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(54) Low magnetostriction amorphous metal alloys.

(57) A magnetic alloy that is at least 50 percent glassy, having the formula $(Co_{1-x-y-z}Fe_xNi_yT_z)_{100-b}(B_{1-w}M_w)_b$, where T is at least one of Mn, Cr, V, Ti, Mo, Nb and W, M is at least one of Si, P, C and Ge, B ist boron x ranges from about 0.05 to 0.25, y ranges from about 0.05 to 0.80, z ranges from about 0 to 0.25, b ranges from about 12 to 30 atom percent, w ranges up to 0.75 when M is Si or Ge and up to 0.5 when M is C or P, said alloy having a value of magnetostriction of about -7×10^{-6} and $+5 \times 10^{-6}$ and a saturation induction of about 0.2 to 1.4T.

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DESCRIPTION

LOW MAGNETOSTRICTION AMORPHOUS METAL ALLOYS

BACKGROUND OF THE INVENTION

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 zeromagnetic 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 are at least about 50 percent glassy and consist essentially of compositions defined by the formula: $(Co_{1-x-y-z}Fe_xNi_yT_z)_{100-b}(B_{1-w}M_w)_b$, where T is at least one of Mn, Cr, V, Ti, Mo, Nb and W, M is at least one of Si, P, C and Ge, B is boron, x ranges from about 0.05 to 0.25, y ranges from about 0.05 to 0.80, z ranges from about 0 to 0.25, b ranges from about 12 to 30 atom percent, w ranges up to 0.75 when M is Si or Ge and up to 0.5 when M is C or P, said alloy having a value of magnetostriction of about -7×10^{-6} and $+5 \times 10^{-6}$ and a saturation induction of about 0.2 to 1.4T.

A preferred magnetic alloy is one, wherein y ranges from about 0.3 to 0.6 or between 0.60 to 0.80 and z is respectively less than 0.2 or less than 0.15 when T is more than 50 percent of at least one of Cr and V, said alloy having a value of magnetostriction of about -6×10^{-6} to $+4 \times 10^{-6}$ and a saturation induction of about 0.1 to 0.9T.

Special magnetic alloys according to the invention have a composition selected from the group consisting of

$Co_{53.7}Ni_{15.3}Fe_{5.5}Mn_{5.5}B_{20}$, $Co_{41}Ni_{30}Fe_{5}Mn_{4}B_{20}$, $Co_{58}Ni_{12}Fe_{6}Mn_{4}B_{20}$, $Co_{58}Ni_{12}Fe_{6}Mn_{4}B_{20}$, $Co_{51}Ni_{18}Fe_{8}Cr_{3}B_{20}$, $Co_{56}Ni_{12}Fe_{6}Cr_{6}B_{20}$, $Co_{40}Ni_{30}Fe_{5}V_{5}B_{20}$, $Co_{52}Ni_{18}Fe_{8}Mn_{2}B_{20}$, $Ni_{45}Co_{26.5}Fe_{7.5}Mn_{1}B_{20}$, $Co_{39}Ni_{30}Cr_{6}Fe_{5}B_{20}$, $Co_{51}Ni_{18}Fe_{9}Cr_{2}B_{20}$ and $Co_{59}Ni_{12}Fe_{6}V_{5}B_{20}$.

The purity of the above composition is that found in normal commercial 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 is a triangular Fe-Co-Ni diagram showing regions of positive and negative magnetostriction, the dotted line isolating therefrom the region of nickel-rich compositions wherein amorphous metals are difficult to form and thermally unstable.

Description of the Preferred Embodiments

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 per cent 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.

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 per cent 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 -4×10^{-6}, respectively. A 50-50 per cent mixture of these glasses gives $Co_{75}Fe_5B_{20}$ which does in fact show $\lambda_s = 0$ (O'Handley et al., IEEE Trans Mag-12, p. 942, 1976). Similarly, for $Co_{40}Ni_{40}B_{40}$ $\lambda_s = -7 \times 10^{-6}$ while for $Fe_{80}B_{20}$ $\lambda_s = 32 \times 10^{-6}$. A linear mixture having $\lambda = 0$ would be $0.18 \times (Fe_{80}B_{20}) + 0.82 \times (Co_{40}Ni_{40}B_{20}) = Co_{33}Ni_{33}Fe_{14}B_{20}$ which is very close to the observed $\lambda_s = 0$ composition, $Co_{33.5}Ni_{33.5}Fe_{13}B_{20}$.

The rule of linear combination of opposing magnetostrictions (LCOM) can be applied across the Co-Ni side of the Fe-Co-Ni triangular magnetostrictions diagram shown in the drawing (see also U.S. Patent No. 4,150,981 to O'Handley). Table I sets forth some typical near-zero magnetostriction compositions.

Table I

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

$Co_{53.7}Ni_{15.3}Fe_{5.5}Mn_{5.5}B_{20}$	$Co_{52}Ni_{18}Fe_8Mn_2B_{20}$
$Co_{41}Ni_{30}Fe_5Mn_4B_{20}$	$Ni_{45}Co_{26.5}Fe_{7.5}Mn_1B_{20}$
$Co_{58}Ni_{12}Fe_6Mn_4B_{20}$	
$Co_{51}Ni_{18}Fe_8Cr_3B_{20}$	$Co_{39}Ni_{30}Cr_6Fe_5B_{20}$
$Co_{56}Ni_{12}Fe_6Cr_6B_{20}$	$Co_{51}Ni_{18}Fe_9Cr_2B_{20}$
$Co_{40}Ni_{30}Fe_5V_5B_{20}$	$Co_{59}Ni_{12}Fe_6V_5B_{20}$

Referring to the drawing, a region of difficult to fabricate and relatively unstable glasses exist in the Ni-rich corner of the triangular Fe-Co-Ni diagram. Yet, glassy alloys of zero or low magnetostriction exist there with potential for various applications.

Ni-rich glasses are more easily made and are more stable if the "late" transition metal Ni is balanced to a certain extent by an "early" TM, e.g., Mn, Cr, V. Examples of such glasses include $Ni_{50}Mn_{30}B_{20}$, $Ni_{60}Cr_{20}B_{20}$, or $Ni_{70}V_{10}B_{20}$.

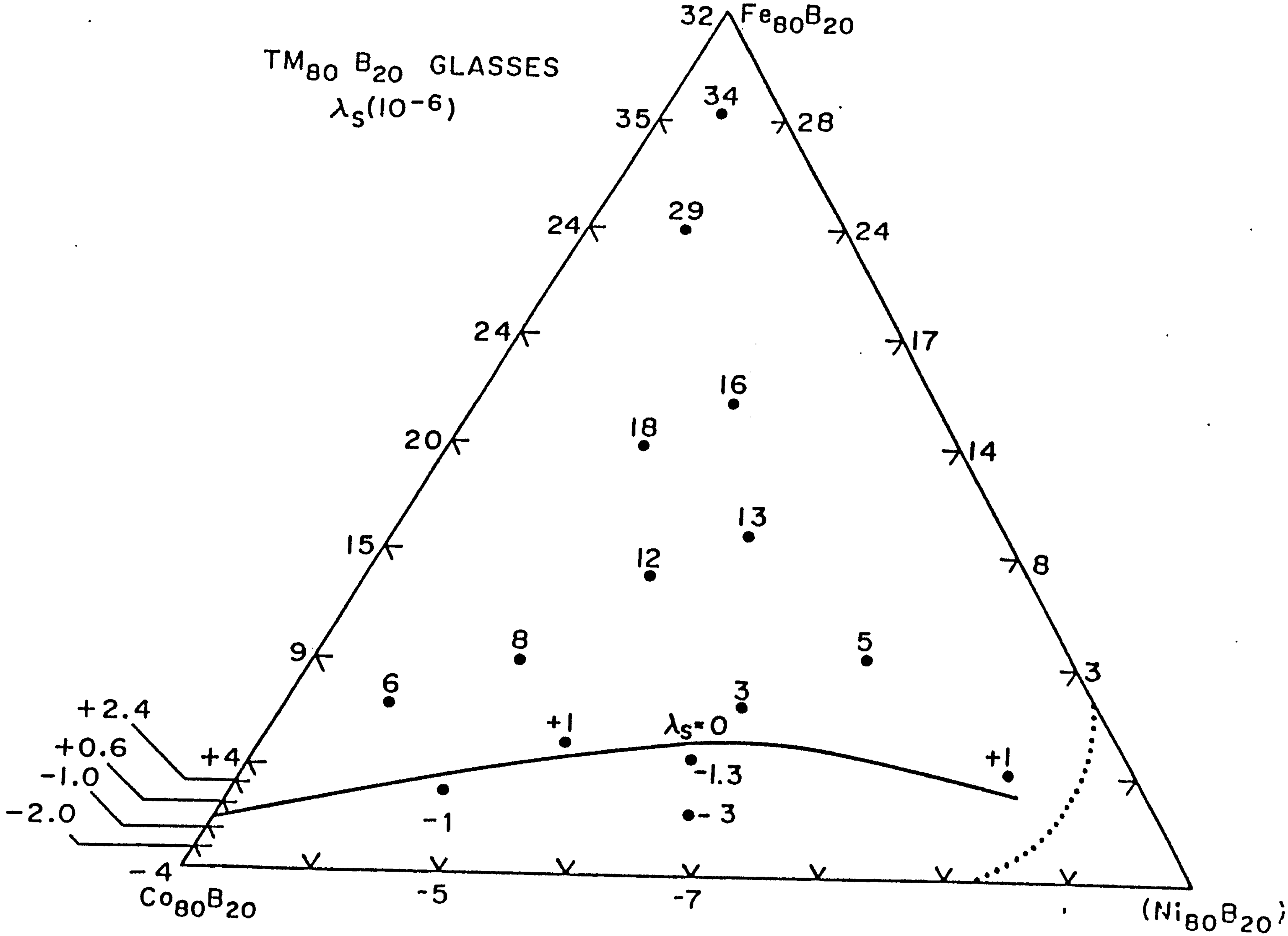
Based on the evidence of $\lambda_s = 0$ alloys set forth above and the known stabilizing effects of light TM's on Ni-rich glasses, new low magnetostriction glasses rich in Ni have been developed in the region below or near the $\lambda_s = 0$ line in the drawing (i.e., glasses initially showing $\lambda_s < 0$) by the addition of Mn, Cr, and/or V. Thus, for example, $(Co_{.25}Ni_{.75})_{80}B_{20}$ can be rendered more fabricable and more stable in the glassy state, and its negative magnetostriction can be increased to near zero by substituting Mn, Cr or V for Co: $(Ni_{.75}Co_{.25-x}T_x)_{80}B_{20}$.

1 Claims:

1. A magnetic alloy that is at least 50 percent glassy, having the formula $(Co_{1-x-y-z}Fe_xNi_yT_z)_{100-b}(B_{1-w}M_w)_b$, where T is at least one of Mn, Cr, V, Ti, Mo, Nb and W, M is at least one of Si, P, C and Ge, B ist boron, x ranges from about 0.05 to 0.25, y ranges from about 0.05 to 0.80, z ranges from about 0 to 0.25, b ranges from about 12 to 30 atom percent , w ranges up to 0.75 when M is Si or Ge and up to 0.5 when M is C or P, said alloy having a value of magnetostriction of about -7×10^{-6} and $+5 \times 10^{-6}$ and a saturation induction of about 0.2 to 1.4T.

2. A magnetic alloy, as recited in claim 1, wherein y ranges from about 0.3 to 0.6 or between 0.60 to 0.80 and z is respectively less than 0.2 or less than 0.15 when T is more than 50 percent of at least one of Cr and V, said alloy having a value of magnetostriction of about -6×10^{-6} to $+4 \times 10^{-6}$ and a saturation induction of about 0.1 to 0.9T.

3. A magnetic alloy having a composition selected from the group consisting of $Co_{53.7}Ni_{15.3}Fe_{5.5}Mn_{5.5}B_{20}$, $Co_{41}Ni_{30}Fe_5Mn_4B_{20}$, $Co_{58}Ni_{12}Fe_6Mn_4B_{20}$, $Co_{51}Ni_{18}Fe_8Cr_3B_{20}$, $Co_{56}Ni_{12}Fe_6Cr_6B_{20}$, $Co_{40}Ni_{30}Fe_5V_5B_{20}$, $Co_{52}Ni_{18}Fe_8Mn_2B_{20}$, $Ni_{45}Co_{26.5}Fe_{7.5}Mn_1B_{20}$, $Co_{39}Ni_{30}Cr_6Fe_5B_{20}$, $Co_{51}Ni_{18}Fe_9Cr_2B_{20}$ and $Co_{59}Ni_{12}Fe_6V_5B_{20}$.



TM80 B20 GLASSES
λs(10-6)
32
Fe80B20
34
35
28
29
24
24
24
17
16
18
20
14
13
12
15
8
9
8
5
6
3
3
+2.4
+1
λs=0
+4
+1
+0.6
-1.3
-1.0
-1
-3
-2.0
-4
Co80B20
-5
-7
(Ni80B20)

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EUROPEAN SEARCH REPORT

0160166
Application number

EP 85101588.3

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,A	US - A - 4 056 411 (CHEN) * Abstract; table I * --	1,3	C 22 C 19/07 H 01 F 1/14
D,A	US - A - 4 038 073 (O'HANDLEY) * Abstract * --	1	
D,A	US - A - 4 150 981 (O'HANDLEY) * Abstract * --	1	
A	US - A - 4 288 260 (SENNO) * Fig. 2 * --	1	
A	US - A - 4 081 298 (MENDELSOHN) * Column 2, lines 47-65 * --	1	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	DE - A1 - 2 553 003 (ALLIED CHEMICAL CORP.) * Page 2, lines 10-21 * --	1-3	C 22 C H 01 F
A	EP - A1 - 0 021 101 (VACUUMSCHMELZE) * Abstract * --	1,2	

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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EUROPEAN SEARCH REPORT

0160166 Application number

EP 85101588.3

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)
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, section C, vol. 2, no. 136, November 11, 1978 THE PATENT OFFICE JAPANESE GOVERNMENT page 2948 C 78 * Kokai-no. 53-102 219 (TOKYO DENKI) * --	1	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, section C, vol. 2, no. 155, December 26, 1978 THE PATENT OFFICE JAPANESE GOVERNMENT page 3718 C 78 * Kokai-no. 53-120 625 (MATSUSHITA DENKI) * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	DE - A1 - 2 824 749 (VACUUM-SCHMELZE) * Claims 2,3 * ----	1-3	

The present search report has been drawn up for all claims

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