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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 c/o Allied Cor-**  
**poration**  
**P.O. Box 2245R**  
**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

This invention relates to glassy metal alloys with Perminvar characteristics that is constant permeabilities at low magnetic field excitations and constricted hysteresis loops. More particularly, this invention provides glassy metal alloys with highly non-linear magnetic properties at low magnetic excitation levels.

The magnetic response, namely magnetic induction caused by magnetic excitation, of a typical ferromagnet, is non-linear characterized by a hysteresis loop. This loop usually does not allow a relatively constant permeability near the zero-excitation point. To realize such a feature, so-called Perminvar alloys were developed [see, for example, R. M. Bozorth, *Ferromagnetism* (Van Nostrand, Co., Inc., New York, 1951) p. 166-180]. These alloys are usually based on crystalline iron-cobalt-nickel system. Typical compositions (weight percent) include 20%Fe-60%Co-20%Ni (20-60 Perminvar) and 30%Fe-25%Co-45%Ni (45-45 Perminvar). Improvements of the crystalline Perminvar alloys have been made. Of significance is the addition of molybdenum, as exemplified by the synthesis of 7.5-45-25 Mo-Perminvar (7.5%Mo-45%Ni-25%Co-22.5%Fe). This material, when furnace cooled from 1110 °C, exhibited a dc coercivity ( $H_c$ ) of 40 A/m (= 0.5 Oe), initial permeability ( $\mu_0$ ) of 100 and the remanence ( $B_r$ ) of 0.75 T.

In the advent of modern electronics technology, it becomes necessary to further improve the Perminvar-like properties. For example, further reduction  $H_c$  and increase of  $\mu_0$  would be desirable when an efficient transformer requiring low field modulations is needed. Furthermore, the usual non-linear characteristic of the conventional Perminvar alloys cannot be utilized without a large level of excitation of well above 80 A/m (= 1 Oe). Also desirable in many applications are low ac magnetic losses. One approach to attain these excellent soft magnetic properties is to reduce the materials' magnetostriction values as low as possible.

Saturation magnetostriction  $\lambda_s$  is related to the fractional change in length  $\Delta l/l$  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  $\lambda_s$  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 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, making 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 reduce the magnetization by dilution and electronic hybridization, 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  $\text{Fe}_{4.0}\text{Ni}_{4.0}\text{P}_{1.4}\text{B}_6$  (the subscripts are in atom percent) has a saturation induction of about 0.8 Tesla, while the glassy alloy  $\text{Ni}_{4.9}\text{Fe}_{2.9}\text{P}_{1.4}\text{B}_6\text{Si}_2$  has a saturation induction of about 0.46 Tesla and the glassy alloy  $\text{Ni}_{8.0}\text{P}_{2.0}$  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,  $\text{Co}_{7.2}\text{Fe}_3\text{P}_{1.6}\text{B}_6\text{Al}_3$  (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  $\text{Co}_{7.4}\text{Fe}_6\text{B}_{2.0}$  [IEEE Trans. MAG-12, 942 (1976)]. However, none of the above-mentioned near-zero magnetostrictive materials show Perminvar-like characteristics. By polishing the surface of a low magnetostrictive glassy ribbon, a surface uniaxial anisotropy was introduced along the polishing direction which resulted in observation of Perminvar-like Kerr hysteresis loops (Applied Physics Letters, vol. 36, pp. 339-341 (1980)). This is only a surface effect and is not of a bulk property of the material, limiting the use of such effect in some selected devices.

Furthermore, to realize the Perminvar properties, the crystalline materials mentioned-above have to be baked for a long time at a given temperature. Typically the heat-treatment is performed at 425 °C for 24 hours. Obviously it is desirable to heat-treat the materials at a temperature as low as possible and for a duration as short as possible.

EP-A-84138 discloses glassy metal alloys of near zero magnetostriction having the formula  $\text{Co}_a\text{Fe}_b\text{Ni}_c\text{Mo}_d\text{B}_e\text{Si}_f$ , where "a" to "f" are in atom percent, a is from 58 to 70, b is from 2 to 75, c is from 0 to 8, d is from 1 to 2, e is from 11 to 15 and f is from 9 to 14, the sum of a, b and c being from 72 to 76 and the sum of e and f being from 23 to 26. There is no description of how to obtain therefrom any alloy having Perminvar characteristics.

Clearly desirable are new magnetic materials with various Perminvar characteristics which are suited for modern electronics technology.

According to the invention there is provided 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 M is at least one of Cr, Mo, Mn and Nb, "a" - "f" are in atom percent and the sums of "a" - "f" equals 100, "a" is from 66 to 71, "b" is from 2.5 to 4.5, "c" is from 0 to 3, "d" is from 0 to 4, "e" is from 6 to 24 and "f" is from 0 to 19, with the provisos that the sum of "a", "b" and "c" is from 71 to 76 and the sum of "e" and "f" is from 25 to 27 and up to 4 atom percent of Si may be replaced by C, Al and Ge, said alloy having a value of magnetostriction between  $-1 \times 10^{-6}$  and  $+1 \times 10^{-6}$ , said alloy having Perminvar characteristics of a relatively constant permeability at low magnetic excitation and a

constricted hysteresis loop as a result of having been heat-treated by heating to a temperature between 50 and 110 °C below the first crystallization temperature thereof for from 15 to 180 minutes and then cooling at a rate slower than about - 60 °C/min.

5 The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and the accompanying drawing, which is a graph depicting the B-H characteristics of an alloy which has been annealed for fifteen minutes at the temperatures (A) 460 °C, (B) 480 °C and (C) 500 °C.

10 The glassy alloy is heat-treated at a temperature  $T_a$  for a duration of time  $t_a$ , where  $\Delta T_{c-a} = (T_{cl} - T_a)$  is between 50 and 110 °C; and  $t_a$  is between 15 and 120 minutes, followed by cooling of the material at a rate slower than about -60 °C/min. The choice of  $T_a$  and  $t_a$  should exclude the case that  $\Delta T_{c-a} \sim 50$  °C and  $t_a \geq 15$  minutes because such combination sometimes results in crystallization of the glassy alloy.

15 The purity of the above composition is that found in normal commercial practice. However, it would be appreciated that the metal M in the alloys may be replaced by at least one other element such as vanadium, tungsten, tantalum, titanium, zirconium and hafnium, and up to 4 atom percent of Si may be replaced by carbon, aluminum or germanium without significantly degrading the desirable magnetic properties of these alloys.

Examples of near-zero magnetostrictive glassy metal alloys for heat treatment in accordance with the invention include  $Co_{70.5}Fe_{4.5}B_{15}Si_{10}$ ,  $Co_{69.0}Fe_{4.1}Ni_{1.4}Mo_{1.5}B_{12}Si_{12}$ ,  $Co_{65.7}Fe_{4.4}Ni_{2.9}Mo_2B_{11}Si_{14}$ ,  $Co_{69.2}Fe_{3.8}Mo_2B_8Si_{17}$ ,  $Co_{67.5}Fe_{4.5}Ni_{3.0}B_8Si_{17}$ ,  $Co_{70.9}Fe_{4.1}B_8Si_{17}$ ,  $Co_{69.9}Fe_{4.1}Mn_{1.0}B_8Si_{17}$ ,  $Co_{69.0}Fe_{4.0}Mn_2B_8Si_{17}$ ,  $Co_{68.0}Fe_{4.0}Mn_3B_8Si_{17}$ ,  $Co_{67.1}Fe_{3.9}Mn_4B_8Si_{17}$ ,  $Co_{68.0}Fe_{4.0}Mn_2Cr_1B_8Si_{17}$ ,  $Co_{69.0}Fe_{4.0}Cr_2B_8Si_{17}$ ,  $Co_{69.0}Fe_{4.0}Nb_2B_8Si_{17}$ ,  $Co_{68.2}Fe_{3.8}Mn_1B_{12}Si_{15}$ ,  $Co_{67.7}Fe_{3.3}Mn_2B_{12}Si_{15}$ ,  $Co_{67.8}Fe_{4.2}Mo_1B_{12}Si_{15}$ ,  $Co_{67.8}Fe_{4.2}Cr_1B_{12}Si_{15}$ ,  $Co_{67.0}Fe_{4.0}Cr_2B_{12}Si_{15}$ ,  $Co_{66.1}Fe_{3.9}Cr_3B_{12}Si_{15}$ ,  $Co_{68.5}Fe_{2.5}Mn_4B_{10}Si_{15}$ ,  $Co_{65.7}Fe_{4.4}Ni_{2.9}Mo_2B_{23}C_2$  and  $Co_{68.6}Fe_{4.4}Mo_2Ge_4B_{21}$ .

25 These alloys possess saturation induction ( $B_s$ ) between 0.5 and 1 Tesla, Curie temperature between 200 and 450 °C and excellent ductility. Some magnetic and thermal properties of these and some of other near-zero magnetostrictive alloys are listed in Table I.

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TABLE I

Saturation induction ( $B_s$ ), Curie temperature ( $\theta_f$ ), saturation magnetostriction ( $\lambda_s$ ) and the first crystallization temperature ( $T_c$ ) of near-zero magnetostrictive alloys for heat treatment in accordance with the present invention.						
Compositions						
Co	Fe	Ni	M	B	Si	
70.5	4.5	-	-	15	10	
69.0	4.1	1.4	Mo = 1.5	12	12	
65.7	4.4	2.9	Mo = 2	11	14	
68.2	3.8	-	Mn = 1	12	15	
67.7	3.3	-	Mn = 2	12	15	
67.8	4.2	-	Mo = 1	12	15	
67.8	4.2	-	Cr = 1	12	15	
69.2	3.8	-	Mo = 2	8	17	
67.5	4.5	3.0	-	8	17	
70.9	4.1	-	-	8	17	
69.9	4.1	-	Mn = 1	8	17	
69.0	4.0	-	Mn = 2	8	17	
68.0	4.0	-	Mn = 3	8	17	
67.1	3.9	-	Mn = 4	8	17	
69.0	4.0	-	Cr = 2	8	17	
68.0	4.0	-	Mn = 2, Cr-1	8	17	
69.0	4.0	-	Nb = 2	8	17	
65.7	4.4	2.9	Mo = 2	23	C = 3*	
65.7	4.4	2.9	Mo = 2	23	2	
69.5	4.1	1.4	-	6	19	
68.6	4.4	-	Mo = 2	21	Ge = 4*	
70.5	4.5	-	-	24	Ge = 1*	
67.0	4.0	-	Cr = 2	12	15	
69.2	3.8	-	Mo = 2	10	15	
68.1	4.0	1.4	Mo = 1.5	8	17	
69.0	3.0	-	Mn = 3	10	15	
68.5	2.5	-	Mn = 4	10	15	
68.8	4.2	-	Cr = 2	10	15	

\* All Si content is replaced by the indicated element and amount.

	B <sub>s</sub> (Tesla)	θ f(° C)	λ s(10 <sup>-6</sup> )	T <sub>cl</sub> (° C)
5	0.82	422	-0.3	517
	0.73	324	0	520
	0.77	246	0	530
	0.70	266	+0.4	558
	0.71	246	+0.4	560
10	0.62	227	+0.4	556
	0.64	234	+0.6	561
	0.67	295	+0.5	515
	0.73	329	+0.5	491
	0.77	343	-0.4	490
15	0.77	331	-0.5	493
	0.75	312	+0.8	502
	0.74	271	+0.9	507
	0.74	269	-0.8	512
	0.63	261	+0.2	503
20	0.69	231	+0.7	511
	0.62	256	+0.4	541
	0.76	393	0	500
	0.79	402	0	512
	0.73	316	-0.1	443
25	0.77	365	0	570
	0.99	451	-0.4	494
	0.57	197	+0.4	480
	0.72	245	+0.4	541
	0.67	276	+0.4	512
30	0.79	305	+1.1	544
	0.78	273	+0.4	548
	0.69	261	+0.4	540

Figure 1 illustrates the B(induction)-H(applied field) hysteresis loops for a near-zero magnetostrictive Co<sub>67.8</sub>Fe<sub>4.2</sub>Cr<sub>1</sub>B<sub>12</sub>Si<sub>15</sub> glassy alloy heat-treated at T<sub>a</sub> = 460 °C (A), T<sub>a</sub> = 480 °C (B) and T<sub>a</sub> = 500 °C (C) for 15 minutes, followed by cooling at a rate of about -5 °C/min. The constricted B-H loops of Figs 1B and 1C are characteristic of the materials with Perminvar-like properties, whereas the B-H loop of Fig. 1A corresponds to that of a typical soft ferromagnet. As evidenced in Figure 1, the choice of the heat-treatment temperature T<sub>a</sub> is very important in obtaining the Perminvar characteristics in the glassy alloys. Table II summarizes the heat-treatment conditions for some of these alloys and some of the resultant magnetic properties.

Table II

Heat-treatment temperature ( $T_a$ ) and duration ( $t_a$ )  
 to obtain Perminvar characteristics in the glassy  
 alloys.  $\Delta T_{C-a}$  is equal to ( $T_{C1}$   
 $-T_a$ ). Cooling rate is about  $-5^\circ\text{C}/\text{min}$ . unless stated  
 otherwise. The quantity  $\mu_0$  is the initial dc  
 permeability and  $H_C$  is the coercivity obtained after the  
 heat-treatment.

Compositions

	Co	Fe	Ni	M	B	Si
15	70.5	4.5	-	-	15	10
	70.5	4.5	-	-	15	10
20	70.5	4.5	-	-	15	10
	69.0	4.1	1.4	Mo=1.5	12	12
	69.0	4.1	1.4	Mo=1.5	12	12
	69.0	4.1	1.4	Mo=1.5	12	12
25	65.7	4.4	2.9	Mo=2	11	14
	68.2	3.8	-	Mn=1	12	15
	68.2	3.8	-	Mn=1	12	15
30	67.7	3.3	-	Mn=2	12	15
	67.7	3.3	-	Mn=2	12	15
	67.8	4.2	-	Mo=1	12	15
35	67.8	4.2	-	Cr=1	12	15
	67.8	4.2	-	Cr=1	12	15
	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
40	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
45	69.2	3.8	-	Mo=2	8	17
	67.5	4.5	3.0	-	8	17
	67.5	4.5	3.0	-	8	17

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Compositions

	Co	Fe	Ni	M	B	Si
	67.5	4.5	3.0	-	8	17
5	67.5	4.5	3.0	-	8	17
	70.9	4.1	-	-	8	17
	70.9	4.1	-	-	8	17
10	69.9	4.1	-	Mn=1	8	17
	69.9	4.1	-	Mn=1	8	17
	69.0	4.0	-	Mn=2	8	17
	69.0	4.0	-	Mn=2	8	17
15	68.0	4.0	-	Mn=3	8	17
	68.0	4.0	-	Mn=3	8	17
	67.1	3.9	-	Mn=4	8	17
	69.0	4.0	-	Cr=2	8	17
20	69.0	4.0	-	Cr=2	8	17
	68.0	4.0	-	Mn=2, Cr=1	8	17
	68.0	4.0	-	Mn=2, Cr=1	8	17
25	69.0	4.0	-	Nb=2	8	17
	68.1	4.0	1.4	Mo=1.5	8	17
	68.1	4.0	1.4	Mo=1.5	8	17
	65.7	4.4	2.9	Mo=2	23	C=3*
30	65.7	4.4	2.9	Mo=2	23	2
	69.5	4.1	1.4	-	6	19
	68.5	4.4	-	Mo=2	21	Ge=4*
35	70.5	4.5	-	-	24	Ge=1*
	69.2	3.8	-	Mo=2	10	15
	69.2	3.8	-	Mo=2	10	15
	69.0	3.0	-	Mo=3	10	15
40	68.5	2.5	-	Mn=4	10	15
	68.8	4.2	-	Cr=2	10	15

\* All of Si content is replaced by the indicated element.

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	$T_a$ (°C)	$t_a$ (min.)	$\Delta T_{C-a}$ (°C)	$H_C$ (A/m)	$\mu_0$
	460	15	57	3.4	7,900
5	460	15**	57	3.1	5,700
	460	15***	57	1.4	7,600
	430	120	90	1.2	4,000
	430	150	90	3.6	4,000
10	420	180	100	6.4	12,250
	420	15	110	4.0	33,000
	480	15	78	0.20	19,000
	500	15	58	7.6	13,000
15	480	15	80	0.20	22,000
	500	15	60	0.20	22,000
	500	15	56	0.44	90,000
	480	15	81	0.20	50,000
20	500	15	61	0.44	30,000
	460	15	55	4.2	9,700
	460	30	55	4.9	10,000
25	460	45	55	4.5	8,000
	460	90	55	5.0	7,500
	460	105	55	3.9	7,900
	380	45	111	4.7	12,700
30	380	60	111	4.5	9,600
	380	90	111	3.6	11,500
	380	105	111	5.0	15,800
	420	15	71	3.6	7,200
35	400	15	90	7.0	5,000
	420	15	70	2.0	2,400
	400	15	93	1.7	2,500
	420	15	73	0.84	3,600
40	400	15	102	3.2	13,000
	420	15	82	0.98	5,000
	400	15	107	2.0	29,000
	420	15	87	3.3	21,500
45	420	15	92	0.70	15,800
	420	15	83	0.80	24,000
	440	15	63	0.84	21,500
50	420	15	91	1.4	31,500
	440	15	71	1.1	24,000
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	$T_a$ (°C)	$t_a$ (min.)	$\Delta T_{c-a}$ (°C)	$H_c$ (A/m)	$\mu_o$
	440	15	101	3.4	28,700
5	440	15	72	2.9	35,800
	460	15	52	3.6	19,300
	440	15	60	5.6	2,300
	450	15	62	10.4	8,000
10	380	15	63	12	3,300
	480	15	90	5.2	17,000
	420	15	74	6	600
15	450	60	91	1.5	21,000
	460	60	81	1.6	19,300
	440	15	104	1.2	17,500
	440	15	108	1.2	23,000
20	460	15	80	0.8	20,000

\*\* cooling rate =  $-3^\circ\text{C}/\text{min.}$

\*\*\* cooling rate =  $-60^\circ\text{C}/\text{min.}$

This table teaches the importance of the quantity  $\Delta T_{c-a}$  being between 50 and  $110^\circ\text{C}$  and relatively slow cooling rates after the heat-treatments at temperature  $T_a$  and for the duration  $t_a$ . It is also noted that  $\mu_o$  values are higher and the  $H_c$  values are lower than those of prior art materials. For example, a properly heat-treated ( $T_a = 480^\circ\text{C}$ ;  $t_a = 15$  min.)  $\text{Co}_{67.8}\text{Fe}_{4.2}\text{Cr}_1\text{B}_{12}\text{Si}_{15}$  glassy alloy exhibits  $\mu_o = 50,000$  and  $H_c = 0.2$  A/m whereas one of the improved prior art alloy, namely 7.5-45-25 Mo-Perminvar, gives  $\mu_o = 100$  and  $H_c = 40$  A/m when furnace cooled from  $1100^\circ\text{C}$  and gives  $\mu_o = 3,500$  when quenched from  $600^\circ\text{C}$ .

In many magnetic applications, lower magnetostriction is desirable. For some applications, however, it may be desirable or acceptable to use materials with a small positive or negative magnetostriction. Such near-zero magnetostrictive glassy metal alloys are obtained for "a", "b", "c" in the ranges of 66 to 71, 2.5 to 4.5 and 0 to 3 atom percent respectively, with the proviso 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 alloys is less than about  $1 \times 10^{-6}$  (i.e. the saturation magnetostriction ranges from  $-1 \times 10^{-6}$  to  $+1 \times 10^{-6}$  or from -1 to +1 microstrains).

The glassy alloys of the invention are conveniently prepared by techniques readily available elsewhere; see e.g. US Patent No. 3,845,805 and No. 3,856,513. In general, the glassy alloys, in the form of continuous ribbon or wire, 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 25 to 27 atom percent of the total alloy composition is sufficient for glass formation with boron ranging from 6 to 24 atom percent. It is preferred, however, that the content of metal M, i.e. the quantity "d" does not exceed very much 2 atom percent except when  $M = \text{Mn}$  to maintain a reasonably high Curie temperature ( $\geq 200^\circ\text{C}$ ).

In addition to the highly non-linear nature of the glassy Perminvar alloys of the present invention, these alloys exhibit high permeabilities and low core loss at high frequencies. Some examples of these features are given in Table III.

Table III

Core loss (L) and impedance permeability ( $\mu$ ) at  
f=50 kHz and induction level of 0.1 Tesla for some of  
the glassy Perminvar-like alloys of the present  
invention.  $T_a$  and  $t_a$  are heat-treatment temperature and  
time. Cooling after the heat-treatment is about  
-5°C/min., unless otherwise stated.

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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>
	70.5	4.5	-	-	15	10
5	70.5	4.5	-	-	15	10
	70.5	4.5	-	-	15	10
	69.0	4.1	1.4	Mo=1.5	12	12
	65.7	4.4	2.9	Mo=2	11	14
10	68.2	3.8	-	Mn=1	12	15
	68.2	3.8	-	Mn=1	12	15
	67.7	3.3	-	Mn=2	12	15
	67.7	3.3	-	Mn=2	12	15
15	67.8	4.2	-	Mo=1	12	15
	67.8	4.2	-	Cr=1	12	15
	67.8	4.2	-	Cr=1	12	15
	69.2	3.8	-	Mo=2	8	17
20	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
	69.2	3.8	-	Mo=2	8	17
25	67.5	4.5	3.0	-	8	17
	67.5	4.5	3.0	-	8	17
	67.5	4.5	3.0	-	8	17
	67.5	4.5	3.0	-	8	17
30	67.5	4.5	3.0	-	8	17
	70.9	4.1	-	-	8	17
	70.9	4.1	-	-	8	17
	69.9	4.1	-	Mn=1	8	17
35	69.9	4.1	-	Mn=1	8	17
	69.0	4.0	-	Mn=2	8	17
	69.0	4.0	-	Mn=2	8	17
	68.0	4.0	-	Mn=3	8	17
40	68.0	4.0	-	Mn=3	8	17
	67.1	3.9	-	Mn=4	8	17
	69.0	4.0	-	Cr=2	8	17
	69.0	4.0	-	Cr=2	8	17
45	68.0	4.0	-	Mn=2, Cr=1	8	17
	68.0	4.0	-	Mn=2, Cr=1	8	17
	69.0	4.0	-	Nb=2	8	17
50	68.1	4.0	1.4	Mo=1.5	8	17

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	<u>Co</u>	<u>Fe</u>	<u>Ni</u>	<u>M</u>	<u>B</u>	<u>Si</u>
	68.1	4.0	1.4	Mo=1.5	8	17
5	65.7	4.4	2.9	Mo=2	23	C=3*
	65.7	4.4	2.9	Mo=2	23	2
	68.6	4.4	-	Mo=2	21	Ge=4*
	69.2	3.8	-	Mo=2	10	15
10	69.0	3.0	-	Mn=3	10	15
	68.5	2.5	-	Mn=4	10	15
	68.8	4.2	-	Cr=2	10	15

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\* All of Si content is replaced by the indicated element.

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	$T_a$ (°C)	$t_p$ (min.)	$L$ (W/kg)	$\mu$
	460	15	35	2,300
	460	15**	39	2,000
5	460	15***	14	3,400
	430	120	14	2,800
	420	15	6.7	6,000
	480	15	4.6	14,000
10	500	15	4.4	9,300
	480	15	4.0	17,600
	500	15	4.5	17,000
15	500	15	4.0	27,600
	480	15	4.0	24,700
	500	15	3.7	22,500
	460	15	9.0	5,400
20	460	30	6.3	14,900
	460	45	6.6	13,800
	460	90	6.7	14,400
	460	105	6.9	14,800
25	380	45	19	3,000
	380	60	20	2,800
	380	90	21	2,900
	380	105	18	2,900
30	420	15	22	3,000
	400	15	31	2,400
	420	15	15	2,000
	400	15	23	2,800
35	420	15	16	2,700
	400	15	11	3,800
	420	15	11	3,800
40	400	15	8.0	5,500
	420	15	10	5,200
	420	15	5.7	9,250
	420	15	5.5	12,500
45	440	15	4.7	13,200
	420	15	4.8	10,000
	440	15	4.7	10,500
	440	15	4.2	11,200
50	440	15	6.6	8,200

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	$T_a$ (°C)	$t_a$ (min.)	L (W/kg)	$\mu$
	460	15	7.2	7,100
5	440	15	20	2,000
	450	15	27	2,800
	480	15	9.7	5,200
	450	60	9.1	9,600
10	460	60	10	7,700
	440	15	8.3	6,500
	440	15	8.3	8,200
15	460	15	5.7	10,300

\*\* Cooling rate =  $-3^\circ\text{C}/\text{min}$ .

20 \*\*\* Cooling rate =  $-60^\circ\text{C}/\text{min}$ .

## EXAMPLES

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### 1. Sample Preparation

The glassy alloys listed in Tables I-III 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  $\mu\text{m}$  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

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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 ( $\theta_f$ ) was measured by inductance method and also monitored by differential scanning calorimetry, which was used primarily to determine the crystallization temperatures.

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 ( $\Delta l/l$ ) and perpendicular ( $\Delta l/l$ ) in-plane fields, according to the formula

$$\lambda = 2/3 [(\Delta l/l) - (\Delta l/l) \text{ ' }].$$

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## 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 M is at least one of Cr, Mo, Mn and Nb, "a" - "f" are in atom percent and the sums of "a" - "f" equals 100, "a" is from 66 to 71, "b" is from 2.5 to 4.5, "c" is from 0 to 3, "d" is from 0 to 4, "e" is from 6 to 24 and "f" is from 0 to 19, with the provisos that the sum of "a", "b" and "c" is from 71 to 76 and the sum of "e" and "f" is from 25 to 27 and up to 4 atom percent of Si may be replaced by C, Al or Ge, said alloy having a value of magnetostriction between  $-1 \times 10^{-6}$  and  $+1 \times 10^{-6}$ , said alloy having Perminvar characteristics of a relatively constant permeability at low magnetic excitation and a constricted hysteresis loop as a result of having been heat-treated by heating to a temperature between 50 and 110°C below the first crystallization temperature thereof for from 15 to 180 minutes and then cooling at a rate slower than about  $-60^\circ\text{C}/\text{min}$ .
2. A magnetic alloy according to claim 1 having the formula  $\text{Co}_{70.5}\text{Fe}_{4.5}\text{B}_{15}\text{Si}_{10}$ .
3. A magnetic alloy according to claim 1 having the formula  $\text{Co}_{65.7}\text{Fe}_{4.4}\text{Ni}_{2.9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$ .
4. A magnetic alloy according to claim 1 having the formula  $\text{Co}_{68.2}\text{Fe}_{3.8}\text{Mn}_1\text{B}_{12}\text{Si}_{15}$ .
5. A magnetic alloy according to claim 1 having the formula  $\text{Co}_{67.7}\text{Fe}_{3.3}\text{Mn}_2\text{B}_{12}\text{Si}_{15}$ .
6. A magnetic alloy according to claim 1 having the formula  $\text{Co}_{67.8}\text{Fe}_{4.2}\text{Mo}_1\text{B}_{12}\text{Si}_{15}$ .
7. A magnetic alloy according to claim 1 having a formula selected from  
 $\text{Co}_{67.8}\text{Fe}_{4.2}\text{Cr}_1\text{B}_{12}\text{Si}_{15}$ ,  $\text{Co}_{69.2}\text{Fe}_{3.8}\text{Mo}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.5}\text{Fe}_{4.5}\text{Ni}_{3.0}\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{70.9}\text{Fe}_{4.1}\text{B}_8\text{Si}_{17}$ ,  
 $\text{Co}_{69.9}\text{Fe}_{4.1}\text{Mn}_{1.0}\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Mn}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{68.0}\text{Fe}_{4.0}\text{Mn}_3\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.1}\text{Fe}_{3.9}\text{Mn}_4\text{B}_8\text{Si}_{17}$ ,  
 $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Cr}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{68.0}\text{Fe}_{4.0}\text{Mn}_2\text{Cr}_1\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Nb}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.0}\text{Fe}_{4.0}\text{Cr}_2\text{B}_{12}\text{Si}_{15}$ ,

## 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 M est au moins l'un des éléments Cr, Mo, Mn et Nb, "a" - "f" - sont des atomes % et la somme de "a" - "f" est égale à 100, "a" est compris entre 66 et 71, "b" est compris entre 2,5 et 4,5, "c" est compris entre 0 et 3, "d" est compris entre 0 et 4, "e" est compris entre 6 et 24 et "f" est compris entre 0 et 19, dans la mesure où la somme de "a", "b" et "c" est comprise entre 71 et 76 et la somme de "e" et "f" est comprise entre 25 et 27 et jusqu'à 4 atomes % de Si peuvent être remplacés par C, Al ou Ge, ledit alliage ayant une valeur de la magnétostriction comprise entre  $-1 \times 10^{-6}$  et  $+1 \times 10^{-6}$ , ledit alliage ayant les caractéristiques d'un Perminvar de perméabilité relativement constante à une faible excitation magnétique et une courbe d'hystérésis rétrécie à la suite de la soumission à un traitement thermique par chauffage à une température comprise entre 50 et 110 ° C au-dessous de sa première température de cristallisation pendant une durée comprise entre 15 et 180 minutes et ensuite par refroidissement à une cadence inférieure à environ  $-60^\circ\text{C}/\text{mn}$ .
2. Alliage magnétique selon la revendication 1, ayant la formule  $\text{Co}_{70.5}\text{Fe}_{4.5}\text{B}_{15}\text{Si}_{10}$ .
3. Alliage magnétique selon la revendication 1, ayant la formule  $\text{Co}_{65.7}\text{Fe}_{4.4}\text{Ni}_{2.9}\text{Mo}_2\text{B}_{11}\text{Si}_{14}$ .
4. Alliage magnétique selon la revendication 1, ayant la formule  $\text{Co}_{68.2}\text{Fe}_{3.8}\text{Mn}_1\text{B}_{12}\text{Si}_{15}$ .
5. Alliage magnétique selon la revendication 1, ayant la formule  $\text{Co}_{67.7}\text{Fe}_{3.3}\text{Mn}_2\text{B}_{12}\text{Si}_{15}$ .
6. Alliage magnétique selon la revendication 1, ayant la formule  $\text{Co}_{67.8}\text{Fe}_{4.2}\text{Mo}_1\text{B}_{12}\text{Si}_{15}$ .
7. Alliage magnétique selon la revendication 1, ayant une formule choisie parmi :  
 $\text{Co}_{67.8}\text{Fe}_{4.2}\text{Cr}_1\text{B}_{12}\text{Si}_{15}$ ,  $\text{Co}_{69.2}\text{Fe}_{3.8}\text{Mo}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.5}\text{Fe}_{4.5}\text{Ni}_{3.0}\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{70.9}\text{Fe}_{4.1}\text{B}_8\text{Si}_{17}$ ,  
 $\text{Co}_{69.9}\text{Fe}_{4.1}\text{Mn}_{1.0}\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Mn}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{68.0}\text{Fe}_{4.0}\text{Mn}_3\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.1}\text{Fe}_{3.9}\text{Mn}_4\text{B}_8\text{Si}_{17}$ ,  
 $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Cr}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{68.0}\text{Fe}_{4.0}\text{Mn}_2\text{Cr}_1\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{69.0}\text{Fe}_{4.0}\text{Nb}_2\text{B}_8\text{Si}_{17}$ ,  $\text{Co}_{67.0}\text{Fe}_{4.0}\text{Cr}_2\text{B}_{12}\text{Si}_{15}$ .

## Patentansprüche

- 5 1. Magnetische Legierung, die zu wenigstens 70 % glasartig ist, mit der Formel  $\text{Co}_a\text{Fe}_b\text{-Ni}_c\text{M}_d\text{B}_e\text{Si}_f$ , worin M wenigstens eines der Elemente Cr, Mo, Mn und Nb ist, "a" - "f" in Atomprozenten angegeben sind und die Summe von "a" - "f" 100 ist, "a" 66 bis 71 ist, "b" 2,5 bis 4,5 ist, "c" 0 bis 3 ist, "d" 0 bis 4 ist, "e" 6 bis 24 ist und "f" 0 bis 19 ist, wobei die Summe von "a", "b" und "c" 71 bis 76 ist und die Summe von "e" und "f" 25 bis 27 ist und bis zu 4 Atom-% von Si durch C, Al oder Ge ersetzt sein können, wobei diese Legierung einen Magnetostruktionswert zwischen  $-1 \times 10^{-6}$  und  $+1 \times 10^{-6}$  hat und wobei die Legierung Perminvar-Eigenschaften einer relativ konstanten Permeabilität bei niedriger magnetischer Erregung und eine eingeengte Hystereseschleife als Ergebnis einer Hitzebehandlung durch Erhitzen auf eine Temperatur zwischen 50 und 110 °C unterhalb ihrer ersten Kristallisationstemperatur während 15 bis 180 min und anschließendes Kühlen mit einer Geschwindigkeit langsamer als etwa -60 °C/min hat.
- 10 2. Magnetische Legierung nach Anspruch 1 mit der Formel  $\text{Co}_{70,5}\text{Fe}_{4,5}\text{B}_{1,5}\text{Si}_{1,0}$ .
3. Magnetische Legierung nach Anspruch 1 mit der Formel  $\text{Co}_{65,7}\text{Fe}_{4,4}\text{Ni}_{2,9}\text{Mo}_2\text{B}_{1,1}\text{Si}_{1,4}$ .
4. Magnetische Legierung nach Anspruch 1 mit der Formel  $\text{Co}_{68,2}\text{Fe}_{3,8}\text{Mn}_1\text{B}_{1,2}\text{Si}_{1,5}$ .
- 20 5. Magnetische Legierung nach Anspruch 1 mit der Formel  $\text{Co}_{67,7}\text{Fe}_{3,3}\text{Mn}_2\text{B}_{1,2}\text{Si}_{1,5}$ .
6. Magnetische Legierung nach Anspruch 1 mit der Formel  $\text{Co}_{67,8}\text{Fe}_{4,2}\text{Mo}_1\text{B}_{1,2}\text{Si}_{1,5}$ .
- 25 7. Magnetische Legierung nach Anspruch 1 mit einer Formel, die unter  $\text{Co}_{67,8}\text{Fe}_{4,2}\text{Cr}_1\text{B}_{1,2}\text{Si}_{1,5}$ ,  $\text{Co}_{69,2}\text{Fe}_{3,8}\text{Mo}_2\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{67,6}\text{Fe}_{4,5}\text{Ni}_{3,0}\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{70,9}\text{Fe}_{4,1}\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{69,9}\text{Fe}_{4,1}\text{Mn}_{1,0}\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{69,0}\text{Fe}_{4,0}\text{Mn}_2\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{68,0}\text{Fe}_{4,0}\text{Mn}_3\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{67,1}\text{Fe}_{3,9}\text{Mn}_4\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{69,0}\text{Fe}_{4,0}\text{Cr}_2\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{68,0}\text{Fe}_{4,0}\text{Cr}_2\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{68,0}\text{Fe}_{4,0}\text{Mn}_2\text{Cr}_1\text{B}_8\text{Si}_{1,7}$ ,  $\text{Co}_{69,0}\text{Fe}_{4,0}\text{Nb}_2\text{B}_8\text{Si}_{1,7}$  oder  $\text{Co}_{67,0}\text{Fe}_{4,0}\text{Cr}_2\text{B}_{1,2}\text{Si}_{1,5}$  ausgewählt ist.
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