger than that of X. The good glass-forming ability of such alloys with large size ratio has been explained by topological effects. In the present invention, this "80-20 concept" has been generalized to quaternary or higher-component alloys and has been successfully applied for developing Ni-free bulk metallic glasses. It has surprisingly been found that alloys with exceptionally good glass-forming ability result when following the principles laid down in claim 1. While it is generally believed in the art that the presence of nickel improves the glass-forming abilities of an alloy, making nickel an essential component of many quaternary bulk glass-forming alloys, and especially of Zr-based alloys, it has been found by the inventors that nickel can be dispensed with by following the principles of the present invention, while still alloys with excellent glass-forming abilities are obtained.

[0042] While the invention is not limited to the particular compositions described hereafter, the underlying principles of the invention will in the following be exemplified for an alloy with general composition Zr-Cu-Fe-Al. Of the four components present in such an alloy, Zr is the element with the largest atomic size ($r = 0.160$ nm). With Fe ($r = 0.128$ nm), it forms a deep eutectic composition near 20 atomic percent (at.%) Fe. This is illustrated in Fig. 1, which shows, in a highly schematic manner, part of the phase diagram of a binary Zr-Fe alloy. The transitions between the various solid phases have been omitted from the diagram for clarity, such that the diagram shows only the expected liquidus line, i.e., the liquidus temperature as a function of composition (S = solid, L = liquid). A deep eutectic feature at 24 at.% Fe is clearly visible. This deep eutectic can be qualitatively explained by topological considerations.

[0043] Also Zr and Cu have eutectic compositions, one of which occurs at 72.5% Zr, as illustrated in Fig. 2. This diagram shows, again in a highly schematic fashion, the liquidus line. At various compositions between 38.2 at.% and 72.5 at.%, several other eutectics are expected.

[0044] The fourth component in the above-mentioned general composition is Al. Fig. 3 shows, again in a highly schematic fashion, part of the phase diagram of a binary Al-Fe alloy. Several solid-solid transitions have been included in this diagram. In particular, a high-temperature phase, the so-called ϵ -phase 301, is present around the composition Al_6Fe_4 . This phase prevents a deep eutectic to be present at around 60 at.% in the Al-Fe phase diagram, which would otherwise be expected by extrapolation, as indicated by the dotted line in Fig. 3. However, since the eutectics of $Zr_{76}Fe_{24}$ and $Zr_{72.5}Cu_{27.5}$ are already below 1000°C , it is likely that the high-temperature ϵ -phase, which spans a temperature range between 1102 and 1232°C , will not form any more in the quaternary alloy.

[0045] These considerations led to the development of the composition $(Zr_{72.5}Cu_{27.5})_{80}(Fe_{40}Al_{60})_{20}$ as a starting point for further investigations as detailed below. It was found that this alloy, even without any further refinement of the composition, exhibits excellent glass-forming ability. In addition, the composition of the alloy was varied, and it was found that the alloy retained its good glass-forming properties in a rather wide range of compositions.

[0046] This shows that the "80-20 concept" can be successfully generalized to quaternary alloys. The concept is believed to be generally applicable and not to be restricted to the particular Zr-Cu-Fe-Al system described above. In particular, the same considerations may be applied to alloys which are based on Ti, Hf, Nb, La, Pd or Pt as a main component. Instead of Cu, other elements having a deep eutectic with the main component may be employed. Particularly good candidates are Be, Ag and Au. The Fe component may be replaced by one or more of the transition metals except Ni, e.g. by Co. The Al component may be replaced by, e.g., Zr or one or more of the metalloids.

[0047] In the following, examples of the manufacture and characterization of inventive alloys will be given.

Example 1:**Preparation and characterization of amorphous $(Zr_xCu_{100-x})_{80}(Fe_{40}Al_{60})_{20}$ samples**

[0048] Several Zr-based Ni-free alloys with composition $(Zr_xCu_{100-x})_{80}(Fe_{40}Al_{60})_{20}$ were prepared, where $x = 60, 62, 64, 66, 68, 72.5, 77, 79, 81, 83$ and 85 . Ingots were prepared by arc melting the constituents (purity $> 99.9\%$) in a titanium-gettered argon atmosphere (99.9999% purity). Using an induction-heating coil, the ingots were remelted in a quartz tube (vacuum $\approx 10^{-5}$ mbar) and injection cast into a copper mold with high-purity argon. Samples were cast into plates with a thickness of 0.5 mm, width of 5 mm and length of 10 mm. To determine the critical casting thickness, some samples were additionally or alternatively cast into various rod- and cone-like shapes with diameters ranging up to 10 mm. Furthermore, several samples were made with a thickness of 1 mm and cross section $1\text{ cm} \times 4\text{ cm}$. The samples were then, where appropriate, cut into various pieces of length 1 cm and investigated by X-ray diffraction (XRD), small-angle neutron scattering (SANS), differential thermal analysis (DTA) and/or hardness measurements. XRD was performed with a Scintag XDS-2000 X-ray diffractometer, using a collimated monochromatic $Cu K_\alpha$ x-ray source. The thermophysical properties were investigated with a Netzsch Proteus C550 DTA and SANS was performed at Paul Scherrer Institute,

Switzerland, using a wavelength of $\lambda = 6 \text{ \AA}$ and sample-detector distances of 1.8 m, 6 m, and 20 m.

[0049] Fig. 4 shows XRD patterns of as-cast alloys of composition $\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$, $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$, and $\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$, i.e., $(\text{Zr}_x\text{Cu}_{100-x})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$ with $x = 68, 72.5$, and 77 . All samples show a typical XRD pattern of an amorphous structure without any Bragg peaks. The amorphicity is also confirmed by SANS. As can be seen in Fig. 5, the same samples do not show any small-angle scattering over a wide Q-range, giving evidence for a homogeneous, amorphous structure.

[0050] The DTA scans in Fig. 6, performed with a heating rate of 20 K/min, reveal for all three alloys a clear glass transition, followed by an extended undercooled liquid region and an exothermic crystallization peak. For comparison, the Ni-bearing alloy $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ was also investigated by DTA. This result is also shown in Fig. 6 for comparison. Additionally, the DTA scan in Fig. 7, which was performed over an extended temperature range, shows the endothermic melting peak of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$.

[0051] Table 2 gives the characteristic values extracted from DTA scans like those of Figs. 6 and 7. The glass transition temperatures T_g were extracted from the onset of the endothermic events in Fig. 6 (arrows pointing up) and the first crystallization temperatures T_{x1} were obtained from the onset of the exothermic peaks (arrows pointing down). The onset of melting T_m and the offset of melting T_l were obtained from scans like that in Fig. 7. The new Ni-free alloys show an undercooled liquid region $\Delta T_x = T_{x1} - T_g$ of 78 to 86 K and a reduced glass transition temperature T_g/T_l between 0.56 and 0.57. Table 2 lists the ratios of T_g/T_m also, since in many publications this ratio has been used as the reduced glass transition temperature. The value of T_g/T_m is 0.59 to 0.62 for the new Ni-free alloys and thus significantly larger than that of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$.

Table 2. Glass transition temperature T_g , first crystallization temperature T_{x1} , undercooled liquid region $\Delta T_x = T_{x1} - T_g$, liquidus temperature (offset of melting) T_l , reduced glass transition temperature T_g/T_l , onset of melting T_m , and ratio T_g/T_m for three Ni-free alloys and for the Ni-bearing alloy $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$, obtained by DTA using a heating rate of 20K/min.

Alloy	T_g (K)	T_{x1} (K)	ΔT_x (K)	T_l (K)	T_g/T_l	T_m (K)	T_g/T_m
$(\text{Zr}_{68}\text{Cu}_{32})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20} = \text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$	687	773	86	1234	0.556	1098	0.62
$(\text{Zr}_{72.5}\text{Cu}_{27.5})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20} = \text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$	677	761	86	1192	0.568	1130	0.60
$(\text{Zr}_{77}\text{Cu}_{23})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20} = \text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$	670	743	78	1189	0.563	1133	0.59
$\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$	630	742	112	1165	0.540	1098	0.573

[0052] Table 3 shows the Vickers hardness HV of the Ni-free alloys that was measured with a load of 500 g. From these measurements, one obtains an estimated yield strength of 1.56 to 1.68 GPa, using the scaling relation $\sigma_y = 3 \text{ HV}$. Indeed, detailed tensile tests show a yield strength of $\sigma_y = 1.71 \text{ GPa}$ and an elastic limit of 2.25% for the alloy $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$.

Table 3. Vickers hardness HV (measured with a load of 500 g) and estimated yield strength σ_y of the Ni-free alloys.

Alloy	HV (kg/mm ²)	σ_y (GPa)
$\text{Zr}_{54.4}\text{Cu}_{25.6}\text{Fe}_8\text{Al}_{12}$	563	1.68
$\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$	542	1.62
$\text{Zr}_{61.6}\text{Cu}_{18.4}\text{Fe}_8\text{Al}_{12}$	521	1.56

[0053] Detailed casting experiments were performed on these Ni-free alloys, and these were compared with the critical casting thicknesses of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ (Vit105™) under equal experimental conditions. The alloy $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ ($x = 72.5$) could be cast into a fully amorphous state up to a rod-diameter of 7 mm. Fig. 8 shows some examples of such cast samples. These examples prove that indeed articles to be used in real-life applications can be manufactured from the inventive alloys. The wedge-shaped sample is fully amorphous up to a diameter of 7 mm.

[0054] Fig. 9 shows X-ray diffraction patterns of $\text{Zr}_{58}\text{Cu}_{22}\text{Fe}_8\text{Al}_{12}$ cast to cylindrical rods of diameters 5, 7 and 8 mm, and to a plate of 1 mm thickness (inset). No Bragg peaks are apparent either in the 5 mm rod sample or in the 1 mm plate, while only very weak Bragg peaks seem to arise in the 7 mm rod sample. In contrast, a clear crystalline component is present in the 8 mm rod sample, as apparent from the strong Bragg peaks from that sample.

[0055] These findings are consistent with the DTA scans shown in Fig. 10, which were performed on the 5 mm, 7mm and 8 mm rod samples. Clear exothermic crystallization peaks are visible for the 5 mm and 7 mm samples, while no such peak is observed for the 8 mm sample.

[0056] Likewise, the alloys with $x = 68, 77$ could be cast in rod shape with a diameter of at least 5 mm with an amorphous structure.

[0057] Fig. 11 shows XRD patterns of $Zr_{54.4}Cu_{25.6}Fe_8Al_{12}$ ($x = 68$) cast to a cone with a maximum outer diameter of 6 mm. The XRD scans were performed on 0.5 mm thick plates cut perpendicularly to the longitudinal axis of the cone. The average diameter of the corresponding plates is given in the figure. The XRD patterns of the plates with diameters of 5 mm or less show typical amorphous structures, while the plate with 6 mm diameter appears to show some Bragg peaks indicating a small volume fraction of crystals in the amorphous matrix. This is perfectly consistent with the findings for rods with uniform diameter.

[0058] Fig. 12 shows a DTA scan of $Zr_{61.6}Cu_{18.4}Fe_8Al_{12}$ ($x = 77$) performed with a heating rate of 20 K/min. Clear glass-transition, crystallization and melting features are observed. Fig. 13 shows a SEM image, showing the fracture surface of glassy $Zr_{61.6}Cu_{18.4}Fe_8Al_{12}$ ($x = 77$) which is typical for an amorphous glass. These findings demonstrate that also $Zr_{61.6}Cu_{18.4}Fe_8Al_{12}$ ($x = 77$) is an excellent bulk metallic glass-former.

[0059] In summary, of the three alloys with $x = 68, 72.5$ and 77 , the alloy $Zr_{58}Cu_{22}Fe_8Al_{12}$ ($x = 72.5$) has the greatest glass-forming ability, comparable to that of Vit105™, followed by $Zr_{61.6}Cu_{18.4}Fe_8Al_{12}$ and $Zr_{54.4}Cu_{25.6}Fe_8Al_{12}$, followed by the prior-art alloy $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$. These experimental results agree well with the Turnbull theory (D. Turnbull, Contemp. Phys. 10, 473 (1969), F. Spaepen and D. Turnbull, Proc. Sec. Int. Conf. on Rapidly Quenched Metals (Cambridge, Mass.: M.I.T. Press, 1976), pp. 205-229), which predicts that the best glass-forming ability is obtained for the alloy with the highest ratio of T_g/T_f (see Table 2).

[0060] Fig. 14 shows the tensile stress-strain curves of an as-cast cylindrical $Zr_{58}Cu_{22}Fe_8Al_{12}$ ($x = 72.5$) sample with a diameter of 5 mm. Hooke's law is well fulfilled for strain up to 2.25%. The excellent elasticity and high tensile strength as visible from this diagram are just one example of the excellent mechanical properties of the inventive alloys.

[0061] The alloys with $x = 60, 62, 64, 66, 79, 81, 83$ and 85 were also investigated by selected similar methods. It was found that the alloys with x between 62 and 81 were amorphous when cast to a thickness of 0.5 mm, the alloy with $x = 60$ was crystalline, the alloy with $x = 83$ was partially amorphous, and the alloy with $x = 85$ was crystalline when cast to a thickness of 0.5 mm.

[0062] It is apparent from this example that the composition of the material can be varied within rather broad limits without losing the good glass-forming properties. Specifically, it may be expected that a variation in the composition with respect to the other constituent elements, in particular a moderate variation of the numbers a and y , will not alter the glass-forming ability dramatically. Furthermore, it is expected that addition of a small amount of an additional component will not negatively affect the glass-forming ability or even possibly improve the glass-forming ability of the inventive materials, while possibly improving certain desired properties.

Example 2: Preparation of mixed-phase samples

[0063] Samples with a mixed-phase structure were prepared as follows: Fully amorphous samples of $Zr_{58}Cu_{22}Fe_8Al_{12}$ were prepared as in Example 1. The samples were subjected to heat treatment (annealing) at various temperatures for 12 hours. XRD patterns and DTA scans were recorded for the heat-treated samples. Fig. 15 shows XRD patterns of the samples in the as-prepared state (bottom trace) and after annealing. The XRD patterns show typical amorphous structures up to an annealing temperature of 683 K. At higher annealing temperatures, however, clear Bragg peaks arising from an icosahedral phase (I.P.) can be observed. At still higher temperatures, peaks which are typical for a Zr_2Fe structure are observed. Fig. 16 shows the XRD pattern of the sample annealed at 708 K for 12 hours in more detail. The indexing indicates the presence of an icosahedral phase with a lattice constant of 0.476 nm. Fig. 17 shows DTA scans of the same samples as in Fig. 15, which are consistent with the development of a structure with both glassy and crystalline components.

[0064] In order to better characterize the structure after annealing, in-situ small-angle neutron scattering (SANS) experiments were performed during annealing at a temperature of 708 K of a $Zr_{58}Cu_{22}Fe_8Al_{12}$ sample which was initially fully amorphous. The results are shown in Fig. 18, for total annealing times as indicated. The results show that crystalline regions develop in the initially fully amorphous sample, with typical sizes on the order of only nanometers. These data were analyzed by applying the Guinier approximation. Fig. 19 shows the time evolution of the particle size, Φ , in this approximation. This clearly demonstrates the emergence of nanocrystals within the glassy matrix. It is believed that the generation of such nanocrystals is fostered by keeping the annealing temperature only slightly above the laboratory glass transition temperature, in particular, in a range between 0 and 150 K above the laboratory glass transition temperature. The laboratory glass transition temperature is to be understood as the glass transition temperature as determined by DSC (differential scanning calorimetry) with a typical heating rate of 20 K/min. Higher annealing temperatures often lead to the precipitation of larger crystals; for example in the range of 0.1 - 20 μm .

[0065] Such mixed-phase materials exhibit somewhat different mechanical properties than a fully glassy material. In particular, ductility is often improved, which can be rationalized by the fact that shear bands which develop as a result of shear forces during forming and which might lead to breaking of the material are disrupted by the crystals. These

properties may be particularly beneficial in applications where the material must be shaped or deformed during manufacture of the end product.

Example 3: Variations of composition

[0066] Samples in a widely varying range of compositions were prepared and investigated. The compositions of the following Tables proved to be at least partially amorphous when cast to a plate with thickness of 1 mm (Table 4), 0.5 mm (table 5), or 0.2 mm (Table 6):

Table 4: Alloys having a partially or fully amorphous structure when cast to a thickness of 1 mm.

$(\text{Zr}_{95}\text{Ti}_5)_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2$	$\text{Zr}_{72}\text{Cu}_{12}\text{Fe}_{12}\text{Al}_4$
$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_3\text{Sn}_1$	$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_4$
$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2\text{Cr}_2$	$\text{Zr}_{72}\text{Cu}_{11}\text{Fe}_{11}\text{Al}_6$
$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2\text{Nb}_2$	$\text{Zr}_{72}\text{Cu}_{11.5}\text{Fe}_{11}\text{Al}_{5.5}$
$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2\text{Zn}_2$	$\text{Zr}_{73}\text{Cu}_{11}\text{Fe}_{11}\text{Al}_5$
$(\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2)_{98}\text{Mo}_2$	$\text{Zr}_{71}\text{Cu}_{11}\text{Fe}_{11}\text{Al}_7$
$(\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2)_{98}\text{P}_2$	$\text{Zr}_{69}\text{Cu}_{11}\text{Fe}_{11}\text{Al}_9$
$(\text{Zr}_{95}\text{Hf}_5)_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2$	$\text{Zr}_{70}\text{Cu}_{10.5}\text{Fe}_{10.5}\text{Al}_9$
$\text{Zr}_{70}\text{Cu}_{11}\text{Fe}_{11}\text{Al}_8$	$\text{Zr}_{70}\text{Cu}_{10}\text{Fe}_{11}\text{Al}_9$
$\text{Zr}_{71}\text{Cu}_{11}\text{Fe}_{10}\text{Al}_8$	$\text{Zr}_{70}\text{Cu}_{11}\text{Fe}_{10}\text{Al}_9$
$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{90}\text{Al}_{10}$	$\text{Zr}_{69}\text{Cu}_{10}\text{Fe}_{10}\text{Al}_{11}$
$\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2$	$\text{Zr}_{69}\text{Cu}_{10}\text{Fe}_{11}\text{Al}_{10}$
$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{98}\text{Al}_2$	$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2\text{Sn}_2$
$\text{Zr}_{73}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_1$	$\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Sn}_2$
$\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2$	$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{98}\text{Sn}_2$
$\text{Zr}_{71}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_3$	

Table 5: Alloys with a partially or fully amorphous structure when cast to a thickness of 0.5 mm.

$(\text{Zr}_{79}\text{Cu}_{21})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$	$(\text{Zr}_{66}\text{Cu}_{34})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$
$(\text{Zr}_{81}\text{Cu}_{19})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$	$(\text{Zr}_{64}\text{Cu}_{36})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$
$(\text{Zr}_{83}\text{Cu}_{17})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$	$(\text{Zr}_{62}\text{Cu}_{38})_{80}(\text{Fe}_{40}\text{Al}_{60})_{20}$

Table 6: Alloys with a partially or fully amorphous structure when cast to a thickness of 0.2 mm.

$\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2$	$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{98}\text{Ge}_2$
$\text{Zr}_{72}\text{Cu}_{13}\text{Fe}_{13}\text{Sn}_2$	$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{98}\text{Sn}_2$

[0067] For comparison, the alloys in Table 7, while being binary, ternary or Ni-containing alloys, were also investigated and developed an at least partially amorphous structure when cast to a thickness of 0.2 mm.

Table 7: Comparative listing of other alloys with a partially or fully amorphous structure when cast to a thickness of 0.2 mm.

$\text{Zr}_{70}\text{Cu}_{13}\text{Fe}_{13}\text{Al}_2\text{Ni}_2$	$\text{Zr}_{76}\text{Fe}_{20}\text{Al}_4$
$\text{Zr}_{70}\text{Cu}_{6.5}\text{Fe}_{13}\text{Al}_2\text{Ni}_{6.5}$	$\text{Zr}_{70}\text{Fe}_{27}\text{Nb}_3$
$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{98}\text{Ni}_2$	$\text{Zr}_{68}\text{Fe}_{27}\text{Nb}_5$
$(\text{Zr}_{74}\text{Cu}_{13}\text{Fe}_{13})_{96}\text{Ni}_4$	$\text{Zr}_{66}\text{Fe}_{28}\text{Nb}_6$
$\text{Zr}_{76}\text{Fe}_{24}$	$\text{Zr}_{68}\text{Fe}_{25}\text{Nb}_7$
$\text{Zr}_{75}\text{Fe}_{23}\text{Sn}_2$	$\text{Zr}_{75}\text{Fe}_{24}\text{Ni}_1$
$\text{Zr}_{70}\text{Fe}_{28}\text{Nb}_2$	$\text{Zr}_{75.5}\text{Fe}_{23.5}\text{Ge}_1$
$\text{Zr}_{76}\text{Fe}_{22}\text{Sn}_2$	$\text{Zr}_{70}\text{Fe}_{28}\text{Nb}_1\text{Sn}_1$
$\text{Zr}_{76}\text{Fe}_{23}\text{Sn}_1$	$\text{Zr}_{75.5}\text{Fe}_{23.5}\text{Si}_1$
$\text{Zr}_{75}\text{Fe}_{24}\text{Sn}_1$	$\text{Zr}_{77}\text{Fe}_{23}$

Table continued

	$Zr_{74}Fe_{24}Sn_2$	$Zr_{69}Fe_{30}Nb_1$
	$Zr_{73.72}Fe_{23.28}Sn_3$	$Zr_{68}Fe_{31}Nb_1$
5	$Zr_{73}Fe_{24}Sn_3$	$Zr_{75}Fe_{25}$
	$Zr_{76}Fe_{21}Sn_3$	$Zr_{68}Fe_{26}Nb_6$
	$Zr_{69}Fe_{29}Nb_1Sn_1$	$Zr_{69}Fe_{27}Nb_4$
	$Zr_{75.5}Fe_{23.5}Al_1$	$Zr_{68}Fe_{28}Nb_4$
10	$Zr_{76}Fe_{23}Al_1$	$Zr_{71}Fe_{26}Nb_3$
	$Zr_{72}Fe_{28}$	$Zr_{70}Fe_{28}Nb_2$
	$Zr_{74}Fe_{26}$	$Zr_{70}Fe_{26}Nb_4$
	$Zr_{70}Fe_{29}Nb_1$	$Zr_{74}Fe_{13}Cu_{13}$
	$Zr_{72}Fe_{27}Nb_1$	$Zr_{71}Fe_{16}Cu_{13}$
15	$Zr_{74}Fe_{25}Nb_1$	$Zr_{74}Fe_{13}Cu_{13}$
	$Zr_{73}Fe_{25}Nb_2$	$Zr_{76}Fe_{23}Cu_1$
	$Zr_{76}Ni_{24}$	$Zr_{76}Fe_{12}Cu_{12}$
	$Zr_{60}Fe_{20}Ni_{20}$	$Zr_{73.5}Fe_{21.5}Cu_5$
	$Zr_{75.5}Fe_{23.5}Si_1$	$Zr_{72}Fe_{14}Cu_{14}$
20	$Zr_{76}Fe_{16}Al_8$	

[0068] Specifically, this list shows that also ternary, nickel-free alloys can be reasonably good glass-formers, especially if composed according to the "80:20 scheme". Specifically, the list shows that ternary alloys of composition $(Zr_xD_{100-x})_aFe_{100-a}$, where the number a is in the range from about 70 to about 90, in particular approximately 80, are good glass formers. Here D is advantageously Cu, Nb, Al or Sn.

[0069] The alloys in Table 8 have also been prepared and were found to be fully amorphous when subjected to splat cooling to a thickness of 20 micrometers at high cooling rates of approximately 10^6 K/s. These alloys may be regarded as candidate materials for bulk metallic glasses, while casting experiments will be necessary to verify which of these are indeed bulk metallic glasses.

Table 8: Alloys having a fully amorphous structure when splat-cooled. All numbers are atomic percentages.

	$Zr_{58}Cu_{22}Fe_{18}Al_2$	$(Zr_{58}Cu_{22}Fe_8Al_{12})_{98}Nb_2$
	$Zr_{58}Cu_{22}Fe_{16}Al_4$	$(Zr_{58}Cu_{22}Fe_8Al_{12})_{98}Ta_2$
35	$Zr_{58}Cu_{22}Fe_{14}Al_6$	$(Zr_{58}Cu_{22}Fe_8Al_{12})_{98}Cr_2$
	$Zr_{58}Cu_{22}Fe_{12}Al_8$	$(Zr_{58}Cu_{22}Fe_8Ag_2)_{98}Co_2$
	$Zr_{58}Cu_{22}Fe_{10}Al_{10}$	$(Zr_{58}Cu_{22}Fe_8Al_{12})_{98}Mo_2$
	$Zr_{58}Cu_{22}Fe_6Al_{14}$	$(Zr_{58}Cu_{22}Fe_8Al_{12})_{98}Sn_2$
40	$Zr_{58}Cu_{22}Fe_4Al_{16}$	$Zr_{58}Cu_{22}Fe_6Al_{12}Nb_2$
	$Zr_{58}Cu_{22}Fe_2Al_{18}$	$(Zr_{72.5}Cu_{27.5})_{76}Fe_8Al_{12}Nb_4$
	$Zr_{62.4}Co_{17.6}Fe_8Al_{12}$	$Zr_{58}Cu_{22}Fe_4Al_{12}Nb_4$
	$Zr_{65}Al_{15}Fe_{15}Nb_5$	$Zr_{58}Cu_{22}Fe_8Al_{10}Nb_2$
	$Zr_{58}Cu_{22}Co_8Al_{12}$	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Co_2$
45	$Zr_{68}Al_{15}Fe_{15}Nb_2$	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Cr_2$
	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Nb_2$	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Ta_2$
	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Sn_2$	$(Zr_{72.5}Cu_{27.5})_{78}Fe_8Al_{12}Mo_2$
	$(Zr_{72.5}Cu_{27.5})_{80}Fe_6Al_{12}Nb_2$	$(Zr_{72.5}Cu_{27.5})_{76}Fe_8Al_{12}Sn_4$

[0070] Also the ternary alloys in Table 9 were found to be fully amorphous when splat-cooled. These are listed for comparative purposes.

Table 9: Ternary alloys having a fully amorphous structure when splat-cooled.

	$Zr_{60}Fe_{15}Al_{15}$	$Zr_{58}Cu_{22}Fe_{20}$
55	$Zr_{75}Fe_{23}Sn_2$	$Zr_{58}Cu_{22}Al_{20}$
	$Zr_{70}Fe_{28}Nb_2$	

[0071] The wide range of alloys according to the present invention which were investigated in these experiments clearly demonstrate that wide variations of composition are possible without losing the glass-forming properties of the alloys.

[0072] It is to be understood that the above examples are only provided for illustrative purposes and that the invention is in no way limited to these examples.

List of abbreviations, symbols and reference signs

[0073]

at. %	atomic percent
XRD	X-ray diffraction
SEM	scanning electron microscopy
SANS	small-angle neutron scattering
DTA	differential thermal analysis
DSC	differential scanning calorimetry
T_g	glass transition temperature
T_{x1}	first crystallization temperature
ΔT_x	undercooled liquid region
T_l	offset of melting (liquidus temperature)
T_m	onset of melting
T	temperature
σ_y	yield strength
HV	Vickers hardness
S	solid
L	liquid
2θ	scattering angle
Int	intensity
a.u.	arbitrary units
Q	wave number
S(Q)	scattering intensity
q	heat transfer
cps	counts per second
σ	tensile stress
ε	strain
I.P.	icosahedral phase
ann.	annealed
Φ	particle size

Claims

1. An alloy having a structure containing at least one amorphous phase, the alloy being represented by the general formula

$$[(A_x D_{100-x})_a (E_y G_{100-y})_{100-a}]_{100-b} Z_b,$$

wherein a, b, x and y are zero or real positive numbers signifying atomic percentages, wherein

- A is at least one element selected from the group consisting of Zr (zirconium), Hf (hafnium), Ti (titanium), Nb (niobium), La (lanthanum), Pd (palladium) and Pt (platinum),
- D, E, G and Z are components each consisting of at least one element, wherein all elements in these components are mutually different and different from all elements in A,

characterized in that said alloy is substantially free of nickel, that $70 \leq a \leq 90$, that $x \geq 50$, that $y > 0$, and that $0 \leq b \leq 6$, with the proviso that, if $A = \text{Zr}$, $D = \text{Cu}$ and $E = \text{Al}$, then $G \neq \text{Pd}$.

2. Alloy according to claim 1, **characterized in that** said at least one amorphous phase is obtainable by cooling from

a temperature above the melting point of the alloy to a temperature below the glass-transition temperature of the amorphous phase at a cooling rate of 1000 K/s or less.

3. Alloy according to claim 1 or 2, **characterized in that** D and/or E are capable of forming deep eutectic compositions with A.
4. Alloy according to one of the preceding claims, **characterized in that** G is capable of forming a deep eutectic composition with A and/or E.
5. Alloy according to one of the preceding claims, **characterized in that** A = Zr (zirconium).
6. Alloy according to one of the preceding claims, **characterized in that** D is at least one element selected from the group consisting of Cu (copper), Be (beryllium), Ag (silver) and Au (gold).
7. Alloy according to claim 6, **characterized in that** A = Zr (zirconium), D = Cu (copper), and that $62 \leq x \leq 83$.
8. Alloy according to one of claims 1 to 4, **characterized in that** A is at least one element selected from the group consisting of Pd (palladium) and Pt (platinum), and that D = Cu (copper).
9. Alloy according to one of the preceding claims, **characterized in that** E is at least one metal selected from the group consisting of the transition metals except Ni (nickel).
10. Alloy according to claim 9, **characterized in that** E is at least one metal selected from Fe (iron) and Co (cobalt).
11. Alloy according to one of the preceding claims, **characterized in that** G is at least one element selected from the group consisting of Al (aluminum), Zr (zirconium) and the metalloids.
12. Alloy according to claim 11, **characterized in that** E = Fe (iron), G = Al (aluminum) and $30 \leq y \leq 50$.
13. Alloy according to one of the claims 1 to 7 or 9 to 12, **characterized in that** A is Zr (zirconium), D is Cu (copper), E is Fe (iron) and G is Al (aluminum).
14. Alloy according to one of the preceding claims, **characterized in that** $b > 0$, and that Z is at least one element selected from the group consisting of Ti, Hf, V, Nb, Y, Cr, Mo, Fe, Co, Sn, Zn, P, Pd, Ag, Au and Pt.
15. Alloy according to claim 1 or 2, **characterized in that** the alloy is represented by the formula $(Zr_xCu_{100-x})_{80}(Fe_{40}Al_{60})_{20}$ with $62 \leq x \leq 83$ or by one of the formulas $Zr_{70}Cu_{13}Fe_{13}Al_3Sn_1$, $Zr_{70}Cu_{13}Fe_{13}Al_2Cr_2$, $Zr_{70}Cu_{13}Fe_{13}Al_2Nb_2$, $Zr_{70}Cu_{13}Fe_{13}Al_2Zn_2$, $(Zr_{72}Cu_{13}Fe_{13}Al_2)_{98}Mo_2$, $(Zr_{72}Cu_{13}Fe_{13}Al_2)_{98}P_2$, $(Zr_{95}Hf_5)_{72}Cu_{13}Fe_{13}Al_2$, $Zr_{70}Cu_{11}Fe_{11}Al_8$, $Zr_{71}Cu_{11}Fe_{10}Al_8$, $(Zr_{74}Cu_{13}Fe_{13})_{90}Al_{10}$, $Zr_{72}Cu_{13}Fe_{13}Al_2$, $(Zr_{74}Cu_{13}Fe_{13})_{98}Al_2$, $Zr_{73}Cu_{13}Fe_{13}Al_1$, $Zr_{72}Cu_{13}Fe_{13}Al_2$, $Zr_{71}Cu_{13}Fe_{13}Al_3$, $Zr_{72}Cu_{12}Fe_{12}Al_4$, $Zr_{70}Cu_{13}Fe_{13}Al_4$, $Zr_{72}Cu_{11}Fe_{11}Al_6$, $Zr_{72}Cu_{11.5}Fe_{11}Al_{5.5}$, $Zr_{73}Cu_{11}Fe_{11}Al_5$, $Zr_{71}Cu_{11}Fe_{11}Al_7$, $Zr_{69}Cu_{11}Fe_{11}Al_9$, $Zr_{70}Cu_{10.5}Fe_{10.5}Al_9$, $Zr_{70}Cu_{10}Fe_{11}Al_9$, $Zr_{70}Cu_{11}Fe_{10}Al_9$, $Zr_{69}Cu_{10}Fe_{10}Al_{11}$, $Zr_{69}Cu_{10}Fe_{11}Al_{10}$, $Zr_{70}Cu_{13}Fe_{13}Al_2Sn_2$, $Zr_{72}Cu_{13}Fe_{13}Sn_2$, and $(Zr_{74}Cu_{13}Fe_{13})_{98}Sn_2$.
16. Alloy according to one of the preceding claims, **characterized in that** the alloy has a structure comprising at least one amorphous phase and at least one crystalline phase.
17. Method of manufacturing an alloy according to one of claims 1 to 16, the method comprising
 - preparing a melt of aliquots of A, D, E, G, and optionally Z, and
 - cooling the melt from a temperature above the melting point of the alloy to a temperature below the glass-transition temperature of the amorphous phase with a cooling rate of 1000 K/s or less to obtain a solidified material.
18. Method according to claim 17, **characterized in that** the method comprises casting of the melt into a mold, in particular into a microstructured mold.
19. Method according to claim 17 or 18, **characterized in that** the method additionally comprises processing of the alloy at a temperature below the onset temperature of melting.

20. Method according to claim 19 of manufacturing an alloy according to claim 16, **characterized in that** the method comprises heat-treating the solidified material at a temperature below the onset temperature of melting for a time period sufficient for the formation of the at least one crystalline phase.

5 21. Method according to claim 19, **characterized in that** the method comprises a step of bringing the alloy into a superplastic state and forming a microstructure in this state.

22. Method of manufacturing an alloy according to one of claims 1 to 16, the method comprising mechanical alloying of a starting material which contains components A, D, E, G, and optionally Z, and/or an alloy thereof.

10 23. Use of an alloy according to one of claims 1 to 16 for manufacturing a product intended for being brought into prolonged contact with a human or animal body.

15 24. Implant for implantation in the human or animal body comprising an alloy according to one of claims 1 to 16.

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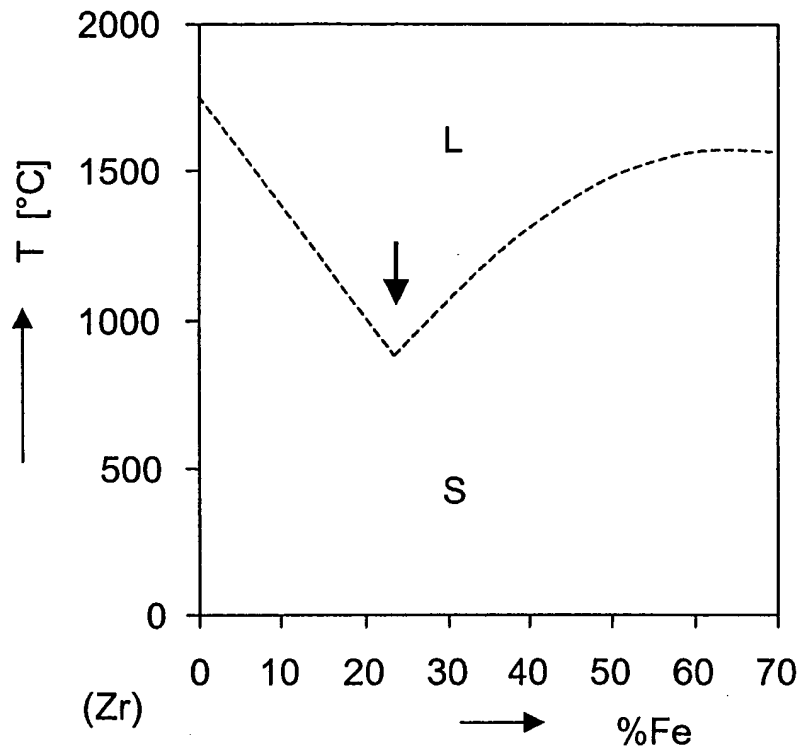


FIG. 1

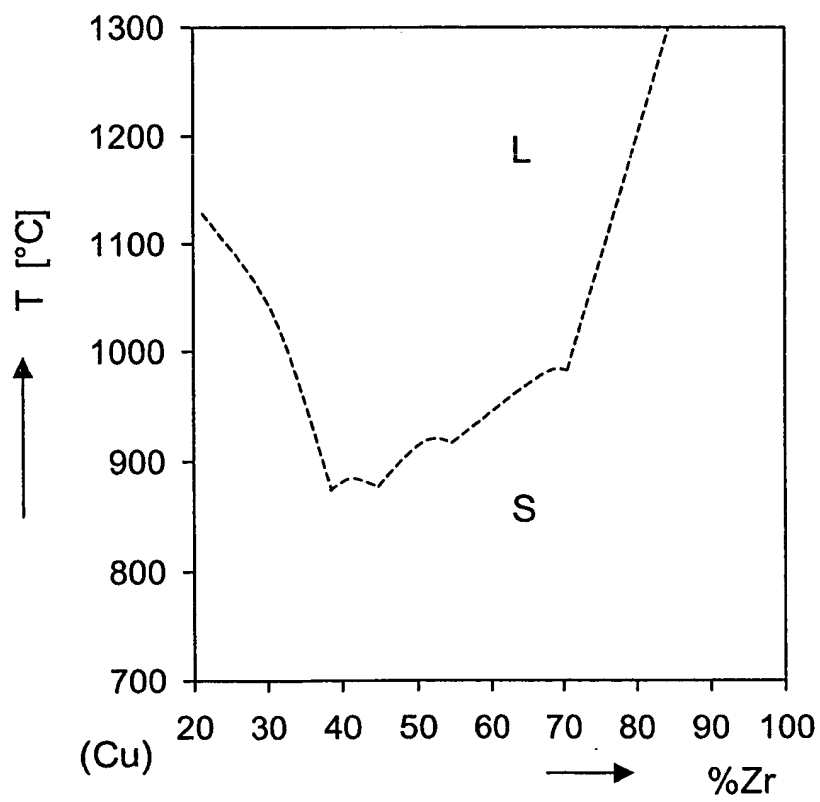


FIG. 2

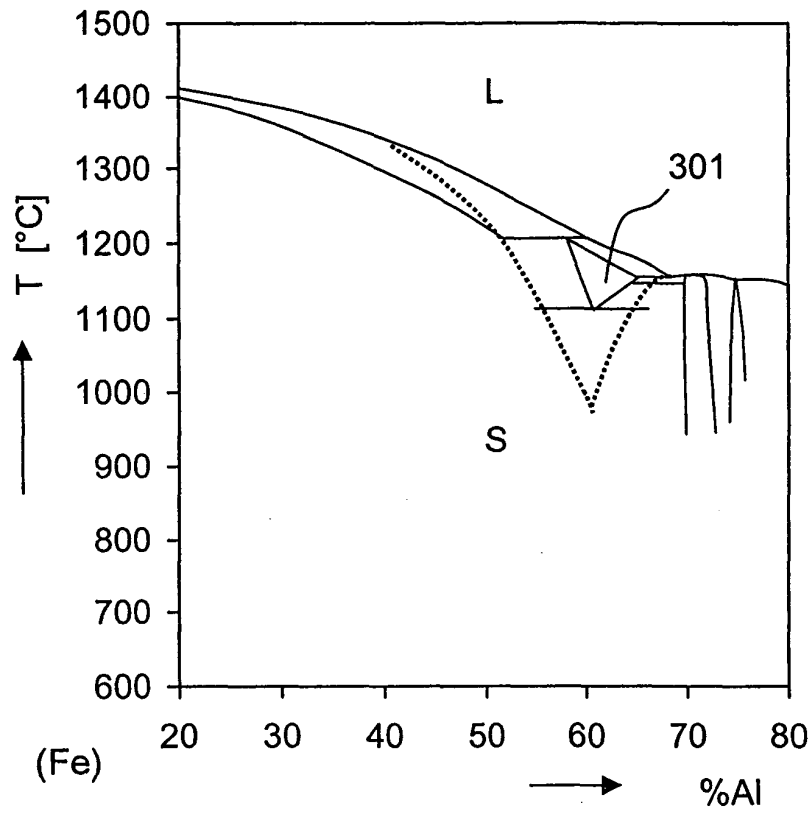


FIG. 3

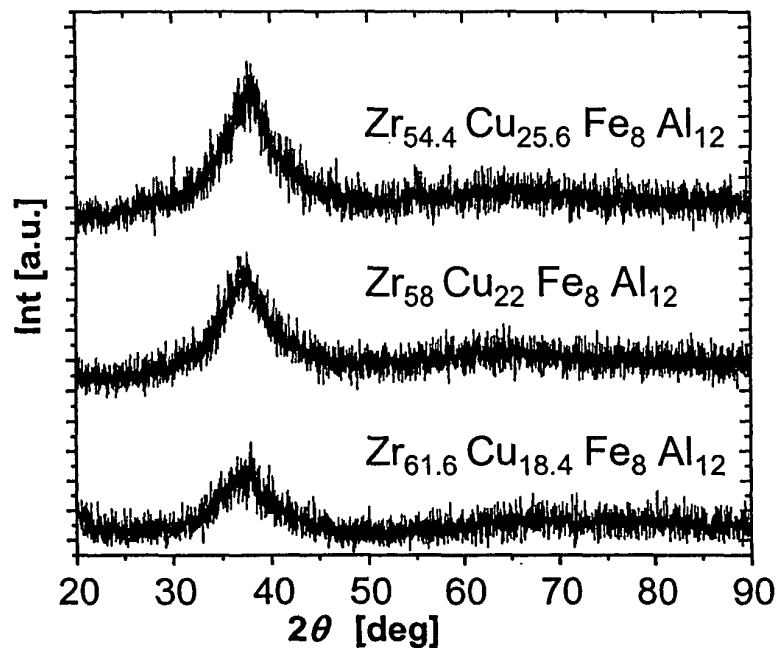


FIG. 4

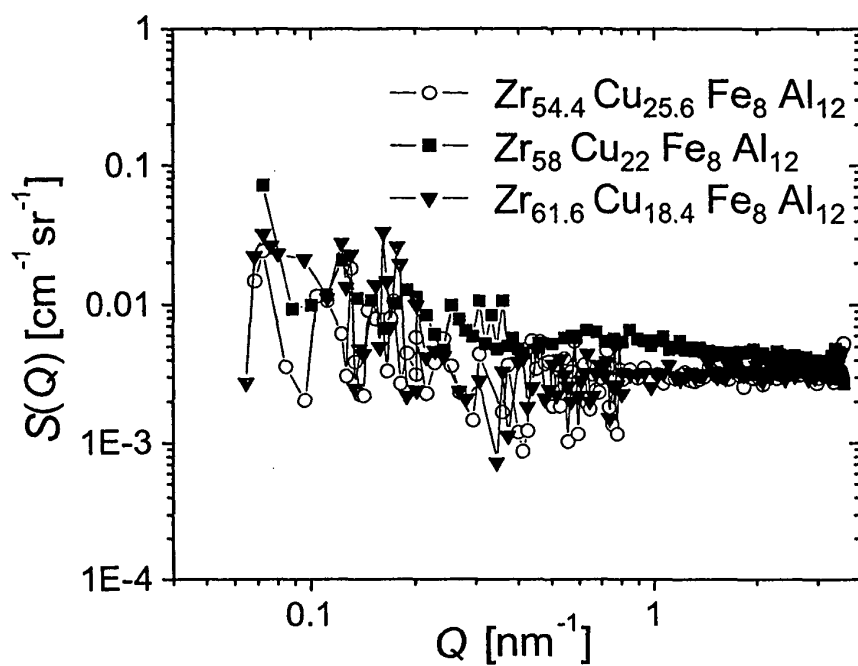


FIG. 5

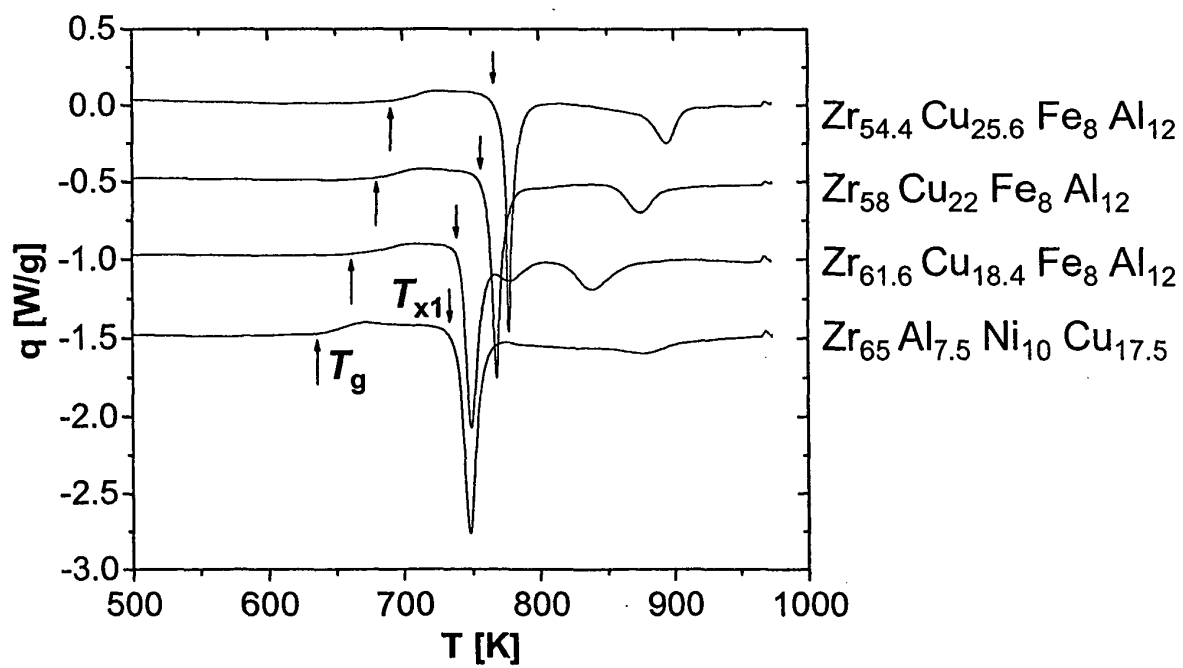


FIG. 6

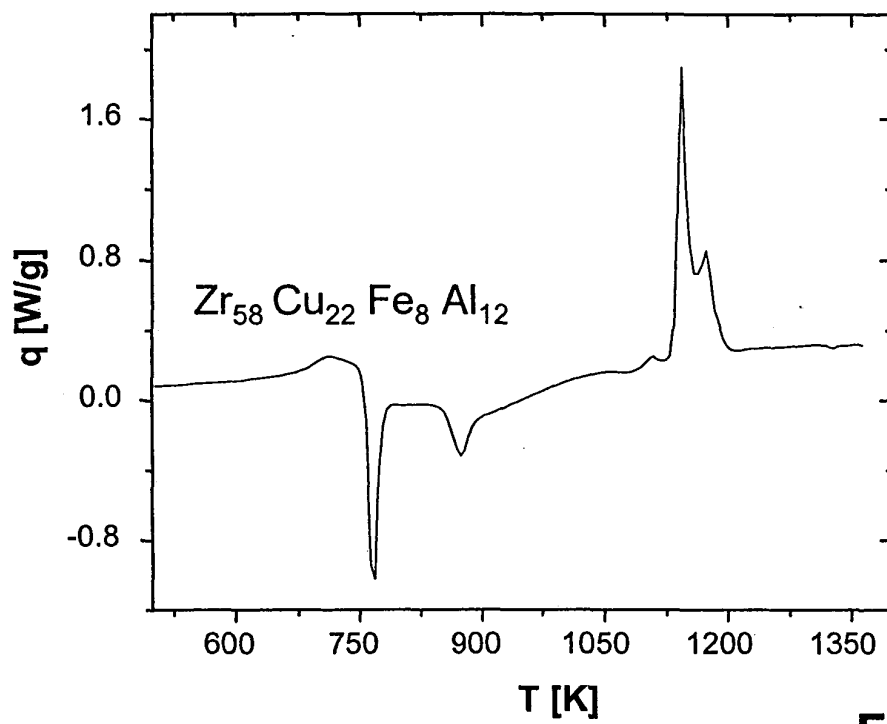


FIG. 7

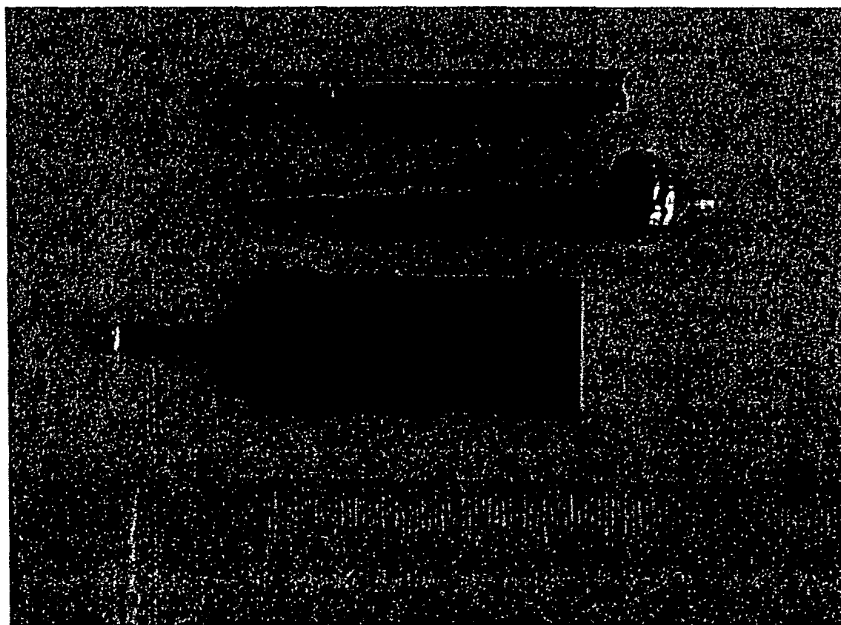


FIG. 8

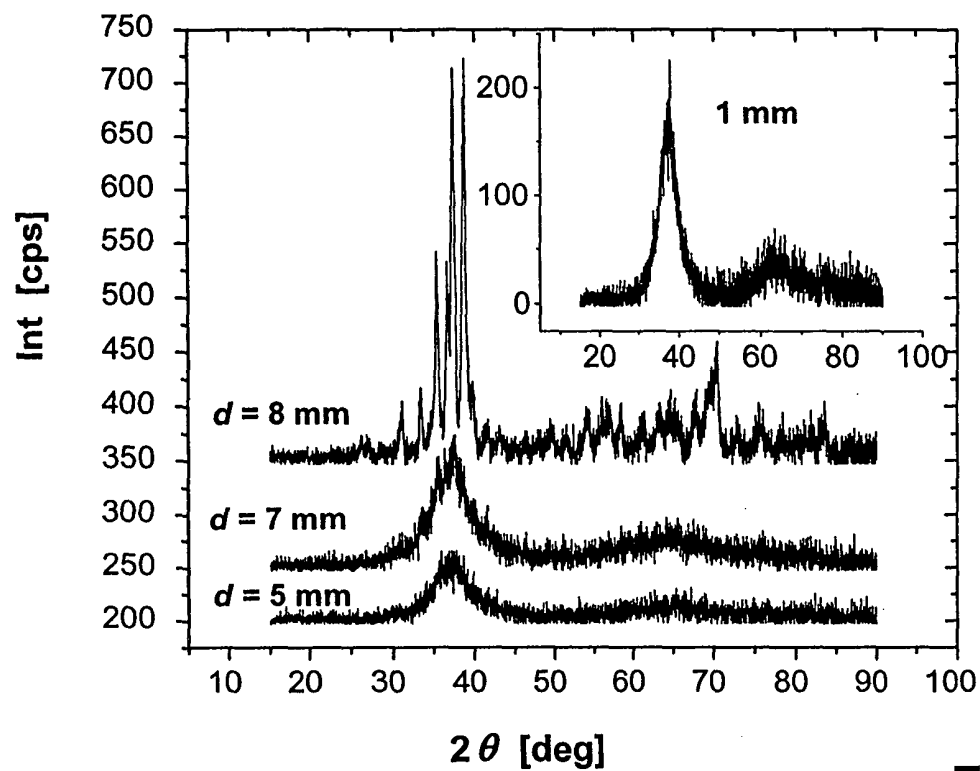


FIG. 9

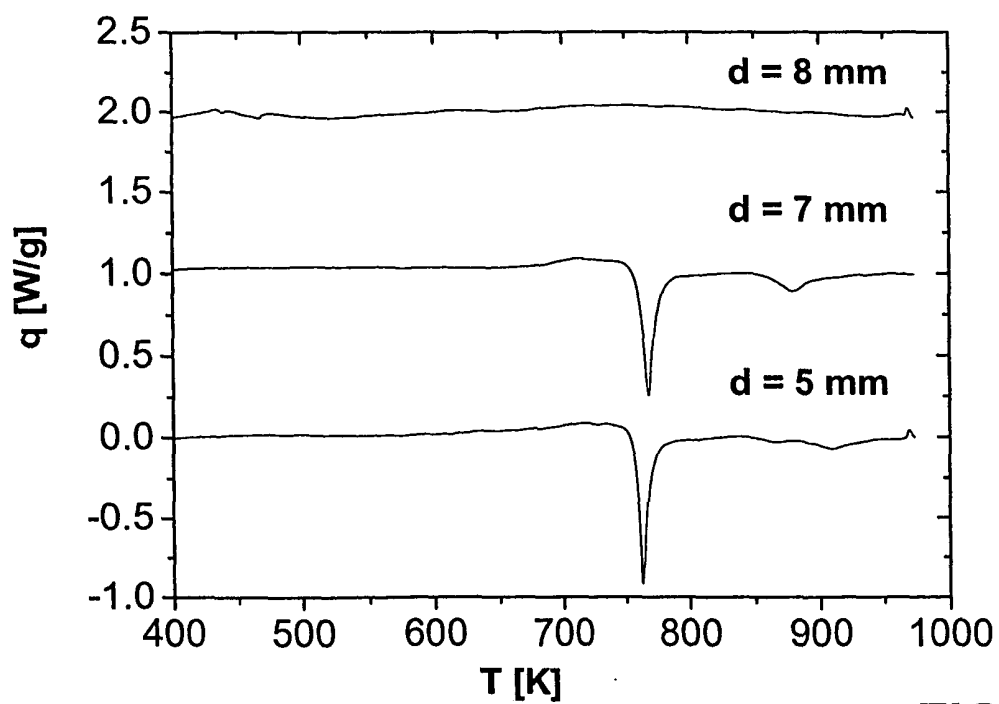


FIG. 10

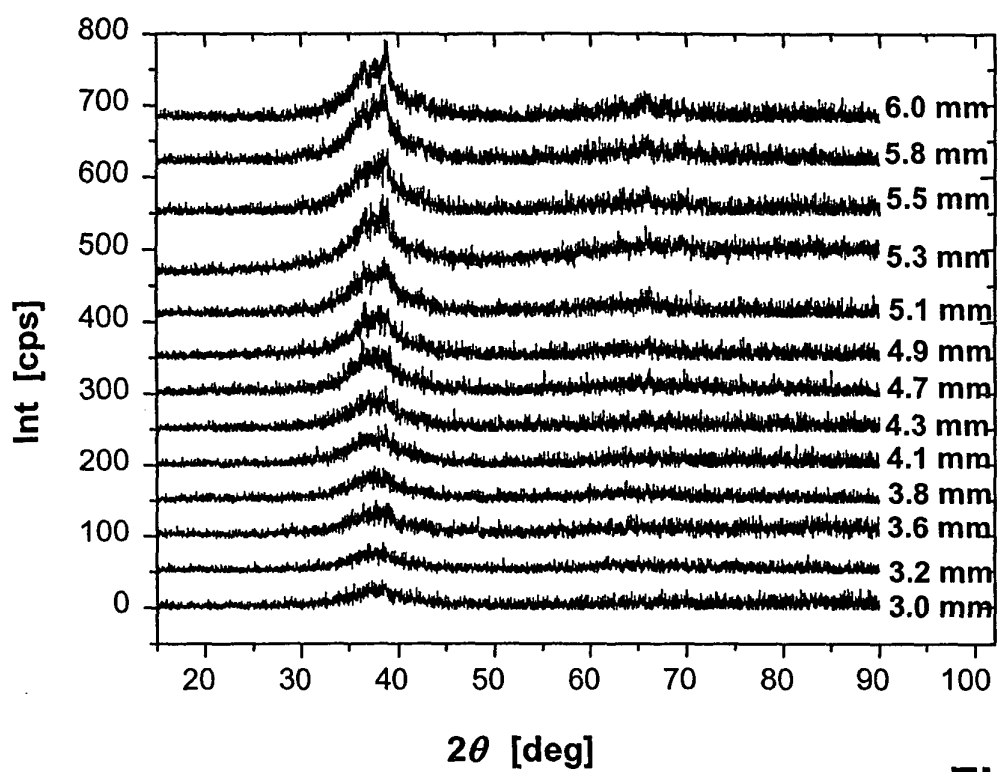


FIG. 11

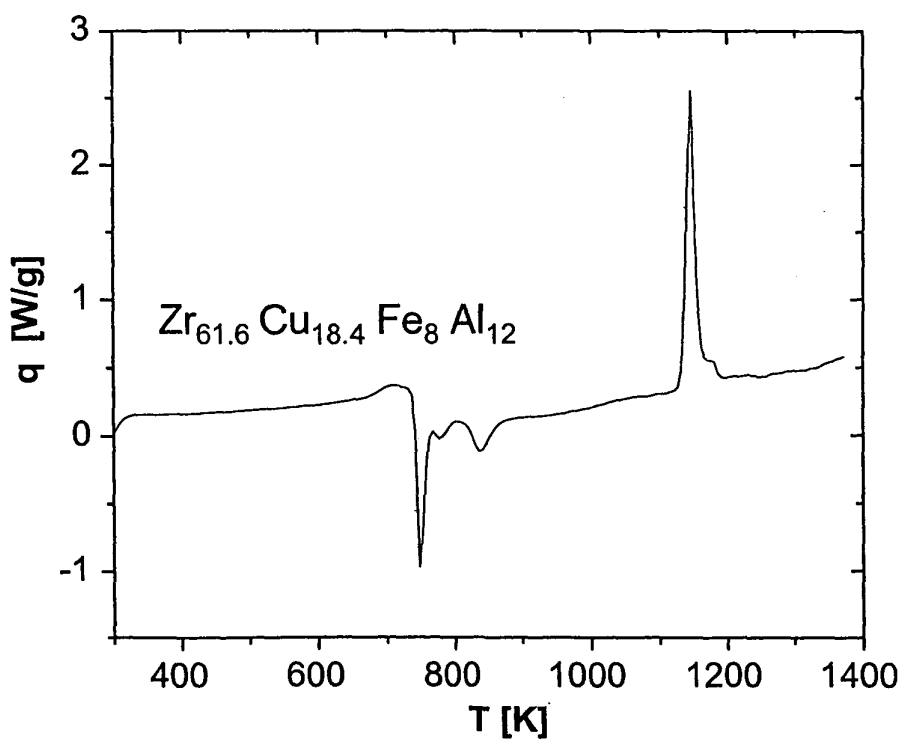


FIG. 12

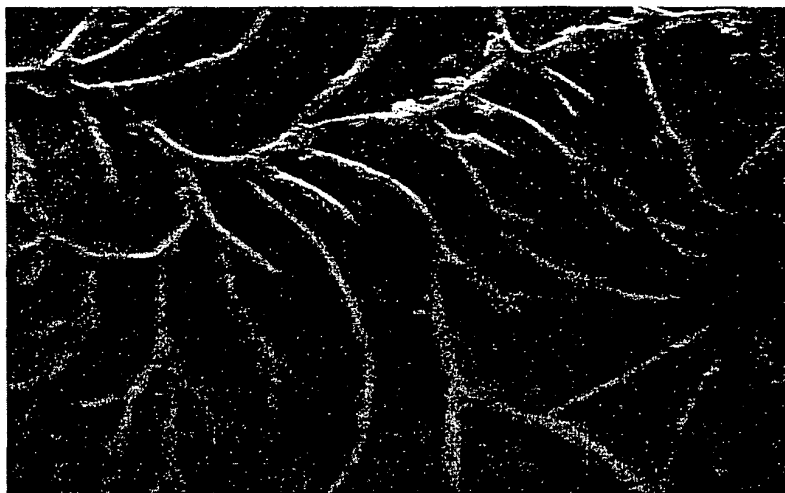


FIG. 13

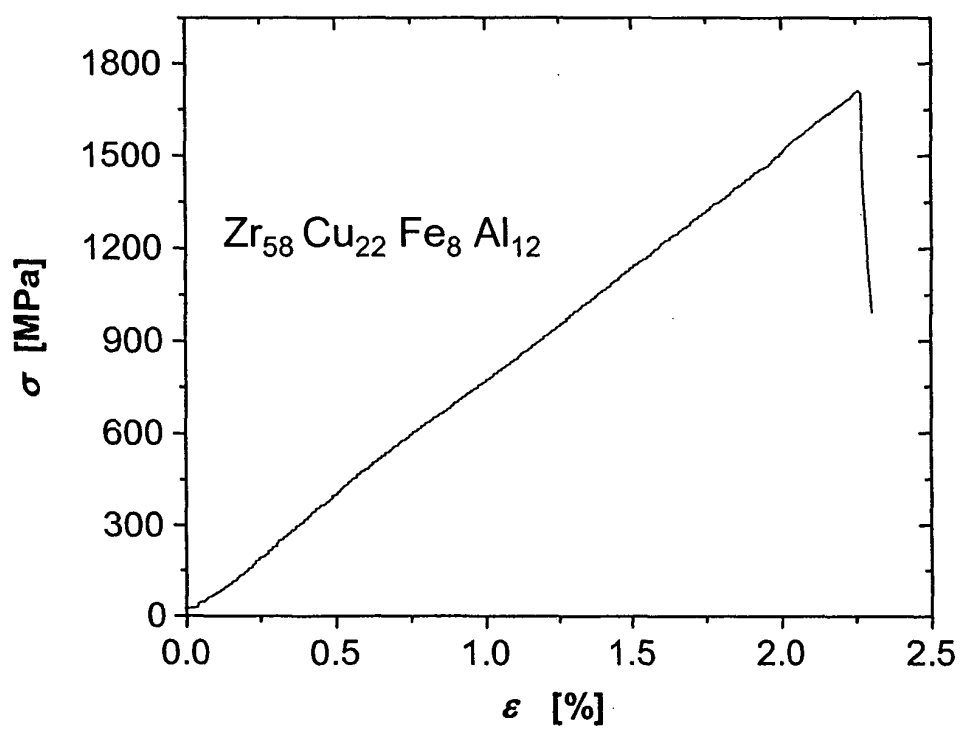


FIG. 14

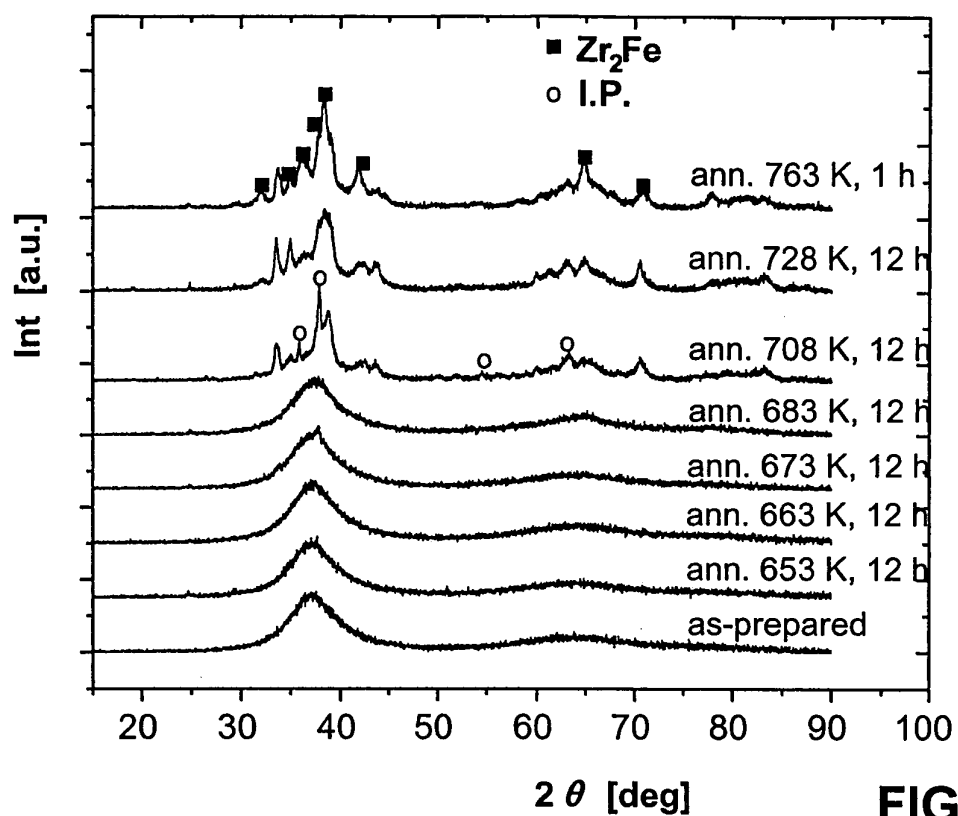


FIG. 15

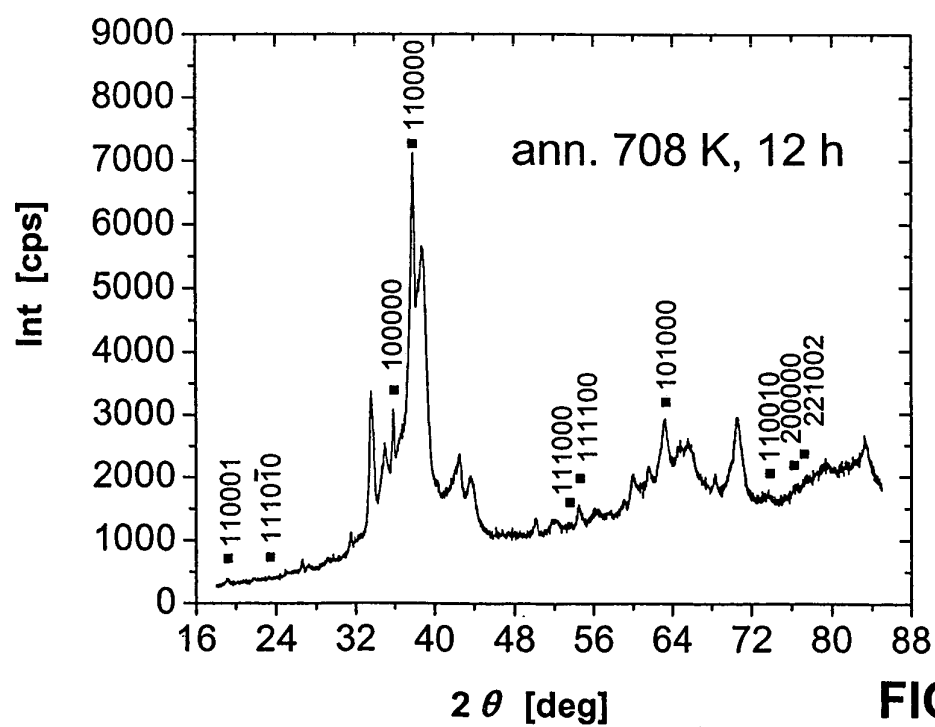


FIG. 16

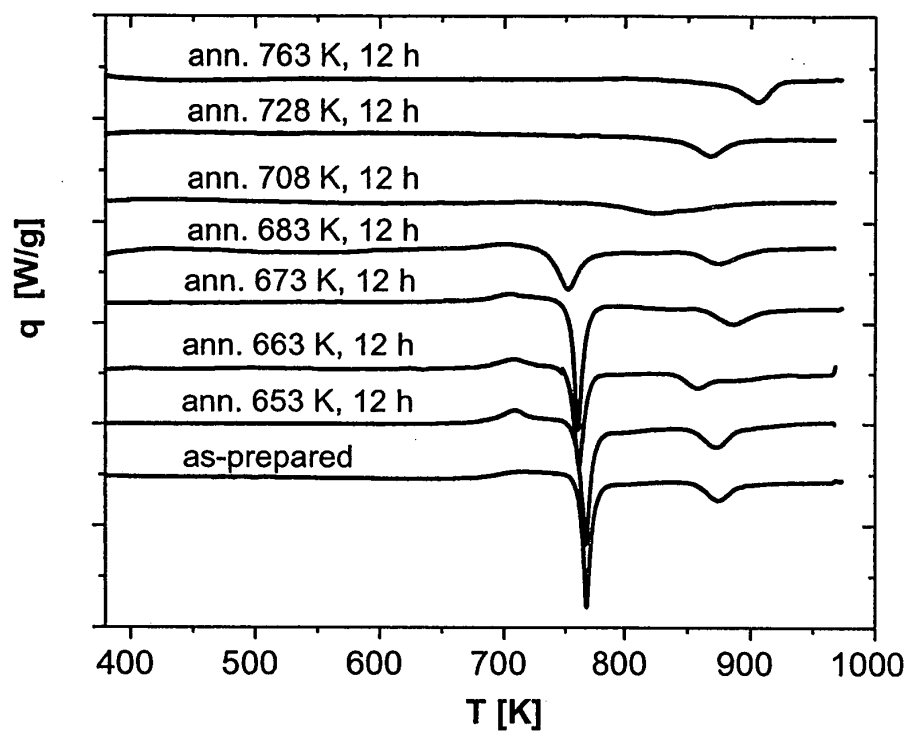


FIG. 17

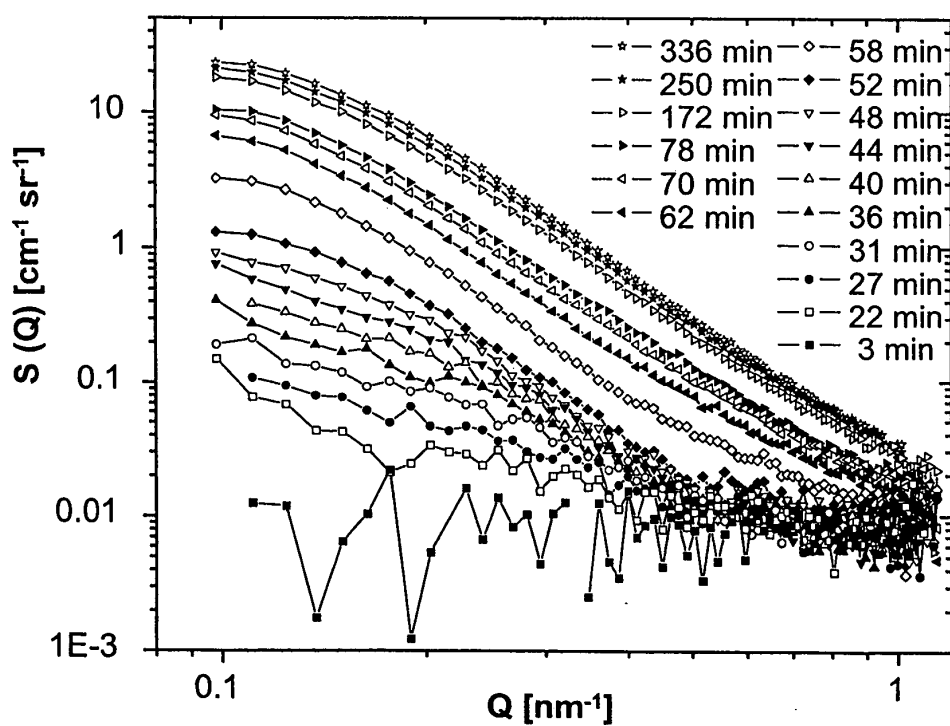


FIG. 18

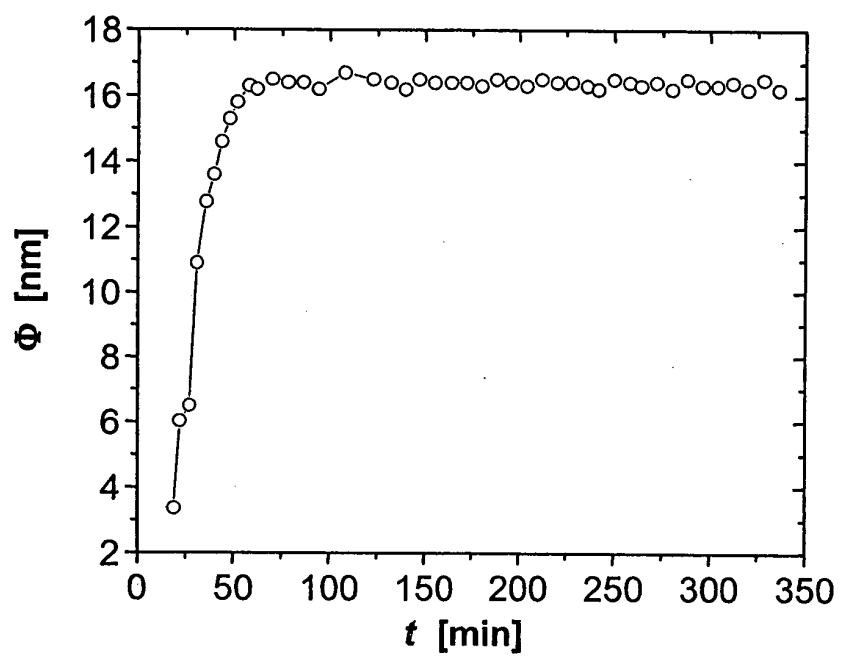


FIG. 19



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 40 5550

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X	US 5 803 996 A (MASUMOTO TSUYOSHI ET AL) 8 September 1998 (1998-09-08) * column 2, lines 48-51 * * column 3, lines 13-37 * * column 4, lines 10-12,65-67 * * column 5, lines 41-47 * * examples A3,A5,B4,B5; table 1 * -----	1-14, 16-22	C22C45/10
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 20 January 2005	Examiner Rolle, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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