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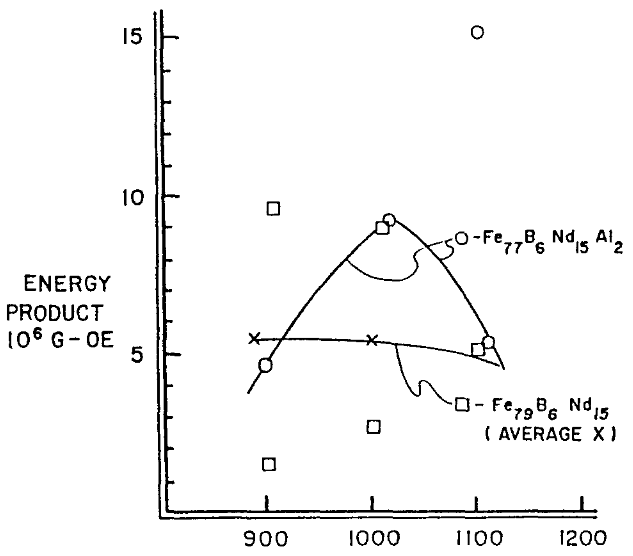
(54) **Method of preparing a hard magnet by addition of a quench rate range broadening additive and a hard magnet prepared thereby.**

(57) Disclosed is a method of forming a glassy, hard magnetic material by rapidly quenching a molten composition of (1) a transition metal, as iron, cobalt, nickel, manganese, or mixtures thereof, (2) a lanthanide, as praesodymium, neodymium, or mixtures thereof, (3) boron, and (4) a quench rate broadening amount of a glass forming additive chosen from the group consisting of aluminium, alumnum-vanadium, zirconium, and zirconium-niobium. Also disclosed are the hard, magnetic materials prepared thereby.



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METHOD OF PREPARING A HARD MAGNET BY ADDITION OF A QUENCH RATE RANGE BROADENING ADDITIVE AND A HARD MAGNET PREPARED THEREBY

FIELD OF THE INVENTION

The invention relates to permanent magnets, i.e. hard magnets, formed of transition metal, a rare earth metal, and boron, and to methods of preparing the permanent magnetic materials.

BACKGROUND OF THE INVENTION

Hard magnets, that is, permanent magnets are characterized by a high coercive force and a high remanence. They may be formed of a transition metal and a rare earth metal, as samarium-cobalt, or a transition metal, a rare earth metal, and boron, as iron-neodymium-boron. The transition metal-rare earth metal-boron hard magnets are characterized by low cost and a precise morphology with the grain size being on the order of from about 1 to about 10 magnetic domains in size. Transition metal-rare earth metal-boron hard magnets and methods of preparing them are described in U.S. Patent 4,402,770 to N.C. Koon for Hard Magnetic Alloys of a Transition Metal And Lantanide, U.S. 4,409,043 to N.C. Koon for Amorphous Transition Metal Lantanide Alloys, and Japanese Published Patent Application 59-64739 of J.J. Croat, claiming the benefit of U.S. Application Serial No. 414,936 of J.J. Croat for High Energy Product Rare-Earth-Iron Magnet Alloys and U.S. Application Serial No. 508,766 of J.J. Croat for High Energy Product Rare Earth-Iron Magnet Alloys.

In order to prepare bulk quantities of transition metal-rare earth metal-boron magnets alloys, the material must be quenched from the melt. However, in order to attain maximum performance, i.e. high coercivity, high remanence, and high energy product, the composition and quenching conditions must be very precisely controlled. That is, the stoichiometry and thermal quenching require control within very narrow limits. Moreover, even very slight deviations from optimum compositions and/or quench conditions lead to weak hard magnets, or even to soft magnetic materials.

The apparent stochiometric composition of the material approaches a minimum melting point composition, for example, a eutectoid. However, the properties of the solidifying melt are not invariant, but are believed to be a strong function of local deviations of the liquid composition from the eutectoid composition. Thus, too slow a quench rate results in a soft magnet material requiring remelting and recasting. Too rapid a quench rate is reported, e.g., in U.S. Patent 4,402,770 to Koon, et al and U.S. Patent Application Serial No. 508,266 of Croat to result in a weak magnet that requires subsequent annealing to obtain a hard magnetic morphology.

Both Koon and Croat demonstrate a preference for a two step process characterized by over-quench and subsequent back annealing.

The two step process of quenching and back annealing, while avoiding the effects of the sensitivity of the magnetic parameters to process parameters, imposes the economic burden of an added series of manufacturing steps.

SUMMARY OF THE INVENTION

The invention herein provides an as-quenched, unannealed, microcrystalline hard magnet prepared with relaxed process parameters. The invention herein further provides a method for preparing an as quenched, unannealed, microcrystalline, hard magnet, not requiring subsequent annealing, and produced with relaxed process parameters.

In a preferred exemplification, the magnetic material is prepared by rapidly quenching a molten composition of:

(1) a transition metal such as iron, cobalt, nickel, manganese, and mixtures thereof;

(2) a rare earth metal, i.e. a lanthanide, ascerium, neodymium, praesodymium, and mixtures thereof;

(3) boron; and

(4) a quench rate range broadening amount of a glass forming additive, for example, chosen from the group consisting of aluminum, aluminium-vanadium, zirconium, and zirconium-niobium.

In a particularly preferred exemplification, the magnetic material is prepared by rapidly quenching a molten composition of iron, neodymium or praesodymium, boron, and aluminum, whereby to form the as-quenched, unannealed, microcrystalline hard magnet, and the as-quenched, unannealed, microcrystalline hard magnet prepared thereby.

THE FIGURES

The invention may be understood by reference to the Figures.

Figure 1 shows the as-quenched energy products of neodymium-iron-boron and praesodymium-iron-boron-aluminum alloys.

Figure 2 shows the as quenched energy products of a praesodymium-iron-boron and neodymium-iron-boron-aluminum alloys.

DETAILED DESCRIPTION OF THE INVENTION

The as-quenched hard magnetic alloys herein contemplated are characterized by morphologies associated with high magnetic remanences, high energy products, high coercivities, and high Curie temperatures and are further characterized in that they do not require annealing to obtain these properties.

The preferred composition has the formula $TM_wRE_xB_yG_z$. TM represents a transition metal or metals chosen from the group consisting of iron, cobalt, nickel, manganese, and mixtures thereof. Preferably iron is the predominant or even sole transition metal. Where iron is not the sole transition metal, it constitutes the major part of the total transition metal content of the alloy, generally being above about 70 atomic percent of the total transition metals present in the magnetic material.

That is, the transition metal content is preferably substantially all iron with inconsequential impurities. Optionally up to 30 atomic percent of cobalt, nickel and/or manganese, basis total transition metal content of the composition, may be present without deleterious effect, and may even provide an additive effect.

RE represents a rare earth metal or metals. The rare earth metal or metals are light rare earth metals chosen from the group consisting of cerium, neodymium, praesodymium, and mixtures thereof.

B represents boron.

G represents a quench rate range broadening glass forming additive or combinations thereof chosen from the group consisting of aluminum, aluminum-vanadium, zirconium, and zirconium-niobium. We have found that certain combinations of glass formers appear to synergistically interact as aluminum-vanadium and zirconium-niobium, which are preferred combinations, while others appear to counteract each other as aluminum-zirconium, aluminum-niobium, vanadium-zirconium and vanadium-niobium.

w, the atomic percent of transition metal is about 60 to about 92. x, the atomic percent of total rare earth metals is from about 8 to about 40. y, the atomic percent of boron is from about traces to about 20. z, the atomic percent of the quench rate range broadening material, is a quench rate range broadening amount of the glass forming material. The content of glass forming material is generally above about one atomic percent and preferably above about two atomic percent, but also generally less than about ten atomic percent.

Hard magnetic properties arise from the interaction of boron, the transition metal, and the rare earth metal. With partial substitution of boron, the transition metal, or the rare earth metal, or any or all of the alloy constituents by the glass former, it is possible to provide processing advantages according to the method of this invention. Notwithstanding the presence of the glass formers, the amount of boron must be high enough to interact with the transition metal and rare earth metal, but not so high as to form non-magnetic phases or to render the alloy soft or even non-magnetic. Moreover, the amount of boron should not be so low as to fail to provide an operative, hard magnet. Within this range of boron composition, the glass former is added to enhance the quench rate range at which a high coercivity, high remanence, high energy product magnetic alloy is formed.

The invention further contemplates the method of forming the alloy. The alloy is formed by a rapid solidification process, i.e. a quench process, to form a hard magnet. In the melt spinning method of quenching molten metals, quench rate is expressed as the product of the rotational velocity of the chill wheel the radius of the chill wheel, and pi. This gives a linear velocity with respect to the molten metal effluent. At constant effluent geometry, effluent spacing, hydrostatic head, and melt temperature, quench rate is monotonic and approximately linear with chill surface linear velocity. For a melt spinner utilizing a 20 inch diameter copper clad chill wheel spaced 1 to 30 millimeters from a 0.2 to 2.0 millimeter diameter aperture with a 0.5 to 10 pounds per square inch head, a chill wheel velocity of 1000 revoltions per minute, i.e., a linear velocity of 1.32×10^3 cm/sec. The quench rate is above 0.5 x 10^5C per second, preferably above about 1 x 10^5C per second, and in a particularly preferred embodiment above about 10 x 10^5C per second. Molten compositions of transition metal-rare earth metal-boron exhibit a relatively sharp local maximum of e.g., coercivity, as a function of chill wheel velocity, with coercivity dropping off to 30 percent of peak value at chill wheel velocities of plus or minus 10 percent of the chill wheel velocity corresponding to peak coercivity. By way of contrast molten compositions of transition metal-rare earth metal-boron-aluminum exhibit a flat local maximum of, e.g., coercivity as a function of chill wheel velocity, with coercivity being 85 to 90 percent of peak value at chill wheel velocities of plus or minus 10 percent of the chill wheel velocity corresponding to peak coercivity, and 60 percent of peak value of at chill wheel velocities of plus or minus 20 percent of the chill wheel velocity corresponding to peak coercivity. As herein contemplated, a molten composition of transition metal, rare earth metal, boron, and glass former is quenched within a quench rate range to form a glassy, hard, magnetic material having optimal grain sizes. The method may optionally include post-quench annealing if a grain size above that obtained by the quenching is required.

The components of the magnetic alloy preferably obtained to 99.9 percent purity and particularly a preferred exemplification to 99.99 percent purity.

The precursor materials, that is, the transition metal, the rare earth metal, boron, and the quench rate range enhancing glass forming material are melted together in an inert atmosphere, for example, an argon helium atmosphere. Melting and remelting may be carried out several times in order to obtain substantially homogeneous alloy.

The substantially homogeneous alloy is discharged to a quenched surface to rapidly quench the material. The quench surface may be a rapidly moving inert surface, that is, a surface moving at a quench speed of about at least 300 centimeters per minute with respect to the molten alloy affluent. Preferably, the rapidly moving surface is a rapidly rotating inert surface such as a polished copper wheel rotating at an angular velocity so as to provide a linear velocity of above about 300 centimeters per second, preferably above about 1000 centimeters per second but less than about 5000 centimeters per second.

The following examples are illustrative of the method of this invention.

EXAMPLES

I. Preparation of the Alloys

Alloys of the examples were prepared by weighing out the appropriate constituents. The praesodymium was Morton Thiokol Alfa praesodymium, having a nominal purity of 99.99 percent. The neodymium was Research Chemicals Inc., neodymium, having a nominal purity of 99.9 percent. The boron was Morton Thiokol Alfa boron, having a nominal purity of 99.9 percent. The aluminum was Atlantic Equipment aluminum, having a nominal purity of 99.99 percent. The iron was Atlantic Equipment electrolytic iron, having a nominal purity of 99.999 percent.

The constituents were placed in a 19 mm o.d., 17 mm i.d. quartz crucible, and heated in an electric induction furnace under a purified argon atmosphere, whereby to form an ingot. The ingots were homogenized by repeated remelting.

II. Quenching

Quenching was carried out using an argon pressurized quartz crucible having an orifice on the bottom. The orifice was vertically spaced from a moving chill surface, i.e., a 20 inch diameter rotating, copper wheel. The molten metal was ejected through the orifice onto the copper chill wheel.

The crucible was purged with argon. Thereafter, a portion of the homogenized ingot was placed in the crucible, and the crucible was heated in an induction furnace. When the ingot was molten, the molten composition was ejected onto the rapicly rotating copper chill wheel. A thin ribbon was recovered.

III. Magnetization

Magnetization measurements were made using a vibrating sample magnetometer. The magnetometer was calibrated using a standard N.B.S. nickelsphere sample.

EXAMPLE I

Samples of $Fe_{82}B_6Pr_{12}$ and $Fe_{79}B_6Pr_{11.5}Al_{3.5}$ were prepared, quenched, and tested as described above. The following results were obtained:

Composition	$Fe_{82}B_6Pr_{12}$	$Fe_{79}B_6Pr_{11.5}Al_{3.5}$

Quench surface
velocity = 1596cm/sec
(600 rpm)

Energy product	.3 x 10^6 G-Oe
Remanence	2.95 x 10^3G
Coercive force	.87 x 10^3Oe

Quench surface
velocity = 1728cm/sec
(650 rpm)

Energy product	2.23 x 10^6G-Oe
Remanence	3.85 x 10^3G
Coercive force	2.40 x 10^3Oe

Quench surface
velocity = 1862cm/sec
(700 rpm)

Energy product	3.8 x 10^6 G-Oe, 1.8 x 10^6G-Oe	3.8 x 10^6G-Oe
Remanence	7.98 x 10^3G, 6.97 x 10^3G	5.73 x 10^3G
Coercive force	7.75 x 10^3Oe, .55 x 10^3Oe	4.3 x 10^3Oe

Quench surface
velocity = 1994cm/sec
(750 rpm)

Energy product		2.6 x 10^6G-Oe
Remanence	4.46 x 10^3G	
Coercive force		3.97 x 10^3Oe

EXAMPLE II

Samples of $Fe_{79}B_6Nd_{15}$ and $Fe_{77}B_6Nd_{15}Al_2$ were prepared, quenched, and tested as described above. The following results, shown graphically in Figure 2, were obtained:

Composition	$Fe_{79}B_6Nd_{15}$	$Fe_{77}B_6Nd_{15}Al_2$
Quench surface velocity = 2394cm/sec (900 rpm)		
Energy product	1.9×10^6G-Oe 9.9×10^6G-Oe	4.9×10^6G-Oe
Remanence	5.69×10^3G 7.44×10^3G	5.57×10^3G
Coercive force	1.04×10^4Oe 1.32×10^4Oe	1.21×10^4Oe
Quench surface velocity = 2660cm/sec (1000 rpm)		
Energy product	2.59×10^6G-Oe 9.0×10^6G-Oe	9.08×10^6G-Oe
Remanence	6.79×10^3G 7.09 x 13G	3.87×10^3G 6.7×10^3G
Coercive force	0.48×10^4Oe 1.32×10^4Oe	1.17×10^4Oe 1.21×10^4Oe

Quench surface velocity = 2926cm/sec (1100 rpm)		
Energy product	5.1×10^6 G-Oe	5.1×10^6 G-Oe 14.8×10^6 G-Oe
Remanence	4.71×10^3 G	5.81×10^3 G 8.8×10^3 G
Coercive force	4.17×10^3 Oe	1.13×10^4 Oe 1.24×10^4 Oe

While the invention has been described with respect to certain preferred exemplifications and embodiments thereof, it is not intended to limit the scope of protection thereby, but solely by the claims appended hereto.

CLAIMS

1. A hard magnetic material comprising:

(a) a transition metal chosen from the group consisting of iron, cobalt, nickel, manganese and mixtures thereof;

(b) a lanthanide chosen from the group consisting of praesodymium, neodymium, and mixtures thereof;

(c) boron;

characterized in that said hard magnetic material includes a quench rate range broadening amount of a glass forming additive chosen from the group consisting of aluminum, aluminum-vanadium, zirconium, and zirconium-niobium.

2. The hard magnetic material of Claim 1, wherein the transition metal is iron.

3. The hard magnetic material of Claim 1, wherein the glass forming additive is aluminum.

4. The hard magnetic material of Claim 3, wherein the aluminum content is from about 2 to about 10 atomic percent.

5. The hard magnetic alloy of Claim 4, wherein the alloy comprises about 8 to about 40 atomic percent lanthanide, about 2 to 10 atomic percent aluminum, up to about 20 percent boron, balance iron.

6. A method of forming the glassy, hard magnetic material of claim 1 characterized by:

(1) forming a molten composition of:

(a) a transition metal chosen from the group consisting of iron, cobalt, nickel, manganese, and mixtures thereof;

(b) a lanthanide chosen from the group consisting of praesodymium, neodymium, and mixtures thereof;

(c) boron; and

(d) a quench rate range broadening amount of a glass forming additive chosen from the group consisting of aluminum, aluminum-vanadium, zirconium, and zirconium-niobium; and

(2) quenching the molten composition within a quench rate range to form a glassy, hard magnetic material.

7. The method of Claim 6, wherein the transition metal is iron.

8. The method of Claim 6, wherein the glass forming additive is aluminum.

9. The method of Claim 8, wherein aluminum content is from about 2 to about 10 atomic percent.

10. The method of Claim 9, wherein the hard magnetic alloy comprises about 8 to about 40 atomic percent lanthanide, up to about 20 atomic percent boron, about 2 to 10 atomic percent aluminum, balance iron.

11. The method of Claim 6 comprising quenching the molten composition on a chill surface.

12. The method of Claim 11 comprising discharging the molten composition onto the chill surface.

13. The method of Claim 12, wherein the chill surface moves with respect to the molten composition.

FIG. 1

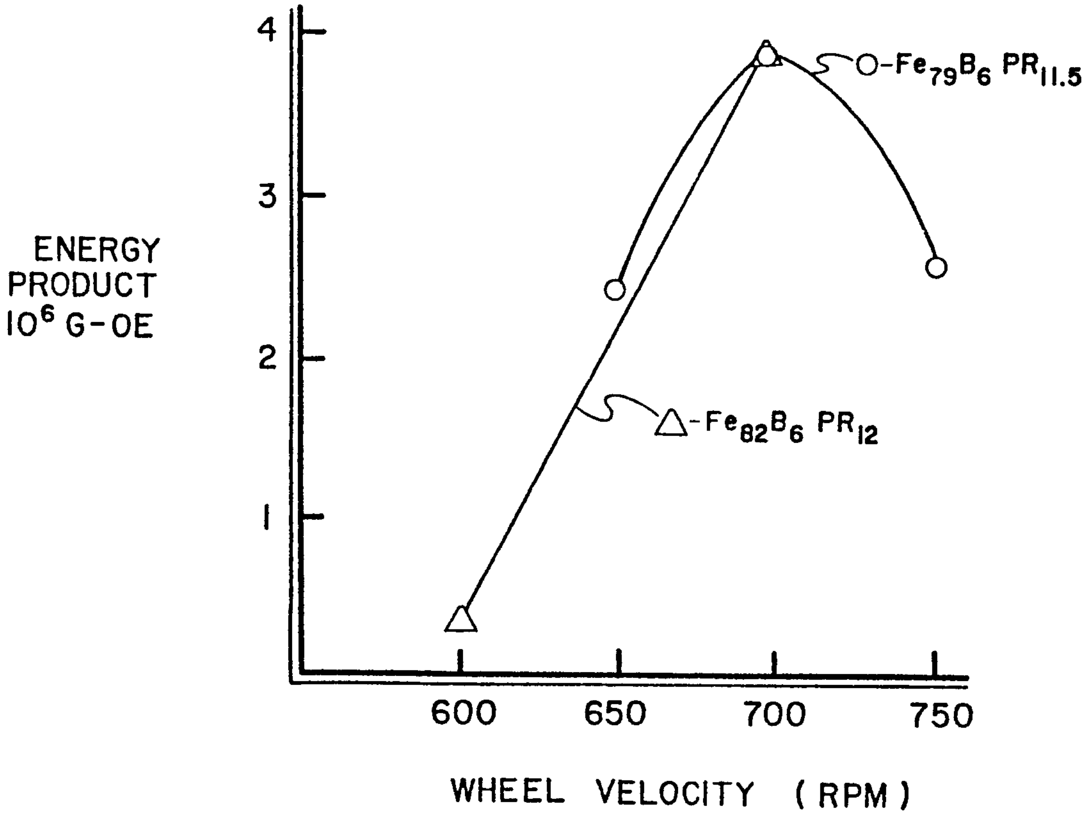
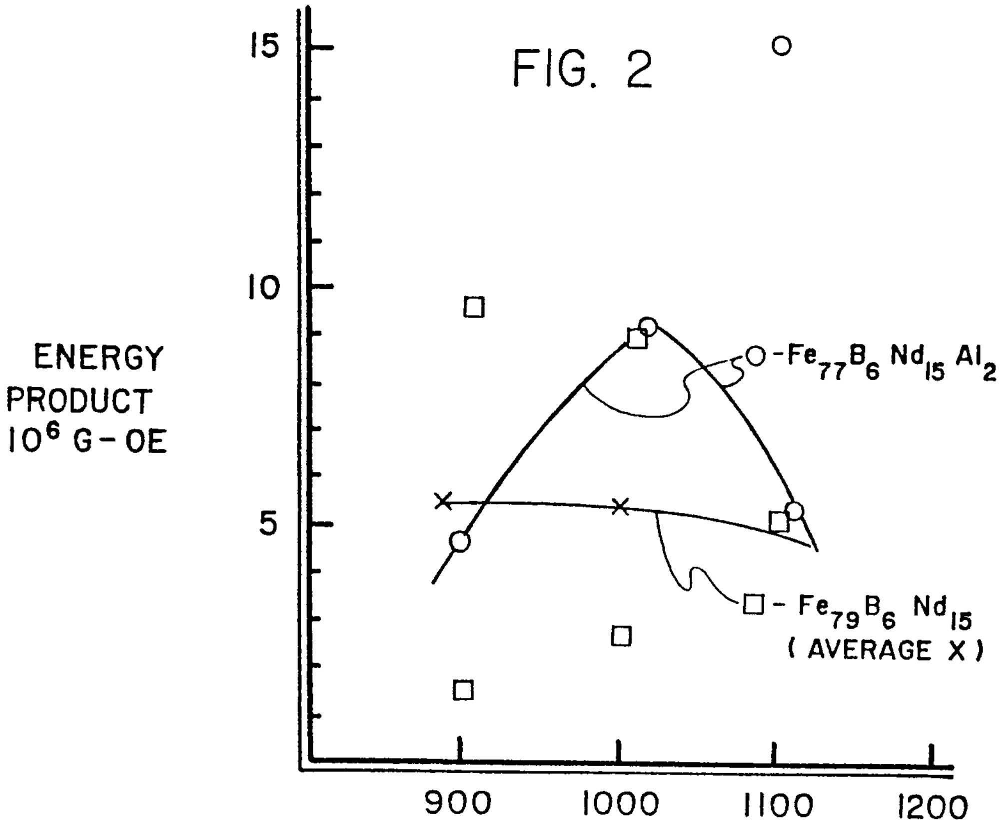

4
3
2
1
ENERGY PRODUCT 10^6 G-OE
○-$Fe_{79}B_6$ $PR_{11.5}$
△-$Fe_{82}B_6$ PR_{12}
600
650
700
750
WHEEL VELOCITY (RPM)

FIG. 2


15
10
5
ENERGY PRODUCT 10^6 G-OE
○-$Fe_{77}B_6$ Nd_{15} Al_2
☐- $Fe_{79}B_6$ Nd_{15}
(AVERAGE X)
900
1000
1100
1200

European Patent
Office

EUROPEAN SEARCH REPORT

0175222
Application number

EP 85111219.3

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 - 4 409 043 (KOON) * Abstract; claims 1-20 * --	1-5	H 01 F 1/04 C 22 C 38/00
D,A	US - A - 4 402 770 (KOON) * Abstract; claims 1-22; fig. 1 * --	1-5	
A	US - A - 4 419 148 (JIN) * Abstract; claims 1-8 * --	1-3,6	
A	US - A - 4 324 597 (KAMINO) * Abstract; claims 1-3 * --	1,6	
A	EP - A1 - 0 072 893 (ALLIED CORPORATION) * Abstract * --	1,6	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	US - A - 4 374 665 (KOON) * Totality * --	1-3	H 01 F 1/00 H 01 F 41/00 C 22 C 38/00 C 22 C 19/00 C 04 B 35/00
A	DE - A1 - 3 103 706 (SUMITOMO) * Abstract; claims 1-8 * ----	1-5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-12-1985	VAKIL

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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