⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 084 138**
A2

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: 82111754.6

㉒ Date of filing: 17.12.82

(51) Int. Cl.^{3}: **H 01 F 1/14**

㉚ Priority: 18.01.82 US 340413

(43) Date of publication of application:
27.07.83 Bulletin 83/30

(84) Designated Contracting States:
DE FR GB IT

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(54) Near-zero magnetostrictive glassy metal alloys with high magnetic and thermal stability.

(57) A new series of glassy metal alloys with near zero magnetostriction is disclosed. The glassy alloys have the composition $Co_aFe_bNi_cMo_dB_eSi_f$, 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, Curie 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.

EP 0 084 138 A2

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DESCRIPTION

NEAR-ZERO MAGNETOSTRICTIVE GLASSY METAL ALLOYS WITH HIGH MAGNETIC AND THERMAL STABILITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to glassy metal alloys with near-zero magnetostriction, high magnetic and thermal stability and excellent soft magnetic properties.

2. Description of the Prior Art

Saturation magnetostriction λ_S is related to the fractional change in length $\Delta \ell / \ell$ 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 magnetocrystalline anisotropy is not too large and the resistivity not too small). Also because energy is not lost to mechanical vibrations when the saturation magametostriction 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 $Co_{90}Fe_{10}$ 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 $Co_{90}Fe_{10}$ 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 tayloring of the alloy composition to achieve near-zero maganetostriction.

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 $Fe_{40}Ni_{40}P_{14}B_6$ (the subscripts are in atom percent) has a saturation induction of about 0.8 Tesla, while the glassy alloy $Ni_{49}Fe_{29}P_{14}B_6Si_2$ has a saturation induction of about 0.46 Tesla and the glassy alloy $Ni_{80}P_{20}$ 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, $Co_{72}Fe_3P_{16}B_6Al_3$ (AIP Conference Proceedings, No. 24, pp. 745-746 (1975)) $Co_{70.5}Fe_{4.5}Si_{15}B_{10}$ (Vol. 14, Japanese Journal of Applied Physics, pp. 1077-1078 (1975)) $Co_{31.2}Fe_{7.8}Ni_{39.0}B_{14}Si_8$ [proceedings of 3rd International Conference on Rapidly Quenched Metals, p. 183, (1979)] and $Co_{74}Fe_6B_{20}$ [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}), as-cast 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_f (K)	T_{c1} (K)	H_c (A/m)	Annealed Values	
					H_c (A/m)	μ (at 1 kHz)
$Co_{72}Fe_3P_{16}B_6Al_3$	0.63	600	-	1.8	1.0*	-
$Co_{70.5}Fe_{4.5}B_{10}Si_{15}$	0.65	688	-	8.0	1.2**	50 000
$Co_{31.2}Fe_{7.8}Ni_{39}B_{14}Si_8$	0.61	503	690	-	0.16***	50 000
$Co_{74}Fe_6B_{20}$	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.

Clearly desirable are zero magnetostrictive glassy alloys with higher magnetic and thermal stability and a saturation induction as high as possible.

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. The glassy metal alloy has the composition $Co_aFe_bNi_cMo_dB_eSi_f$, 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 about 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 and 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 glassy alloy has a value of magnetostriction ranging from about -1×10^{-6} to $+1 \times 10^{-6}$ a saturation induction ranging from about 0.6 to 0.8 Tesla, a Curie temperature ranging from about 550 to 670K and a first crystallization temperature ranging from about 790 to 870 K.

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 core loss and low coercivity. The glassy metal alloy has the composition $Co_aFe_bNi_cMo_dB_eSi_f$, 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 and d ranges from about 1 to about 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 and 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 glassy alloy has a value of magnetostriction ranging from about -1×10^{-6} to $+1 \times 10^{-6}$ and a saturation induction ranging from about 0.6 to 0.8 Tesla, Curie Temperature, ranging from 550 to 670K and the first crystallization temperature ranging from about 790 to 870 K.

The purity of the above composition is that found in normal commercial practice. However, it will be appreciated that molybdenum in the alloys of the invention may be replaced by at least one other transition metal element, such as tungsten, niobium, tantalum, titanium, zirconium and hafnium, and up to about 2 atom percent of Si may be replaced by carbon, aluminum or germanium without significantly degrading the desirable magnetic properties of these glassy alloys.

Examples of essentially zero magnetostrictive glassy metal alloys of the invention include $Co_{67.4}Fe_{4.1}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$, $Co_{67.1}Fe_{4.4}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$, $Co_{64.0}Fe_{4.5}Ni_{6.0}Mo_{1.5}B_{12.5}Si_{11.5}$, $Co_{67.0}Fe_{4.5}Ni_{3.0}Mo_{1.5}B_{12}Si_{12}$, $Co_{67.0}Fe_{4.5}Ni_{3.0}Mo_{1.5}B_{13}Si_{11}$ and $Co_{67.5}Fe_{4.5}Ni_{3.0}Mo_{1.0}B_{12}Si_{12}$. These glassy alloys possess saturation induction between about 0.7 and 0.8 Tesla, Curie temperature between 600 and 670K, the first crystallization temperature of about 800K and excellent ductility. Some magnetic and thermal properties of these and some of other near-zero magnetostrictive glassy alloys of the present invention are listed in Table II. These may be compared with properties listed in Table I for previously-reported glassy metal alloys of zero magnetostriction.

The activation energy (E_a) for the reorientation of the magnetization is listed in Table III for some representative near-zero magnetostrictive glassy alloys. This table indicates that Si tends to increase E_a and also that E_a tends to be higher when Si/B ratio is close to 1. The higher values of E_a, indicating higher magnetic stability of the system, is desired. Combining these information based Table II and III, preferred Si content is between 9 and 14 atom percent when (Si + B) is between 23 and 26 atom percent.

The presence of Mo is to increase T_{c1} and hence the thermal stability of the alloy system. The content of Mo beyond 2 atom percent, however, reduces the Curie temperature to a level lower than 550 K, which is undesirable in convention magnetic devices.

Table II

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

Compositions									
Co	Fe	Ni	Mo	B	Si	B_s(Tesla)	θ_f(K)	$s(10^{-6})$	T_{c1}(K)
67.4	4.1	3.0	1.5	12.5	11.5	0.72	603	-0.0	798
67.1	4.4	3.0	1.5	12.5	11.5	0.75	626	+0.0	798
64.0	4.5	6.0	1.5	12.5	11.5	0.70	620	-0.0	796
65.5	4.5	4.5	1.5	12.5	11.5	0.74	620	+0.8	799
70.0	4.5	0	1.5	12.5	11.5	0.77	649	+0.8	800
68.5	4.5	1.5	1.5	12.5	11.5	0.78	639	-0.9	801
63.3	3.7	7.5	1.5	12.5	11.5	0.66	575	-0.7	798
67.0	4.5	3.0	1.5	11	13	0.72	582	+0.4	801
67.0	4.5	3.0	1.5	12	12	0.70	598	+0.0	803
67.0	4.5	3.0	1.5	13	11	0.74	654	+0.0	797
67.0	4.5	3.0	1.5	14	10	0.74	637	+0.4	800
67.8	3.7	3.0	1.5	11	13	0.70	558	-0.4	799
67.8	3.7	3.0	1.5	12	12	0.70	585	-0.2	804
67.8	3.7	3.0	1.5	13	11	0.70	600	-0.4	797
67.8	3.7	3.0	1.5	14	10	0.72	623	-0.6	798
67.8	3.7	3.0	1.5	15	9	0.72	640	-0.6	794
66.3	5.2	3.0	1.5	12	12	0.72	586	+0.6	800
68.5	3.0	3.0	1.5	12	12	0.70	609	-0.3	796
69.3	2.2	3.0	1.5	12	12	0.70	580	-1.1	794
67.5	4.5	3.0	1.0	12	12	0.75	672	+0.0	810
66.6	4.4	3.0	2.0	12	12	0.69	610	+0.6	802
68.0	3.0	3.0	2.0	12	12	0.68	567	+0.8	867
62.2	5.9	5.9	2.0	12	12	0.69	578	+1.1	806
63.6	5.9	4.4	2.0	12	12	0.65	563	+0.8	808
65.1	5.9	3.0	2.0	12	12	0.68	549	+0.8	810
66.6	5.9	1.5	2.0	12	12	0.71	581	+1.1	808
63.0	6.0	6.0	2.0	12	11	0.71	673	+0.2	795
67.1	5.4	0	2.0	12.5	13	0.72	643	+0.5	820
58.4	7.3	7.3	2.0	13	12	0.62	570	+0.7	824

TABLE III

Activation energy (E_a) for reorientation of the magnetic anisotropy of representative near-zero magnetostrive glassy alloys.

Alloy Compositions						E_a
Co	Fe	Ni	Mo	B	Si	(10^{-19}J)
64.0	8.0	8.0	2.0	18	0	1.1
64.0	8.0	8.0	2.0	16	2	1.2
64.0	8.0	8.0	2.0	10	8	2.6
60.0	7.5	7.5	2.0	17	6	0.82
60.0	7.5	7.5	2.0	11	12	2.1

For some applications, it may be desirable or acceptable to use a material with a small positive or a small negative magnetostriction. Such near-zero magnetostrictive glassy metal alloys are obtained for a, b and c in the ranges of about 58 to 70, 2 to 7.5 and 0 to 8 atom percent respectively, with the provision that the sum of a, b and c ranges between 72 and 76 atom percent. The absolute value of saturation magnetostriction $|\lambda_s|$ of these glassy metal alloys is less than about 1 x 10^{-6} (i.e., the saturation magnetostriction ranges from about -1 x 10^{-6} to +1 x 10^{-6}, or -1 to +1 microstrains). The saturation induction of these glassy alloys ranges between about 0.6 and 0.8 Tesla.

Values of λ_s even closer to zero may be obtained for values of a, b and c ranging respectively from about 63 to 69, 3 to 6 and 0 to 6, with the provision that the sum of a, b and c ranges between about 72 and 76 atom percent. For such preferred compositions, $|\lambda s|$ is less than 0.5 x 10^{-6}. Essentially zero values of magnetostriction are obtained for values of a, b and c ranging from about 64 to 68, 4 to 5 and 0 to 6 atom percent respectively with the provision that the sum of a, b and c ranges between about 72 and 76 atom percent and also when f is between 11 and 12 atom percent and (e + f) is close to 24 atom percent and, accordingly, such compositions are most preferred.

The glassy metal alloys of the invention are conveniently prepared by techniques readily available elsewhere; see, e.g., U.S. Patents 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 23 to 26 atom percent of the total alloy composition is sufficient for glass formation, with boron ranging from about 11 to 15 atom percent and silicon ranging from about 9 to about 14 atom percent. As noted hereinabove, a ratio Si/B close to 1 and a Si content ("f") between 11 and 12 atom percent are most favorable because they lead to higher stability and relative insensitiveness of the magnetostriction value (which is close to zero) to the metalloid composition. For example, the rate of change of magnetostriction value with respect to silicon content, $d\lambda_s/df$, is close to zero for "f" between 11 and 12 atom percent while $|d\lambda_s/df|$ is about 0.8×10^{-6}/at.%Si near f=10 or 13 atom percent when a=67.1, b=4.5, c=3.0 and d=1.5 atom percent. The quantity $|d\lambda_s/df|$ becomes zero near f=12 atom percent and about 0.1×10^{-6}/at.%Si near f=10 or 13 atom percent when a=67.8, b=3.7,c=3.0 and d=1.5 atom percent.

The small amount of Ni is relatively ineffective to alter the magnetostriction values in the present alloy system and Co:Fe ratios essentially determine the resultant maganetostriction values. Zero magnetostriction is realized for the Co:Fe ratio of about (14 ∿ 16.5) to 1 in the present alloy system. In the prior art glassy metal alloys such as $Co_{70.5}Fe_{4.5}B_{10}Si_{15}$ and $Co_{74}Fe_{6}B_{20}$, the ratios are narrowly set at about 14 and 12 respectively. The above range of the Co:Fe ratio between about 14:1 to 16.5:1 and the tolerance of about ±0.5 atom percent near f=11.5 atom percent to achieve $\lambda_s=0$ and $d\lambda_s/df=0$ are advantageous from materials synthesis standpoint.

Table IV gives ac core loss (L), exciting power (P_e) 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 temperatures (T_a).

Table IV

Examples of core loss (L), exciting power (P_e) and permeability of near-zero magnetostrictive glassy alloys annealed at different temperatures (T_a).

Composition									
Co	Fe	Ni	Mo	B	Si	L(W/kg)	Pe(Va/kg)	μ	T_a(°C)
67.4	4.1	3.0	1.5	12.5	11.5	5.0	7.8	21300	375
67.1	4.4	3.0	1.5	12.5	11.5	8.3	12	14400	400
68.5	4.5	1.5	1.5	12.5	11.5	5.2	7.4	21200	400
70.0	4.5	0	1.5	12.5	11.5	7.9	12	13000	400
65.5	4.5	4.5	1.5	12.5	11.5	5.1	7.5	20900	400
64.0	4.5	6.0	1.5	12.5	11.5	6.8	9.3	16900	400
63.3	3.7	7.5	1.5	12.5	11.5	6.8	12	13500	400
67.1	5.4	0	2.0	12.5	13	7.0	12	11000	300 *
58.4	7.3	7.3	2.0	13	12	10	11	8200	350**

* Holding time = 5 min.;
Cooling rate = -0.5°C/min.; H_{11} = 20 Oe and Hl = 350

**Holding time = 2 hours;
Cooling rate = -0.5°C/min.; H_{11} = 20 Oe and Hl = 35 Oe

Table V shows the effects of the annealing temperature (T_a) and annealing field (H_{11}) applied along the circumferential cirection of the toroidal samples on the dc coercivity (H_c) and remanence (B_r), ac coercivity (H_c') and squareness ratio (B_r/B_1), where B_1 is the induction at an applied field of 1 Oe at 50 kHz and μ at 50 kHz and 0.1 T induction for one of the zero magnetostrictive alloys of the present invention. Low coercivity and high squareness ratio close to 1 at high frequencies (e.g. 50 kHz) are desirable in some magnetic device applications such as switch-mode power supplies.

Table V

Effects of annealing temperature (T_a) and circumferential field (H_{11}) on the dc coercivity (H_c) and remanence (B_r), ac (50 kHz) coercivity (H_c') and BH loop squareness ratio (B_r/B_1), and permeability at 50 kHz and B_m=0.1 T for $Co_{67.4}Fe_{4.1}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$.

Annealing Conditions		dc		50 kHz		
T_a (°C)	H_{11}(A/m)	H_c(A/m)	B_r(T)	H_c'(A/m)	B_r/B_1	μ
350	0	0.56	0.54	24	1	15600
350	1600	0.49	0.63	21	1	10000
375	0	0.49	0.38	18	1	21300
375	1600	0.42	0.59	22	1	10900
400	0	0.42	0.38	17	1	20000
400	1600	0.28	0.50	26	0.95	11300
425	0	0.56	0.40	21	0.89	14000
425	1600	0.49	0.45	24	1	13300
440	0	0.56	0.39	21	0.92	14400
440	1600	0.56	0.59	24	1	10600

Table VI shows the effects of the annealing time (t_a) on L, Pe and μ for one of the zero magnetostrictive alloys of the present invention.

Table VI

Effects on annealing time (t_a) on core less (L), exciting power (P_e) and permeability (μ) at induction of 0.1 Tesla and frequency of 1 kHz and 50 kHz for $Co_{67.4}Fe_{4.1}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$ annealed at T_a=380°C.

Annealing time	1 kHz			50 kHz		
t_a (min.)	L(W/kg)	Pe(VA/kg)		L(W/kg)	Pe(VA/kg)	μ
10	0.024	0.056	56 500	4.2	7.1	22 100
20	0.027	0.056	56 300	3.6	6.8	23 200
30	0.027	0.055	56 800	3.7	6.7	23 600
60	0.031	0.053	59 000	4.9	7.2	21 700

The results set forth in Tables IV-VI above indicate that L=4 W/kg, P_e=7 Va/kg and μ=23 000 at 0.1 T and 50 kHz can be achieved for 25-30 μm thick zero magnetostrictive glassy alloys of the present invention. Compared with these values, a prior art crystalline nonmagnetostrictive supermalloy of the similar thickness (25 μm) gives L= 8 W/kg, P_e= 10 VA/kg and μ =19 000 at 0.1 T and 50 kHz. It is clear that the properties of the nonmagnetostrictive glassy alloys of the present invention are superior to those of the crystalline supermalloys. Examples of amorphous alloys outside the scope of the invention are set forth in Table VII. The advantageous combination of properties provided by the alloys of the present invention cannot be achieved in the prior art nonmagnetostrictive glassy alloys with high saturation induction such as $Co_{74}Fe_6B_{20}$ 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 $Co_{31.2}Fe_{7.8}Ni_{39.0}B_{14}Si_8$ tend to be magnetically unstable at relatively low temperature of about 150°C as pointed earlier.

Table VII shows the magnetic properties of some of the representative glassy alloys of the composition $Co_aFe_bNi_cMo_dB_eSi_f$ 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 at least one of the following undesirable properties: (i) The value of $|\lambda_s|$ is larger than 1x10-6, (ii) The Curie temperature (θ_f) is higher than the crystallization temperature (T_{c1}), which makes the post-fabrication field annealing less effective and (iii) The Curie temperature and saturation induction (B_s) become too low to be practical.

Table VII

Magnetic properties of some representative $Co_aFe_bNi_cMo_dB_eSi_f$ glassy alloys in which at least one of a, b, c, d, e and f is outside the range defined in the present invention.

Composition									
Co	Fe	Ni	Mo	B	Si	B_s(Tesla)	θ_f(K)	s(10^{-6})	T_{c1}(K)
69.4	5.6	0	0	25	0	1.0	760	+0.0	715
64.0	8.0	8.0	2	10	8	0.97	725	+2.5	700
64.0	8.0	8.0	2	12	6	0.95	735	+1.7	713
60.0	7.5	7.5	2	19	4	0.83	715	+1.6	760
43.8	7.3	14.6	2	13	12	0.52	507	+2.7	817

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-magnetic-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 B_s ($=4\pi M_s D$) 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_{c1}) 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 $(\Delta\ell/\ell)_{\parallel}$ and perpendicular $(\Delta\ell/\ell)_{\perp}$ in-plain fields, according to the formula $\lambda = 2/3[(\Delta\ell/\ell)_{\parallel} - (\Delta\ell/\ell)_{\perp}]$.

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

What is claimed is:

1. A magnetic alloy that is at least 70% glassy, having the formula $Co_aFe_bNi_cMo_dB_eSi_f$ where a ranges from about 58 to 70 atom percent, b ranges from about 2 to 7.5 atom percent, c rangaes from 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 and c ranges from about 72 to 76 atom percent and the sum of e and f ranges from about 23 to 26 atom percent, said alloy having a value of magnetostriction between $-1x10^{-6}$ and $+1x10^{-6}$.

2. The magnetic alloy of claim 1 in which a ranges from about 63 to 69 atom percent, b ranges from about 3 to 6 atom percent and c ranges from about 0 to 6 atom percent.

3. The magnetic alloy of claim 1 in which a ranges from about 64 to 68 atom percent, b ranges from 4 to 5 atom percent and c ranges from 0 to 6 atom percent when f is between 11 and 12 atom percent and the sum of e and f is near 24 atom percent.

4. The magnetic alloy of claim 3 having the formula $Co_{67.4}Fe_{4.1}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$.

5. The magnetic alloy of claim 3 having the formula $Co_{67.1}Fe_{4.4}Ni_{3.0}Mo_{1.5}B_{12.5}Si_{11.5}$.

6. The magnetic alloy of claim 3 having the formula $Co_{64.0}Fe_{4.5}Ni_{6.0}Mo_{1.5}B_{12.5}Si_{11.5}$.

7. The magnetic alloy of claim 3 having the formula $Co_{67.0}Fe_{4.5}Ni_{3.0}Mo_{1.5}B_{12}Si_{12}$.

8. The magnetic alloy of claim 3 having the formula $Co_{67.0}Fe_{4.5}Ni_{3.0}Mo_{1.5}B_{13}Si_{11}$.

9. The magnetic alloy of claim 3 having the formula $Co_{67.5}Fe_{4.5}Ni_{3.0}Mo_{1.0}B_{12}Si_{12}$.