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(54) **NEAR-ZERO MAGNETOSTRICTIVE GLASSY METAL ALLOYS FOR HIGH FREQUENCY APPLICATIONS.**

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(73) Proprietor : **ALLIED-SIGNAL INC. (a Delaware corporation)**
Columbia Road and Park Avenue P.O. Box
2245R
Morristown New Jersey 07960 (US)

(72) Inventor : **HASEGAWA, Ryusuke**
29 Hill Street
Morristown, NJ 07960 (US)

(74) Representative : **Myerscough, Philip Boyd et al**
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 5EU (GB)

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Description**BACKGROUND OF THE INVENTION**5 **1. Field of the Invention**

This invention relates to glassy metal alloys with near-zero magnetostriction which are especially suited for use in high frequency applications.

10 **2. Description of the Prior Art**

Saturation magnetostriction λ_s is related to the fractional change in length of $\Delta\ell/\ell$ that occurs in a magnetic material on going from the demagnetized to the saturated, ferromagnetic state. The value of magnetostriction, a dimensionless quantity, is often given in units of microstrains (i.e., a microstrain is a fractional change in length of one part per million).

Ferromagnetic alloys of low magnetostriction are desirable for several interrelated reasons:

1. Soft magnetic properties (low coercivity, high permeability) are generally obtained when both the saturation magnetostriction λ_s and the magnetocrystalline anisotropy K approach zero. Therefore, given the same anisotropy, alloys of lower magnetostriction will show lower dc coercivities and higher permeabilities. Such alloys are suitable for various soft magnetic applications.

2. Magnetic properties of such zero magnetostrictive materials are insensitive to mechanical strains. When this is the case, there is little need for stress-relief annealing after winding, punching or other physical handling needed to form a device from such material. In contrast, magnetic properties of stress-sensitive materials, such as the crystalline alloys, are seriously degraded by such cold working and such materials must be carefully annealed.

3. The low dc coercivity of zero magnetostrictive materials carries over to ac operating conditions where again low coercivity and high permeability are realized (provided the magneto-crystalline anisotropy is not too large and the resistivity not too small). Also because energy is not lost to mechanical vibrations when the saturation magnetostriction is zero, the core loss of zero magnetostrictive materials can be quite low. Thus, zero magnetostrictive magnetic alloys (of moderate or low magnetocrystalline anisotropy) are useful where low loss and high ac permeability are required. Such applications include a variety of tape-wound and laminated core devices, such as power transformers, signal transformers, magnetic recording heads and the like.

4. Finally, electromagnetic devices containing zero magnetostrictive materials generate no acoustic noise under AC excitation. While this is the reason for the lower core loss mentioned above, it is also a desirable characteristic in itself because it eliminates the hum inherent in many electromagnetic devices.

There are three well-known crystalline alloys of zero magnetostriction (in atom percent, unless otherwise indicated):

- (1) Nickel-iron alloys containing approximately 80% nickel ("80 nickel permalloys");
- (2) Cobalt-iron alloys containing approximately 90% cobalt; and
- (3) Iron-silicon alloys containing approximately 6 wt. % silicon.

Also included in these categories are zero magnetostrictive alloys based on the binaries but with small additions of other elements such as molybdenum, copper or aluminum to provide specific property changes. These include, for example, 4% Mo, 79% Ni, 17% Fe (sold under the designation Moly Permalloy) for increased resistivity and permeability; permalloy plus varying amounts of copper (sold under the designation Mumetal) for magnetic softness and improved ductility; and 85 wt. % Fe, 9 wt. % Si, 6 wt. % Al (sold under the designation Sendust) for zero anisotropy.

The alloys included in category (1) are the most widely used of the three classes listed above because they combine zero magnetostriction with low anisotropy and are, therefore, extremely soft magnetically; that is they have a low coercivity, a high permeability and a low core loss. These permalloys are also relatively soft mechanically and their excellent magnetic properties, achieved by high temperature (above 1000°C) anneal, tend to be degraded by relatively mild mechanical shock.

Category (2) alloys such as those based on $\text{Co}_{90}\text{Fe}_{10}$ have a much higher saturation induction (B_s about 1.9 Tesla) than the permalloys. However, they also have a strong negative magnetocrystalline anisotropy, which prevents them from being good soft magnetic materials. For example, the initial permeability of $\text{Co}_{90}\text{Fe}_{10}$ is only about 100 to 200.

Category (3) alloys such as Fe/6 wt% Si and the related ternary alloy Sendust (mentioned above) also show higher saturation inductions (B_s about 1.8 Tesla and 1.1 Tesla, respectively) than the permalloys. However

these alloys are extremely brittle and have, therefore, found limited use in powder form only. Recently both Fe/6.5 wt. % Si [IEEE Trans. MAG-16, 728 (1980)] and Sendust alloys (IEEE Trans. MAG-15 1149 (1970)) have been made relatively ductile by rapid solidification. However, compositional dependence of the magnetostriction is very strong in these materials, difficult precise tailoring of the alloy composition to achieve near-zero magnetostriction.

It is known that magnetocrystalline anisotropy is effectively eliminated in the glassy state. It is therefore desirable to seek glassy metal alloys of zero magnetostriction. Such alloys might be found near the compositions listed above. Because of the presence of metalloids which tend to quench the magnetization by the transfer of charge to the transition-metal d-electron states, however, glassy metal alloys based on the 80 nickel permalloys are either non-magnetic at room temperature or have unacceptably low saturation inductions. For example, the glassy alloy $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (the subscripts are in atom percent) has a saturation induction of about 0.8 Tesla, while the glassy alloy $\text{Ni}_{49}\text{Fe}_{29}\text{P}_{14}\text{B}_6\text{Si}_2$ has a saturation induction of about 0.46 Tesla and the glassy alloy $\text{Ni}_{80}\text{P}_{20}$ is non-magnetic. No glassy metal alloys having a saturation magnetostriction approximately equal to zero have yet been found near the iron-rich Sendust composition. A number of near-zero magnetostrictive glassy metal alloys based on the Co-Fe crystalline alloy mentioned above in (2) have been reported in the literature. These are, for example, $\text{Co}_{72}\text{Fe}_3\text{P}_{16}\text{B}_6\text{Al}_3$ (AIP Conference Proceedings, No. 24, pp. 745-746 (1975)) $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{15}\text{B}_{10}$ (Vol. 14, Japanese Journal of Applied Physics, pp. 1077-1078 (1975)) $\text{Co}_{31.2}\text{Fe}_{7.8}\text{Ni}_{39.0}\text{B}_{14}\text{Si}_8$ [proceedings of 3rd International Conference on Rapidly Quenched metals, p. 183, (1979)] and $\text{Co}_{74}\text{Fe}_6\text{B}_{20}$ [IEEE Trans. MAG-12, 942 (1976)]. Table I lists some of the magnetic properties of these materials.

Table I

Saturation induction (B_s), Curie temperature (θ_f), the first crystallization temperature (T_{c1}), ascast dc coercivity (H_C), and dc coercivity and permeability (μ) in the annealed states of some of the prior art zero magnetostrictive glassy alloys.

Alloy	B_s (Tesla)	θ (K)	T_{c1} (K)	H_C (A/m)	Annealed Values	
					H_C (A/m)	μ (at 1 kHz)
$\text{Co}_{72}\text{Fe}_3\text{P}_{16}\text{B}_6\text{Al}_3$	0.63	600	-	1.8	1.0*	-
$\text{Co}_{70.5}\text{Fe}_{4.5}\text{B}_{10}\text{Si}_{15}$	0.65	688	-	8.0	1.2**	50 000
$\text{Co}_{31.2}\text{Fe}_{7.8}\text{Ni}_{39.0}\text{B}_{14}\text{Si}_8$	0.61	503	690	-	0.16***	50 000
$\text{Co}_{74}\text{Fe}_6\text{B}_{20}$	1.18	700	660	2.8	-	-

* annealed at 270°C for 45 min., in 2400 A/m field (H_{11}) applied along the circumferential direction of the toroidal sample.

** annealed at 350°C and cooled at 175°C/hour in $H_{11} = 32$ kA/m.

*** annealed at about 330°C.

The saturation induction (B_s) of these alloys ranges between 0.6 and 1.2 Tesla. The glassy alloys with B_s close to 0.6 T show low coercivities and high permeabilities comparable to crystalline supermalloys. However, these alloys tend to be magnetically unstable at relatively low (150°C) temperatures. On the other hand, the glassy alloys with $B_s \sim 1.2$ Tesla tend to have their ferromagnetic Curie temperatures (θ_f) near or above their first crystallization temperatures (T_{c1}). This makes heat-treatment of these materials very difficult to achieve desired soft magnetic properties because such annealing is most effective when carried out at temperatures near θ_f .

A recent prior art (Journal of Applied Physics 53, 7819 (1983)) discloses near-zero magnetostrictive glassy alloys with excellent soft magnetic properties and magnetic stability. These glassy alloys were designed with the idea of a saturation induction as high as possible. Recent trends in the applied magnetics do not necessarily require high saturation inductions but a high squareness ratio, a low ac core loss and a high permeability at high frequencies. In view of this, glassy metal alloys exhibiting these features are desirable.

EP-A-84 138 describes a new series of glassy metal alloys with near-zero magnetostriction is disclosed. The glassy alloys have the composition $\text{CO}_a\text{Fe}_b\text{Ni}_c\text{Mo}_d\text{B}_e\text{Si}_f$, where a ranges from about 58 to 70 atom percent, b ranges from about 2 to 7.5 atom percent, c ranges from about 0 to 8 atom percent, d ranges from about 1 to

2 atom percent, e ranges from about 11 to 15 atom percent and f ranges from about 9 to 14 atom percent with the proviso that the sum of a, b, c ranges from about 72 to 76 atom percent and the sum of e and f ranges from about 23 to 26 atom percent. The magnetostriction of these alloys ranges from about -1×10^{-6} to $+1 \times 10^{-6}$ and the saturation induction is between about 0.6 and 0.8 Tesla. The transition metal content is responsible for the low magnetostriction in these alloys. The metalloid content strongly affects the saturation induction. Curies temperature, and magnetic stability. Magnetostriction is mildly affected by the metalloid composition and a particular range of Si/B ratio for certain iron, cobalt containing alloys wherein the magnetostriction is near-zero and relatively insensitive to the Si/B ratio. The same Si/B ratios also provide high magnetic stability.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a magnetic alloy that is at least 70% glassy, and which has a near-zero magnetostriction, high magnetic and thermal stability and excellent soft magnetic properties at high frequencies. The glassy metal alloy has the composition $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$, where subscripts are in atom percents and "a" ranges from 65.5 to 70.5, "b" ranges from 3.8 to 4.5, "c" ranges from 0 to 3, "d" ranges from 1 to 2, "e" ranges from 10 to 12 and "f" ranges from 14 to 15 when M is selected from a group consisting of vanadium, chromium, molybdenum, niobium and tungsten; when M is manganese, "a" ranges from 68.0 to 70.0, "b" ranges from 2.5 to 4.0, "c" ranges from 0 to 3, "d" ranges from 1 to 4, "e" ranges from 10 to 12 and "f" ranges from 14 to 15. The glassy alloy has a value of saturation magnetostriction ranging from -1×10^{-6} to $+1 \times 10^{-6}$, a saturation induction of at least 0.65 Tesla, a Curie temperature ranging from 245 to 310°C and the first crystallization temperature ranging from 530 to 575°C.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, there is provided a magnetic alloy that is at least 70% glassy and which has an outstanding combination of properties, including a near-zero magnetostriction, high magnetic and thermal stability and such soft magnetic properties as high permeability, low ac core loss and low coercivity.

The purity of the above composition is that found in normal commercial practice. However, it will be appreciated that up to about 2 atom percent of (Si + B) may be replaced by carbon, aluminum or germanium without significantly degrading the desirable magnetic properties of these alloys.

Examples of essentially zero magnetostrictive glassy metal alloys of the invention include

$\text{Co}_{65.7}\text{Fe}_{4.4}\text{Ni}_{2.9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$ and

$\text{Co}_{68.13}\text{Fe}_{4.0}\text{Ni}_{1.37}\text{Mo}_{1.5}\text{B}_{10}\text{Si}_{15}$. These glassy alloys possess saturation induction between about 0.65 and 0.70 Tesla, Curie temperature of about 270°C and the first crystallization temperature of about 530°C. Some magnetic and thermal properties of other near-zero magnetostrictive glassy alloys of the present invention are listed in Table II.

TABLE II

5 Saturation induction (B_s), Curie temperature (θ_c), saturation magnetostriction (λ_s) and the first crystallization temperature (T_{c1}) of near-zero magnetostrictive glassy alloys.

<u>compositions</u>										
10	65.7	4.4	2.9	Mo=2	11	14	0.65	266	0	530
	68.13	4.0	1.37	Mo=1.5	10	15	0.70	268	0	530
	68.7	4.3	0	Mo=2	11	14	0.65	292	0.7	544
	69.6	4.4	0	Mo=1	10	15	0.73	305	0.4	544
15	68.75	4.25	0	Mo=2	10	15	0.65	254	0.6	555
	69.6	4.4	0	Cr=1	10	15	0.74	295	-0.4	531
	68.75	4.25	0	Cr=2	10	15	0.69	261	0.4	540
20	68.2	3.8	0	Mn=1	12	15	0.70	266	0.4	558
	67.7	3.3	0	Mn=2	12	15	0.70	246	0.4	560
	70.0	4.0	0	Mn=1	10	15	0.80	326	0.4	532
25	69.5	3.5	0	Mn=2	10	15	0.80	308	0.9	538
	69.0	3.0	0	Mn=3	10	15	0.78	305	1.0	544
	68.5	2.5	0	Mn=4	10	15	0.78	273	0.4	548
30	69.6	4.4	0	V=1	10	15	0.72	309		535
	68.75	4.25	0	V=2	10	15	0.65	256		546
	69.6	4.4	0	Nb=1	10	15	0.74	314		551
	68.75	4.25	0	Nb=2	10	15	0.66	259		574
35	69.6	4.4	0	W=1	10	15	0.72	309		548
	68.75	4.25	0	W=2	10	15	0.65	259		545

40 The presence of the metal element M is to increase T_d and hence the thermal stability of the alloy system. The content of M beyond 2 atom percent, however, reduces the Curies temperature to a level lower than 245°C, which is undesirable in conventional magnetic devices.

45 For some applications, it may be desirable or acceptable to use a material with a small positive or a small negative magnetostriction. When this is the case, all of the glassy alloys of Table II exhibiting the saturation magnetostriction value ranging from -1×10^{-6} to $+10^{-6}$ may qualify. The value of the magnetostriction is essentially determined by the ratio of $Fe/(Co+Fe)$ or $(Fe+Mn)/(Co+Fe+Mn)$. These ratios are about 0.06 and 0.07-0.09 respectively. The small amount of the element Ni and the metal M excepting Mn which is present in the glassy alloys of the present invention is relatively ineffective to alter the magnetostriction of these alloys.

50 The glassy alloy of the invention are conveniently prepared by techniques readily available elsewhere; see, e.g., U.S. Patent 3,845,805, issued November 5, 1974 and 3,856,513, issued December 24, 1974. In general, the glassy alloys, in the form of continuous ribbon, wire, etc., are rapidly quenched from a melt of the desired composition at a rate of at least about 10^5 K/sec.

A metalloid content of boron and silicon in the range of about 24 to 27 atom percent of the total alloy composition is sufficient for glass formation, with boron ranging from about 10 to 12 atom percent and silicon ranging from about 14 to about 15 atom percent.

55 Tables III and IV give ac core loss (L), exciting power (P_s) and permeability (μ) at 0.1 Tesla induction and at 50 kHz of the near-zero magnetostrictive glassy alloys of the present invention annealed at different temperature (T_o). Summarizing, by water quenching subsequent to the heat-treatments given in Table III, the glassy alloys of the present invention exhibit, on the average, $L=4$ W/kg, $P_s=6$ VA/kg and $\mu=28,000$. One of them,

namely, $\text{Co}_{68.13}\text{Fe}_{4.0}\text{Ni}_{1.37}\text{Mo}_{1.5}\text{B}_{10}\text{Si}_{15}$, can attain $L=3.0\text{ W/kg}$, $P_8=4.2\text{ VA/kg}$ and $\mu=38,000$. Slower cooling after the heat-treatments generally results in higher value for the loss and the exciting power, and lower permeabilities. Some of the glassy alloys of the present invention, when cooled slowly subsequent to the heat-treatments, however, show results comparable to or better than those exhibited by the materials quenched rapidly after the heat-treatments. One such example is shown by a glassy $\text{Co}_{68.75}\text{Fe}_{4.25}\text{W}_2\text{B}_{10}\text{Si}_{15}$, which gives $L=2.7\text{ W/kg}$, $P_8=4.6\text{ VA/kg}$ and $\mu=34,100$ at 50 kHz and 0.1 Tesla induction when heat-treated at 400°C for 15 min. without a field and cooled slowly at a rate of about -4°C/min. Compared with these values, a prior art crystalline non-magnetostrictive supermalloy of the similar thickness (25 μm) given $L=1\text{ W/kg}$, $P_8=10\text{ VA/kg}$ and $\mu=19,000$ at 0.1 Tesla and 50 kHz. Examples of glassy alloys outside the scope of the invention are set forth in Table V. The advantageous combination of properties provided by the alloys of the present invention cannot be achieved in prior art nonmagnetostrictive glassy alloys with high saturation induction, such as $\text{Co}_{74}\text{Fe}_6\text{B}_{20}$, because their Curie temperatures are higher than the first crystallization temperatures and the heat-treatment to improve their properties are not so effective as in those with lower saturation inductions. The above properties, achieved in the glassy alloys of the present invention, may be obtained in low induction glassy alloys of the prior art. However, these alloys of the prior art such as $\text{Co}_{31.2}\text{Fe}_{7.8}\text{Ni}_{39.0}\text{B}_{14}\text{Si}_8$ tend to be magnetically unstable at relatively low temperature of about 150°C as pointed out earlier. The best combined properties of another glassy alloy of a prior art were $L=4\text{ W/kg}$, $P_8=7\text{ VA/kg}$ and $\mu=23,000$ obtained for a glassy $\text{Co}_{67.4}\text{Fe}_{4.1}\text{Ni}_{3.0}\text{Mo}_{1.5}\text{B}_{12.5}\text{Si}_{11.5}$ annealed at 380°C for 15 min. and cooled rapidly. It is again clear that the glassy alloys of the present invention are generally superior to this class of glassy alloys.

TABLE III

Examples of core loss (L), exciting power (P_g) and permeability (μ) at 50 kHz and 0.1 Tesla of near-zero magnetostrictive glassy alloys of the present invention annealed at different temperature (T). Annealing time was 15 min., after which the glass alloy samples were quenched into water at room temperature. No field was applied during the heat-treatment.

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<u>compositions</u>									
<u>Co</u>	<u>Fe</u>	<u>Ni</u>	<u>M</u>	<u>B</u>	<u>Si</u>	<u>T_g(°C)</u>	<u>L(W/kg)</u>	<u>P_g(VA/kg)</u>	<u>μ</u>
65.7	4.4	2.9	Mo=2	11	14	420	3.8	5.8	27 300
68.13	4.0	1.37	Mo=1.5	10	15	380	3.0	4.2	38 000
69.6	4.4	0	Mo=1	10	15	400	4.5	5.9	27 100
68.75	4.25	0	M=2	10	15	420	4.3	5.7	28 200
69.6	4.4	0	Cr=1	10	15	440	4.1	5.5	29 700
68.75	4.25	0	Cr=2	10	15	400	4.2	5.6	27 500
68.2	3.8	0	Mn=1	12	15	420	4.1	5.7	28 400
67.7	3.3	0	Mn=2	12	15	440	4.0	6.1	26 600
70.0	4.0	0	Mn=1	10	15	420	3.6	5.5	29 300
69.5	3.5	0	Mn=2	10	15	420	4.4	6.1	26 900
69.0	3.0	0	Mn=3	10	15	440	4.2	5.9	27 800
68.5	2.5	0	Mn=4	10	15	420	4.5	6.3	25 800
69.6	4.4	0	V=1	10	15	400	4.2	5.7	29 000
68.75	4.25	0	V=2	10	15	400	4.2	6.2	27 000
69.6	4.4	0	Nb=1	10	15	420	5.5	7.3	22 600
68.75	4.25	0	Nb=2	10	15	400	4.2	5.9	27 500
69.6	4.4	0	W=1	10	15	420	4.1	5.3	30 500
68.75	4.25	0	W=2	10	15	400	5.2	6.1	26 100

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TABLE IV

Core loss (L), exciting power (P_e) and permeability (μ) measured at 50 kHz and 0.1 Tesla induction for near-zero magnetostrictive glassy alloys of the present invention annealed under different conditions. The annealing time was 15 min., after which the samples were cooled, unless otherwise stated, at a rate of about $-4^\circ\text{C}/\text{min.}$ to room temperature. No field was applied during the anneal except for the cases indicated by asterisks.

<u>compositions</u>									
Co	Fe	Ni	M	B	Si	$T_a(^{\circ}\text{C})$	L(W/kg)	$P_e(\text{VA/kg})$	μ
65.7	4.4	2.9	Mo=2	11	14	440*	3.9	5.6	29 000
68.13	4.0	1.37	Mo=1.5	10	15	400*	4.9	7.4	21 900
68.13	4.0	1.37	Mo=1.5	10	15	440	4.8	10.8	14 900
68.75	4.25	0	Mo=2	10	15	460	5.0	8.1	19 700
68.2	3.8	0	Mn=1	12	15	420	6.7	11.8	13 300
67.7	3.3	0	Mn=2	12	15	460	4.0	8.6	18 700
68.75	4.25	0	V=2	10	15	440	4.2	9.2	18 100
68.75	4.25	0	Nb=2	10	15	460	3.5	9.0	17 800
68.75	4.25	0	W=2	10	15	400	2.7	4.6	34 100

* A field of 1600 A/m was applied along the direction of the ribbon during heat-treatment, after which the sample was quenched into water at room temperature.

TABLE V

Magnet properties of some representative $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$ glassy alloys in which at least one of a, b, c, d, e, and f is outside the range defined in the present invention.

<u>compositions</u>							
Co	Fe	Ni	M	B	Si	$B_R(\text{T})$	$\theta_c(^{\circ}\text{C})$
64.2	3.8	0	Mo=3	14	15	0.33	64
65.05	3.95	0	Mo=4	10	15	0.56	209
66.1	3.9	0	Cr=3	12	15	0.50	154
65.8	3.2	0	Mn=2	14	15	0.58	170
66.2	1.8	0	Mn=5	12	15	0.65	194
67.9	4.1	0	V=3	10	15	0.58	199
67.9	4.1	0	Nb=3	10	15	0.57	195
67.9	4.1	0	W=3	10	15	0.54	179

Table V shows the magnetic properties of some of the representative glassy alloys of the composition $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$ (M is selected from the group consisting of V, Cr, Mn, Mo, Nb and W), in which at least one of a, b, c, d, e and f is outside the composition range defined in the present invention. The table indicates that the alloys with at least one of the constituents outside the defined ranges exhibit either Curie temperature or saturation induction too low to be practical in many magnetic applications

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

1. Sample Preparation

The glassy alloys listed in Tables II-VII were rapidly quenched (about 10^6 K/sec) from the melt following the techniques taught by Chen and Polk in U.S. Patent 3,856,513. The resulting ribbons, typically 25 to 30 μm thick and 0.5 to 2.5 cm wide, were determined to be free of significant crystallinity by x-ray diffractometry (using CuK radiation) and scanning calorimetry. Ribbons of the glassy metal alloys were strong, shiny, hard and ductile.

2. Magnetic Measurements

Continuous ribbons of the glassy metal alloys prepared in accordance with the procedure described in Example I were wound onto bobbins (3.8 cm O.D.) to form closed-magnet-path toroidal samples. Each sample contained from 1 to 3 g of ribbon. Insulated primary and secondary windings (numbering at least 10 each) were applied to the toroids. These samples were used to obtain hysteresis loops (coercivity and remanence) and initial permeability with a commercial curve tracer and core loss (IEEE Standard 106-1972).

The saturation magnetization, M_s , of each sample, was measured with a commercial vibrating sample magnetometer (Princeton Applied Research). In this case, the ribbon was cut into several small squares (approximately 2 mm x 2 mm). These were randomly oriented about their normal direction, their plane being parallel to the applied field (0 to 720 kA/m. The saturation induction $R_s (=4 \pi 4M_s D)$ was then calculated by using the measured mass density D.

The ferromagnetic Curie temperature (θ_f) was measured by inductance method and also monitored by differential scanning calorimetry, which was used primarily to determine the crystallization temperatures. The first or primary crystallization temperature (T_{cl}) was used to compare the thermal stability of various glassy alloys of the present and prior art inventions.

Magnetic stability was determined from the reorientation kinetics of the magnetization, in accordance with the method described in Journal of Applied Physics, Vol. 49, p. 6510 (1978), which method is incorporated herein by reference thereto.

Magnetostriction measurements employed metallic strain gauges (BLH Electronics), which were bonded (Eastman - 910 Cement) between two short lengths of ribbon. The ribbon axis and gauge axis were parallel. The magnetostriction was determined as a function of applied field from the longitudinal strain in the parallel ($\Delta\ell/\ell$) and perpendicular ($\Delta\ell'/\ell$) in-plane fields, according to the formula $\lambda = 2/3[(\Delta\ell/\ell) - \Delta\ell'/\ell]$.

Claims

1. A magnetic alloy that is at least 70% glassy, having the formula $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$ where the subscripts are in atom percent and "a" ranges from 65.5 to 70.5, "b" ranges from 3.8 to 4.5, "c" ranges from 0 to 3, "d" ranges from 1 to 2, "e" ranges from 10 to 12 and "f" ranges from 14 to 15 when M is selected from the group consisting of vanadium, chromium, molybdenum, niobium and tungsten; when M is manganese, "a" ranges from 68.0 to 70.0, "b" ranges from 2.5 to 4.0, "c" ranges from 0 to 3, "d" ranges from 1 to 4, "e" ranges from 10 to 12 and "f" ranges from 14 to 15, said alloy having a value of the saturation magnetostriction between -1×10^{-6} to $+1 \times 10^{-6}$, a Curie temperature ranging from 245°C to 310°C, a first crystallization temperature ranging from 530°C to 575°C and a saturation induction of at least 0.65 Tesla.

2. The magnetic alloy of claim 1 having the formula $\text{Co}_{65.7}\text{Fe}_{4.4}\text{Ni}_{2.9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$.

3. The magnetic alloy of claim 1 having the formula $\text{Co}_{68.13}\text{Fe}_{4.0}\text{Ni}_{1.37}\text{Mo}_{1.5}\text{B}_{10}\text{Si}_{15}$.

4. The magnetic alloy of claim 1 having the formula $\text{Co}_{69.6}\text{Fe}_{4.4}\text{Mo}_1\text{B}_{10}\text{Si}_{15}$.

5. The magnetic alloy of claim 1 having the formula $\text{Co}_{68.75}\text{Fe}_{4.25}\text{Mo}_2\text{B}_{10}\text{Si}_{15}$.

6. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,6}\text{Fe}_{4,4}\text{Cr}_1\text{B}_{10}\text{Si}_{15}$.
 7. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,75}\text{Fe}_{4,25}\text{Cr}_2\text{B}_{10}\text{Si}_{15}$.
 8. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,2}\text{Fe}_{3,8}\text{Mn}_1\text{B}_{12}\text{Si}_{15}$.
 9. The magnetic alloy of claim 1 having the formula $\text{Co}_{67,7}\text{Fe}_{3,3}\text{Mn}_2\text{B}_{12}\text{Si}_{15}$.
 10. The magnetic alloy of claim 1 having the formula $\text{Co}_{70,0}\text{Fe}_{4,0}\text{Mn}_1\text{B}_{10}\text{Si}_{15}$.
 11. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,5}\text{Fe}_{3,5}\text{Mn}_2\text{B}_{10}\text{Si}_{15}$.
 12. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,0}\text{Fe}_{3,0}\text{Mn}_3\text{B}_{10}\text{Si}_{15}$.
 13. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,5}\text{Fe}_{2,5}\text{Mn}_4\text{B}_{10}\text{Si}_{15}$.
 14. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,6}\text{Fe}_{4,4}\text{V}_1\text{B}_{10}\text{Si}_{15}$.
 15. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,75}\text{Fe}_{4,25}\text{V}_2\text{B}_{10}\text{Si}_{15}$.
 16. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,6}\text{Fe}_{4,4}\text{Nb}_1\text{B}_{10}\text{Si}_{15}$.
 17. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,75}\text{Fe}_{4,25}\text{Nb}_2\text{B}_{10}\text{Si}_{15}$.
 18. The magnetic alloy of claim 1 having the formula $\text{Co}_{69,6}\text{Fe}_{4,4}\text{W}_1\text{B}_{10}\text{Si}_{15}$.
 19. The magnetic alloy of claim 1 having the formula $\text{Co}_{68,75}\text{Fe}_{4,25}\text{W}_2\text{B}_{10}\text{Si}_{15}$.

Patentansprüche

1. Eine zu zumindest 70% glasähnliche magnetische Legierung mit der Formel $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$, in der die tiefgestellten Indices Atomprozent sind und "a" von 65,5 bis 70,5, "b" von 3,8 bis 4,5, "c" von 0 bis 3, "d" von 1 bis 2, "e" von 10 bis 12 und "f" von 14 bis 15 reichen, falls M aus der Gruppe bestehend aus Vanadium, Chrom, Molybdän, Niob und Wolfram ausgewählt ist, wobei, falls M Mangan ist, "a" von 68,0 bis 70,0, "b" von 2,5 bis 4,0, "c" von 0 bis 3, "d" von 1 bis 4, "e" von 10 bis 12 und "f" von 14 bis 15 reichen, wobei die Legierung einen Sättigungsmagnetostriktionswert zwischen -1×10^{-6} bis $+1 \times 10^{-6}$, eine Curietemperatur im Bereich von 245°C bis 310°C, eine erste Kristallisationstemperatur im Bereich von 530°C bis 575°C und eine Sättigungsinduktion von zumindest 0,65 Tesla aufweist.

2. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{65,7}\text{Fe}_{4,4}\text{Ni}_{2,9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$.
 3. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,13}\text{Fe}_{4,0}\text{Ni}_{1,37}\text{Mo}_{1,5}\text{B}_{10}\text{Si}_{15}$.
 4. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,6}\text{Fe}_{4,4}\text{Mo}_1\text{B}_{10}\text{Si}_{15}$.
 5. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,75}\text{Fe}_{4,25}\text{Mo}_2\text{B}_{10}\text{Si}_{15}$.
 6. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,6}\text{Fe}_{4,4}\text{Cr}_1\text{B}_{10}\text{Si}_{15}$.
 7. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,75}\text{Fe}_{4,25}\text{Cr}_2\text{B}_{10}\text{Si}_{15}$.
 8. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,2}\text{Fe}_{3,8}\text{Mn}_1\text{B}_{12}\text{Si}_{15}$.
 9. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{67,7}\text{Fe}_{3,3}\text{Mn}_2\text{B}_{12}\text{Si}_{15}$.
 10. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{70,0}\text{Fe}_{4,0}\text{Mn}_1\text{B}_{10}\text{Si}_{15}$.
 11. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,5}\text{Fe}_{3,5}\text{Mn}_2\text{B}_{10}\text{Si}_{15}$.
 12. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,0}\text{Fe}_{3,0}\text{Mn}_3\text{B}_{10}\text{Si}_{15}$.
 13. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,5}\text{Fe}_{2,5}\text{Mn}_4\text{B}_{10}\text{Si}_{15}$.
 14. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,6}\text{Fe}_{4,4}\text{V}_1\text{B}_{10}\text{Si}_{15}$.
 15. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,75}\text{Fe}_{4,25}\text{V}_2\text{B}_{10}\text{Si}_{15}$.
 16. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,6}\text{Fe}_{4,4}\text{Nb}_1\text{B}_{10}\text{Si}_{15}$.
 17. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,75}\text{Fe}_{4,25}\text{Nb}_2\text{B}_{10}\text{Si}_{15}$.
 18. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{69,6}\text{Fe}_{4,4}\text{W}_1\text{B}_{10}\text{Si}_{15}$.
 19. Magnetische Legierung nach Anspruch 1 der Formel $\text{Co}_{68,75}\text{Fe}_{4,25}\text{W}_2\text{B}_{10}\text{Si}_{15}$.

Revendications

1. Alliage magnétique qui est au moins vitreux à 70 %, répondant à la formule $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$ dans laquelle les indices sont des pourcentages atomiques et "a" est compris entre 65,5 et 70,5, "b" entre 3,8 et 4,5, "c" entre 0 et 3; "d" entre 1 et 2, "e" entre 10 et 12 et "f" entre 14 et 15 lorsque M est choisi dans le groupe constitué du vanadium, du chrome, du molybdène, du niobium et du tungstène; lorsque M est le manganèse, "a" est compris entre 68,0 et 70,0, "b" entre 2,5 et 4,0, "c" entre 0 et 3, "d" entre 1 et 4, "e" entre 10 et 12 et "f" entre 14 et 15, ledit alliage ayant une valeur de la magnétostriction de saturation comprise entre -1×10^{-6} et $+1 \times 10^{-6}$, une température de Curie comprise entre 245°C et 310°C, une première température de cristallisation comprise entre 530°C et 575°C et une induction de saturation d'au moins 0,65 Tesla.

2. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{65,7}\text{Fe}_{4,4}\text{Ni}_{2,9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$.

3. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{68,13}\text{Fe}_{4,0}\text{Ni}_{1,37}\text{Mo}_{1,5}\text{B}_{10}\text{Si}_{15}$.

4. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,6}\text{Fe}_{4,4}\text{Mo}_1\text{B}_{10}\text{Si}_{15}$.
5. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,75}\text{Fe}_{4,25}\text{Mo}_2\text{B}_{10}\text{Si}_{15}$.
6. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,6}\text{Fe}_{4,4}\text{Cr}_1\text{B}_{10}\text{Si}_{15}$.
7. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,75}\text{Fe}_{4,25}\text{Cr}_2\text{B}_{10}\text{Si}_{15}$.
- 5 8. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,2}\text{Fe}_{3,8}\text{Mn}_1\text{B}_{12}\text{Si}_{15}$.
9. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{87,7}\text{Fe}_{3,3}\text{Mn}_2\text{B}_{12}\text{Si}_{15}$.
10. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{70,0}\text{Fe}_{4,0}\text{Mn}_1\text{B}_{10}\text{Si}_{15}$.
11. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,5}\text{Fe}_{3,5}\text{Mn}_2\text{B}_{10}\text{Si}_{15}$.
12. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,0}\text{Fe}_{3,0}\text{Mn}_3\text{B}_{10}\text{Si}_{15}$.
- 10 13. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,5}\text{Fe}_{2,5}\text{Mn}_4\text{B}_{10}\text{Si}_{15}$.
14. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,6}\text{Fe}_{4,4}\text{V}_1\text{B}_{10}\text{Si}_{15}$.
15. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,75}\text{Fe}_{4,25}\text{V}_2\text{B}_{10}\text{Si}_{15}$.
16. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,6}\text{Fe}_{4,4}\text{Nb}_1\text{B}_{10}\text{Si}_{15}$.
17. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,75}\text{Fe}_{4,25}\text{Nb}_2\text{B}_{10}\text{Si}_{15}$.
- 15 18. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{89,6}\text{Fe}_{4,4}\text{W}_1\text{B}_{10}\text{Si}_{15}$.
19. Alliage magnétique selon la revendication 1, répondant à la formule $\text{Co}_{88,75}\text{Fe}_{4,25}\text{W}_2\text{B}_{10}\text{Si}_{15}$.

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