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<p>(54) Title: NEAR-ZERO MAGNETOSTRICTIVE GLASSY METAL ALLOYS FOR HIGH FREQUENCY APPLICATIONS</p>		
<p>(57) Abstract</p> <p>A glassy metal alloy has a value of magnetostriction near-zero and the composition <math>Co_aFe_bNi_cM_dB_eSi_f</math>, where "a" ranges from about 65.5 to 70.5 atom percent, "b" ranges from about 3.8 to 4.5 atom percent, "c" ranges from about 0 to 3 atom percent, "d" ranges from about 1 to about 2 atom percent, "e" ranges from about 10 to about 12 atom percent and "f" ranges from about 14 to 15 atom percent when M is selected from vanadium, chromium, molybdenum, niobium and tungsten, when M is manganese, "a" ranges from about 68.0 to 70.0 atom percent, "b" ranges from about 2.5 to 4.0 atom percent, "c" ranges from 0 to 3 atom percent, "d" ranges from 1 to about 4 atom percent, "e" ranges from about 10 to 12 atom percent and "f" ranges from about 14 to about 15 atom percent. The alloy has a saturation magnetostriction value ranging from about <math>-1 \times 10^{-6}</math> to <math>+1 \times 10^{-6}</math>, a saturation induction ranging from about 0.65 to about 0.80 Tesla and a Curie temperature ranging from about 245 to 310°C.</p>		

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NEAR-ZERO MAGNETOSTRICTIVE GLASSY METAL ALLOYS  
FOR HIGH FREQUENCY APPLICATIONS

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  $\lambda_s$  is related to the fractional change in length of  $\Delta l/l$  that occurs in a magnetic material on going from the demagnetized to the saturated, ferromagnetic state. The value of magneto-  
15 striction, 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:

20 1. Soft magnetic properties (low coercivity, high permeability) are generally obtained when both the saturation magnetostriction  $\lambda_s$  and the magnetocrystalline anisotropy  $K$  approach zero.

Therefore, given the same anisotropy, alloys of lower  
25 magnetostriction will show lower dc coercivities and higher permeabilities. Such alloys are suitable for various soft magnetic applications.

30 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  
35 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  
5 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  
10 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  
15 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))  
20  $Co_{31.2}Fe_{7.8}Ni_{39.0}B_{14}Si_8$  [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  
25 of these materials.

Table I

Saturation induction ( $B_s$ ), Curie temperature ( $\theta_f$ ), the first crystallization temperature ( $T_{C1}$ ), as-cast dc coercivity ( $H_C$ ), and dc coercivity and  
30 permeability ( $\mu$ ) in the annealed states of some of the prior art zero magnetostrictive glassy alloys.

Alloy	$B_s$ (Tesla)	$\theta$ (K)	$T_{C1}$ (K)	$H_C$ (A/m)	Annealed Values	
					$H_C$ (A/m)	$\mu$ (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
5 $Co_{31.2}Fe_{7.8}Ni_{39}$ $B_{14}Si_8$	0.61	503	690	-	0.16***	50 000
$Co_{74}Fe_6P_{20}$	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.

10 \*\*\* 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.

15 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 ( $\theta_f$ ) near or above their first crystallization temperatures ( $T_{C1}$ ).

20 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  $\theta_f$ .

A recent prior art [Journal of Applied Physics 53,  
25 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  
30 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.

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#### 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  $Co_aFe_bNi_cM_dBeSi_f$ , where subscripts are in atom percents and "a" ranges from about 65.5 to about 70.5, "b" ranges from about 3.8 to about 4.5, "c" ranges from about 0 to about 3, "d" ranges from about 1 to about 2, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15 when M is selected from a group consisting of vanadium, chromium, molybdenum, niobium and tungsten; when M is manganese, "a" ranges from about 68.0 to about 70.0, "b" ranges from about 2.5 to about 4.0, "c" ranges from about 0 to about 3, "d" ranges from about 1 to about 4, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15. The glassy alloy has a value of saturation magnetostriction ranging from about  $-1 \times 10^{-6}$  to  $+1 \times 10^{-6}$ , a saturation induction ranging from about 0.65 to about 0.80 Tesla, a Curie temperature ranging from about 245 to about 310°C and the first crystallization temperature ranging from about 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 glassy metal alloy has the composition  $Co_aFe_bNi_cM_dBeSi_f$ , where the subscripts are in atom percent and "a" ranges from about 65.5 to about 70.5, "b" ranges from about 3.8 to about 4.5, "c" ranges from about 0 to about 3, "d" ranges from about 1 and to about 2, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15 when M is selected from the group consisting of vanadium, chromium, molybdenum, niobium and tungsten; and when M is manganese, "a" ranges from about 68.0 to



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about 70.0, "b" ranges from about 2.5 to about 4.0, "c" ranges from about 0 to about 3, "d" ranges from about 1 to 4, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15. The glassy alloy has a value of saturation magnetostriction ranging from about  $-1 \times 10^{-6}$  to about  $+1 \times 10^{-6}$ , a saturation induction ranging from about 0.65 to 0.80 Tesla, a Curie temperature ranging from about 245 to about 310°C and the first crystallization temperature ranging from about 530 to 575°C.

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

Saturation induction ( $B_S$ ), Curie temperature ( $\theta_f$ ), saturation magnetostriction ( $\lambda_s$ ) and the first crystallization temperature ( $T_{C1}$ ) of near-zero magnetostrictive glassy alloys.

	compositions						$B_S$ (Tesla)	$\theta_f$ (°C)	$\lambda_s$ (10 <sup>-6</sup> )	$T_{C1}$ (°C)
	Co	Fe	Ni	M	B	Si				
5	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
10	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
	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
15	70.0	4.0	0	Mn=1	10	15	0.80	326	0.4	532
	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
	69.6	4.4	0	V=1	10	15	0.72	309		535
20	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
	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

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The presence of the metal element M is to increase  $T_{C1}$  and hence the thermal stability of the alloy system. The content of M beyond 2 atom percent, however, reduces the Curie temperature to a level lower than 245°C, which is undesirable in conventional

30

magnetic devices.

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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  $-1 \times 10^{-6}$  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.

5 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  
10 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.

15 Tables III and IV give ac core loss (L), exciting power ( $P_g$ ) and permeability ( $\mu$ ) at 0.1 Tesla induction and at 50 kHz of the near-zero magnetostrictive glassy alloys of the present invention annealed at different temperature ( $T_0$ ). Summarizing, by water quenching subsequent to the heat-treatments given in Table III, the  
20 glassy alloys of the present invention exhibit, on the average,  $L=4$ W/kg,  $P_g=6$ 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  $L=3.0$ W/kg,  $P_g=4.2$ 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  
25 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  
30 gives  $L=2.7$ W/kg,  $P_g=4.6$ 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  $-4^\circ\text{C}/\text{min}$ . Compared with these values, a prior art crystalline non-magnetostrictive supermalloy of the similar thickness (25  $\mu\text{m}$ ) gives  $L=10$ W/kg,  $P_g=10$ VA/kg and  $\mu=$   
35 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  
5 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  $150^\circ\text{C}$   
10 as pointed out earlier. The best combined properties of another glassy alloy of a prior art were  $L=4\text{W/kg}$ ,  $P_g=7\text{ VA/kg}$  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  $380^\circ\text{C}$  for 15 min. and cooled rapidly. It is again clear that the glassy alloys of the present invention are generally superior to  
15 this class of glassy alloys.

TABLE III

Examples of core loss (L), exciting power ( $P_g$ ) and permeability ( $\mu$ ) 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.

	<u>compositions</u>						<u><math>T_g</math>(°C)</u>	<u>L(W/kg)</u>	<u><math>P_g</math>(VA/kg)</u>	<u><math>\mu</math></u>
	<u>Co</u>	<u>Fe</u>	<u>Ni</u>	<u>M</u>	<u>B</u>	<u>Si</u>				
10	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
15	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
20	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
25	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

TABLE IV

Core loss (L), exciting power ( $P_e$ ) and permeability ( $\mu$ ) 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  $-4$  °C/min. to room temperature. No field was applied during the anneal except for the cases indicated by asterisks.

		compositions						L(W/kg)	$P_e$ (VA/kg)	$\mu$	
		Co	Fe	Ni	M	B	Si				$T_a$ (°C)
10		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
15		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

20

\* 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

25

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

		compositions						$B_a$ (T)	$\theta_f$ (°C)
		Co	Fe	Ni	M	B	Si		
30		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
35		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  $Co_aFe_bNi_cM_dRe_eSi_f$  (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  $\mu$ m 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  
5 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  $B_s$  ( $=4 \pi 4M_s D$ ) was then calculated by using the measured  
10 mass density  $D$ .

The ferromagnetic Curie temperature ( $\theta_f$ ) was measured by inductance method and also monitored by differential scanning calorimetry, which was used primarily to determine the crystallization tempera-  
15 tures. 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  
20 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  
25 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  
30 parallel ( $\Delta l/l$ ) and perpendicular ( $\Delta l/l$ ) in-plane fields, according to the formula  $\lambda = 2/3[(\Delta l/l) - \Delta l/l]$ .

Having thus described the invention in rather full  
35 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  $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{M}_d\text{B}_e\text{Si}_f$  where the subscripts are in atom percent and "a" ranges from about 65.5 to  
5 70.5, "b" ranges from 3.8 to about 4.5, "c" ranges from about 0 to about 3, "d" ranges from about 1 to about 2, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15 when M is selected from the group consisting of vanadium, chromium, molybdenum, niobium  
10 and tungsten; when M is manganese, "a" ranges from about 68.0 to about 70.0, "b" ranges from about 2.5 to about 4.0, "c" ranges from about 0 to about 3, "d" ranges from about 1 to about 4, "e" ranges from about 10 to about 12 and "f" ranges from about 14 to about 15, said alloy  
15 having a value of the saturation magnetostriction between  $-1 \times 10^{-6}$  to  $+1 \times 10^{-6}$ .

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  
20 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  $\text{Co}_{68.75}\text{Fe}_{4.25}\text{Mo}_2\text{B}_{10}\text{Si}_{15}$ .

25 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  
30 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  $\text{Co}_{70.0}\text{Fe}_{4.0}\text{Mn}_1\text{B}_{10}\text{Si}_{15}$ .

35 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  $\text{Co}_{69.6}\text{Fe}_{4.4}\text{V}_1\text{B}_{10}\text{Si}_{15}$ .

5 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  $\text{Co}_{69.6}\text{Fe}_{4.4}\text{Nb}_1\text{B}_{10}\text{Si}_{15}$ .

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

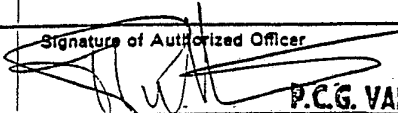
18. The magnetic alloy of claim 1 having the formula  $\text{Co}_{69.6}\text{Fe}_{4.4}\text{W}_1\text{B}_{10}\text{Si}_{15}$ .

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

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 87/02802

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : H 01 F 1/16; C 22 C 1/00; C 22 C 19/07		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	H 01 F; C 22 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP, A, 0084138 (ALLIED CORP.) 27 July 1983 see claims 1,2	1
A	--	2-5
X	US, A, 4411716 (K. SHIKI et al.) 25 October 1983 see claim 1	1
A	--	6,7
X	DE, A, 3021536 (MATSUSHITA) 18 December 1980 see claims 1,3	1
A	--	8-13
X	Patent Abstracts of Japan, volume 8, no. 243 (E-277)(1680), 8 November 1984, & JP, A, 59121805 (TOSHIBA K.K.) 14 July 1984	1
A	--	16,17
A	Patent Abstracts of Japan, volume 8, no. 193 (C-241)(1630), 5 September 1984, & JP, A, 5985835 (TOSHIBA K.K.) 17 May 1984	1-29
	./.	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
4th February 1988	14 MAR 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 <b>P.C.G. VAN DER PUTTEN</b>	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A, 0160166 (ALLIED CORP.) 6 November 1985	
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A	Patent Abstracts of Japan, volume 9, no. 193 (E-334)(1916), 9 August 1985, & JP, A, 6059708 (HITACHI KINZOKU K.K.) 6 April 1984	
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A	Patent Abstracts of Japan, volume 10, no. 1 (E-371)(2058), 7 January 1986 & JP, A, 60165705 (HITACHI) 28 August 1985	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8702802

SA 19608

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/02/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0084138	27-07-83	JP-A- 58123851	23-07-83
US-A- 4411716	25-10-83	JP-A- 57019361	01-02-82
DE-A- 3021536	18-12-80	JP-A- 55164051	20-12-80
		JP-A- 56081651	03-07-81
		JP-A- 56102541	17-08-81
EP-A- 0160166	06-11-85	None	