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㉓ References cited:
EP-A-0 020 937
DE-A-2 746 238
DE-A-2 839 626
FR-A-2 423 547
FR-A-2 423 548
FR-A-2 442 894
US-A-3 856 513
US-A-4 217 135
US-A-4 219 355

**Japanese Journal of Applied Physics, Vol. 17,
No. 10, October 1978, pp. 1755-1763**

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㉗ References cited:
Applied Physics 20 (1979), pp. 125-127

EP 0 055 327 B2

⑤⑥ References cited

Magnetische Werkstoffe und Bauelemente in der Nachrichten- und Datentechnik, Vorträge der Frühjahrstagung vom 16.-18.04.1980 in Bad Nauheim, published in NTG-Fachberichte, Bd. 76, VDE-Verlag GmbH, pp. 307-311

Journal of Magnetism und Magnetic Materials 9 (1978), pp. 200-202

Annealing Study of 2605S-2, Allied Corporation, 02.02.84

Journal of Magnetism und Magnetic Materials 19(1980), pp. 177-182, made public orally at the 4th European Conference on Soft Magnetic Materials on 11.-14.10.79

Proc. 4th. Int. Conf. on Rapidly Quenched Metals, Sendai 1981, pp. 1031-1033

IEEE Transactions on Magnetics, Vol. 15, No. 4, 1979, pp. 1146-1148

IEEE Transactions on Magnetics, Vol. 15, No. 6, 1979, pp. 1939-1945

Description

Field of the Invention

The invention relates to amorphous metal alloy compositions and, in particular, to amorphous alloys containing iron, silicon and boron having enhanced A.C. magnetic properties.

Description of the Prior Art

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.

Novel amorphous metal alloys have been disclosed by H. S. Chen and D. E. Polk in U.S. Pat. No. 3,856,513, issued Dec. 24, 1974. These amorphous alloys have the formula $M_aY_bZ_c$ where M is at least one metal selected from the group of iron, nickel, cobalt, chromium and vanadium, Y is at least one element selected from the group consisting of phosphorus, boron and carbon, Z is at least one element selected from the group consisting of aluminum, antimony, beryllium, germanium, indium, tin and silicon, "a" ranges from about 60 to 90 atom percent, "b" ranges from about 10 to 30 atom percent and "c" ranges from about 0.1 to 15 atom percent. These amorphous alloys have been found suitable for a wide variety of applications in the form of ribbon, sheet, wire, powder, etc. 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 the group consisting of aluminum, antimony, beryllium, boron, germanium, carbon, indium, phosphorus, silicon and tin, "i" ranges from about 70 to 87 atom percent and "j" ranges from about 13 to 30 atom percent. These amorphous alloys have been found suitable for wire applications.

At the time that the amorphous alloys described above were discovered, they evidenced magnetic properties that were superior to then known polycrystalline alloys. Nevertheless, new applications requiring improved magnetic properties and higher thermal stability have necessitated efforts to develop additional alloy compositions.

US—A—4 219 355 discloses amorphous alloys consisting of iron, boron, silicon and carbon, the atomic percentages of iron and carbon being in the range of 80.0 to 82.0 and 1.5 to 2.5, respectively. The document also discloses that the magnetic properties can be enhanced by heating them to a temperature sufficient to achieve stress relief, cooling and applying a magnetic field during heating and cooling.

The document "Magnetische Werkstoffe und Bauelemente in der Nachrichten- und Datentechnik", published in NTG-Fachberichte, Volume 76, VDE-Verlag GmbH, Berlin, pages 307 to 311, reports about the results of an investigation into the magnetic properties of amorphous FeSiB alloys. The shown area of Fig. 1 on page 307 comprises some alloys of the invention but this figure represents non-heat treated alloys. Furthermore, on pages 310 and 311 there is reported about the thermal stability of the maximum permeability of the alloy $Fe_{77}Si_{10}B_{12}$. But the document does not provide any information with regard to the magnetic properties intended according to the invention.

Summary of the Invention

In accordance with the present invention, there is provided a metal alloy which is at least 90% amorphous containing apart from incidental impurities iron, silicon and boron and is producible by a process comprising the steps of heating said amorphous alloy to a temperature in the range of about 340 to 440°C and sufficient to achieve stress relief but less than that required to initiate crystallization; cooling said alloy at a rate of about 0.5°C/min to 7°C/min; and applying a magnetic field to said alloy during said heating and cooling, and which is characterized in that it consists of a composition having the formula $Fe_aSi_bB_c$ wherein "a", "b" and "c" are atomic percentages ranging from about 75 to 78.5, 4 to 10.5 and 11 to 21, respectively, with the proviso that the sum of "a", "b" and "c" equals 100. Moreover, the invention provides a magnetic core comprising a metal alloy identified above.

The alloys of this invention exhibit improved A.C. magnetic properties at temperatures up to about 150°C. As a result, the alloys are particularly suited for use in power transformers, aircraft transformers, current transformers, high frequency transformers (e.g. transformers having operating frequencies ranging from about 400 Hz to 100 kHz), switch cores, high gain magnetic amplifiers and low frequency inverters.

Detailed Description of the Invention

The composition of the new amorphous Fe-Si-B alloy, in accordance with the invention, consists of 75 to 78.5 atom percent iron, 4 to 10.5 atom percent silicon and 11 to 21 atom percent boron. Such compositions exhibit enhanced A.C. magnetic properties. The improved magnetic properties are evidenced by high magnetization, low core loss and low volt-ampere demand which remain constant and stable at

temperatures up to 125°C. A further composition consists of 78 atom percent iron, 6 to 10 atom percent silicon, the balance being boron.

The alloys of the present invention are preferably at least about 97% amorphous and most preferably 100% amorphous. Magnetic properties are improved in alloys possessing a greater volume percent of amorphous material. The volume percent of amorphous material is conveniently determined by X-ray diffraction.

The amorphous metal alloys from which those according to the invention are producible, are formed by cooling a melt at a rate of about 10⁵°C to 10⁶°C/sec. The purity of all materials is that found in normal commercial practice. A variety of techniques is available for fabricating splat-quenched foils and rapid-quenched continuous ribbons, wire, sheet, etc. Typically, a particular composition is selected, powders or granules of the requisite elements (or of materials that decompose to form the elements, such as ferroboration, ferrosilicon, etc.) 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 most preferred process for fabricating continuous metal strip containing the alloys of the invention is that set forth in U.S.P. 4,142,571 to Narasimhan. The Narasimhan patent sets forth a method of forming a continuous metal strip by depositing molten metal onto the surface of a moving chill body. The method comprises the steps of (a) moving the surface of a chill body in a longitudinal direction at a constant predetermined velocity of from about 100 to about 2000 meters per minute past the orifice of a slotted nozzle defined by a pair of generally parallel lips located proximate to the surface such that the gap between the lips and the surface is from about 0.03 to about 1 millimeter, the orifice being arranged generally perpendicular to the direction of movement of the chill body, and (b) forcing a stream of molten metal through the orifice of the nozzle into contact with the surface of the moving chill body to permit the metal to solidify thereon to form a continuous strip. Preferably, the nozzle slot has a width of from about 0.34 to 1 millimeter, the first lip has a width at least equal to the width of the slot and the second lip has a width of from about 1.5 to 3 times the width of the slot amorphous metal strip produced in accordance with the Narasimhan process has a width of at least about 7 millimeters, preferably at least about 1 centimeter and, more preferably yet, a width of at least about 3 centimeters. The strip is at least 0.02 millimeter thick but may be as thick as about 0.14 millimeter, or thicker, depending on the melting point, solidification and crystallization characteristics of the alloy employed.

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

The method of annealing comprises heating the alloy to a temperature sufficient to achieve stress relief but less than that required to initiate crystallization, cooling the alloy, and applying a magnetic field to the alloy during the heating and cooling. Preferably, a rate of cooling range of about 1°C/min to 16°C/min is employed.

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

When cores comprising the subject 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 subject 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 savings 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 subject alloys result in cores of reduced weight for a given capacity rating.

The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of 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, silicon and boron 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 a temperature ranging from 340°C to 440°C with the 795.8 A/m field applied during heating and cooling to determine the optimum field annealing conditions for each composition. The optimum field annealing condition for each

EP 0 055 327 B2

composition is that at which the exciting power of the core is lowest. The samples were cooled at a rate of approximately 10°C/min.

The A.C. magnetic properties, i.e., power loss (watts/kilogram) and exciting power (RMS Volt-amperes/kilogram), of the samples were measured at a frequency of 60 Hz and a magnetic intensity of 1.4 Tesla by the sine-flux method.

Field annealed 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 A.C. magnetic measurements for amorphous metal alloys within the scope of the invention

Ex.	Composition			A.C. properties: 60Hz, 1.4T Room temperature: 100°C			
	Fe	B (atom %) (weight %)	Si	Power loss (W/kg)	Exciting power (VA/kg)	Power loss (W/kg)	Exciting power (VA/kg)
1.	75	15	10	0.25	1.81	0.23	2.34
	91.4	3.5	6.1				
2.	76	14	10	0.20	0.67	0.20	0.92
	90.8	3.2	6.0				
3.	77	13	10	0.21	1.31	0.18	2.06
	91.0	3.0	6.0				
4.	78	12	10	.27	.39	.30	.37
	91.4	2.7	5.9				
5.	78	18	4	.21	.47	.22	.95
	93.4	4.2	2.4				
6.	78	17	5	0.18	0.24	0.20	0.27
	93.1	3.9	3.0				
7.	78	16	6	0.33	0.41	0.37	0.67
	92.7	3.7	3.6				
8.	78	14	8	.23	.34	.28	.42
	92.1	3.2	4.7				
9.	78	12	10	.27	.39	.23	.24
	91.4	2.7	5.9				

For comparison, the compositions of some amorphous metal alloys lying outside the scope of the invention and their field annealed A.C. measurements are listed in Table II. These alloys, in contrast to those within the scope of the present invention, have higher core loss and higher volt-ampere demand at room temperature and at 100°C.

TABLE II
Field annealed A.C. magnetic measurements for amorphous metal alloys not within
the scope of the invention

Ex.	Composition			A.C. properties: 60Hz, 1.4T Room temperature: 100°C			
	Fe	B (atom %) (weight %)	Si	Power loss (W/kg)	Exciting power (VA/kg)	Power loss (W/kg)	Exciting power (VA/kg)
10.	80	10	10	>.2*	>.2*	—**	—**
	92.0	2.2	5.8				
11.	81	10	9	—**	—**	—**	—**
	92.6	2.2	5.2				
12.	82	9	9	—**	—**	—**	—**
	92.9	2	5.1				
13.	78	10	12	.27	2.08	.19	2.58
	90.7	2.3	7				
14.	78	8	14	—***	—***	—***	—***
	90.1	1.8	8.1				

*Values indicated are at 1.26T and are expected to be higher at 1.4T.

**VA/kg at 1.4T > 10; Power Loss corresponding to such high VA demand is inaccurate.

***Not castable into ductile ribbon.

Claims

1. A metal alloy which is at least 90% amorphous, containing apart from incidental impurities iron, silicon and boron and is producible by a process comprising the steps of heating said amorphous alloy to a temperature in the range of about 340 to 440°C and sufficient to achieve stress relief but less than that required to initiate crystallization; cooling said alloy at a rate of about 0,5°C/min to 75°C/min; and applying a magnetic field to said alloy during said heating and cooling, characterized in that it consists of a composition having the formula $Fe_aSi_bB_c$ wherein "a", "b" and "c" are atomic percentages ranging from about 75 to 78,5, 4 to 10,5 and 11 to 21, respectively, with the proviso that the sum of "a", "b" and "c" equals 100.
2. An amorphous metal alloy as recited in claim 1, wherein said alloy is at least about 97% amorphous.
3. An amorphous metal alloy as recited in claim 1, whereby said alloy is 100% amorphous.
4. An amorphous metal alloy as recited in claim 1, being at least 90% amorphous and consisting of a composition having the formula $Fe_aSi_bB_c$, wherein "a" and "b" are 78 and 6 to 10 respectively, the balance being boron.
5. An amorphous metal alloy as recited in claim 1, being producible by cooling said alloy at a rate of about 1°C/min to 16°C/min.
6. A magnetic core comprising a metal alloy which is at least 90% amorphous, containing apart from incidental impurities iron, silicon and boron and is producible by a process comprising the steps of heating said amorphous alloy to a temperature in the range of about 340 to 440°C and sufficient to achieve stress relief but less than that required to initiate crystallization; cooling said alloy at a rate of about 0,5°C/min to 75°C/min; and applying a magnetic field to said alloy during said heating and cooling, characterized in that it consists of a composition having the formula $Fe_aSi_bB_c$, wherein "a", "b" and "c" are atomic percentages ranging from about 75 to 78,5 4 to 10,5 and 11 to 21, respectively, with the proviso that the sum of "a", "b" and "c" equals 100.

Patentansprüche

1. Metallegierung, die zu wenigstens 90% amorph ist und außer beiläufigen Verunreinigungen Eisen, Silicium und Bor enthält und durch ein Verfahren herstellbar ist, in dem man die amorphe Legierung auf eine Temperatur im Bereich von etwa 340 bis 440°C und ausreichend, um Spannungsbeseitigung zu erreichen, aber geringer als zur Einleitung von Kristallisation erforderlich wäre, erhitzt, die Legierung mit einer Geschwindigkeit von etwa 0,5°C/min bis 75°C/min kühlt und an die Legierung während des Erhitzens und Kühlens ein magnetisches Feld anlegt, dadurch gekennzeichnet, daß sie aus einer Zusammensetzung der Formel $Fe_aSi_bB_c$ besteht, worin "a", "b" und "c" Atomprozentsätze sind und im Bereich von etwa 75 bis 78,5 bzw. 4 bis 10,5 bzw. 11 bis 21 liegen, wobei die Summe von "a", "b" und "c" 100 ist.
2. Amorphe Metallegierung nach Anspruch 1, worin die Legierung zu wenigstens etwa 97% amorph ist.

EP 0 055 327 B2

3. Amorphe Metallegierung nach Anspruch 1, worin die Legierung zu 100% amorph ist.

4. Amorphe Metallegierung nach Anspruch 1, die zu wenigstens 90% amorph ist und aus einer Zusammensetzung der Formel $\text{Fe}_a\text{Si}_b\text{B}_c$ besteht, worin "a" und "b" 78 bzw. 6 bis 10 sind und der Rest Bor ist.

5. Amorphe Metallegierung nach Anspruch 1, die durch Kühlen der Legierung mit einer Geschwindigkeit von etwa 1°C/min bis 16°C/min herstellbar ist.

6. Magnetkern mit einer Metallegierung, die zu wenigstens 90% amorph ist, außer beiläufigen Verunreinigungen Eisen, Silicium und Bor enthält und durch ein Verfahren herstellbar ist, bei dem man die amorphe Legierung auf eine Temperatur im Bereich von etwa 340 bis 440°C und ausreichend, um Spannungs-beseitigung zu erreichen, aber geringer als zur Einleitung von Kristallisation erforderlich wäre, erhitzt, die Legierung mit einer Geschwindigkeit von etwa 0,5°C/min bis 75°C/min kühlt und an die Legierung während des Erhitzens und Kühlens ein Magnetfeld anlegt, dadurch gekennzeichnet, daß sie aus einer Zusammensetzung der Formel $\text{Fe}_a\text{Si}_b\text{B}_c$ besteht, worin "a", "b" und "c" Atomprozentätze im Bereich von 75 bis 78,5 bzw. 4 bis 10,5 bzw. 11 bis 21 sind, wobei die Summe von "a", "b" und "c" 100 ist.

15 Revendications

1. Alliage métallique au moins à 90% amorphe contenant à l'exception des impuretés accidentelles du fer, du silicium et du bore et peut être obtenu par un procédé comprenant les étapes de chauffage du dit alliage amorphe à une température comprise entre 340 et 440°C et suffisante pour réaliser l'élimination des tensions mais inférieure à celle requise pour provoquer la cristallisation; le refroidissement du dit alliage à une vitesse comprise entre environ 0,5°C/min à 75°C/min; et à appliquer un champ magnétique au dit alliage pendant le chauffage et le refroidissement, caractérisé en ce qu'il consiste en une composition ayant pour formule $\text{Fe}_a\text{Si}_b\text{B}_c$ dans laquelle "a", "b" et "c" sont des pourcentages atomiques de allant de 75 à 78,5, de 4 à 10,5 et 11 à 21, respectivement, étant entendu que la somme de "a" plus "b" plus "c" est égale à 100.

2. Alliage métallique amorphe selon la revendication 1, caractérisé en ce que le dit alliage est au moins amorphe à 97%.

3. Alliage métallique amorphe selon la revendication 1, caractérisé en ce que le dit alliage est à 100% amorphe.

4. Alliage métallique amorphe selon la revendication 1, qui est au moins à 90% amorphe et consiste en une composition ayant pour formule $\text{Fe}_a\text{Si}_b\text{B}_c$, caractérisé en ce que les valeurs "a" et "b" sont de 78 et 6 à 10 respectivement, le complément étant du bore.

5. Alliage métallique amorphe selon la revendication 1, caractérisé en ce qu'il peut être produit par refroidissement du dit alliage à une vitesse d'environ 1°C/min à 16°C/min.

6. Noyau magnétique comportant un alliage métallique qui est au moins à 90% amorphe, et comprenant exception faite des impuretés accidentelles du fer, du silicium et du bore, et qui est produit par un procédé comprenant les phases de chauffage du dit alliage amorphe à une température comprise entre 340 et 440°C et suffisante pour réaliser l'élimination des tensions mais inférieure à celle qui est requise pour provoquer la cristallisation; le refroidissement du dit alliage à une vitesse de 0,5°C/min à 75°C/min; et l'application d'un champ magnétique au dit alliage pendant le chauffage et le refroidissement, caractérisé en ce qu'il consiste en une composition ayant la formule $\text{Fe}_a\text{Si}_b\text{B}_c$ dans laquelle "a", "b" et "c" sont des pourcentages atomiques compris entre 75 et 78,5, 4 et 10,5 et 11 et 21, respectivement, étant entendu que la somme de "a" plus "b" plus "c" est égale à 100.