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(54) Low magnetostriction amorphous metal alloys.

(57) A magnetic alloy having a composition selected from the group consisting of $Co_{73}Fe_{4.5}Mn_{2.5}B_{20}$, $Co_{73}Fe_{2.5}Mn_{4.5}B_{20}$, $Co_{73}Fe_2Mn_5B_{20}$, $Co_{66}Mn_9Ni_5B_{20}$ and $Co_{68.4}Mn_{8.3}Ni_{3.3}B_{20}$.

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Low Magnetostriction Amorphous Metal Alloys

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1. Field of the Invention

This invention relates to amorphous metal alloys and, more particularly, to cobalt rich amorphous metal alloys that include certain transition metal and metalloid elements.

2. Description of the Prior Art

There are three physical parameters which can inhibit the easy magnetization and demagnetization of magnetic materials: strong anisotropy, non-zero magnetostriction and, at high frequencies, low resistivity. Metallic glasses generally show resistivities greater than 100 micro ohm cm, whereas crystalline and polycrystalline magnetic metals generally show resistivities below 50 micro ohm cm. Also, because of their randomly disordered structures, metallic glasses are typically isotropic in their physical properties, including their magnetization. Because of these two characteristics, metallic glasses have an initial advantage over conventional magnetic metals. However, metallic glasses do not generally show zero magnetostriction. When zero magnetostriction glasses can be found they are generally good soft magnetic metals (R.C. O'Handley, B.A. Nesbitt, and L.I. Mendelsohn, IEEE Trans Mag-12, p. 942, 1976, U.S. Patents Nos. 4,038,073 and 4,150,981), because they satisfy the three approved criteria. For this reason, interest in zero magnetostriction glasses has been intense as indicated by the many publications on low magnetostriction metallic glasses (A.W. Simpson and W.G. Clements, IEEE Trans Mag-11, p. 1338, 1975; N. Tsuya, K.I. Arai, Y. Shiraga and T. Masumoto, Phys. Lett. A51, p. 121, 1975; H.A. Brooks, Jour. Appl. Phys. 47, p. 334, 1975; T. Egami, P.J. Flanders and C.D. Graham, Jr., Appl. Phys. Lett. 26, p. 128, 1975 and AIP Conf. Proc. No. 24, p. 697, 1975; R.C. Sherwood, E.M. Gyorgy, H.S. Chen, S.D. Ferris, G. Norman and H.J. Leamy, AIP Conf. Proc. No. 24, p. 745, 1975; H. Fujimori, K.I. Arai, H. Shiraga, M. Yamada, T. Masumoto and N. Tsuya, Japan, Jour. Appl. Phys. 15, p. 705, 1976; L. Kraus and J. Schneider, phys. stat. sol. a39, p. K161, 1977; R.C. O'Handley in Amorphous Magnetism, edited by R. Levy and R. Hasegawa (Plenum Press, New York 1977), p. 379; R.C. O'Handley, Solid State Communications 21, p. 1119, 1977;

R.C. O'Handley, Solid State Communications 22, p. 458, 1977; R.C. O'Handley, Phys. Rev. 18, p. 930, 1978; H.S. Chen, E.M. Gyorgy, H.J. Leamy and R.C. Sherwood, U.S. Patent No. 4,056,411, Nov. 1, 1977).

The existence of a zero in the magnetostriction of Co-Mn-B glasses has been observed by H. Hiltzinger of Vacuumschmeltze A.G., Hanau, Germany.

Reference to Co-rich glasses containing 6 atom percent of Cr is made by N. Heiman, R.D. Hempstead and N. Kazama in Journal of Applied Physics, Vol. 49, p. 5663, 1978. Their interest was in improving the corrosion resistance of Co-B thin films. No reference to magnetostriction is made in that article.

Saturation moments and Curie temperatures of $Co_{80-x}T_xP_{10}B_{10}$ glasses (T = Mn, Cr, or V) were recently reported by T. Mizoguchi in the Supplement to the Scientific Reports of RITU (Research Institutes of Tonoku University), A June 1978, p. 117. No reference to their magnetostrictive properties was reported.

In Journal of Applied Physics, Vol. 50, p. 7597, 1979, S. Ohnuma and T. Masumoto outline their studies of magnetization and magnetostriction in Co-Fe-B-Si glasses with light transition metal (Mn, Cr, V, W, Ta, Mo and Nb) substitutions. They show that the coercivity decreases and the effective permeability increases in the composition range near zero magnetostriction.

New applications requiring improved soft zero-magnetic materials that are easily fabricated and have excellent stability have necessitated efforts to develop further specific compositions.

SUMMARY OF THE INVENTION

The present invention provides low magnetostriction and zero magnetostriction glassy alloys that are easy to fabricate and thermally stable. The alloys have a composition selected from the group consisting of $Co_{73}Fe_{4.5}Mn_{2.5}B_{20}$, $Co_{73}Fe_{2.5}Mn_{4.5}B_{20}$, $Co_{73}Fe_2Mn_5B_{20}20$, Co_{66}-$Mn_9Ni_5B_{20}$ and $Co_{68.4}Mn_{8.3}Ni_{3.3}B_{20}$.

The purity of the above composition is that found in normal commerial practice.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiments of the invention and the accompanying drawing, which shows the cobalt-rich corners of triangular diagrams for compositions defined by the formula $(Co_{1-x-y}Fe_xT_y)_{80}B_{20}$, where T is Mn.

The amorphous alloys of the invention can be formed by cooling a melt of the composition at a rate of at least about 10^5°C/sec. A variety of techniques are available, as is now well-known in the art, for fabricating splat-quenched foils and rapid-quenched continuous ribbons, wire, sheet, etc. Typically, a particular composition is selected, powders of the requisite elements (or of materials that decompose to form the elements, such as nickel-borides, etc.) in the desired proportions are melted and homogenized, and the molten alloy is rapidly quenched either on a chill surface, such as a rotating cooled cylinder, or in a suitable fluid medium, such as a chilled brine solution. The amorphous alloys may be formed in air. However, superior mechanical properties are achieved by forming these amorphous alloys in a partial vacuum with absolute pressure less than about 5.5 cm of Hg, and preferably about 100 μm to 1 cm of Hg, as disclosed in U.S. Patent No. 4,154,283 to Ray et al.

The amorphous metal alloys are at least 50 percent amorphous, and preferably at least 80 percent amorphous, as measured by X-ray diffraction. However, a substantial degree of amorphousness approaching 100 percent amorphous is obtained by forming these amorphous metal alloys in a partial vacuum. Ductility is thereby improved, and such alloys possessing a substantial degree of amorphousness are accordingly preferred.

Ribbons of these alloys find use in soft magnetic applications and in applications requiring low magnetostriction, high thermal stability (e.g., stable up to about 100°C) and excellent fabricability.

The following example is 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.

EXAMPLE

An alloy melt of known composition was rapidly quenched to form non-crystalline ribbons, presumably of the same composition as the melt. The ribbons, typically 40 micrometers (μm) by 2 mm in cross section, were cut into squares for vibration-sample magnetometer measurements of specific magnetization σ(4.2K, 9 KOe) and σ(T, 9 KOe) with 295 K < T < T_x, the crystallization temperature. Curie temperatures were obtained from the inflection points in the σ(T, 9 KOe) curves.

The magnetostriction measurements were made in fields up to 4 KOe with metal foil strain gauges (as reported in more detail by R.C. O'Handley in Solid State Communications, Vol. 22, p. 485, 1977). The accuracy of these measurements is considered to be within 10 percent of full strain and their strain sensitivity is on the order of 10^{-7}.

Co-rich glass compositions with positive and negative magnetostriction can be added linearly to give zero magnetostriction. For example, λ_s for $Co_{70}Fe_{10}B_{20}$ and $Co_{80}B_{20}$ glasses are +4 and -4 x 10^{-6}, respectively. A 50-50 percent mixture of these glasses gives $Co_{75}Fe_{5}B_{20}$ which does in fact show λ_s = 0 (O'Handley et al., IEEE Trans Mag-12, p. 942, 1976). Similarly, for $Co_{40}Ni_{40}B_{40}$ λ_s = -7 x 10^{-6} while for $Fe_{80}B_{20}$ λ_s = 32 x 10^{-6}. A linear mixture having λ = 0 would be 0.18 x ($Fe_{80}B_{20}$) + 0.82 x ($Co_{40}Ni_{40}B_{20}$) = $Co_{33}Ni_{33}Fe_{14}B_{20}$ which is very close to the observed λ_s = 0 composition, $Co_{33.5}Ni_{33.5}Fe_{13}B_{20}$.

The rule of linear combination of opposing magnetostrictions (LCOM) has been applied to develop additional zero magnetostriction glasses. Table I lists several such glasses and the drawing shows where they fall in the Co-rich corner of a triangular composition diagram. The lines connecting these newly developed $\lambda_s = 0$ compositions closely follow the observations of Ohnuma and Masumoto (cited above) for $(Co\ Fe\ X)_{78}B_{14}Si_8$ glasses (with X = Mn, Cr, V) despite the different metalloids used in the two cases.

TABLE I

Some Near-zero Magnetostriction Cobalt-rich Glasses Developed by the LCOM Method

$Co_{73}Fe_{4.5}Mn_{2.5}B_{20}$	$Co_{73}Fe_{2}Mn_{5}B_{20}$
$Co_{73}Fe_{2.5}Mn_{4.5}B_{20}$	

The magnetostriction of Co-rich glasses is small because of the near-cancellation of two independent mechanisms for the magnetostriction, a positive two-ion interaction and a negative single-TM-ion term (O'Handley, Phys. Rev. B 18, p. 930, 1978). As a result, the TM makeup for $\lambda_s = 0$ is nearly independent of TM/M ratio.

An improvement on this approximation can be realized by taking into account the fact that the strength of the negative single-ion term varies linearly with the concentration of magnetic ions. The two-ion term should vary as the number of TM pairs at short range. However, observed trends in $Co_{100-x}B_x$ glasses (K. Narita, J. Yamasaki, and H. Fukunaga, Jour. Appl. Phys. Vol. 50, p. 7591, 1979 and J. Aboaf and E. Klokholm, ICM Munich Sept. 1979 to appear in Jour. Magnetism and Magnetic Materials), are best described by assuming the number of nearest neighbor TM pairs to be independent of x. This implies that the nearest-neighbor coordination of cobalt atoms by cobalt atoms does not vary strongly with x. Thus the compositional dependence of magnetostriction in Co-rich glasses is well described at room temperature by: $\lambda_s \propto + 6.8 \times 10^{-6} - 10.2 \times 10^{-6} \times (100-x)/80$ where the first term is the observed two-ion component of magnetostriction (independent of composition x) and the second is the single-ion component of magnetostriction (which varies linearly with the TM concentration). Thus the magnetostriction becomes less negative as metalloid content increases, the change in λ being $+0.13 \times 10^{-6}$ per atom percent more metalloid. Alternatively, the zero magnetostriction composition is shifted to glasses richer in iron as 100-x increases, the shift being approximately +0.23 percent Fe per 1 percent decrease in x.

As a result, the Co-Fe-T ratios (T = Mn) for $\lambda_s = 0$ in the drawing hold approximately for other TM/M ratios in the glass-forming range $12 \leq x < 28$ atom percent. A first order correction shifts the $\lambda_s = 0$ lines toward Fe by approximately 1 percent for every 4 percent decrease in x.

Metalloid type has little effect on the magnitude or sign of magnetostriction in Co-rich glasses (O'Handley in Amorphous Magnetism eds. R. Levy and R. Hasegawa, Plenum Press 1977, p. 379).

Table II sets forth some typical near-zero magnetostriction compositions.

TABLE II

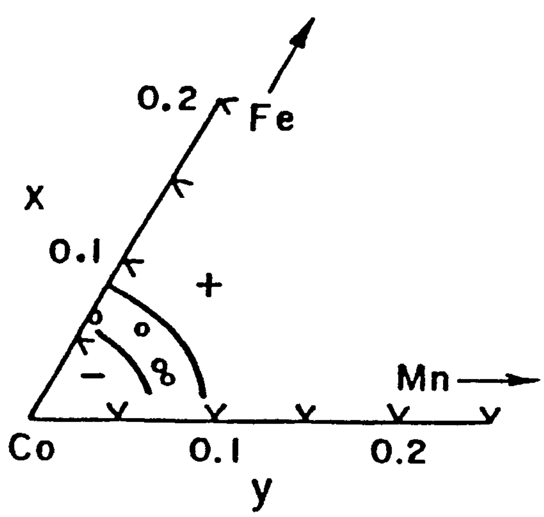
New Co-Ni Base Glassy Alloys or Near-zero Magnetostriction Developed by LCOM Method.

$Co_{66}Mn_9Ni_5B_{20}$	$Co_{68.4}Mn_{8.3}Ni_{3.3}B_{20}$

Claim

A magnetic alloy having a composition selected from the group consisting of $Co_{73}Fe_{4.5}Mn_{2.5}B_{20}$, $Co_{73}Fe_{2.5}Mn_{4.5}B_{20}$, $Co_{73}Fe_{2}Mn_{5}B_{20}$, $Co_{66}Mn_{9}Ni_{5}B_{20}$ and $Co_{68.4}Mn_{8.3}Ni_{3.3}B_{20}$.

$(Co_{1-x-y}Fe_xT_y)_{80}B_{20}$



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EUROPEAN SEARCH REPORT

0161394

Application number

EP 85101590.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,X	US - A - 4 056 411 (CHEN) * Abstract; fig. I * --	1	C 22 C 19/07 H 01 F 1/14
A	DE - A1 - 2 553 003 (ALLIED CHEMICAL CORP.) * Page 2, lines 10-21 * --	1	
A	EP - A1 - 0 021 101 (VACUUMSCHMELZE) * Abstract * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
C 22 C H 01 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-07-1985	ONDER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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