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(54) **Metallic glasses having a combination of high permeability, low coercivity, low AC core loss, low exciting power and high thermal stability.**

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Description

The invention relates to metallic glasses having high permeability, low magnetostriction, low coercivity, low ac core loss, low exciting power and high thermal stability.

As is known, metallic glasses are metastable materials lacking any long range order. X-ray diffraction scans of glassy metal alloys show only a diffuse halo similar to that observed for inorganic oxide glasses.

Metallic glasses (amorphous metal alloys) have been disclosed in US—A—3 856 513. These alloys include compositions having the formula $M_aY_bZ_c$, where M is a metal selected from the group consisting of iron, nickel, cobalt, vanadium and chromium, Y is an element selected from the group consisting of phosphorus, boron and carbon and Z is an element selected from the group consisting of aluminum, silicon, tin, germanium, indium, antimony and beryllium, "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. Also disclosed are metallic glassy wires having the formula T_iX_j, where T is at least one transition metal and X is an element selected from the group consisting of phosphorus, boron, carbon, aluminum, silicon, tin, germanium, indium, beryllium and antimony, "i" ranges from about 70 to 87 atom percent and "j" ranges from about 13 to 30 atom percent. Such materials are conveniently prepared by rapid quenching from the melt using processing techniques that are now well-known in the art.

Metallic glasses are also disclosed in US—A—4 067 732 issued January 10, 1978. These glassy alloys include compositions having the formula $M_aM'_bCr_cM''_dB_e$, where M is one iron group element (iron, cobalt and nickel), M' is at least one of the two remaining iron group elements, M'' is at least one element of vanadium, manganese, molybdenum, tungsten, niobium and tantalum, Bis boron, "a" ranges from about 40 to 85 atom percent, "b" ranges from 0 to about 45 atom percent, "c" and "d" both range from 0 to about 20 atom percent and "e" ranges from about 15 to 25 atom percent, with the provision that "b", "c" and "d" cannot be zero simultaneously. Such glassy alloys are disclosed as having an unexpected combination of improved ultimate tensile strength, improved hardness and improved thermal stability.

By the FR—A—2 376 218 glassy alloys comprising about 63 to 83 atom percent iron and/or cobalt, 0 to about 60 atom percent of which may be replaced by nickel, about 2 to 12 atom percent at least one element selected from the group consisting of molybdenum, tungsten, niobium and titanium and about 15 to 25 atom percent at least one element selected from the group consisting of boron, phosphorus and carbon, but containing no silicon are known. The US—A—4 140 525 discloses glassy alloys consisting of 56 to 68 atom percent iron, 4 to 9 atom percent chromium, 1 to 6 atom percent molybdenum and 27 to 29 atom percent boron.

The EP—A—20 937 discloses at least 90% amorphous metal alloys consisting essentially 80 to 82 atom percent iron, 12.5 to 14.5 atom percent boron, 2.5 to 5.0 atom percent silicon and 1.5 to 2.5 atom percent carbon. Finally the EP—A—49 770 discloses special amorphous alloys having the formulae $Fe_{81}B_{13.5}Si_{3.5}C_2$, $Fe_{81}B_{14}Si_5$ and $Fe_{79}B_{16}Si_5$.

These disclosures also mention unusual or unique magnetic properties for many metallic glasses which fall within the scope of the broad claims. However, metallic glasses possessing a combination of higher permeability, lower magnetostriction, lower coercivity, lower core loss, lower exciting power and higher thermal stability than prior art metallic glasses are required for specific applications such as tape recorder head, relay cores, transformers and the like.

In accordance with the invention, metallic glasses having a combination of high permeability, low saturation magnetostriction, low coercivity, low ac core loss, low exciting power and high thermal stability are provided. The metallic glasses consist of 62 to 79 atom percent of iron, 2 to 8 atom percent of at least one element selected from the group consisting of nickel, cobalt, and mixtures thereof, 2 to 4 atom percent of at least one element selected from the group consisting of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, zirconium and hafnium, 17 to 28 atom percent of boron, from 0.5 to 6 atom percent of said boron being replaced with silicon and up to 2 atom percent of boron being, optionally, replaced with carbon, plus incidental impurities. The metallic glasses of the invention are suitable for use in tape recorder heads, relay cores, transformers and the like.

A concentration of less than about 1 atom percent of Cr, Mo, W, V, Nb, Ta, Ti, Zr and/or Hf does not result in sufficient improvement of the properties of permeability, saturation magnetostriction, coercivity, ac core loss and thermal stability. A concentration greater than about 6 atom percent of at least one of these elements results in an unacceptably low Curie temperature.

Iron provides high saturation magnetization at room temperature. Accordingly the metal content is preferably substantially iron, with up to about 8 atom percent nickel and/or cobalt in order to compensate the reduction of the room temperature saturation magnetization due to the presence of chromium, molybdenum, tungsten, niobium, tantalum, titanium, zirconium and/or hafnium. The addition of nickel increases permeability.

Preferably the replacement of boron with silicon and carbon provides said glass with a metalloid element selected from the group consisting of substantially boron and from 0.5 to 4 atom percent silicon, and boron plus silicon together with from 0 to 2 atom percent carbon.

Suitably the metallic glasses according to the invention consist of 70 to 79 atom percent iron, 2 to 4 atom percent of at least one element selected from the group consisting of nickel, cobalt and mixtures thereof, 2 to 4 atom percent of an element selected from the group consisting of molybdenum and

chromium and 17 to 22 percent of an element selected from the group consisting of boron, silicon and mixtures thereof.

Preferably the alloys according to the invention are at least 85 percent amorphous and comprise discrete particles of its constituents, said particles having an average size ranging from 0.1 μm to 0.3 μm and an average said discrete particles occupy an average volume fraction of 0.005 to 0.01.

Examples of metallic glasses of the invention include

$Fe_{76}Ni_4Mo_2B_{17.5}Si_{0.5}$, $Fe_{75}Ni_2Co_2Mo_3B_{16}Si_2$, $Fe_{75}Co_4Mo_3B_{16}Si_2$, $Fe_{75}Ni_4Mo_3B_{16}Si_2$,

$Fe_{77}Ni_2Mo_3B_{16}Si_2$, $Fe_{75}Ni_4Mo_3B_{14}Si_4$, $Fe_{71}Ni_4Mo_3B_{17}Si_5$,

$Fe_{74}Ni_4Mo_4B_{16}Si_2$, $Fe_{75}Ni_4V_3B_{14}Si_2C_2$, $Fe_{71}Ni_4Mo_3B_{16}Si_4C_2$,

$Fe_{78}Ni_2Mo_2B_{12}Si_4C_2$, $Fe_{78}Ni_2Cr_2B_{16}Si_2$, $Fe_{75}Ni_4Nb_3B_{16}Si_2$,

$Fe_{75}Ni_4W_3B_{16}Si_2$, $Fe_{75}Ni_4V_3B_{16}Si_2$, $Fe_{75}Ni_4Ti_3B_{16}Si_2$, $Fe_{75}Ni_4Zr_3B_{16}Si_2$,

$Fe_{72}Ni_2Mo_2B_{22}Si_2$, $Fe_{70}Ni_2Mo_2B_{22}Si_4$, and $Fe_{70}Ni_2Mo_2B_{24}Si_2$

(the subscripts are in atom percent). The purity of all alloys is that found in normal commercial practice.

The presence of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium and/or hafnium raises the crystallization temperature while simultaneously lowering the Curie temperature of the glassy alloy. The increased separation of these temperatures provided ease of magnetic annealing, that is, thermal annealing at a temperature near the Curie temperature. As is well-known, annealing a magnetic material close to its Curie temperature generally results in improved properties. As a consequence of the increase in crystallization temperature with increase in the concentration of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, and/or hafnium, annealing can be easily accomplished at elevated temperatures near the Curie temperature and below the crystallization temperature. Such annealing cannot be carried out for many alloys similar to those of the invention but lacking these elements. On the other hand, too high a concentration of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium and/or hafnium reduces the Curie temperature to a level that may be undesirable in certain applications.

Preferably, the metalloid content ranges from 17 to 26 atom percent for maximum thermal stability.

Preferred metallic glass systems are as follows:

1. Fe-M-Mo-B-Si: $Fe_{100-a-b-c-d}M_aMo_bB_cSi_d$, where M is at least one of nickel and cobalt. When (c+d) is about 18, the preferred ranges of a, b, c and d are from about 2 to 8, from about 2 to 4, from about 14 to 17.5 and from about 0.5 to 4, respectively. When (c+d) is about 22, the preferred ranges for a, b, c and d are from about 2 to 8, from about 2 to 6, from about 15 to 20.5 and from about 0.5 to 6, respectively. When (c+d) is close to 25, the preferred ranges of a, b, c and d are from about 2 to 8, from about 2 to 6, from about 21 to 25 and from about 1 to 6 respectively. These metallic glasses have a combination of saturation induction (B_s) of 1.0—1.4 Tesla, saturation magnetostriction (λ_s) between 12 and 24 ppm, Curie temperature (θ_f) between about 475 and 705 K and first crystallization temperature of 750—880 K. When optimally heat-treated, these alloys have excellent ac magnetic properties especially at high frequencies ($f>10^3$ Hz). The ac core loss (L) and exciting power (P_e) taken at f=50 kHz[f] and the induction level of B_m=0.1 Tesla of, for example, a heat-treated $Fe_{75}Ni_4Mo_3B_{16}Si_2$ metallic glass are 6.5 W/kg and 13.4 VA/kg, respectively. These values are to be compared with L=7 W/kg and P_e=20 VA/kg for a heat treated prior art metallic glass of the same thickness having the composition $Fe_{79}B_{16}Si_5$. The permeability μ at B_m=0.1 Tesla is 10 500 and 8000 for the heat-treated $Fe_{75}Ni_3Mo_4B_{16}Si_2$ and $Fe_{79}B_{16}Si_5$, respectively. The smaller saturation magnetostriction (λ_s) of about 20 ppm) of the present alloy as compared to λ_s=30 ppm for the aforesaid prior art alloy makes the alloys of the present invention especially suited for magnetic device applications such as cores for high frequency transformers. Beyond f=50 kHz, the alloys of the present invention have permeabilities comparable or higher than those for crystalline supermalloys which have B_s near 0.8 Tesla. The higher values of B_s for the present alloys make these alloys better suited than supermalloy for magnetic applications of f>50 kHz.

2. Fe-M-M'-B-Si: $Fe_{100-a-b-c-d}M_aM'_bB_cSi_d$ where M is nickel and/or cobalt and M' is selected from Cr, W, V, Nb, Ta, Ti, Zr or Hf. When (c+d) is about 18, the preferred ranges of a, b, c and d are about 2 to 8, from about 2 to 4, from about 14 to 17.5 and from about 0.5 to 4, respectively. When (c+d) is about 22, the preferred ranges for a, b, c and d are from about 2 to 8, from about 2 to 6, from about 16 to 21.5 and from about 0.5 to 6, respectively. When (c+d) is close to 25, the preferred ranges for a, b, c and d are from about 2 to 8, from about 2 to 6, from about 21 to 25 and from about 1 to 6, respectively.

3. Fe-M-M'-B-Si-C: $Fe_{100-a-b-c-d-e}M_aM'_bB_cSi_dC_e$ wherein M is nickel and/or cobalt, and M' is selected from the group consisting of Cr, Mo, W, V, Nb, Ta, Ti, Zr or Hf. When (c+d) is about 18, the preferred ranges for a, b, c, d and e are from about 2 to 8, from about 2 to 4, from about 12 to 17.5, from about 0.5 to 4 and from 0 to 2, respectively. When (c+d) is about 22, the preferred ranges for a, b, c, d and e are from about 2 to 8, from about 2 to 6, from about 14 to 21.5, from about 0.5 to 6 and from about 0 to 2, respectively. When

(c+d) is close to 25, the preferred ranges for a, b, c, d and e are from about 2 to 8, from about 2 to 6, from about 20 to 27, from about 1 to 6 and from about 0 to 2, respectively.

Magnetic permeability is the ratio of induction to applied magnetic field. A higher permeability renders a material more useful in certain applications such as tape recorder heads, due to the increased response. The frequency dependence of permeability of the glassy alloys of the invention is similar to that of the 4—79 Permalloys in the medium-to-high frequency range (1—50 kHz), and at higher frequencies (about 50 kHz to 1 MHz), the permeability is comparable to that of the supermalloys. Especially noted is the fact that a heat-treated $Fe_{75}Ni_4Mo_3B_{16}Si_2$ metallic glass has permeability of 24,000 while the best-heat-treated prior art $Fe_{40}Ni_{36}Mo_4B_{20}$ metallic glass has a permeability of 14,000 at 1 kHz and the induction level of 0.01 Tesla.

Saturation magnetostriction is the change in length under the influence of a saturating magnetic field. A lower saturation magnetostriction renders a material more useful in certain application such as tape recorder heads. Magnetostriction is usually discussed in terms of the ratio of the change in length to the original length, and is given in ppm. Prior art iron rich metallic glasses evidence saturation magnetostrictions of about 30 ppm as do metallic glasses without the presence of the any of the elements belonging to the IVB, VB and VIB columns of the periodic table such as molybdenum. For example, a prior art iron rich metallic glass designated for use in high frequency applications and having the composition $Fe_{79}B_{16}Si_5$ has a saturation magnetostriction of about 30 ppm. In contrast, a metallic glass of the invention having the composition $Fe_{75}Ni_4Mo_3B_{16}Si_2$ has a saturation magnetostriction of about 20 ppm. A lower saturation magnetostriction leads to a lower phase angle between the exciting field and the resulting induction. This results in lower exciting power as discussed below.

Ac core loss is that energy loss dissipated as heat. It is the hysteresis in an ac field and is measured by the area of a B—H loop for low frequencies (less than about 1 kHz) and from the complex input power in the exciting coil for high frequencies (about 1 kHz to 1 MHz). The major portion of the ac core loss at high frequencies arises from the eddy current generated during flux change. However, a smaller hysteresis loss and hence a smaller coercivity is desirable. A lower core loss renders a material more useful in certain applications such as tape recorder heads and transformers. Core loss is discussed in units of watts/kg. Prior art heat-treated metallic glasses typically evidence ac core losses of about 0.05 to 0.1 watts/kg at an induction of 0.1 Tesla and at the frequency range of 1 kHz. For example, a prior art heat-treated metallic glass having the composition $Fe_{40}Ni_{36}Mo_4B_{20}$, has an ac core loss of 0.07 watts/kg at an induction of 0.1 Tesla and at the frequency of 1 kHz, while a metallic glass having the composition $Fe_{76}Mo_4B_{20}$ has an ac core loss of 0.08 watts/kg at an induction of 0.1 Tesla and at the same frequency. In contrast, a metallic glass alloy of the invention having the composition $Fe_{75}Ni_4Mo_3B_{16}Si_2$ has an ac core loss of 0.02 watts/kg at an induction of 0.1 Tesla and at the same frequency.

Exciting power is a measure of power required to maintain a certain flux density in a magnetic material. It is therefore desirable that a magnetic material to be used in magnetic devices has an exciting power as low as possible. Exciting power (P_e) is related to the above-mentioned core loss (L) through the relationship $L=P_e \cos \delta$ where δ is the phase shift between the exciting field and the resultant induction. The phase shift is also related to the magnetostriction in such a way that a lower magnetostriction value leads to a lower phase shift. It is than advantageous to have the magnetostriction value as low as possible. As mentioned earlier, prior art iron-rich metallic glasses such as $Fe_{79}B_{16}Si_5$ have the magnetostriction value near 30 ppm, in contrast to the magnetostriction value of about 20 ppm of the metallic glasses of the present invention. This difference results in a considerable phase shift difference. For example, optimally annealed prior art metallic glass $Fe_{79}B_{16}Si_5$ has δ near 70° while the metallic glasses of the present invention have δ near 50°. This results, for a given core loss, in a higher exciting power by a factor of two for the prior art metallic glass than the metallic glass of the present invention.

Crystallization temperature is the temperature at which a metallic glass begins to crystallize. A higher crystallization temperature renders a material more useful in high temperature applications and, in conjunction with a Curie temperature that is substantially lower than the cyrstallization temperature, permits magnetic annealing just above the Curie temperature. Some metallic glasses crystallize in multiple steps. In such cases, the first crystallization temperature (the lowest value of the crystallization temperatures) is the meaningful one as far as the materials' thermal stability is concerned. The crystallization temperature as discussed herein is measured by differential scanning calorimetry. Prior art glassy alloys evidence crystallization temperatures of about 660 K to 750 K. For example, a metallic glass having the composition $Fe_{78}Mo_2B_{20}$ has a crystallization temperature of 680 K, while a metallic glass having the composition $Fe_{74}Mo_6B_{20}$ has a crystallization temperature of 750 K. In contrast, metallic glasses of the invention evidence increases in crystallization temperatures to a level above 750 K.

The magnetic properties of the metallic glasses of the present invention are improved by thermal treatment, characterized by choice of annealing temperatures (T_a), holding time (t_a), applied magnetic field (either parallel or perpendicular to the ribbon direction and in the ribbon plane), and post-treatment cooling rate. For the present alloys, the optimal properties are obtained after an anneal which causes the controlled precipitation of a certain number of crystalline particles from the glassy matrix. Under these conditions, for compositions having boron content ranging from about 17 to 20 atom percent, the discrete particles have a body-centered cubic structure. The particles are composed essentially of iron, up to 22 atom percent of the iron being adapted to be replaced by at least one of nickel, cobalt, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, hafnium, silicon and carbon. For compositions having

boron content ranging from about 21 to 25 atom percent and iron content ranging from about 69 to 78 atom percent, the discrete particles consist essentially of a mixture of particles, a major portion of which mixture contains particles having a crystalline Fe_3B structure. The particles of such portion are composed of iron and boron, up to 14 atom percent of the iron being adapted to be replaced by at least one of nickel, cobalt, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium and hafnium and up to 2 atom percent of the boron being adapted to be replaced by carbon. A small number of such particles introduces a certain decrease in the average domain wall spacing with concomitant decrease in core loss. Too large a number of particles increases the coercivity and thus the hysteresis loss. A metallic glass of the present invention with composition $Fe_{75}Ni_4Mo_3B_{16}Si_2$ has a combination of low loss and high permeability with a coercivity of only 2 A/m when optimally annealed. In contrast to this, an optimally annealed prior art metallic glass $Fe_{79}B_{16}Si_5$ has a coercivity of about 8 A/m. The crystalline particle size in the optimally heat-treated materials of the present invention ranges between 100 and 300 nm, and their volume fraction is less than 1%. The interparticle spacing is of the order of 1—10 μm.

In summary, the metallic glasses of the invention have a combination of high permeability, low saturation magnetostriction, low coercivity, low ac core loss, low exciting power and high crystallization temperature and are useful as tape heads, relay cores, transformers and the like.

The metallic glasses of the invention are prepared by cooling a melt of the desired composition at a rate of at least about $10^{5°}$C/sec, employing quenching techniques well known to the metallic glass art; see e.g., US—A—3,856,513. The metallic glasses are substantially completely glassy, that is, at least 90% glassy, and consequently possess lower coercivities and are more ductile than less glassy alloys.

A variety of techniques are available for fabricating continuous ribbon, wire, sheet, etc. Typically, a particular composition is selected, powders or granules of the requisite elements in the desired portions are melted and homogenized and the molten alloy is rapidly quenched on a chill surface such as a rapidly rotating cylinder.

Examples

Example 1: Fe-Ni-Mo-B-Si

Ribbons having compositions given by $Fe_{100-a-b-c-d}Ni_aMo_bB_cSi_d$ and having dimensions about 1 to 2.5 cm wide and about 25 to 50 μm thick were formed by squirting a melt of the particular composition by overpressure of argon onto a rapidly rotating copper chill wheel (surface speed about 1500 to 3000 cm/sec).

Molybdenum content was varied from 1 to 6 atom percent, for which substantially glassy ribbons were obtained. Molybdenum content higher than 6 atom percent reduced the Curie temperature to an unacceptable low value.

Permability, magnetostriction, core loss, magnetization and coercive force were measured by conventional techniques employing B—H loops, metallic strain gauges and a vibrating sample magnetometer. Curie temperature and crystallization temperature were measured respectively by an induction method and differential scanning calorimetry. The measured values of room temperature saturation induction, Curie temperature, room temperature saturation magnetostriction and the first crystallization temperature are summarized in Table I below. The magnetic properties of these glassy alloys are annealing are presented in Table II. Optimum annealing conditions for the metallic glass $Fe_{75}Ni_4Mo_3B_{16}Si_2$ and the obtained results are summarized in Table III. Frequency dependence of permeability and ac core loss of this optimally annealed alloy are listed in Table IV.

The presence of molybdenum is seen to increase the permeability and the crystallization temperature and to lower the ac core loss, exciting power and magnetostriction. Especially noted is the fact that the optimally heat-treated metallic glass $Fe_{75}Ni_4Mo_3B_{16}Si_2$ of the present invention has a coercivity reaching as low as 2.5 A/m and yet has a low core loss of 6.5 W/kg and permeability of 12500 at 50 kHz and at the induction level of 0.1 Tesla. The combination of these properties make these compositions suitable for high frequency transformer and tape-head applications.

TABLE I

Examples of basic magnetic properties of Fe-Ni-Mo-B-Si alloys. B_s and λ_s are room temperature saturation induction and saturation magnetostriction, respectively. θ_f and T_{cl} are ferromagnetic Curie and the first crystallization temperatures, respectively.

Composition								
Fe	Ni	Mo	B	Si	B_s (Tesla)	θ_f(K)	$\lambda_s(10^{-6})$	T_{cl}(K)
76	4	2	17.5	0.5	1.38	590	23	760
78	2	2	16	2	1.34	580	21	763
76	4	2	14	4	1.33	598	20	766
74	6	2	14	4	1.32	616	24	761
72	8	2	14	4	1.32	622	23	758
77	2	3	17.5	0.5	1.27	535	19	773
75	4	3	17.5	0.5	1.28	550	20	769
73	6	3	17.5	0.5	1.28	560	20	765
71	8	3	17.5	0.5	1.30	568	22	762
77	2	3	16	2	1.26	545	22	768
75	4	3	16	2	1.27	570	19	769
73	6	3	16	2	1.26	583	21	765
71	8	3	16	2	1.25	600	19	759
77	2	3	14	4	1.24	549	17	768
75	4	3	14	4	1.23	554	21	766
73	6	3	14	4	1.23	566	21	761
71	8	3	14	4	1.22	575	20	758
77	2	3	12	6	1.24	544	21	766
75	4	3	12	6	1.23	561	19	761
73	6	3	12	6	1.22	570	20	758
71	8	3	12	6	1.22	580	21	770
71	4	3	17	5	1.24	573	21	830
74	4	4	17.5	0.5	1.16	514	16	780
76	2	4	16	2	1.12	502	17	775
74	4	4	16	2	1.13	517	17	774
72	6	4	16	2	1.14	540	17	768
70	8	4	16	2	1.14	560	19	766
72	6	4	14	4	1.11	517	17	769

TABLE I (contd.)

Composition								
Fe	Ni	Mo	B	Si	B_s (Tesla)	θ_f(K)	$\lambda_s(10^{-6})$	T_{cl}(K)
70	8	4	14	4	1.14	518	18	774
74	2	2	20	2	1.29	632	23	804
72	2	2	22	2	1.25	657	22	824
70	4	2	22	2	1.30	665	22	823
68	6	2	22	2	1.26	671	20	819
66	8	2	22	2	1.27	687	20	816
70	2	2	22	4	1.21	668	21	848
68	2	2	22	6	1.18	658	18	869
71	2	2	24	1	1.25	705	20	810
69	2	4	24	1	1.12	556	16	854
70	2	2	24	2	1.24	674	19	831
68	4	2	24	2	1.24	706	20	829
66	6	2	24	2	1.26	680	20	824
64	8	2	24	2	1.18	706	20	829
66	4	4	24	2	1.10	626	16	848
68	2	2	24	4	1.21	690	14	855

TABLE II

Examples of ac core loss, L; exciting power, P_e and permeability μ at f=50 kHz and the maximum induction level of B_m=0.1 Tesla for Fe-Ni-Mo-B-Si alloys annealed without fields at the temperature T_a for about 15 min. and subsequently cooled at a rate of about −1°C/min. The values with asterisks are for B_m=0.01 Tesla.

Composition								
Fe	Ni	Mo	B	Si	L(W/kg)	P_e(VA/kg)	μ	T_a(°C)
76	4	2	17.5	0.5	28	35	5200	400
78	2	2	16	2	20	26	3340	380
76	4	2	14	4	20	29	2170	360
74	6	2	14	4	18	26	3260	380
72	8	2	14	4	18	25	2460	400
77	2	3	17.5	0.5	16	20	8100	400
75	4	3	17.5	0.5	18	20	8500	400
73	6	3	17.5	0.5	19	23	7000	400
71	8	3	17.5	0.5	21	38	5000	400
77	2	3	16	2	11	16	9200	420
75	4	3	16	2	12	17	9000	420
73	6	3	16	2	12	22	8000	420
71	8	3	16	2	16	27	5500	420
77	2	3	14	4	17	21	7400	420
75	4	3	14	4	21	24	6600	420
73	6	3	14	4	19	24	6800	420
71	8	3	14	4	16	21	6500	420
77	2	3	12	6	19	24	5950	400
75	4	3	12	6	18	20	5320	400
73	6	3	12	6	19	25	5750	400
71	8	3	12	6	19	24	5680	400
71	4	3	17	5	14	23	7000	440
74	4	4	17.5	0.5	15	17	8800	400
76	2	4	16	2	14	20	7400*	435
74	4	4	16	2	15	21	7600*	435
72	6	4	16	2	15	21	7200*	435
70	8	4	16	2	21	31	7100*	435

TABLE II (contd.)

Composition								
Fe	Ni	Mo	B	Si	L(W/kg)	P_e(VA/kg)	μ	T_a(°C)
72	6	4	14	4	17	22	6600*	435
70	8	4	14	4	15	22	7050*	435
74	2	2	20	2	12	28	5880	450
72	2	2	22	2	12	28	6050	450
72	2	2	22	2	14	32	4230	490
72	2	2	22	2	13	34	4930	490
70	4	2	22	2	12	31	5430	490
68	6	2	22	2	15	34	4930	490
66	8	2	22	2	14	37	4550	490
70	2	2	22	4	12	28	5950	450
70	2	2	22	4	14	28	5860	490
70	2	2	22	4	14	31	5470	510
70	2	2	22	4	12	32	5170	490
68	2	2	22	6	13	27	6290	490
69	2	4	24	1	9	18	9130	490
70	2	2	24	2	10	27	6070	450
70	2	2	24	2	10	27	6080	490
66	6	2	24	2	13	35	5220	450

TABLE III

Optimum annealing conditions for 32 μm-thick $Fe_{75}Ni_4Mo_3B_{16}Si_2$ ribbon and the obtained results of core loss (L), permeability (μ) at f=50 kHz and B_m=0.1 T and ac coercivity (H_c)

Conditions				
Anneal temp.	Holding time	L (W/kg)	μ	H_c(A/m)
380°C	120 min.	11.8	8 200	2.35
400	150	6.5	12 500	2.5
420	90	11.2	8 200	4.5

TABLE IV

Frequency dependence of the permeability (μ) and ac core loss (L) at the induction level B_m=0.01 and 0.1 Tesla, for an optimally annealed 32 μm-thick $Fe_{75}Ni_4Mo_3B_{16}Si_2$ alloy ribbon.

Frequency (Hz)	10^3	5×10^3	10^4	5×10^4	10^5
μ (B_m=0.01 T)	24 000	23 000	18 500	11 500	8000
μ (B_m=0.1 T)	50 000	37 000	29 000	12 500	9000
L (B_m=0.1 T) (W/kg)	0.02	0.24	0.83	6.5	20

Example 2: Fe-Ni-M-B-Si system

Ribbons having compositions given by $Fe_{100-a-b-c-d}M_a$-M'_b-B_c-Si_d when M is nickel and/or cobalt, M' is one of the elements chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium and hafnium, and having dimensions about 1 cm wide and about 25 to 50 μm thick were formed as in Example 1.

Metal "M'" content was varied from 1 to 6 atom percent, for which substantially glassy ribbons were obtained. Higher metal "M'" content reduced the Curie temperature to an unacceptably low value.

The magnetic and thermal data are summarized in Table V below. The magnetic properties of these glassy alloys after annealing are presented in Table VI.

Low field magnetic properties of these metallic glasses were comparable to those for the metallic glasses containing molybdenum (Example 1).

A combination of low ac core loss and high permeability at high frequency is achieved in the metallic glasses of the present invention. The thermal stability is also shown to be excellent as evidenced by high crystallization temperature. These improved combination of properties of the metallic glasses of the present invention renders these compositions suitable in the magnetic cores of transformers, tape-recording heads and the like.

TABLE V

Examples of the room temperature saturation induction, B_s, Curie temperature, θ_f, saturation magnetostriction, λ_s, and the first crystallization temperature, T_c, for the metallic glasses having the composition $Fe_{100-a-b-c-d}M_aM'_bB_cSi_d$ where M is at least one of nickel and cobalt, and M'=Cr, Mo, W, V, Nb, Ta, Ti, Zr or Hf.

Composition	B_s (Tesla)	θ_f (K)	λ_s (ppm)	T_{cl} (K)
$Fe_{76.5}Ni_{3.9}Cr_2B_{15.6}Si_2$	1.46	631	18	773
$Fe_{76.5}Ni_{3.9}Cr_2B_{13.7}Si_4$	1.42	620	24	773
$Fe_{76.5}Ni_{3.9}Cr_2B_{11.7}Si_6$	1.37	621	21	762
$Fe_{75}Ni_4Cr_3B_{16}Si_2$	1.33	559	19	762
$Fe_{75}Ni_4V_3B_{16}Si_2$	1.33	597	24	762
$Fe_{75}Ni_4Nb_3B_{16}Si_2$	1.03	534	18	785
$Fe_{75}Ni_4Ta_3B_{16}Si_6$	1.38	622	21	756
$Fe_{75}Ni_4Ti_3B_{16}Si_2$	1.42	573	21	720
$Fe_{75}Ni_4Zr_3B_{16}Si_6$	1.39	597	27	808
$Fe_{75}Ni_4Hf_3B_{16}Si_2$	1.38	599	22	770
$Fe_{77}Co_2Mo_3B_{16}Si_2$	1.30	540	19	779
$Fe_{75}Co_4Mo_3B_{16}Si_2$	1.32	560	18	777
$Fe_{75}Co_2Ni_2Mo_3B_{16}Si_2$	1.29	534	19	776
$Fe_{71}Co_4Ni_4Mo_3B_{16}Si_2$	1.33	600	22	772
$Fe_{69}Co_5Ni_1Mo_3B_{16}Si_6$	1.27	650	21	830

TABLE VI

Core loss (L), exciting power (P_e) and permeability (μ) taken at f=50 kHz, and B_m=0.1 Tesla on the heat-treated metallic glasses having the composition $Fe_{100-a-b-c-d}M_aM'_bB_cSi_d$ where M=Ni, and/or Co, and M'=Cr, Mo_1, W, V, Nb, Ta, Ti, Zr or Hf. The annealing temperatures are indicated by t_a and the holding time is 15 min. for all the materials.

Composition	L(W/kg)	P_e(VA/kg)	(μ)	T_a(°C)
$Fe_{76.5}Ni_{3.9}Cr_2B_{15.6}Si_2$	18	25	7400	395
$Fe_{76.5}Ni_{3.9}Cr_2B_{13.7}Si_4$	17	23	5800	410
$Fe_{76.5}Ni_{3.9}Cr_2B_{11.7}Si_6$	19	27	6200	410
$Fe_{78}Ni_2Cr_2B_{16}Si_2$	14	21	8440	400
$Fe_{75}Ni_4Cr_3B_{16}Si_2$	19	27	6130	400
$Fe_{75}Ni_4V_3B_{16}Si_2$	25	28	5800	400
$Fe_{75}Ni_4Nb_3B_{16}Si_2$	20	24	7000	400
$Fe_{75}Ni_4Ti_3B_{16}Si_2$	40	49	3500	400
$Fe_{75}Ni_4Zr_3B_{16}Si_2$	38	47	4000	400
$Fe_{77}Co_2Mo_3B_{16}Si_2$	23	28	6000	400
$Fe_{75}Co_4Mo_3B_{16}Si_2$	27	32	5000	400
$Fe_{75}Co_2Ni_2B_{16}Si_2$	13	22	7300	400
$Fe_{71}Co_4Ni_4Mo_3B_{16}Si_2$	17	26	6200	400
$Fe_{69}Co_5Ni_1Mo_3B_{16}Si_6$	18	28	5700	400

TABLE VII

Saturation induction (B_s), Curie temperature (θ_f), saturation magnetostriction (λ_s) and the first crystallization temperature (T_{cl}) of the metallic glasses having the composition $Fe_{100-a-b-c-d-e}Ni_aM_bB_cSi_dC_e$ where M=Cr, Mo, W, V, Nb, Ta, Ti or Zr.

Composition	B_s (Tesla)	θ_f (K)	λ_s (ppm)	T_{cl} (K)
$Fe_{75}Ni_4Cr_3B_{14}Si_2C_2$	1.32	585	23	755
$Fe_{78}Ni_2Cr_2B_{14}Si_2C_2$	1.40	597	25	753
$Fe_{78}Ni_2Mo_2B_{12}Si_4C_2$	1.34	580	24	766
$Fe_{73}Ni_2Mo_3B_{16}Si_4C_2$	1.25	578	20	823
$Fe_{71}Ni_4Mo_3B_{16}Si_4C_2$	1.26	573	16	822
$Fe_{69}Ni_6Mo_3B_{16}Si_4C_2$	1.22	617	17	817
$Fe_{75}Ni_4W_3B_{14}Si_2C_2$	1.30	563	21	776
$Fe_{75}Ni_4V_3B_{14}Si_2C_2$	1.35	640	21	755
$Fe_{75}Ni_4Nb_3B_{14}Si_2C_2$	1.38	580	24	760
$Fe_{75}Ni_4Ta_3B_{14}Si_2C_2$	1.54	640	24	758
$Fe_{75}Ni_4Ti_3B_{14}Si_2C_2$	1.46	583	17	749
$Fe_{75}Ni_4Zr_3B_{14}Si_2C_2$	1.57	649	24	741

Example 3: Fe-Ni-M-B-Si-C system

Ribbons having compositions given by $Fe_{100-a-b-c-d-e}Ni_aM'_bB_cSi_dC_e$ where M'=Cr, Mo, W, V, Nb, Ta, Ti, or Zr and having dimensions about 1 cm wide and about 25 to 50 µm thick were formed as in Example 1. The metal "M'" content was varied from 1 to 6 atom percent, and the carbon content "e" was up to 2 atom percent for which substantially glassy ribbons were obtained. The metal "M'" content greater than about 6 atom percent reduced the Curie temperature to an unacceptably low value.

The magnetic and thermal data are summarized in Table VII below. The magnetic properties of these metallic glasses after annealing are presented in Table VIII. A combination of low ac core loss, high permeability, and high thermal stability of the metallic glasses of the present invention renders these compositions suitable in the magnetic cores of transformers, recording heads and the like.

TABLE VIII

Core loss (L), exciting power (P_e) and permeability (μ) taken at f=50 kHz and B_m=0.1 Tesla on the heat-treated metallic glasses having the composition $Fe_{100-a-b-c-d-e}Ni_aM'_bB_cSi_dC_e$ where M'=Cr, Mo, W, V, Nb or Ta. Annealing temperatures are indicated by T_a and the holding time is 15 min. for all the materials.

Composition	L(W/kg)	P_e(VA/kg)	(μ)	T_a(°C)
$Fe_{75}Ni_4Cr_3B_{14}Si_2C_2$	30	34	4600	400
$Fe_{78}Ni_2Cr_2B_{14}Si_2C_2$	43	48	3800	400
$Fe_{78}Ni_2Mo_2B_{12}Si_4C_2$	34	39	4300	400
$Fe_{73}Ni_2Mo_3B_{16}Si_4C_2$	15	24	7000	440
$Fe_{71}Ni_4Mo_3B_{16}Si_4C_2$	13	26	6700	440
$Fe_{69}Ni_6Mo_3B_{16}Si_4C_2$	18	31	5200	440
$Fe_{75}Ni_4W_3B_{14}Si_2C_2$	32	38	4200	400
$Fe_{75}Ni_4V_3B_{14}Si_2C_2$	23	26	6300	400
$Fe_{75}Ni_4Nb_3B_{14}Si_2C_2$	26	29	5700	400
$Fe_{75}Ni_4Ta_3B_{14}Si_2C_2$	19	49	2600	400

Having thus described the invention in rather full detail, it will be understood that this detail need not be strictly adhered to but that various changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the present invention as defined by the subjoined claims.

Claims

1. A metallic glass having a combination of high permeability, low magnetostriction, low coercivity, low ac core loss, low exciting power and high thermal stability consisting of 62 to 79 atom percent iron, 2 to 8 atom percent of at least one element selected from the group consisting of nickel, cobalt and mixtures thereof, 2 to 4 atom percent of at least one element selected from the group consisting of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium and hafnium, 17 to 28 atom percent of boron, from 0.5 to 6 atom percent of said boron being replaced with silicon and up to 2 atom percent of boron being, optionally, replaced with carbon, plus incidental impurities.

2. The metallic glass of claim 1, in which the replacement of boron with silicon and carbon provides said glass with a metalloid element selected from the group consisting of substantially boron and from 0.5 to 4 atom percent silicon and boron plus silicon together with from 0 to 2 atom percent carbon.

3. The metallic glass of claim 2, in which said metalloid element ranges from 17 to 26 atom percent.

4. The metallic glass of claim 1, consisting of 70 to 79 atom percent iron, 2 to 4 atom percent of at least one element selected from the group consisting of nickel, cobalt and mixtures thereof, 2 to 4 atom percent of an element selected from the group consisting of molybdenum and chromium and 17 to 22 percent of an element selected from the group consisting of boron, silicon and mixtures thereof.

5. An alloy of claim 1 which is at least 85 percent amorphous, said alloy being characterized by the presence therein of discrete particles of its constituents, said particles having an average size ranging from 0.1 µm to 0.3 µm and an average interparticle spacing of 1 µm to 10 µm.

6. An alloy of claim 5, in which said discrete particles occupy an average volume fraction of 0.005 to 0.01.

7. A method of enhancing the magnetic properties of the metallic glass recited in claim 1, comprising the step of annealing said alloy at a temperature and for a time sufficient to induce precipitation of discrete particles in said amorphous metal matrix.

8. A method as recited in claim 7, wherein the discrete particles consist essentially of a mixture of particles a portion of which mixture contains particles having a body-centered cubic structure, said particles being composed essentially of iron, up to 22 atom percent of said iron being adapted to be replaced by at least one of nickel, cobalt, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, hafnium, silicon and carbon.

9. A method as recited in claim 7, wherein the discrete particles consist essentially of a mixture of particles a portion of which mixture contains particles having a crystalline Fe_3B structure, said particles of

said portion being composed of iron and boron, up to 14 atom percent of said iron being adapted to be replaced by at least one of nickel, cobalt, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, and hafnium, and up to 2 atom percent of said boron being adapted to be replaced by carbon.

Patentansprüche

1. Metallisches Glas mit einer Kombination hoher Permeabilität, niedriger Magnetostriktion, niedriger Koerzitivkraft, niedrigen Wechselstrom-Kernverlustes, niedriger Erregerkraft und hoher thermischer Stabilität, bestehend aus 63 bis 79 Atom-% Eisen, 2 bis 8 Atom-% wenigstens eines Elementes aus der Gruppe Nickel, Kobalt und von Gemischen derselben, 2 bis 4 Atom-% wenigstens eines Elementes aus der Gruppe Chrom, Molybdän, Wolfram, Vanadin, Niob, Tantal, Titan, Zirkon und Hafnium, 17 bis 28 Atom-% Bor, wobei 0,5 bis 6 Atom-% des Bors durch Silizium ersetzt sind und bis zu 2 Atom-% des Bors gegebenenfalls durch Kohlenstoff ersetzt sind, sowie beiläufigen Verunreinigungen.

2. Metallisches Glas nach Anspruch 1, in welchem der Austausch von Bor gegen Silizium und Kohlenstoff das Glas mit Metalloidelementen versieht, der entweder im wesentlichen aus Bor und zusätzlich 0,5 bis 4 Atom-% Silizium oder aus Bor plus Silizium zusammen mit 0 bis 2 Atom-% Kohlenstoff bestehen.

3. Metallisches Glas nach Anspruch 2, in welchem die Metalloidelemente im Bereich von 17 bis 26 Atom-% liegen.

4. Metallisches Glas nach Anspruch 1, bestehend aus 70 bis 79 Atom-% Eisen, 2 bis 4 Atom-% wenigstens eines Elementes aus der Gruppe Nickel, Kobalt und von Gemischen hiervon, 2 bis 4 Atom-% eines Elementes aus der Gruppe Molybdän und Chrom sowie 17 bis 22 Atom% eines Elementes aus der Gruppe Bor, Silizium und von Gemischen hiervon.

5. Legierung nach Anspruch 1, die zu wenigstens 85 % amorph ist, wobei diese Legierung durch das Vorhandensein einzelner Teilchen seiner Bestandteile darin gekennzeichnet ist und wobei diese Teilchen eine mittlere Größe im Bereich von 0,1 µ bis 0,3 µm und einen mittleren Abstand zwischen den Teilchen von 1 µm bis 10 µm haben.

6. Legierung nach Anspruch 5, in welcher die einzelnen Teilchen einen mittleren Volumenanteil von 0,005 bis 0,01 einnehmen.

7. Verfahren zur Verbesserung der magnetischen Eigenschaften des metallischen Glases nach Anspruch 1 mit der Stufe eines Erhitzens der Legierung auf eine Temperatur und während einer Zeit, die ausreichen, um eine Ausfällung einzelner Teilchen in der amorphen Metallmatrix einzuleiten.

8. Verfahren nach Anspruch 7, bei dem die einzelnen Teilchen im wesentlichen aus einem Teilchengemisch bestehen, von dem ein Teil Teilchen mit einer raumzentrierten kubischen Struktur enthält, wobei diese Teilchen im wesentlichen aus Eisen aufgebaut sind, wobei bis zu 22 Atom-% dieses Eisens durch wenigstens eines der Elemente Nickel, Kobalt, Chrom, Molybdän, Wolfram, Vanadin, Niob, Tantal, Titan, Zirkon, Hafnium, Silizium und Kohlenstoff ersetzbar sein können.

9. Verfahren nach Anspruch 7, bei dem die einzelnen Teilchen im wesentlichen aus einem Teilchengemisch bestehen, von dem ein Teil Teilchen mit einer kristallinen Fe_3B-Struktur enthält, wobei diese Teilchen des besagten Anteils aus Eisen und Bor aufgebaut sind, bis zu 14 Atom-% des Eisens durch wenigstens eines der Elemente Nickel, Kobalt, Chrom, Molybdän, Wolfram, Vanadin, Niob, Tantal, Titan, Zirkon und Hafnium austauschbar sind und bis zu 2 Atom-% des Bors durch Kohlenstoff austauschbar sind.

Revendications

1. Verre métallique présentant une combinaison de perméabilité élevée, faible magnétostriction, faible champ coercitif, faible perte en fer en courant alternatif, puissance d'excitation réduite et grande stabilité thermique, se composant de 62 à 79 pour-cent atomiques de fer, 2 à 8 pour-cent atomiques d'au moins un élément choisi dans le groupe composé du nickel, cobalt et leurs mélanges, 2 à 4 pour-cent atomiques d'au moins un élément choisi dans le groupe composé du chrome, molybdène, tungstène, vanadium, niobium, tantale, titane, zirconium et hafnium, 17 à 28 pour-cent atomiques de bore, 0,5 à 6 pour-cent atomiques dudit bore étant remplacés par du silicium et jusqu'à 2 pour-cent atomiques de bore étant, en option, remplacés par du carbone, le reste étant des impuretés inévitables.

2. Verre métallique suivant la revendication 1, dans lequel le remplacement de bore par du silicium et du carbone introduit dans ledit verre un élément métalloïde choisi dans le groupe composé substantiellement du bore et de 0,5 à 4 pour-cent atomiques de silicium, et de bore plus du silicium ensemble avec de 0 à 2 pour-cent atomiques de carbone.

3. Verre métallique suivant la revendication 2, dans lequel ledit élément métalloïde a une teneur de 17 à 26 pour-cent atomiques.

4. Verre métallique suivant la revendication 1, se composant de 70 à 79 pour-cent atomiques de fer, 2 à 4 pour-cent atomiques d'au moins un élément choisi dans le groupe composé du nickel, cobalt et leurs mélanges, 2 à 4 pour-cent atomiques d'un élément choisi dans le groupe composé du molybdène et du chrome et 17 à 22 pour-cent atomiques d'un élément choisi dans le groupe composé du bore, silicium et leurs mélanges.

5. Alliage suivant la revendication 1 qui est amorphe à au moins 85 %, ledit alliage étant charactérisé par la présence de particules discrètes de ses constituants, lesdits particules ayant une taille moyenne comprise entre 0,1 µm et 0,3 µm et un écartement moyen entre les particules de 1 µm à 10 µm.

6. Alliage suivant la revendication 5, dans lequel lesdites particules discrètes occupent une fraction volumique moyenne de 0,005 à 0,01.

7. Procédé pour accroître les propriétés magnétiques du verre métallique décrit dans la revendication 1, comprenant l'étape de recuit dudit alliage à une température et pendant un temps suffisants pour induire la précipitation de particules discrètes dans ladite matrice métallique amorphe.

8. Procédé suivant la revendication 7, dans lequel les particules discrètes se composent essentiellement d'un mélange de particules dont une portion contient des particules ayant une structure cubique centrée, lesdites particules étant composées essentiellement de fer, jusqu'à 22 pour-cent atomiques dudit fer pouvant être remplacés par au moins un des éléments nickel, cobalt, chrome, molybdène, tungstène, vanadium, niobium, tantale, titane, zirconium, hafnium, silicium et carbone.

9. Procédé suivant la revendication 7, dans lequel les particules discrètes consistent essentiellement en un mélange de particules dont une portion contient des particules ayant une structure cristalline Fe_3B, lesdites particules de ladite portion étant composées de fer et de bore, jusqu'à 14 pour-cent atomiques dudit fer pouvant être remplacés par au moins un des éléments nickel, cobalt, chrome, molybdène, tungstène, vanadium, niobium, tantale, titane, zirconium et hafnium, et jusqu'à 2 pour-cent atomiques dudit bore pouvant être remplacés par du carbone.