

Method of enhancing the magnetic properties of amorphous metal alloys

The invention relates to a method of enhancing the D.C. and A.C. magnetic properties of amorphous metal alloy compositions and, in particular, amorphous alloys containing iron, boron, silicon and carbon.

Investigations have demonstrated that it is possible to obtain solid amorphous materials from certain metal alloy compositions. An amorphous material substantially lacks any long range atomic order and is characterized by an X-ray diffraction profile consisting of broad intensity maxima. Such a profile is qualitatively similar to the diffraction profile of a liquid or ordinary window glass. This is in contrast to a crystalline material which produces a diffraction profile consisting of sharp, narrow intensity maxima.

These amorphous materials exist in a metastable state. Upon heating to a sufficiently high temperature, they crystallize with evolution of the heat of crystallization, and the X-ray diffraction profile changes from one having amorphous characteristics to one having crystalline characteristics.

Amorphous metal alloys have been disclosed in US—A—3,856,513 (Chen and Polk). These amorphous alloys have the formula $M_aY_bZ_c$ where M is at least one of iron, nickel, cobalt, chromium and vanadium, Y is at least one element selected from phosphorus, boron and carbon, Z is at least one element selected from aluminum, antimony, beryllium, germanium, indium, tin and silicon, "a" is from 60 to 90 atom percent, "b" is from 10 to 30 atom percent and "c" is from 0.1 to 15 atom percent. These amorphous alloys have been found suitable for use in a wide variety of applications in the form of ribbon, sheet, wire and powder. The Chen and Polk patent also discloses amorphous alloys having the formula T_iX_j , where T is at least one transition metal, X is at least one element selected from aluminum, antimony, beryllium, boron, germanium, carbon, indium, phosphorus, silicon and tin, "i" is from 70 to 87 atom percent and "j" is from 13 to 30 atom percent. These amorphous alloys have been found suitable for wire applications.

DE—A—2553003 discloses the use in the core of a magnetic device of an amorphous metal alloy of the formula $M_aT_bX_c$ where M can be iron, T is an optional element, X is at least one element selected from a group including boron, silicon and carbon, and a, b and c are atomic percentages with a being from 70 to 85%, b being from 0 to 15% and c being from 15 to 25%.

DE—A—2605615 discloses the use in the core of a magnetic device of an amorphous metal alloy of the formula M_aY_b where M can be iron and Y is at least one of phosphorus, boron, carbon and silicon, and a and b are atomic percentages with a being from 60 to 95% and b being from 5 to 40%.

US—A—4081298 describes a process for improving the magnetic properties of glassy metal alloys of the composition $Fe_aNi_bP_cB_d$ where a to d are atomic percentages with a being 38 to 42%, b being 38 to 42%, c being 12 to 16% and d being 4 to 8%. The process involves immersing a toroidally wound filament of the alloy in a heat transfer liquid heated to 310 to 350°C and cooling at a rate not greater than 30°C/min through its Curie temperature, optionally applying a magnetic field to the filament during the cooling.

US—A—4116728 describes the treatment of ferrous amorphous alloys to modify their magnetic properties by heating to a temperature sufficient to achieve stress relief but insufficient to initiate crystallization and then cooling at a rate of 0.1°C/min to 100°C/min, optionally carrying out the cooling in a directed magnetic field.

Applied Physics Letters, 34, No. 1, 1979, S. Hatta et al. describes the heat treatment of Fe—B—C amorphous alloys to improve their saturation magnetization.

In accordance with the present invention there is provided a method of enhancing the magnetic properties of a metal alloy which is at least 90% amorphous and has a composition of the formula $Fe_aB_bSi_cC_d$ wherein "a", "b", "c" and "d" are atomic percentages ranging from 80.0 to 82.0, 12.5 to 14.5, 2.5 to 5.0 and 1.5 to 2.5, respectively, with the proviso that the sum of "a", "b", "c" and "d" equals 100, wherein the metal alloy is annealed by:

heating said alloy to a temperature sufficient to achieve stress relief but less than that required to initiate crystallization;

cooling said alloy at a rate of 0.5°C/min to 75°C/min; and

applying a magnetic field to said alloy during said heating and cooling.

The starting alloys are at least 90% amorphous, preferably at least 97% amorphous, and most preferably 100% amorphous, as determined by X-ray diffraction. Preferred starting alloys are those wherein "a", "b", "c" and "d" are 81, 13.5, 3.5 and 2, respectively. The starting alloys are fabricated by a known process which comprises forming a melt of the desired composition and quenching at a rate of at least 10⁵°C/sec by casting molten alloy onto a rapidly rotating chill wheel.

The annealed alloys produced by the method of this invention exhibit improved A.C. and D.C. magnetic properties that remain stable at temperatures up to 150°C. As a result, the annealed alloys are particularly suited for use as cores in electromagnetic devices, and find use in power transformers, aircraft transformers, current transformers, 400 Hz transformers, switch cores, high gain magnetic amplifiers and low frequency inverters. The enhanced magnetic properties of the annealed alloys are evidenced by high magnetization, low core loss and low volt-ampere demand. Magnetic properties are

improved in alloys possessing a greater volume percent of amorphous material.

The starting amorphous metal alloys are formed by cooling a melt at a rate of $10^{5^{\circ}}$ to $10^{6^{\circ}}$ C/sec. The purity of all materials is that found in normal commercial practice. Various techniques are available for fabricating splat-quenched foils and rapid-quenched continuous ribbons, wire and sheet. Typically, a particular composition is selected, powders or granules of the requisite elements (or of materials that decompose to form the elements, such as ferrobore and ferrosilicon) in the desired proportions are melted and homogenized, and the molten alloy is rapidly quenched on a chill surface, such as a rotating cylinder.

The starting alloys used in the method of the present invention have an improved processability as compared to other iron-based metallic glasses, since they demonstrate a minimized melting point and maximized undercooling.

The magnetic properties of the starting alloys are enhanced by the annealing method of the invention. Generally, a temperature of 340°C to 385°C is employed during heating, with temperatures of 345°C to 380°C being preferred. A rate of cooling of $0.5^{\circ}\text{C}/\text{min}$ to $75^{\circ}\text{C}/\text{min}$ is employed, with a rate of $1^{\circ}\text{C}/\text{min}$ to $16^{\circ}\text{C}/\text{min}$ being preferred.

As discussed above, the annealed alloys produced by the method of the present invention exhibit improved magnetic properties that are stable at temperatures up to 150°C , rather than a maximum of 125°C as evidenced by prior art alloys. The increased temperature stability of the annealed alloys allows them to be used in high temperature applications, such as cores in transformers for distributing electrical power to residential and commercial consumers.

When cores comprising the annealed alloys are utilized in electromagnetic devices, such as transformers, they evidence high magnetization, low core loss and low volt-ampere demand, thus resulting in more efficient operation of the electromagnetic device. The loss of energy in a magnetic core as the result of eddy currents, which circulate through the core, results in the dissipation of energy in the form of heat. Cores made from the annealed alloys require less electrical energy for operation and produce less heat. In applications where cooling apparatus is required to cool the transformer cores, such as transformers in aircraft and large power transformers, an additional saving is realized since less cooling apparatus is required to remove the smaller amount of heat generated by cores made from the subject alloys. In addition, the high magnetization and high efficiency of cores made from the annealed alloys result in cores of reduced weight for a given capacity rating.

The following Examples serve to illustrate the invention.

Examples

Toroidal test samples were prepared by winding approximately 0.030 kg of 0.0254 m wide alloy ribbon of various compositions containing iron, boron, silicon and carbon on a steatite core having inside and outside diameters of 0.0397 m and 0.0445 m, respectively. One hundred and fifty turns of high temperature magnetic wire were wound on the toroid to provide a D.C. circumferential field of 795.8 ampere/meter for annealing purposes. The samples were annealed in an inert gas atmosphere for 2 hours at 365°C with the 795.8 A/m field applied during heating and cooling. The samples were cooled at rates of $1^{\circ}\text{C}/\text{min}$ and $16^{\circ}\text{C}/\text{min}$.

The D.C. magnetic properties, i.e., coercive force (H_c) and remanent magnetization at zero A/m ($B_{(0)}$) and at eighty A/m ($B_{(80)}$), of the samples were measured by a hysteresisgraph. The A.C. magnetic properties, i.e., core loss (watts/kilogram) and RMS volt-ampere demand (RMS volt-amperes/kilogram), of the samples were measured at a frequency of 60 Hz and a magnetic intensity of 1.26 tesla by the sine-flux method.

Field annealed D.C. and A.C. magnetic values for a variety of alloy compositions that are within the scope of the present invention are shown in Table I.

TABLE I
Field Annealed D.C. and A.C. Magnetic Measurements for Amorphous
Metal Alloys within the Scope of the Invention

Example	Composition				D.C.			60 Hz A.C. 1.26 T	
	Fe	B (atom %) (weight %)	Si	C	Hc (A/m)	B ₍₀₁₎ (T)	B ₍₀₀₁₎ (T)	w/kg	VA/kg
1	81.0 94.2	13.0 2.9	4.0 2.4	2.0 0.5	4.0	1.40	1.56	0.19	0.29
2	80.8 94.0	12.8 2.9	4.2 2.5	2.2 0.6	4.0	1.40	1.54	0.22	0.29
3	80.1 93.8	13.3 3.0	4.6 2.7	2.0 0.5	3.2	1.38	1.52	0.31	0.35
4	80.5 94.5	14.3 3.3	2.7 1.6	2.5 0.6	3.2	1.26	1.46	0.32	0.79
5	81.0 94.2	13.2 3.0	3.9 2.3	1.9 0.5	4.8	1.22	1.48	0.24	0.79
6	81.9 94.9	13.7 3.1	2.7 1.6	1.7 0.4	7.2	1.20	1.52	0.24	0.29

For comparison, the compositions of some amorphous metal alloys lying outside the scope of the invention and their field annealed D.C. and A.C. measurements are listed in Table II. These alloys, in contrast to those within the scope of the present invention, evidenced low magnetization, high core loss and high volt-ampere demand.

TABLE II
Field Annealed D.C. and A.C. Magnetic Measurements for Amorphous
Metal Alloys not within the Scope of the Invention

Example	Composition				D.C.			60 Hz A.C. 1.26 T	
	Fe	B (atom %) (weight %)	Si	C	Hc (A/m)	B ₍₀₁₎ (T)	B ₍₀₀₁₎ (T)	w/kg	VA/kg
7	81.0 93.6	12.0 2.7	6.0 3.5	1.0 0.2	4.8	0.98	1.27	0.29	3.53
8	80.0 93.5	10.0 2.3	5.0 2.9	5.0 1.3	4.8	0.78	0.96	0.35	5.28
9	83.3 95.3	12.3 2.8	2.6 1.5	1.8 0.4	18.4	0.07	0.28	0.73	22.22
10	83.5 96.0	13.5 3.0	0.8 0.5	2.2 0.5	11.2	0.20	0.60	0.35	11.31
11	77.5 91.7	12.0 2.8	8.3 4.9	2.2 0.6	4.8	1.06	1.30	0.24	1.47
12	82.0 94.9	15.0 3.4	3.0 1.7	0.0 0.0	4.0	0.62	0.97	0.33	3.30



Claims

1. A method of enhancing the magnetic properties of a metal alloy which is at least 90% amorphous and has a composition of the formula $Fe_aB_bSi_cC_d$ wherein "a", "b", "c" and "d" are atomic percentages ranging from 80.0 to 82.0, 12.5 to 14.5, 2.5 to 5.0 and 1.5 to 2.5, respectively, with the proviso that the sum of "a", "b", "c" and "d" equals 100, characterised in that the metal alloy is annealed by:
 - heating said alloy to a temperature sufficient to achieve stress relief but less than that required to initiate crystallization;
 - cooling said alloy at a rate of 0.5°C/min to 75°C/min; and
 - applying a magnetic field to said alloy during said heating and cooling.
2. A method according to claim 1, wherein the alloy is heated at 340°C to 385°C.
3. A method according to claim 1, wherein the alloy is heated to a temperature of 345°C to 380°C and is cooled at a rate of 1°C/min to 16°C/min.
4. A method according to claim 1, 2 or 3, wherein said alloy is at least 97 percent amorphous.
5. A method according to claim 1, 2 or 3, wherein said alloy is 100 percent amorphous.
6. A method according to any one of claims 1 to 5, wherein "a", "b", "c" and "d" are 81, 13.5, 3.5 and 2, respectively.
7. A core for use in an electromagnetic device comprising a metal alloy which is at least 90% amorphous, has a composition of the formula $Fe_aB_bSi_cC_d$ wherein "a", "b", "c" and "d" are atomic percentages ranging from 80.0 to 82.0, 12.5 to 14.5, 2.5 to 5.0 and 1.5 to 2.5, respectively, with the proviso that the sum of "a", "b", "c" and "d" equals 100, and has been annealed by a method as claimed in any one of the preceding claims.

Revendications

1. Procédé permettant d'améliorer les propriétés magnétiques d'un alliage métallique qui est au moins amorphe à 90 % et a une composition ayant la formule $Fe_aB_bSi_cC_d$, où "a", "b", "c" et "d" sont des pourcentages atomiques compris entre 80,0 et 82,0; entre 12,5 et 14,5; entre 2,5 et 5,0 et entre 1,5 et 2,5, respectivement, dans la mesure où la somme de "a", "b", "c" et "d" est égale à 100, caractérisé en ce que l'alliage métallique est recuit par:
 - chauffage de l'alliage à une température suffisante pour obtenir la libération des contraintes mais inférieure à la valeur requise pour amorcer la cristallisation;
 - refroidissement de l'alliage à une cadence comprise entre 0,5°C/mn et 75°C/mn; et
 - application d'un champ magnétique à l'alliage pendant le chauffage et le refroidissement.
2. Procédé selon la revendication 1, caractérisé en ce que l'alliage est chauffé à une température comprise entre 340°C et 385°C.
3. Procédé selon la revendication 1, caractérisé en ce que l'alliage est chauffé à une température comprise entre 345°C et 380°C, et est refroidi à une cadence comprise entre 1°C/mn et 16°C/mn.
4. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que l'alliage est au moins amorphe à 97 %.
5. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que l'alliage est amorphe à 100 %.
6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que "a", "b", "c" et "d" sont égaux à 81; 13,5; 3,5 et 2, respectivement.
7. Noyau destiné à être utilisé dans un dispositif électromagnétique constitué d'un alliage métallique qui est au moins amorphe à 90 %, a une composition ayant la formule $Fe_aB_bSi_cC_d$, où "a", "b", "c" et "d" sont des pourcentages atomiques compris entre 80,0 et 82,0; entre 12,5 et 14,5; entre 2,5 et 5,0 et entre 1,5 et 2,5, respectivement, dans la mesure où la somme de "a", "b", "c" et "d" est égale à 100 et qui a été recuit par un procédé selon l'une quelconque des revendications précédentes.

Patentansprüche

1. Verfahren zur Verbesserung des magnetischen Eigenschaften einer Metallegierung, die zu wenigstens 90 % amorph ist und eine Zusammensetzung der Formel $Fe_aB_bSi_cC_d$ besitzt, worin "a", "b", "c" und "d" Atomprozentsätze im Bereich von 80,0 bis 82,0, 12,5 bis 14,5, 2,5 bis 5,0 bzw. 1,5 bis 2,5 sind, wobei die Summe von "a", "b", "c" und "d" gleich 100 ist, dadurch gekennzeichnet, daß man die Metallegierung durch
 - Erhitzen dieser Legierung auf eine ausreichende Temperatur, um Spannungen zu beseitigen, doch auf eine geringere Temperatur, als sie erforderlich ist, um Kristallisation einzuleiten,
 - Kühlen der Legierung mit einer Geschwindigkeit von 0,5° C je Minute bis 75° C je Minute und Anlegen eines Magnetfeldes an die Legierung während des Erhitzens und Kühlens glüht.
2. Verfahren nach Anspruch 1, bei dem die Legierung auf 340° C bis 385° C erhitzt wird.
3. Verfahren nach Anspruch 1, bei dem die Legierung auf eine Temperatur von 345° C bis 380° C erhitzt und mit einer Geschwindigkeit von 1° C je Minute bis 16° C je Minute gekühlt wird.
4. Verfahren nach Anspruch 1, 2 oder 3, bei dem die Legierung zu wenigstens 97 % amorph ist.

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5. Verfahren nach Anspruch 1, 2 oder 3, bei dem die Legierung zu 100 % amorph ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin "a", "b", "c" und "d" 81, 13,5, 3,5 bzw. 2 sind.

7. Kern für die Verwendung in einer elektromagnetischen Vorrichtung, bestehend aus einer Metallegierung, die zu wenigstens 90 % amorph ist, eine Zusammensetzung der Formel $Fe_aB_bSi_cC_d$ hat, worin "a", "b", "c" und "d" Atomprozentsätze im Bereich von 80,0 bis 82,0, 12,5 bis 14,5, 2,5 bis 5,0 bzw. 1,5 bis 2,5 sind, wobei die Summe von "a", "b", "c" und "d" gleich 100 ist, und nach einem Verfahren gemäß einem der vorausgehenden Ansprüche gegläht wurde.

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