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(54) Permanently magnetizable alloys, magnetic materials and permanent magnets comprising FeBR or (Fe,Co)BR (R=vave earth).

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Description

Field of the invention

The present invention relates to improvements in the temperature dependency of the magnetic properties of magnetic materials and permanent magnets based on Fe—B—R systems. In the present disclosure, R denotes rare earth elements inclusive of yttrium.

Background of the invention

Magnetic materials and permanent magnet materials are one of the important electric and electronic materials applied in an extensive range from various electrical appliances for domestic use to peripheral terminal devices of large-scaled computers. In view of recent needs for miniaturization and high efficiency of electric and electronic equipments, there has been an increasing demand for upgrading of permanent magnet materials and generally magnetic materials.

The permanent magnet materials developed yet include alnico, hard ferrite and samarium-cobalt (SmCo) base materials which are well-known and used in the art. Among these, alnico has a high residual magnetic flux density (hereinafter referred to Br) but a low coercive force (hereinafter referred to Hc), whereas hard ferrite has high Hc but low Br.

Advance in electronics has caused high integration and miniaturization of electric components. However, the magnetic circuits incorporated therein with alnico or hard ferrite increase inevitably in weight and volume, compared with other components. On the contrary, the SmCo base magnets meet a demand for miniaturization and high efficiency of electric circuits due to their high Br and Hc. However, samarium is rare natural resource, while cobalt should be included 50—60 wt% therein, and is also distributed at limited areas so that its supply is unstable.

Thus, it is desired to develop novel permanent magnet materials free from these drawbacks.

If it could be possible to use, as the main component for the rare earth elements R light rare earth elements that occur abundantly in ores without employing much cobalt, the rare earth magnets could be used abundantly and with less expense in a wider range. In an effort made to obtain such permanent magnet materials, R—Fe_2 base compounds, wherein R is at least one of the rare earth metals, have been investigated.

(1) Regarding the following explanations, it is to be noted that the unit $1G=10^{-4}$ T, that the unit 1Oe=0.0796k A/m and that the unit $1MGOe=7.96k\ J/m^3$.

(2) In JP—A—52—50598 rare earth cobalt magnets are disclosed obtained by compacting a powder of an intermetallic compound comprising 32—42 weight% of rare earth elements and 58—68 weight% of the sum of Co, Fe and Ni, to which at least one of Ta, V, B, Mn, Cr, Zr, Ti and Nb is added in an amount of no more than 2.0 weight% and sintering the resultant compact. As far as the examples are concerned this reference only deals with Sm—Co magnets.

In addition, JP—A—56—47538 discloses an improvement of the magnetic properties by adding Cr, Hf and B to the low rare earth (mainly Sm and/or Ce) cobalt type permanent magnet alloy.

A. E. Clark has discovered that sputtered amorphous $TbFe_2$ has an energy product of 29.5 MGOe at 4.2°K, and shows a coercive force Hc=3.4 kOe and a maximum energy product (BH)max=7 MGOe at room temperature upon heat-treating at 300—500°C. Reportedly, similar investigations on $SmFe_2$ indicated that 9.2 MGOe was reached at 77°K. However, these materials are all obtained by sputtering in the form of thin films that cannot be generally used as magnets, e.g., speakers or motors. It has further been reported that melt-quenched ribbons of PrFe base alloys show a coercive force Hc as high as 2.8 kOe.

(3) From Appl. Phys. Lett. *39* (10), 1981, pages 840—842, Koon et al amorphous and crystallized $(Fe_{0.82}B_{0.18})_{0.9}Tb_{0.05}La_{0.05}$ materials are known containing multiphase microstructures. With the melt-quenched amorphous ribbons H_c of 9 kOe was reached upon annealing at 627°C (Br=5 kG). However, (BH)max is then low due to the unsatisfactory loop squareness of magnetization curves. The magnetic properties are reported to result from binary systems Fe_3B and R_6Fe_{23} as can be seen from the document IEEE Trans. Magn., Vol. MAG-18, No. 6, 1982 of the same authors.

L. Kabacoff et al (J. Appl. Phys. *53* (3), 1982, pages 2255—2257), reported that certain binary meltspun Fe—Pr show H_c in the kOe order at room temperature. This article furthermore describes melt-quenched ribbons of $(Fe_{0.8}B_{0.2})_{1-x}Pr_x$(x=0 to 0.03 atomic ratio) in the amorphous state. Even though he can determine a separate phase resulting from crystallization within the amorphous material, no permanent magnetic properties were identified.

In EP—A—101552, an alloy is disclosed which contains at least one stable compound of the ternary Fe—B—R type having a tetragonal structure and being capable of being magnetized to become a permanent magnet at room temperature or above.

The non-prepublished EP—A—108474, as far as it is based on its earlier claimed priority, describes permanent magnetic materials with substantially elevated Curie temperature derived by spinning or quenching a melt of Fe, B and R having a substantially "amorphous to finely crystalline structure", which term refers to solids having X-ray diffraction patterns which do not indicate the presence of fully crystalline phases.

In JP—A—57—141901 a finely particulated permanent magnet powder is disclosed containing one or a combination of two or more transition metals for which, besides others, Fe and Co are listed, rare earth

elements, and one or a combination of two or more metalloid elements for which B, Si, P and C are listed having a high coercive force obtained by heat treating an amorphous alloy in the presence or absence of a magnetic field.

These melt-quenched ribbons or sputtered thin films are not any practical permanent magnets (bodies) that can be used as such. It would be practically impossible to obtain practical permanent magnets from these ribbons or thin films.

That is to say, no bulk permanent magnet bodies of any desired shape and size are obtainable from the conventional Fe—B—R base melt-quenched ribbons or R—Fe base sputtered thin films. Due to the unsatisfactory loop squareness (or rectangularity) of the demagnetization curves, the Fe—B—R base ribbons heretofore reported are not taken as the practical permanent magnet materials comparable with the conventional, ordinary magnets. Since both the sputtered thin films and the melt-quenched ribbons are magnetically isotropic by nature, it is indeed almost impossible to obtain therefrom magnetically anisotropic (hereinbelow referred to "anisotropic") permanent magnets for the practical purpose comparable to the conventional hard ferrite of SmCo magnets.

Summary of the disclosure

An essential object of the present invention is to provide novel magnetic materials and permanent magnets based on the fundamental composition of Fe—B—R having an improved temperature dependency of the magnetic properties and methods for making such.

Another object of the present invention is to provide novel practical permanent magnets and magnetic materials which do not share any disadvantages of the prior art magnetic materials hereinabove mentioned.

A further object of the present invention is to provide novel magnetic materials and permanent magnets having good temperature dependency and magnetic properties at room or elevated temperatures.

A still further object of the present invention is to provide novel magnetic materials and permanent magnets which can be formed into any desired shape and practical size.

A still further object of the present invention is to provide novel permanent magnets having magnetic anisotropy and excelling in both magnetic properties and mechanical strength.

A still further object of the present invention is to provide novel magnetic materials and permanent magnets in which as R use can effectively be made of rare earth element occurring abundantly in nature.

Other objects of the present invention will become apparent from the entire disclosure given herein.

The present invention provides an alloy comprising Fe—B—R according to claim 1 characterized in that it contains at least one stable compound of the Fe—Co—B—R type, which compound can be magnetized to become a permanent magnet at room temperature and above, wherein R stands for Nd and/or Pr.

The present invention provides an alloy of the Fe—B—R type according to claim 3, characterized in that it contains 8—30 at% of R, wherein R represents one or more rare earth elements including Y, 2—28 at% B, the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole material containing at least one compound of the Fe—Co—B—R type having a tetragonal crystal structure, a process of preparing such alloys according to claim 12 and the use of such alloys according to claim 17. Besides this, the invention provides a magnetic material according to claim 18, a sintered magnetic material of a special composition according to claim 25 and a process of making a magnetic material powder showing a tetragonal structure according to claim 26. Furthermore, the invention provides a permanent magnet material according to claim 28, a permanent magnetic material according to claim 32 comprising at least 50 vol.% of a phase comprising at least one Fe—Co—B—R type compound having a tetragonal structure, wherein R is at least one rare earth element including Y, an anisotropic permanent magnetic material of a special composition according to claim 40, and a process for producing an anisotropic permanent magnetic material according to claim 50, as well as a permanent magnet according to claim 56, a sintered permanent magnet according to claim 71 and a process of making the same according to claim 85.

The magnetic materials and permanent magnets according to the present invention are essentially formed of alloys comprising novel intermetallic compounds, and are crystalline, said intermetallic compounds being characterized at least by new Curie points Tc.

In the followings the term "percent" or "%" denotes the atomic percent (abridged as "at %") if not otherwise specified.

According to the first aspect of the present invention, there is provided a magnetic material comprising Fe, B, R (at least one of the rare earth elements including Y) and Co, and having its major phase formed of Fe—Co—B—R type compound that is of the substantially tetragonal system crystal structure.

According to the second aspect of the present invention, there is provided a sintered magnetic material having its major phase formed of a compound consisting essentially of, in atomic ratio, 8 to 30% of R (wherein R represents at least one of the rare earth elements including Y), 2 to 28% of B, no more than 50% of Co (except zero % of Co and the balance being Fe and impurities.

According to the third aspect of the present invention, there is provided a sintered magnetic material having a composition similar to that of the aforesaid sintered magnetic material, wherein the major phase is formed of an Fe—Co—B—R type compound that is of the substantially tetragonal system.

According to the fourth aspect of the present invention, there is provided a sintered permanent magnet

(an Fe—Co—B—R base permanent magnet) consisting essentially of, in atomic ratio, 8 to 30% of R (at least one of the rare earth elements including Y), 2 to 28% of B, no more than 50% of Co (except zero % of Co) and the balance being Fe and impurities. This magnet is anisotropic.

According to the fifth aspect of the present invention, there is provided a sintered anisotropic permanent magnet having a composition similar to that of the fourth permanent magnet, wherein the major phase is formed by an Fe—Co—B—R type compound that is of the substantially tetragonal system crystal structure.

Fe—Co—B—R base magnetic materials according to the 6th to 8th aspects of the present invention are obtained by adding to the first—third magnetic materials the following additional elements M, provided, however, that the additional elements M shall individually be added in amounts less than the values as specified below, and that, when two or more elements M are added, the total amount thereof shall be less than the upper limit of the element that is the largest, among the elements actually added (for instance, Ti, V and Nb are added, the sum of these must be no more than 12.5% in all):

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

Fe—B—R—Co base permanent magnets according to the 9th to and 10th aspects of the present invention are obtained by adding respectively to the 4th and 5th permanent magnets the aforesaid additional elements M on the same condition.

Due to the inclusion of Co, the invented magnetic materials and permanent magnets have a Curie point higher than that of the Fe—B—R type system or the Fe—B—R—M type system.

With the permanent magnets of the present invention, practically useful magnetic properties are obtained if the mean crystal grain size of the intermetallic compound is in a range of about 1 to about 100 µm for both the Fe—Co—B—R and Fe—Co—B—R—M systems.

Furthermore, the inventive permanent magnets can exhibit good magnetic properties by containing 1 vol.% or higher of nonmagnetic intermetallic compound phases.

The inventive magnetic materials are advantageous in that they can be obtained in the form of at least as-cast alloys, or powdery or granular alloys or sintered bodies in any desired shapes, and applied to magnetic recording media (such as magnetic recording tapes) as well as magnetic paints, thermosensitive materials and the like. Besides, the magnetic materials are useful as the intermediaries for the production of permanent magnets.

The magnetic materials and permanent magnets according to the present invention are superior in mechanical strength and machinability to the prior art alnico, R—Co type magnets, ferrite, etc., and have a high resistance against chipping-off on machining.

In the following the present invention will be elucidated with reference to the accompanying Drawings which, however, are being presented for illustrative purpose.

Brief description of the drawings

Fig. 1 is a graph showing relationship between the Curie point and the amount of Co of one embodiment of the present invention, with the atomic percent of Co as abscissa;

Fig. 2 is a graph showing the relationship between the amount of B and Br as well as iHc (kOe) of one embodiment of Fe—10Co—xB—15Nd, with the atomic percent of B as abscissa;

Fig. 3 is a graph showing the relationship between the amount of Nd and Br (kG) as well as iHc (kOe) of one embodiment of Fe—10Co—8B—xNd, with the atomic percent of Nd as abscissa;

Fig. 4 is a view showing the demagnetization curves of one embodiment of the present invention (1 is the initial magnetization curve and 2 the demagnetization curve), with $4\pi I$ (kG) as ordinate and a magnetic field H (kOe) as abscissa;

Fig. 5 is a graph showing the relationship between the amount of Co (abscissa) and the Curie point of one embodiment of the present invention;

Fig. 6 is a graph showing the demagnetization curves of one embodiment of the present invention, with a magnetic field H (kOe) as abscissa and $4\pi I$ (kG) as ordinate;

Figs. 7 to 9 are graphs showing the relationship between the amount of additional elements M and the residual magnetization Br (kG);

Fig. 10 is a graph showing the relationship between iHc and the mean crystal grain size D (log-scale abscissa in µm) of one embodiment of the present invention;

Fig. 11 is a graph showing the demagnetization curves of one embodiment of the present invention;

Fig. 12 is a Fe—B—R ternary system diagram showing compositional ranges corresponding to the maximum energy products (BH)max (MGOe) for one embodiment of an Fe—5Co—B—R system;

Fig. 13 is a graph showing the relationship between the amount of Cu, C, P and S (abscissa) and Br of one embodiment of the present invention;

Fig. 14 is an X-ray diffraction pattern of one embodiment of the invention;

Fig. 15 is a flow chart of the experimental procedures of powder X-ray analysis and demagnetization curve measurements; and

Fig. 16 is a graph plotting the values of samples *2 and 8 to 12 of Table 1.

Detailed description of the preferred embodiments

The present inventors have found magnetic materials and permanent magnets of the Fe—B—R system and the magnets comprised of magnetically anisotropic sintered bodies to be new high-performance permanent magnets without employing expensive Sm and Co, and have disclosed them in EP—A—101552. The Fe—B—R base permanent magnets contain Fe as the main component and light-rare earth elements as R, primarily Nd and Pr, which occur abundantly in nature, and contain no Co. Nonetheless, they are excellent in that they can show an energy product reaching as high as 25—35 MGOe or higher. The Fe—B—R base permanent magnets possess high characteristics at costs lower than those required in the case with the conventional alnico and rare earth-cobalt alloys. That is to say, they offer higher cost-performance and, hence, greater advantages as they stand.

As disclosed in the above Application, the Fe—B—R base permanent magnets have a Curie temperature of generally about 300°C and at most 370°C. The entire disclosure of said Application is herewith incorporated herein with reference thereto with respect to the Fe—B—R type magnets and magnetic materials. Such a Curie point is considerably low, compared with the Curie points amounting to about 800°C of the prior art alnico or R—Co base permanent magnets. Thus, the Fe—B—R base permanent magnets have their magnetic properties more dependent upon temperature, as compared with the alnico or R—Co base magnets, and are prone to deteriorate magnetically when used at elevated temperatures.

As mentioned above, the present invention has for its principal object to improve the temperature dependency of the magnetic properties of the Fe—B—R base magnets and generally magnetic materials. According to the present invention, this object is achieved by substituting part of Fe, a main component of the Fe—B—R base magnets, with Co so as to increase the Curie point of the resulting alloy. The results of researches have revealed that the Fe—B—R base magnets are suitably used in a usual range of not higher than 70°C, since the magnetic properties deteriorate at a temperature higher than about 100°C. As a result of various experiments and studies, it has thus been found that the substitution of Co for Fe is effective for improving the resistance to the temperature dependency of the Fe—B—R base permanent magnets and magnetic materials.

More specifically, the present invention provides permanent magnets comprised of anisotropic sintered bodies consisting essentially of, in atomic percent, 8 to 30% R (representing at least one of the rare earth elements including yttrium), 2 to 28% of B and the balance being Fe and inevitable impurities, in which part of Fe is substituted with Co to incorporate 50 at% or less of Co in the alloy compositions, whereby the temperature dependency of said permanent magnets are substantially improved to an extent comparable to those of the prior art alnico® and R—Co base alloys.

According to the present invention, the presence of Co does not only improve the temperature dependency of the Fe—B—R base permanent magnets, but also offer additional advantages. That is to say, it is possible to attain high magnetic properties through the use of light-rare earth elements such as Nd and Pr which occur abundantly in nature. Thus, the present Co-substituted Fe—B—R base magnets are superior to the existing R—Co base magnets from the standpoints of both natural resource and cost as well as magnetic properties.

It has further been revealed from extensive experiments that the resistance to the temperature dependency and the magnetic properties best-suited for permanent magnets are attained in the case where part of Fe is replaced by Co, the crystal structure is substantially of the tetragonal system, and the mean crystal grain size of the sintered body having a substantially tetragonal system crystal structure is in a certain range. Thus, the present invention makes it possible to ensure industrial production of high-performance sintered permanent magnets based on the Fe—Co—B—R system in a stable manner.

By measurements, it has been found that the Fe—Co—B—R base alloys have a high crystal magnetic anisotropy constant Ku and an anisotropic magnetic field Ha which compare favorably with those of the existing Sm—Co base magnets.

According to the theory of the single domain particles, magnetic substances having high anisotropy field Ha potentially provide fine particle type magnets with high-performance as is the case with the hard ferrite or SmCo base magnets. From such a viewpoint, sintered, fine particle type magnets were prepared with wide ranges of composition and varied crystal grain size after sintering to determine the permanent magnet properties thereof.

As a consequence, it has been found that the obtained magnet properties correlate closely with the mean crystal grain size after sintering. In general, the single magnetic domain, fine particle type magnets have magnetic walls which are formed within each of the particles, if the particles are large. For this reason, inversion of magnetization easily takes place due to shifting of the magnetic walls, resulting in a low Hc. On the contrary, if the particles are reduced in size to below a certain value, no magnetic walls are formed within the particles. For this reason, the inversion of magnetization proceeds only by rotation, resulting in high Hc. The critical size defining the single magnetic domain varies depending upon diverse materials, and has been throught to be about 0.01 μm for iron, about 1 μm for hard ferrite, and about 4 μm for SmCo.

The Hc of various materials increases around their critical size. In the Fe—Co—B—R base permanent magnets of the present invention, Hc of 1 kOe or higher is obtained when the mean crystal grain size ranges from 1 to 100 μm, while Hc of 4 kOe or higher is obtained in a range of 1.5 to 50 μm.

The permanent magnets according to the present invention are obtained as sintered bodies. Thus, the crystal grain size of the sintered body after sintering is of the primary concern. It has experimentally been ascertained that, in order to allow the Hc of the sintered compact to exceed 1 kOe, the mean crystal grain size should be no less than about 1 μm after sintering. In order to obtain sintered bodies having a smaller crystal grain size than this, still finer powders should be prepared prior to sintering. However, it is then believed that the Hc of the sintered bodies decrease considerably, since the fine powders of the Fe—Co—B—R alloys are susceptible to oxidation, the influence of distortion applied upon the fine particles increases, superparamagnetic substances rather than ferromagnetic substances are obtained when the grain size is excessively reduced, or the like. When the crystal grain size exceeds 100 μm, the obtained particles are not single magnetic domain particles, and include magnetic walls therein, so that the inversion of magnetization easily takes place, thus leading to a drop in Hc. A grain size of no more than 100 μm is required to obtain Hc of no less than 1 kOe. Particular preference is given to a range of 1.5 to 50 μm, within which Hc of 4 kOe or higher is attained.

It should be noted that the Fe—Co—B—R—M base alloys to be discussed later also exhibit the magnetic properties useful for permanent magnets, when the mean crystal grain size is between about 1 and about 100 μm, preferably 1.5 and 50 μm.

It is generally observed that, as the amount of Co incorporated in Fe-alloys increases, some Fe alloys increase in Curie point (Tc), while another decrease in that point. For this reason, the substitution of Fe with Co generally causes complicated results which are almost unexpected. As an example, reference is made to the substitution of Fe in RFe_3 compounds with Co. As the amount of Co increases, Tc first increases and peaks substantially at a point where a half of the Fe is replaced by Co, say, $R(Fe_{0.5}Co_{0.5})_3$ is obtained, and thereafter decreases. In the case of Fe_2B alloys, Tc decreases with certain gradient by the substitution of Fe with Co.

According to the present invention, it has been noted that, as illustrated in Fig. 1, Tc increases with increases in the amount of Co, when Fe of the Fe—B—R system is substituted with Co. Parallel tendencies have been observed in all the Fe—B—R type alloys regardless of the type of R. Even a slight amount of Co is effective for the increase in Tc and, as will be seen from a (77—x)Fe—xCo—8B—15Nd alloy shown as an example in Fig. 1, it is possible to obtain alloys having any desired Tc between about 310 and about 750°C by regulation of x. In the Co-substituted Fe—B—R base permanent magnets according to the present invention, the total composition of B, R and (Fe plus Co) is essentially identical with that of the Fe—B—R base alloys (without Co).

Boron (B) shall be used on the one hand in an amount no less than 2% so as to meet a coercive force of 1 kOe or higher and, on the other hand, in an amount of not higher than 28% so as to exceed the residual magnetic flux density Br of about 4 kG of hard ferrite. R shall be used on the one hand in an amount no less than 8% so as to obtain a coercive force of 1 kOe or higher and, on the other hand, in an amount of 30% or less since it is otherwise easy to burn, incurs difficulties in handling and preparation, and is expensive.

The present invention offers an advantage in that less expensive light-rare earth element occurring abundantly in nature can be used as R since Sm is not necessarily requisite nor necessarily requisite as a main component.

The rare earth elements used in the magnetic materials and the permanent magnets according to the present invention include light- and heavy-rare earth elements inclusive of Y, and may be applied alone or in combination. Namely, R includes Nd, Pr, La, Ce, Tb, Dy, Ho, Er, Eu, Sm, Gd, Pm, Tm, Yb, Lu and Y. Preferably, the light rare earth elements amount to no less than 50 at% of the overall rare earth elements R, and particular preference is given to Nd and/or Pr. More preferably Nd and/or Pr amounts to no less than 50 at% of the overall R. Usually, the use of one rare earth element will suffice, but, practically, mixtures of two or more rare earth elements such as mischmetal, didymium, etc. may be used due to their ease in availability, Sm, Y, La, Ce, Gd and the like may be used in combination with other rare earth elements such as Nd, Pr, etc. These rare earth elements R are not always pure rare earth elements and, hence, may contain impurities which are inevitably entrained in the production process, as long as they are technically available.

Boron represented by B may be pure boron or boron present as ferroboron, and those containing as impurities Al, Si, C etc. may be used.

Having a composition of 8—30 at% R, 2—28 at% B, 50 at% or less Co, and the balance Fe with the substantially tetragonal system crystal structure after sintering and a mean crystal grain size of 1—100 μm, the permanent magnets according to the present invention have magnetic properties such as coercive force Hc of ≥1 kOe, and residual magnetic flux density Br of ≥4 kG, and provide a maximum energy product (BH)max value which is at least equivalent or superior to the hard ferrite (ferrite being up to 4 MGOe). Due to the presence of Co in an amount of 5% or more the temperature coefficient of Br is about 0.1%/°C or less. If R ranges from 12 to 24%, and B from 3 to 27%, (BH)max≥ about 7 MGOe is obtainable so far as R and B concern.

When the light rare earth elements are mainly used as R (i.e., those elements amount to 50 at% or higher of the overall R) and a composition is applied of 12—24 (preferably 12—20) at% R, 4—24 at% B,

5—45 at% Co, with the balance being Fe, maximum energy product (BH)max of ≥10 MGOe and said thermal coefficient of Br as above are attained. These ranges are more preferable, and (BH)max reaches 33 MGOe or higher.

Referring to the Fe—5Co—B—R system for instance, the ranges surrounded with contour lines of (BH)max 10, 20, 30 and 33 MGOe in Fig. 12 define the respective energy products. The Fe—20Co—B—R system can provide substantially the same results.

Compared with the Fe—B—R ternary magnets, the Co-containing Fe—B—R base magnets of the present invention have better resistance against the temperature dependency, substantially equivalent Br, equivalent or slightly less iHc, and equivalent or higher (BH)max since the loop squareness or rectangularity is improved due to the presence of Co.

Since Co has a corrosion resistance higher than Fe, it is possible to afford corrosion resistance to the Fe—B—R base magnets by incorporation of Co. Particularly, oxidation resistance will simplify the handling of the powdery materials and for the final powdery products.

As stated in the foregoing, the present invention provides embodiments of magnetic materials and permanent magnets which comprise 8 to 30 at % R (R representing at least one of rare earth element including yttrium), 2 to 28 at% B, 50 at% or less Co (except that the amount of Co is zero), and the balance being Fe and impurities which are inevitably entrained in the process of production (referred to "Fe—Co—B—R type".

The present invention provides further embodiments which contain one or more additional elements M selected from the group given below in the amounts of no more than the values specified below wherein when two or more elements of M are contained, the sum of M is no more than the maximum value among the values specified below of said elements M actually added and the amount of M is more than zero:

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

The incorporation of the additional elements M enhances Hc resulting in an improved loop squareness.

The typical impurities contained in magnetic materials or magnets include Cu, S, C, P, O and may be present in total up to 4,0, preferably 3.0, at%. Above the upper limits, no energy product of 4 MGOe is obtained, so that such magnets as contemplated in the present invention are not obtained (see Fig. 13). With respect to Ca, Mg and Si, they are allowed to exist each in an amount up to about 8 at%, preferably with the proviso that their total amount shall not exceed about 8 at%. It is noted that, although Si has effect upon increases in Curie point, its amount is preferably about 5 at% or less, since iHc decreases sharply in an amount exceeding 5 at%. In some cases, Ca and Mg may abundantly be contained in R raw materials such as commercially available Neodymium or the like.

Iron as a starting material for instance includes following impurities (by wt%) not exceeding the values below: 0.03 C, 0.6 Si, 0.6 Mn, 0.5 P, 0.02 S, 0.07 Cr, 0.05 Ni, 0.06 Cu, 0.05 Al, 0.05 O_2 and 0.003 N_2.

Electrolytic iron generally with impurities as above mentioned of 0.005 wt% or less is available.

Impurities included in starting ferroboron (19—13% B) alloys are not exceeding the values below, by wt%: 0.1 C, 2.0 Si, 10.0 Al, etc.

Starting neodymium material includes impurities, e.g., other rare earth element such as La, Ce, Pr and Sm; Ca, Mg, Ti, Al, O, C or the like; and further Fe, Cl, F or Mn depending upon the refining process.

The permanent magnets according to the present invention are prepared by a so-called powder metallurgical process, i.e., sintering, and can be formed into any desired shape and size, as already mentioned. However, desired practical permanent magnets (bodies) were not obtained by such a melt-quenching process as applied in the preparation of amorphous thin film alloys, resulting in no practical coercive force at all.

On the other hand, no desired magnetic properties (particularly coercive force) were again obtained at all by melting, casting and aging used in the production of alnico magnets, etc., The reason is presumed to be that crystals having a coarser grain size and a nonuniform composition are obtained. Other various techniques have been attempted, but none have given any results as contemplated.

In accordance with the present invention, however, practical permanent magnets (bodies) of any desired shape are obtained by forming and sintering powder alloys, which magnets have good magnetic properties and mechanical strength. For instance, the powder alloys are obtainable by melting, casting and grinding or pulverization.

The sintered bodies can be used in the as-sintered state as useful permanent magnets, and may of course be subjected to aging as is the case in the conventional magnets.

The foregoing discussions also hold for both the Fe—Co—B—R system and the Fe—Co—B—R—M system.

Preparation of magnetic materials

Typically, the magnetic materials of the present invention may be prepared by the process forming the previous stage of the powder metallurgical process for the preparation of the permanent magnets of the present invention. For example, various elemental metals are melted and cast into alloys having a tetragonal system crystal structure, which are then finely ground into fine powders.

As a starting material use may be made of the powdery rare earth oxide R_2O_3 (a raw material for R). This may be heated with powdery Fe, powdery Co, powdery FeB and a reducing agent (Ca, etc) for direct reduction. The resultant powder alloys show a tetragonal system as well.

The powder alloys can further be sintered into magnetic materials. This is true for both the Fe—Co—B—R base and the Fe—Co—B—R—M base magnetic materials.

The Fe—Co—B—R base magnets of the present invention will now be explained with reference to the Examples, which are given for the purpose of illustration alone, and are not intended to limit the invention.

Fig. 1 typically illustrates changes in Curie point Tc of 77Fe—8B—15Nd wherein part of Fe is substituted with Co(x), and (77—x)Fe—xCo—8B—15Nd wherein x varies from 0 to 77. The samples were prepared in the following steps.

(1) Alloys were melted by high-frequency melting-and cast in a water-cooled copper mold. As the starting materials for Fe, B and R use was made of, by weight ratio for the purity, 99.9% electrolytic iron, ferroboron alloys of 19.38% B, 5.32% Al, 0.74% Si, 0.03% C and the balance Fe, and a rare earth element or elements having a purity of 99.7% or higher with the impurities being mainly other rare earth elements, respectively. As Co, electrolytic Co having a purity of 99.9% was used.

(2) Pulverization: The castings were coarsely ground in a stamp mill until they passed through a 0.42 mm (35-mesh) sieve, and then were finely pulverized in a ball mill for 3 hours to 3—10 µm.

(3) The resultant powders were oriented in a magnetic field of 10 kOe and compacted under a pressure of 14.71×10^7 Pa (1.5 t/cm^2).

(4) The resultant compacts were sintered at 1000—1200°C for about one hour in an argon atmosphere and, thereafter, allowed to cool.

Blocks weighing about 0.1 g were obtained from the sintered bodies by cutting, and measured on their Curie points using a vibrating sample magnetometer in the following manner. A magnetic field of 10 kOe was applied to the samples, and changes in 4πI depending upon temperature were determined in a temperature range from 250°C to 800°C. A temperature at which 4πI reduced virtually to zero was taken as Curie point Tc.

In the above-mentioned systems, Tc increased rapidly with the increase in the amount of Co replaced for Fe, and exceeded 600°C in Co amounts of no less than 30%.

In the permanent magnets, increases in Tc are generally considered to be the most important factor for reducing the changes in the magnetic properties depending upon temperature. To ascertain this point, a number of permanent magnet samples as tabulated in Table 1 were prepared according to the procedures as applied for the preparation of those used in Tc measurements to determine the temperature dependency of Br.

(5) The changes in Br depending upon temperature were measured in the following manner. Magnetization curves are obtained at 25°C, 60°C and 100°C, respectively, using a BH tracer, and the changes in Br at between 25 and 60°C and between 60 and 100°C were averaged. Table 1 shows the thermal coefficient of Br and the measurement results of magnetization curves at 25°C, which were obtained of various Fe—B—R and Fe—Co—B—R base magnets.

From Table 1, it is evident that the changes in Br depending upon temperature are reduced by incorporation of Co into the Fe—B—R base magnets. Namely, thermal coefficients of about 0.1%/°C or less are obtained if Co is 5% or more.

Table 1 also shows the magnetic properties of the respective samples at room temperature.

In most of the compositions, iHc generally decreases due to the Co substitution, but (BH)max increases due to the improved loop rectangularity of the magnetization curves. However, iHc decreases if the amount of Co increases from 25 to 50% finally reaching about the order of 1.5 kOe. Therefore the amount of Co shall be no higher than 50% so as to obtain iHc≥1 kOe suitable for permanent magnets.

From Table 1 and Fig. 1 the relationship between the Co amount and the magnetic properties is apparent. Namely, even a small amount of Co is correspondingly effective for the improvement of Tc. In a range of 25% or less Co, other magnetic properties (particularly, the energy product) are substantially not affected. (See, samples *2, and 8—12 of Table 1). If Co exceeds 25%, (BH)max also decreases.

The reasons already given in connection with the upper and lower limits of B and the lower limit of R will be confirmed from Table 1, Fig. 2 and Fig. 3.

TABLE 1

No.	Compositions (at%)	Thermal coefficient of Br (%/°C)	iHc(kOe)*	Br(kG)*	(BH)max* (MGOe)
*1	Fe—2B—15Nd	0.14	1.0	9.6	4.0
*2	Fe—8B—15Nd	0.14	7.3	12.1	32.1
*3	Fe—17B—15Nd	0.15	7.6	8.7	17.6
*4	Fe—17B—30Nd	0.16	14.8	4.5	4.2
*5	Fe—20Co—15Nd	—	0	0	0
*6	Fe—10Co—19B—5Pr	—	0	0	0
*7	Fe—60Co—8B—15Nd	0.05	0.8	8.2	3.5
8	Fe—10Co—8B—15Nd	0.09	5.2	12.0	33.0
9	Fe—20Co—8B—15Nd	0.07	8.8	12.0	33.1
10	Fe—30Co—8B—15Nd	0.06	4.5	12.0	24.2
11	Fe—40Co—8B—15Nd	0.06	3.1	11.8	17.5
12	Fe—50Co—8B—15Nd	0.06	1.5	8.7	7.7
13	Fe—15Co—17B—15Nd	0.10	7.4	8.9	18.2
14	Fe—30Co—17B—15Nd	0.08	6.3	8.6	16.5
15	Fe—20Co—8B—10Tb—3Ce	0.08	6.1	6.3	8.8
16	Fe—20Co—12B—14Pr	0.07	7.2	10.5	25.0
17	Fe—15Co—17B—8Nd—5Pr	0.08	7.4	8.3	15.7
18	Fe—20Co—11B—3Sm—13Pr	0.07	6.5	9.6	17.5
19	Fe—10Co—15B—8Nd—7Y	0.09	6.0	7.5	11.0
20	Fe—10Co—14B—7Nd—3Pr—5La	0.09	6.8	7.8	14.2
21	Fe—30Co—17B—28Nd	0.09	12.2	4.6	4.7

N.B.: prefix * refers to comparative tests
*1kOe=79.6 kh/m
1kG=10^{-1} Tesla
1MGOe=7.96 k · J/m^3
Fe=balance Fe

As a typical embodiment of the sintered magnetic magnets of the Fe—Co—B—R system in which part of Fe is substituted with Co, Fig. 4 shows an initial magnetization curve 1 for 57Fe—20Co—8B—15Nd at room temperature.

The initial magnetization curve 1 rises steeply in a low magnetic field, and reaches saturation. The demagnetization curve 2 shows very high loop rectangularity, which indicates that the magnet is a typical high-performance anisotropic magnet. From the form of the initial magnetization curve 1, it is thought that this magnet is a so-called nucleation type permanent magnet since the SmCo type magnets of the nucleation type shows an analogous curve, wherein the coercive force of which is determined by nucleation occurring in the inverted magnetic domain. The high loop rectangularity of the demagnetization

curve 2 indicates that this magnet is a typical high-performance anisotropic magnet. Other samples according to the present invention set forth in Table 1 all showed magnetization curves similar to that of Fig. 4.

A number of magnets using primarily as R light-rare earth elements such as Nd, Pr, etc., are shown in Table 1, from which it is noted that they possess high magnetic properties, and have their temperature dependency further improved by the substitution of Fe with Co. It is also noted that the use of a mixture of two or more rare earth element as R is also useful.

Permanent magnet samples of Fe—Co—B—R—M alloys containing as M one or two additional elements were prepared in a manner similar to that applied for the preparation of the Fe—Co—B—R base magnets.

The additional elements M used were Ti, Mo, Bi, Mn, Sb, Ni, Sn, Ge and Ta each having a purity of 99%, by weight so far as the purity concerns as hereinbelow, W having a purity of 98%, Al having a purity of 99.9%, and Hf having a purity of 95%. As V ferrovanadium containing 81.2% of V; as Nb ferroniobium containing 67.6% of Nb; as Cr ferrochromium containing 61.9% of Cr; and as Zr ferrozirconium containing 75.5% of Zr were used, respectively.

A close examination of the samples having a variety of compositions was carried out by the measurement of iHc, Br, (BH)max, etc. As a result, it has been found that, in quintinary or multicomponent systems based on Fe—Co—B—R—M (wherein M represents one or two or more additional elements), there is a certain region in which high permanent magnet properties are developed.

Table 2 shows the maximum energy product (BH)max, which is the most important factor of the permanent magnet properties, of typical samples. In Table 2, Fe is the balance.

From Table 2, it has been appreciated that the Fe—Co—B—R—M base magnets have high energy product of 10 MGOe or greater over a wide compositional range.

This table mainly enumerates the Examples of alloys containing Nd and/or Pr, but any of 15 rare earth element (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) give rise to increase in (BH)max. However, the alloys containing Nd and Pr according to the present invention are more favorable than those containing as the main materials other rarer rare earth element (Sm, Y and heavy-rare element), partly because Nd and Pr occur relatively abundantly in rare earth ores, and especially because no applications of Nd in larger amounts have been found.

Also in the Fe—Co—B—R—M alloys, Co has no noticeable influence upon (BH)max, when it is added in an amount of 25% or less and Co contributes to the increase in the Curie points with the increasing Co amount as is the case for the Fe—Co—B—R alloys. For instance, comparisons of Sample Nos. 48 with 50, 58 with 60, and 68 with 70 reveal that a compositional difference in the amount of Co (1 to 10 Co) between these alloys causes no noticeable difference in (BH)max. Fig. 5 shows the relationship between the Curie point and the amount of Co (by at%) of the Fe—Co—B—R—M alloys wherein M is V, Nb, Zr and Cr, and indicates that the Curie point increases with increase in the amount of Co, but the addition of M gives rise to substantially no remarkable change in the Curie point.

Parallel tendencies have been observed in the Fe—Co—B—R—M fundamental alloys regardless of the type of R. Even a slight amount of Co, e.g., 1% is effective for Tc increases, and it is possible to obtain alloys having any desired Tc between about 310°C and about 750°C by varying x, as will be evident from the (76—x) Fe—xCo—8B—15Nd—1M system exemplified in Fig. 5.

Accordingly, it has turned out that with respect to the Fe—Co—B—R—M system the relationships between the Co amount and the magnetic properties, and between the ranges of B and R and the magnetic properties are established analogously to the Fe—Co—B—R system previously discussed, provided that the effect of the additional elements M acts additionally.

The Fe—Co—B—R—M magnets according to the present invention have Curie points higher than the Fe—B—R—M magnets without Co.

In the Fe—Co—B—R—M magnets, most of M have an effect upon increases in Hc. Fig. 6 shows the demagnetization curves of the typical Examples of the Fe—Co—B—R—M magnets and M-free Fe—Co—B—R magnets given for the purpose of comparison. In this figure, reference numerals 1 to 3 denote the demagnetization curves of a M-free magnet, a Nb-containing magnet (Table 1 No. 3) and a W-containing magnet (Table 1 No. 83), respectively.

An increase in Hc due to the addition of M provides an increased stability and wide applicability of the permanent magnets. However, the greater the amount of M, the lower the Br and (BH)max will be, due to the fact that they are nonmagnetic materials (except Ni). Since permanent magnets having slightly reduced (BH)max but high Hc have recently been often required in certain fields, the addition of M is very useful, however, provided that (BH)max is at least 4 MGOe.

To ascertain the effect of M upon Br, Br was measured in varied amounts of M. The results are summarized in Figs. 7 to 9. As seen from Figs. 7 to 9, the upper limits of the additional elements M (Ti, Zr, Hf, V, Ta, Nb, Cr, W, Mo, Sb, Sn, Ge and Al) other than Bi, Ni, and Mn may be chosen such that Br is at least equivalent to about 4 kG of hard ferrite. A preferable range in view of Br should be appreciated from Figs. 7 and 9 by defining the Br range into 6.5 kG, 8 kG, 10 kG or the like stages.

Based on these figures, the upper limits of the amounts of additional elements M are fixed at the following values at or below which (BH)max is at least equivalent or superior to about 4 MGOe of hard ferrite:

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

When two or more elements M are employed, the resulting characteristic curve will be depicted between the characteristic curves of the individual elements in Figs. 7 to 9. Thus each amount of the individual elements M are within each aforesaid range, and the total amount thereof is no more than the maximum values among the values specified for the individual elements which are actually added and present in a system. For instance, if Ti, V and Nb are added the total amount of these must be no more than 12.5% in all.

A more preferable range for the amount of M is determined from a range of (BH)max within which it exceeds 10 MGOe of the highest grade alnico. In order that the (BH)max is no less than 10 MGOe, Br of 6.5 kG or higher is required.

From Figs. 7 to 9, the upper limits of the amounts of M are preferably defined at the following values:

4.0% Ti,	6.5% Ni,	5.0% Bi,
8.0% V,	10.5% Nb,	9.5% Ta,
6.5% Cr,	7.5% Mo,	7.5% W,
6.0% Mn,	7.5% Al,	1.5% Sb,
5.5% Ge,	2.5% Sn,	4.5% Zr,
and 4.5% Hf		

wherein two or more additional elements M are used, the preferable ranges for M are obtained when the individual elements are no higher than the aforesaid upper limits, and the total amount thereof is no higher than the maximum values among the values allowed for the individual pertinent elements which are actually added and present.

Within the upper limits of M, when the Fe—Co—B—R base system preferably comprises 4 to 24% of B, 12 to 24 (preferably 12—20)% of R (light-rare earth elements, primarily Nd and/or Pr), and the balance being the given amounts of Fe and Co, (BH)max of 10 MGOe or higher is obtained within the preferable ranges of the additional elements M, and reaches or exceeds the (BH)max level of hard ferrite within the upper limit of M.

Even when the Fe—Co—B—R base system departs from the above-mentioned preferable range, (BH)max exceeding that of hard ferrite is obtained, if the additional element M are in the above-mentioned preferable range. According to more preferable embodiments of the present invention, the permanent magnets have (BH)max of 15, 20, 25, 30 and even 33 MGOe or higher.

In general, the more the amount of M, the lower the Br; however, most elements of M serve to increase iHc. Thus, (BH)max assumes a value practically similar to that obtained with the case where no M is applied, through the addition of an appropriate amount of M, and may reach at most 33 MGOe or higher. The increase in coercive force serves to stabilize the magnetic properties, so that permanent magnets are obtained which are practically very stable and have a high energy product.

If large amounts of Mn and Ni are incorporated, iHc will decrease; there is only slight decrease in Br due to the fact that Ni is a ferromagnetic element (see Fig. 8). Therefore, the upper limit of Ni is 8%, preferably 6.5%, in view of Hc.

The effect of Mn upon decrease in Br is not strong but larger than is the case with Ni. Thus, the upper limit of Mn is 8%, preferably 6%, in view of iHc.

With respect to Bi, its upper limit shall be 5%, since any alloys having a Bi content exceeding 5% cannot practically be produced due to extremely high vapor pressure.

TABLE 2—1

Sample No.	Compositions (at%)	(BH)max (MGOe)*
1	Fe—2Co—8B—15Nd—2Al	29.5
2	Fe—5Co—8B—15Nd—0.5Al	35.2
3	Fe—5Co—17B—15Nd—4Al	11.5
4	Fe—10Co—17B—17Nd—0.5Al	12.7
5	Fe—10Co—8B—15Nd—1Al	31.6
6	Fe—20Co—8B—12Nd—0.5Al	23.0
7	Fe—35Co—6B—24Nd—5Al	10.5
8	Fe—5Co—17B—15Nd—2.5Ti	11.0
9	Fe—10Co—13B—14Nd—2Ti	18.1
10	Fe—20Co—12B—16Nd—1Ti	22.1
11	Fe—35Co—8B—15Nd—0.5Ti	20.5
12	Fe—35Co—6B—25Nd—0.3Ti	12.4
13	Fe—2Co—8B—16Nd—2V	24.0
14	Fe—5Co—6B—15Nd—0.3V	31.1
15	Fe—5Co—8B—14Nd—6V	16.3
16	Fe—10Co—17B—15Nd—1V	14.8
17	Fe—20Co—8B—12Nd—0.5V	21.6
18	Fe—20Co—15B—17Nd—1V	17.2
19	Fe—35Co—6B—25Nd—1V	15.2
20	Fe—2Co—8B—16Nd—2Cr	22.4

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—2

Sample No.	Compositions (at%)	(BH)max (MGOe)*
21	Fe—5Co—20B—15Nd—0.5Cr	12.0
22	Fe—5Co—7B—14Nd—4Cr	18.1
23	Fe—10Co—8B—15Nd—0.5Cr	32.7
24	Fe—10Co—17B—12Nd—0.2Cr	17.2
25	Fe—20Co—8B—15Nd—0.5Cr	31.7
26	Fe—20Co—8B—15Nd—1Cr	30.5
27	Fe—35Co—6B—25Nd—1Cr	14.7
28	Fe—2Co—8B—13Nd—0.5Mn	30.1
29	Fe—5Co—7B—14Nd—1Mn	25.1
30	Fe—10Co—9B—15Nd—1Mn	21.0
31	Fe—20Co—8B—16Nd—1Mn	24.9
32	Fe—20Co—16B—14Nd—0.2Mn	17.1
33	Fe—20Co—7B—14Nd—4Mn	14.5
34	Fe—35Co—9B—20Nd—1Mn	14.2
35	Fe—5Co—8B—15Nd—1Zr	32.3
36	Fe—10Co—9B—14Nd—1Zr	32.2
37	Fe—10Co—17B—16Nd—6Zr	12.9
38	Fe—10Co—6B—20Nd—0.5Zr	18.1
39	Fe—20Co—8B—12Nd—0.5Zr	25.6
40	Fe—20Co—20B—14Nd—0.3Zr	13.2

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—3

Sample No.	Compositions (at%)	(BH)max (MGOe)*
41	Fe—35Co—6B—20Nd—1Zr	16.0
42	Fe—5Co—8B—15Nd—1Hf	32.2
43	Fe—10Co—9B—14Nd—1Hf	32.0
44	Fe—10Co—17B—16Nd—6Hf	13.1
45	Fe—20Co—8B—12Nd—0.5Hf	17.9
46	Fe—20Co—20B—14Nd—0.3Hf	25.2
47	Fe—35Co—6B—20Nd—1Hf	15.7
48	Fe—1Co—8B—16Nd—0.5Nb	33.3
49	Fe—2Co—8B—14Nd—1Nb	35.5
50	Fe—10Co—8B—15Nd—0.5Nb	33.4
51	Fe—10Co—7B—14Nd—1Nb	33.1
52	Fe—20Co—9B—14Nd—0.5Nb	33.1
53	Fe—20Co—8B—15Nd—1Nb	31.3
54	Fe—20Co—17B—13Nd—6Nb	10.7
55	Fe—20Co—8B—15Nd—8Nb	14.8
56	Fe—20Co—6B—25Nd—1Nb	16.8
57	Fe—35Co—7B—15Nd—3Nb	21.6
58	Fe—1Co—8B—16Nd—0.5Ta	32.5
59	Fe—2Co—8B—14Nd—1Ta	31.5
60	Fe—10Co—8B—15Nd—0.5Ta	32.3

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—4

Sample No.	Compositions (at%)	(BH)max (MGOe)*
61	Fe—10Co—7B—14Nd—1Ta	31.2
62	Fe—20Co—9B—14Nd—0.5Ta	31.5
63	Fe—20Co—7B—16Nd—1Ta	30.3
64	Fe—20Co—15B—13Nd—6Ta	10.5
65	Fe—20Co—8B—15Nd—8Ta	11.6
66	Fe—20Co—6B—25Nd—1Ta	15.6
67	Fe—35Co—7B—15Nd—3Ta	20.0
68	Fe—1Co—8B—15Nd—0.5Mo	35.1
69	Fe—2Co—8B—15Nd—1Mo	34.7
70	Fe—10Co—8B—16Nd—0.5Mo	33.0
71	Fe—10Co—7B—14Nd—1Mo	31.0
72	Fe—20Co—9B—14Nd—0.5Mo	31.0
73	Fe—20Co—6B—16Nd—1Mo	32.2
74	Fe—20Co—17B—13Nd—2Mo	14.6
75	Fe—20Co—8B—13Nd—6Mo	14.3
76	Fe—20Co—6B—25Nd—1Mo	16.4
77	Fe—35Co—7B—15Nd—3Mo	18.8
78	Fe—1Co—8B—15Nd—0.5W	33.6
79	Fe—2Co—8B—16Nd—1W	33.2
80	Fe—10Co—8B—16Nd—0.5W	33.7

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—5

Sample No.	Compositions (at%)	(BH)max (MGOe)*
81	Fe—10Co—7B—14Nd—1W	33.3
82	Fe—20Co—9B—14Nd—0.5W	32.5
83	Fe—20Co—8B—15Nd—1W	32.4
84	Fe—20Co—17B—13Nd—2W	14.5
85	Fe—20Co—8B—13Nd—6W	16.2
86	Fe—20Co—6B—25Nd—1W	16.0
87	Fe—35Co—7B—15Nd—3W	18.4
88	Fe—5Co—8B—15Nd—1Ge	22.2
89	Fe—10Co—9B—14Nd—2Ge	11.4
90	Fe—10Co—17B—16Nd—0.5Ge	14.2
91	Fe—20Co—6B—20Nd—0.5Ge	17.2
92	Fe—20Co—8B—12Nd—0.3Ge	25.3
93	Fe—20Co—20B—14Nd—0.5Ge	10.5
94	Fe—35Co—6B—20Nd—1Ge	10.1
95	Fe—5Co—8B—15Nd—1Sb	13.2
96	Fe—10Co—9B—14Nd—0.5Sb	15.4
97	Fe—10Co—17B—16Nd—1Sb	11.1
98	Fe—20Co—6B—20Nd—0.1Sb	21.2
99	Fe—20Co—8B—12Nd—1.2Sb	12.0
100	Fe—20Co—20B—14Nd—0.5Sb	10.5

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—6

Sample No.	Compositions (at%)	(BH)max (MGOe)*
101	Fe—35Co—6B—20Nd—0.5Sb	10.2
102	Fe—5Co—8B—15Nd—1Sn	20.2
103	Fe—10Co—9B—14Nd—0.5Sn	26.1
104	Fe—10Co—17B—16Nd—0.5Sn	11.2
105	Fe—20Co—6B—20Nd—0.5Sn	15.1
106	Fe—20Co—8B—12Nd—1Sn	15.0
107	Fe—20Co—20B—14Nd—0.5Sn	10.4
108	Fe—35Co—6B—20Nd—0.5Sn	10.9
109	Fe—5Co—8B—15Nd—0.2Bi	31.5
110	Fe—10Co—9B—14Nd—0.5Bi	29.6
111	Fe—10Co—17B—16Nd—1Bi	16.0
112	Fe—20Co—6B—20Nd—3Bi	15.8
113	Fe—20Co—8B—12Nd—1.5Bi	21.9
114	Fe—20Co—20B—14Nd—1Bi	10.9
115	Fe—35Co—6B—20Nd—0.5Bi	18.2
116	Fe—5Co—8B—15Nd—1Ni	24.3
117	Fe—10Co—9B—14Nd—4Ni	17.1
118	Fe—10Co—17B—16Nd—0.2Ni	16.2
119	Fe—20Co—6B—20Nd—5Ni	15.8
120	Fe—20Co—8B—12Nd—0.5Ni	25.3

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 2—7

Sample No.	Compositions (at%)	(BH)max (MGOe)*
121	Fe—20Co—20B—14Nd—1Ni	15.3
122	Fe—35Co—6B—20Nd—3Ni	15.3
123	Fe—5Co—8B—15Pr—1Al	24.8
124	Fe—10Co—9B—14Pr—1W	26.5
125	Fe—5Co—17B—14Pr—2V	10.7
126	Fe—10Co—8B—16Pr—0.5Cr	23.2
127	Fe—20Co—8B—17Pr—0.5Mn	21.3
128	Fe—20Co—8B—15Pr—1Zr	25.4
129	Fe—10Co—7B—14Pr—1Mo—1Zr	20.3
130	Fe—10Co—7B—14Nd—0.5Al—1V	29.1
131	Fe—10Co—9B—15Nd—2Nb—0.5Sn	22.8
132	Fe—20Co—8B—16Nd—1Cr—1Ta—0.5Al	22.5
133	Fe—20Co—8B—14Nd—1Nb—0.5W—0.5Ge	22.1
134	Fe—20Co—15B—15Pr—0.5Zr—0.5Ta—0.5Ni	10.9
135	Fe—10Co—17B—10Nd—5Pr—0.5W	16.2
136	Fe—10Co—8B—8Nd—7Ho—1Al	19.9
137	Fe—10Co—7B—9Nd—5Er—1Mn	20.1
138	Fe—5Co—8B—10Nd—5Gd—1Cr	21.5
139	Fe—10Co—9B—10Nd—5La—1Nb	19.3
140	Fe—20Co—10B—10Nd—5Ce—0.5Ta	20.1
141	Fe—20Co—7B—11Nd—4Dy—1Mn	19.5

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

The relationship between the crystal gain size and the magnetic properties of the Fe—Co—B—R base magnets will be described in detail hereinbelow.

The pulverization procedure as previously mentioned was carried out for varied periods of time selected in such a manner that the measured mean particle sizes of the powder ranged from 0.5 to 100 µm. In this manner, various samples having the compositions as specified in Table 3 were obtained.

Comparative Examples: To obtain a crystal grain size of 100 µm or greater, the sintered bodies were maintained for prolonged time in an argon atmosphere at a temperature lower than the sintered temperature by 5—20°C.

From the thus prepared samples having the compositions as specified in table 3 were obtained magnets which were studied to determine their magnetic properties and their mean crystal grain sizes. The results are set forth in Table 3. The mean crystal grain size referred to herein was measured in the following manner:

The samples were polished and corroded on their surfaces, and photographed through an optical microscope at a magnification ranging from ×100 to ×1000. Circles having known areas were drawn on the

photographs, and divided by lines into eight equal sections. The number of grains present on the diameters were counted and averaged. However, grains on the borders (circumferences) were counted as half grains (this method is known as Heyn's method). Pores were omitted from calculation.

In Table 3, the samples marked * represent Comparative Examples.

From the Sample Nos. *7 and *8, it is found that Hc drops to less 1 kOe if the crystal grain size departs from the scope as defined in the present invention.

Samples designated as Nos. 13 and 16 in Table 3 were studied in detail in respect of the relationship between their mean crystal grain size D and Hc. The results are illustrated in Fig. 10, from which it is found that Hc peaks when D is approximately in a range of 3—10 μm, decrease steeply when D is below that range, and drops moderately when D is above that range. Even when the composition varies within the scope as defined in the present invention, the relationship between the mean crystal grain size D and Hc is substantially maintained. This indicates that the Fe—Co—B—R system magnets are the single domain particle type magnets.

From the results given in Table 3 and Fig. 10, it is evident that, in order for the Fe—Co—B—R base magnets to possess Br of about 4 kG of hard ferrite or more and Hc of no less than 1 kOe, the composition comes within the range as defined in the present invention and the mean crystal grain size D is 1—100 μm, and that, in order to obtain Hc of no less than 4 kOe, the mean crystal grain size should be in a range of 1.5—50 μm.

Control of the crystal grain size of the sintered compact can be carried out by controlling process conditions such as pulverization, sintering, post heat treatment, etc.

TABLE 3

No.	Compositions (at%)	Mean crystal grain size D (μm)	Thermal coefficient of Br (%/°C)	Magnetic properties		
				iHc(kOe)*	Br(kG)*	(BH)max (MGOe)*
*1	Fe—2B—15Nd	6.0	0.14	1.0	9.6	4.0
*2	Fe—8B—15Nd	5.5	0.14	9.5	12.3	33.2
*3	Fe—32B—15Nd	10.1	0.16	11.0	2.5	1.3
*4	Fe—17B—30Nd	7.3	0.16	14.8	4.5	4.2
*5	Fe—10Co—15B—5Pr	22.0	—	0	0	0
*6	Fe—60Co—10B—13Nd	15.7	0.07	0.6	7.9	2.8
*7	Fe—20Co—12B—14Pr	110	0.09	<1	5.7	1.8
*8	Fe—40Co—17B—15Nd	0.85	0.07	<1	6.1	1.4
9	Fe—20Co—12B—14Pr	8.8	0.09	6.8	10.4	19.5
10	Fe—40Co—17B—15Nd	2.8	0.06	6.5	9.2	17.1
11	Fe—50Co—8B—15Nd	4.7	0.06	1.5	8.7	5.5
12	Fe—5Co—8B—15Nd	29.0	0.11	6.4	11.3	25.2
13	Fe—30Co—17B—15Nd	36.5	0.08	5.2	8.6	13.6
14	Fe—15Co—16B—16Pr	68.0	0.09	3.6	10.2	9.4
15	Fe—20Co—7B—15Nd	5.6	0.09	8.6	12.1	31.9
16	Fe—5Co—7B—15Nd	6.5	0.11	9.0	12.5	34.2
17	Fe—20Co—11B—8Nd—7Pr	17.5	0.09	6.3	9.5	14.7
18	Fe—10Co—11B—7Nd—3Pr—5La	22.3	0.10	4.8	7.7	9.8
19	Fe—30Co—17B—22Nd	13.5	0.08	4.4	5.4	4.8
20	Fe—10Co—10B—5Ho—10Nd	19.0	0.10	6.6	8.9	15.7
21	Fe—10Co—10B—13Nd—2Dy—1La	15.5	0.10	6.8	10.0	22.3
22	Fe—20Co—9B—10Nd—6Pr—1Sm	10.3	0.10	5.7	10.4	21.5
23	Fe—15Co—7B—14Nd—2Gd	7.5	0.10	4.7	9.7	16.7

*1kOe=79.6 kA/m
1kG=10^{-1} Tesla
1MGOe=7.96 kJ/m^3
Fe=balance Fe

The embodiments and effects of the M-containing Fe—Co—B—R base magnets (Fe—Co—B—R—M magnets) will now be explained with reference to the following Examples given for the purpose of illustration alone and intended not to limit the invention.

Tables 4—1 to 4—3 show properties of the permanent magnets comprising a variety of Fe—Co—B—R—M compounds, which were prepared by melting and pulverization of alloys, followed by forming of the resulting powders in a magnetic field then sintering. Permanent magnets departing from the scope of the

present invention are also shown with mark *. It is noted that the preparation of samples were substantially identical with that of the Fe—Co—B—R base magnets.

From the samples having the compositions as shown in Tables 4—1 to 4—3 were obtained magnets whose magnetic properties and mean crystal grain size were measured. The results are set out in Table 4—1 to 4—3.

TABLE 4—1

No.	Compositions (at%)	Mean crystal grain size D (μm)	(BH)max (MGOe)*
1	Fe—2Co—8B—15Nd—2Al	4.8	29.5
2	Fe—30Co—17B—13Nd—4Al	7.4	17.6
3	Fe—10Co—13B—14Nd—2Ti	10.1	16.6
4	Fe—10Co—13B—14Nd—2Ti	75.0	4.3
5	Fe—20Co—13B—16Nd—0.5Ti	3.2	27.5
6	Fe—35Co—8B—20Nd—1Ti	25.0	11.2
7	Fe—2Co—17B—16Nd—2V	55.0	8.3
8	Fe—20Co—12B—12Nd—0.5V	5.2	21.5
9	Fe—35Co—6B—20Nd—5V	13.5	10.7
10	Fe—5Co—7B—14Nd—3Cr	8.7	16.0
11	Fe—35Co—6B—23Nd—1Cr	18.8	7.4
12	Fe—15Co—16B—15Nd—1.5Mn	21.2	14.6
13	Fe—5Co—8B—17Nd—3Zr	37.5	23.1
14	Fe—10Co—20B—15Nd—0.5Hf	28.0	12.6
15	Fe—35Co—7B—20Nd—2Hf	11.2	15.4
16	Fe—3Co—8B—14Nd—1Nb	5.0	36.0
17	Fe—10Co—7B—17Nd—5Nb	10.7	18.8
18	Fe—5Co—15B—14Nd—1Ta	16.2	11.4
19	Fe—35Co—7B—15Nd—3Ta	7.6	20.8
20	Fe—2Co—8B—15Nd—0.5Mo	6.5	33.5

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 4—2

No.	Compositions (at%)	Mean crystal grain size D (μm)	(BH)max (MGOe)*
21	Fe—10Co—9B—14Nd—2Mo	9.2	28.5
22	Fe—20Co—17B—15Nd—2Mo	26.2	22.4
23	Fe—20Co—17B—14Nd—6Mo	15.7	14.7
24	Fe—20Co—7B—25Nd—1Mo	9.5	15.4
25	Fe—35Co—8B—17Nd—3Mo	22.8	16.9
26	Fe—2Co—7B—17Nd—0.5W	11.2	32.2
27	Fe—5Co—12B—17Nd—3W	35.1	26.3
28	Fe—10Co—8B—14Nd—1W	3.8	35.4
29	Fe—20Co—17B—15Nd—1W	47.0	13.2
30	Fe—20Co—8B—14Nd—6W	27.3	14.8
31	Fe—35Co—7B—15Nd—3W	12.7	12.0
32	Fe—20Co—8B—14Nd—1Ge	18.2	10.7
33	Fe—10Co—9B—16Nd—0.5Sb	9.7	17.8
34	Fe—20Co—17B—15Nd—1Sn	6.0	18.8
35	Fe—20Co—6B—20Nd—3Bi	6.2	16.6
36	Fe—5Co—8B—15Nd—3Ni	16.8	14.8
37	Fe—20Co—10B—17Nd—1Ni	8.4	19.2
38	Fe—20Co—7B—16Nd—1Cu	23.2	13.8
39	Fe—5Co—8B—15Pr—1Al	4.4	27.3
40	Fe—10Co—10B—17Pr—1W	5.7	26.4

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 4—3

No.	Compositions (at%)	Mean crystal grain size D (μm)	(BH)max (MGOe)*
41	Fe—20Co—8B—15Pr—2Zr	4.6	25.4
42	Fe—15Co—8B—10Nd—5Pr—1Nb—1W	7.3	28.1
43	Fe—10Co—7B—15Nd—1La—1Ta—0.5Mn	12.3	17.8
44	Fe—20Co—12B—12Nd—3Ho—2W—0.5Hf	2.8	22.3
45	Fe—20Co—8B—11Nd—4Dy—1Al—0.5Cr	14.1	18.6
46	Fe—10Co—7B—10Nd—5Gd—1W—0.5Cu	28.3	11.4
47	Fe—12Co—8B—13Nd—1Sm—1Nb	6.0	20.5
48	Fe—5Co—7B—14Nd—1Ce—1Mo	9.4	18.3
49	Fe—20Co—8B—13Nd—2Pr—1Y—1Al	12.5	22.3

*1MGOe=7.96 kJ/m^3
Fe=balance Fe

TABLE 5

No.	Compositions (at%)	Mean crystal grain size D (μm)	Magnetic properties		
			iHc(kOe)*	Br(kG)*	(BH)max* (MGOe)
*1	80Fe—20Nd	15	0	0	0
*2	53Fe—32B—15Nd	10	11.0	2.5	1.3
*3	48Fe—17B—35Nd	4	>15	1.4	<1
*4	73Fe—10B—17Nd	0.7	<1	5.0	<1
*5	82Fe—5B—13Nd	140	<1	6.3	2.2

N.B.: Prefix* refers to comparative tests
*1kOe=79.6 kA/m
1kG=10^{-1} Tesla
1MGOe=7.96 kJ/m^3

Fig. 11 shows the demagnetization curves of the typical Examples of the invented Fe—Co—B—R—M base magnets and the M-free Fe—Co—B—R base magnets. In this figure, reference numerals 1—3 denote the demagnetization curves of a M-free magnet, a Mo-containing magnet (Table 4—1 No. 20) and a Nb-containing magnet (Table 4—1 No. 16), all of which show the loop squareness useful for permanent magnet materials.

The curve 4 represents ones with a mean crystal grain size D of 52 μm for the same composition as 3.

In Table 5 comparative samples with marks * are shown, wherein *1—*3 are samples departing from the scope of the present invention.

From *4 and *5, it is found that Hc drops to 1 kOe or less if the mean crystal grain size departs from the scope of the present invention.

Samples designated as Nos. 21 and 41 in Tables 4—2 and 4—3 samples were studied in detail in respect of the relationship between their mean crystal grain size D and Hc. The results are illustrated in Fig. 11, from which it is found that Hc peaks when D is approximately in a range of 3—10 μm, decreases steeply when D is below that range, and drops moderately when D is above that range. Even when the composition varies within the scope as defined in the present invention, the relationship between the average crystal

grain size D and Hc is substantially maintained. This indicates that the Fe—Co—B—R—M base magnets are the single domain particle type magnets.

Apart from the foregoing samples, an alloy having the same composition as Sample No. 20 of Table 4—1 was prepared by the (casting) procedure (1) as already stated. However, the thus cast alloy had Hc of less than 1 kOe in spite of its mean crystal grain size being in a range of 20—80 μm.

From the results given in Table 4—1 and Fig. 10, it is evident that, in order for the Fe—Co—B—R—M base magnets to possess Br of about 4 kG of hard ferrite or more and Hc of no less than 1 kOe, the composition comes within the range as defined in the present invention and the mean crystal grain size is about 1—about 100 μm, and that, in order to obtain Hc of no less than 4 kOe, the mean crystal grain size should be in a range of about 1.5—about 50 μm.

Control of the crystal grain size of the sintered compact can be controlled as is the case of the Fe—Co—B—R system.

As mentioned in the foregoing, the invented permanent magnets of the Fe—Co—B—R—M base magnetically anisotropic sintered bodies may contain, in addition to Fe, Co, B, R and M, impurities which are entrained therein in the process of production as is the case for the Fe—Co—B—R system.

Crystal structure

It is believed that the magnetic materials and permanent magnets based on the Fe—Co—B—R base alloys according to the present invention can satisfactorily exhibit their own magnetic properties due to the fact that the major phase is formed by the substantially tetragonal crystals of the Fe—B—R type. As already discussed, the Fe—Co—B—R type alloy is a novel alloy in view of its Curie point. As will be discussed hereinafter, it has further been experimentally ascertained that the presence of the substantially tetragonal crystals of the Fe—Co—B—R type contributes to the exhibition of magnetic properties. The Fe—Co—B—R type tetragonal system alloy is unknown in the art, and serves to provide a vital guiding principle for the production of magnetic materials and permanent magnets having high magnetic properties as aimed at in the present invention.

According to the present invention, the desired magnetic properties can be obtained, if the Fe—Co—B—R crystals are of the substantially tetragonal system. In most of the Fe—Co—B—R base compounds, the angles between the axes a, b and c are 90° within the limits of measurement error, and $a_o=b_o\neq c_o$. Thus, these compounds can be referred to as the tetragonal system crystals. The term "substantially tetragonal" encompasses ones that have a slightly deflected angle between a, b and c axes, e.g., within about 1°, or ones that have a_o slightly different from b_o, e.g., within about 1%.

To obtain the useful magnetic properties in the present invention, the magnetic materials and permanent magnets of the present invention are required to contain as the major phase an intermetallic compound of the substantially tetragonal system crystal structure. By the term "major phase", it is intended to indicate a phase amounting to 50 vol% or more of the crystal structure, among phases constituting the crystal structure.

The Fe—Co—B—R base permanent magnets having various compositions and prepared by the manner as hereinbelow set forth as will as other various manners were examined with an X-ray diffractometer, X-ray microanalyser (XMA) and optical microscopy.

Experimental procedures

(1) Starting materials (purity is given by weight%)

Fe: electrolytic iron 99.9%

B: ferroboron, or B having a purity of 99%

R: 99.7% or higher with impurities being mainly other rare earth elements

Co: electrolytic cobalt having purity of 99.9%

(2) The experimental producedures are shown in Fig. 15.

The experimental results obtained are illustrated as below:

(1) Fig. 14 illustrates a typical X-ray diffraction pattern of the Fe—Co—B—Nd (67Fe—10Co—8B—15Nd in at%) sintered body showing high properties as measured with a powder X-ray diffractometer. This pattern is very complicated, and can not be explained by any R—Fe, Fe—B or R—B type compounds developed yet in the art.

(2) XMA measurement of the sintered body of (1) hereinabove under test has indicated that it comprises three or four phases. The major phase simultaneously contains Fe, Co, B and R, the second phase is a R-concentrated phase having a R content of 70 weight% or higher, and the third phase is an Fe-concentrated phase having an Fe content of 80 weight% or higher. The fourth phase is a phase of oxides.

(3) As a result of analysis of the pattern given in Fig. 14, the sharp peaks included in this pattern may all be explained as the tetragonal crystals of $a_o=0.880$ nm (8.80 Å) and $c_o=1.223$ nm=(12.23 Å).

In Fig. 14, indices are given at the respective X-ray peaks. The major phase simultaneously containing Fe, Co, B and R, as confirmed in the XMA measurement, has turned out to exhibit such a structure. This structure is characterized by its extremely large lattice constants. No tetragonal system compounds having such large lattice constants are found in any one of the binary system compounds such as R—Fe, Fe—B and B—R.

(4) Fe—Co—B—R base permanent magnets having various compositions and prepared by the aforesaid manner as well as other various manners were examined with an X-ray diffractometer, XMA and optical microscopy. As a result, the following matters have turned out:

(i) Where a tetragonal system compound having macro unit cells occurs, which contains as the essential components R, Fe, Co and B and has lattice constants a_o of about 0.9 nm (9 Å) and c_o of about 1.2 nm (12 Å), good properties suitable for permanent magnets are obtained. Table 6 shows the lattice constants of tetragonal system compounds which constitute the major phase of typical Fe—Co—B—R type magnets, i.e., occupy 50 vol% or more of the crystal structure.

In the compounds based on the conventional binary system compounds such as R—Fe, Fe—B and B—R, it is thought that no tetragonal system compounds having such macro unit cells as mentioned above occur. It is thus presumed that no good permanent magnet properties are achieved by those known compounds.

TABLE 6

Crystal structure of various Fe—B—R/Fe—Co—B—R type compounds

No.	Alloy compositions	Structure of major phase (system)	Lattice constants of major phase	
			a_o (Å)*	c_o (Å)*
1	Fe—15Pr—8B	tetragonal	8.84	12.30
2	Fe—15Nd—8B	"	8.80	12.23
3	Fe—15Nd—8B—1Nb	"	8.82	12.25
4	Fe—15Nd—8B—1Ti	"	8.80	12.24
5	Fe—10Co—15Nd—8B	"	8.79	12.21
6	Fe—20Co—15Nd—8B	"	8.78	12.20
7	Fe—20Co—15Nd—8B—1V	"	8.83	12.24
8	Fe—20Co—15Nd—8B—1Si	"	8.81	12.19
9	Fe—6Nd—6B	body-centered cubic	2.87	—
10	Fe—15Nd—2B	rhombohedral	8.60*	12.50*

N.B.: (*) indicated as hexagonal
*1Å=10^{-1} nm
Fe=balance Fe

(ii) Where said tetragonal system compound has a suitable crystal grain size and, besides, nonmagnetic phases occur which contain much R, good magnetic properties suitable for permanent magnets are obtained.

With the permanent magnet materials, the fine particles having a high anisotropy constant are ideally separated individually from one another by nonmagnetic phases, since a high Hc is then obtained. To this end, the presence of 1 vol% or higher of nonmagnetic phases contributes to the high Hc. In order that Hc is no less than 1 kOe, the nonmagnetic phases should be present in a volume ratio between 1 and 45 vol%, preferably between 2 and 10 vol%. The presence of 45% or higher of the nonmagnetic phases is not preferable. The nonmagnetic phases are mainly comprised of intermetallic compound phases containing much of R, while oxide phases serve partly effectively.

(iii) The aforesaid Fe—Co—B—R type tetragonal system compounds occur in a wide compositional range.

Alloys containing, in addition to the Fe—Co—B—R base components, one or more additional elements M and/or impurities entrained in the process of production can also exhibit good permanent magnet properties, as long as the major phases are comprised of tetragonal system compounds.

As apparent from Table 6 the compounds added with M based on the Fe—B—R system exhibit the tetragonal system as well as the Fe—Co—B—R—M system compounds also does the same. Detailed disclosure regarding other additional elements M as disclosed in EP—A—101 552 is herewith referred to and herein incorporated.

The aforesaid fundamental tetragonal system compounds are stable and provide good permanent magnets, even when they contain up to 1% of H, Li, Na, K, Be, Sr, Ba, Ag, Zn, N, F, Se, Te, Pb, or the like.

As mentioned above, the Fe—Co—B—R type tetragonal system compounds are new ones which have been entirely unknown in the art. It is thus new fact that high properties suitable for permanent magnets are obtained by forming the major phases with these new compounds.

In the field of R—Fe alloys, it has been reported to prepare ribbon magnets by melt-quenching. However, the invented magnets are different from the ribbon magnets in the following several points. That is to say, the ribbon magnets can exhibit permanent magnet properties in a transition stage from the amorphous or metastable crystal phase to the stable crystal state. Reportedly, the ribbon magnets can exhibit high coercive force only if the amorphous state still remains, or otherwise metastable Fe_3B and R_6Fe_{23} are present as the major phases. The invented magnets have no sign of any alloy phase remaining in the amorphous state, and the major phases thereof are not Fe_3B and R_6Fe_{23}.

The present invention will now be further explained with reference to the following example.

Example

An alloy of 10 at% Co, 8 at% B, 15 at% Nd and the balance Fe was pulverized to prepare powders having an average particle size of 1.1 µm. The powders were compacted under a pressure of 19.62×10^7 Pa (2 t/cm^2) and in a magnetic field of 12 kOe, and the resultant compact was sintered at 1080°C for 1 hour in argon of 200 Pa (1.5 Torr).

X-ray diffraction has indicated that the major phase or the sintered body is a tetragonal system compound with lattice constants a_o=0.879 nm (8.79 Å) and c_o=1.221 nm (12.21 Å). As a consequence of XMA and optical microscopy, it has been found that the major phase contains simultaneously Fe, Co, B and Pr, which amount to 90 volume% thereof. Nonmagnetic compound phases having a R content of no less than 80% assumed 4.5% in the overall with the remainder being substantially oxides and pores. The mean crystal grain size was 3.1 µm.

The magnetic properties measured are: Br=12.0 kG, iHc=9.2 kOe, and (BH)max=34 MGOe, and are by far higher than those of the conventional amorphous ribbon magnet.

By measurement, the typical sample of the present invention has also been found to have high mechanical strengths such as bending strength of 25 kg/mm^2, compression strength of 75 kg/mm^2 and tensile strength of 8 kg/mm^2. This sample could effectively be machined, since chipping hardly took place in machining testing.

As is understood from the foregoing, the present invention makes it possible to prepare magnetic materials and sintered anisotropic permanent magnets having high remanence, high coercive force and high energy product with the use of less expensive alloys containing light-rare earth elements, a relatively small amount of Co and based on Fe, and thus present a technical breakthrough.

Claims

1. An alloy comprising Fe—B—R characterized by containing at least one stable compound of the Fe—Co—B—R-type which compound can be magnetized to become a permanent magnet at room temperature and above where R stands for Nd and/or Pr.

2. The alloy of claim 1 in which the compound has a tetragonal structure.

3. An alloy of the Fe—B—R-type characterized by containing 8—30 at% of R, where R represents one or more rare earth elements including Y, 2—28 at% B, the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole material containing at least one compound of the Fe—Co—B—R-type having a tetragonal crystal structure.

4. The alloy of claim 2 or 3 wherein the Co axis of the tetragonal structure is about 1.2 nm (12 Å).

5. The alloy of claim 2, 3 or 4 wherein the ao axis is about 0.9 nm (9 Å).

6. The alloy of one of claims 3 to 5 wherein at least 50% of the overall R are Nd and/or Pr.

7. The alloy of one of the preceding claims having a Curie temperature T_c between 310°C and 750°C.

8. The alloy of one of the preceding claims having crystals with a mean grain size of 1 µm to 100 µm, preferably 1.5 µm to 50 µm.

9. The alloy of one of the preceding claims further comprising additional elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

10. The alloy of one of the preceding claims wherein the Fe—Co—B—R system comprises 4—24 at% of B and 12—24 at% of R.

11. The alloy of one of claims 1 to 10 in which Co is 5—45 at%, preferably 5—25 at%.

12. A process of preparing an alloy containing at least one stable compound of the Fe—Co—B—R—type which compound can be magnetized to become a permanent magnet at room temperature and above by melting and casting a composition containing 2—28 at% of B, 8—30 at% of R, where R stands for at least one rare earth element including yttrium, and the balance being iron substituted by Co, wherein Co amounts to no more than 50 at% of the whole material.

13. The process of claim 12 wherein as the starting materials iron, Co, ferroboron alloys for B and rare earth elements are used.

14. The process of claim 12 or 13 wherein the castings are pulverized.

15. The process of claim 14 wherein the pulverization is effected to 0.5—100 µm, preferably to 3—10 µm.

16. The process of one of claims 12 to 15 in which said alloy further comprises one or more of the elements evident from the list below, the amounts of these elements being respectively limited to no more than the value specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

17. Use of the alloys of one of the preceding claims for being applied to magnetic recording media, magnetic paints, thermo-sensitive materials and intermediaries for the production of permanent magnets.

18. A magnetic material comprising 8—30 at% R, wherein R is at least one rare earth element including Y, 2—28 at% B, and the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole material and comprising at least 50 vol% of a phase comprising at least one Fe—Co—B—R-type compound having a tetragonal structure.

19. The magnetic material of claim 18 wherein the Co axis of the tetragonal structure is about 1.2 nm (12 Å).

20. The magnetic material of claim 18 or 19 wherein the ao axis of the tetragonal structure is about 0.9 nm (9 Å).

21. The magnetic material of one of claims 18 to 20 wherein the mean crystal grain size ranges from 1.0 to 100 µm, preferably from 1.5 to 50 µm.

22. The magnetic material of one of claims 18 to 21 further comprising one or more of the elements evident from the list below, the amounts of these elements being respectively limited to no more than the value specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, and total amount of M is limited to the highest value of one of the individual elements M added.

23. The magnetic material of one of claims 18 to 22 wherein the light rare earth elements are used for the rare earth elements R.

24. The magnetic material of claim 23 wherein Nd and/or Pr are used for the rare earth elements R.

25. A sintered magnetic material consisting of a magnetic material powder showing crystals of a tetragonal structure and comprising 8—30 at% of R, R being one or more of the rare earth elements including Y, 2—28 at% of B, and the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole composition.

26. A process of making a magnetic material powder showing a tetragonal structure and comprising 8—30 at% of R, R being one or more rare earth elements including Y, 2—28 at% of B, and the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole composition by heating a powdery rare earth oxide R_2O_3 as raw material for R, with powdery Fe, powdery Co, powdery Fe—B and a reducing agent for direct reduction.

27. The process of claim 26 including a further step of sintering the powder alloys.

28. A permanent magnet material comprising 8—30 at% R, R being one or more rare earth elements

including Y, Nd and/or Pr amounting to no less than 50 at% of R, 2—28 at% of B, the balance being iron substituted by Co, wherein the Co amounts to no more than 50 at% of the whole material.

29. The permanent magnet material of claim 28 wherein R amounts from 11—24 at% and B from 4—24 at%.

30. A permanent magnet material of claim 28 or 29 comprising 12—20 at% R and 4—24 at% B.

31. The permanent magnet material of one of claims 28 to 30 which contains more than 50 vol% of a phase containing at least one stable Fe—Co—B—R compound having a tetragonal structure.

32. A permanent magnet material comprising at least 50 vol.% of a phase comprising at least one Fe—Co—B—R-type compound having a tetragonal structure, wherein R is at least one rare earth element including Y.

33. The permanent magnet material of claim 31 or 32 wherein the Co axis of the tetragonal structure is about 1.2 nm (12 Å).

34. The permanent magnet material of one of claims 31 to 33 wherein the ao axis of the tetragonal structure is about 0.9 nm (9 Å).

35. The permanent magnet material of one of claims 28 to 34 having a mean crystal grain size of 1 to 100 µm, preferably 1.5 to 50 µm.

36. The permanent magnet material of one of claims 28 to 35 wherein the fine particle of the phase containing at least one stable Fe—Co—B—R compound are separated from one another by nonmagnetic phases.

37. The permanent magnet material of claim 36 wherein the nonmagnetic phases are present in a volume of 1 to 45 vol.%.

38. The permanent magnet material of claim 37 wherein the nonmagnetic phases contain much of R.

39. A permanent magnet material of one of claims 28 to 38 further comprising additional elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

40. An anisotropic permanent magnetic material comprising 8—30 at% of R, R being one or more rare earth elements including Y, 2—28 at% of boron, the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole material.

41. The anisotropic permanent magnetic material of claim 40 comprising 12—20 at% R and 4—24 at% B.

42. The anisotropic permanent magnetic material of claim 40 or 41 which contains more than 50 vol.% of a phase containing at least one stable Fe—Co—B—R compound having a tetragonal structure.

43. The anisotropic permanent magnetic material of claim 42 wherein the Co axis of the tetragonal structure is about 1.2 nm (12 Å).

44. The anisotropic permanent magnetic material of claim 42 or 43 wherein the ao axis of the tetragonal structure of about 0.9 nm (9 Å).

45. The anisotropic permanent magnetic material of one of claims 40 to 44 having a mean crystal grain size of 1 to 100 µm, preferably 1.5 to 50 µm.

46. The anisotropic permanent magnetic material of one of claims 40 to 45 wherein the fine particles of the phase containing at least one stable Fe—Co—B—R compound are separated from one another by nonmagnetic phases.

47. The anisotropic permanent magnetic material of claim 46 wherein the nonmagnetic phases are present in a volume of 1 to 45 vol.%.

48. The anisotropic permanent magnetic material of claim 47 wherein the nonmagnetic phases contain much of R.

49. The anisotropic permanent magnetic material of one of claims 40 to 48 further comprising additional elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

50. A process for producing an anisotropic permanent magnetic material by providing a melt comprising 8—30 at% of R, R being one or more rare earth elements including Y, 2—28 at% of boron, the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole composition, cooling the melt to crystallize and powderizing the crystalline product.

51. The process for producing an anisotropic permanent magnetic material according to claim 50 wherein the balance is Fe substituted by Co, and one or more of the elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

52. The process of claim 50 or 51 wherein the crystalline product is pulverized to 3—10 µm.

53. The process of one of claims 50 to 52 wherein the pulverized product is sintered.

54. The process of claim 53 wherein the sintering is effected at a temperature of 1000 to 1200°C.

55. The process of claim 54 wherein the sintering is effected in an inert gas atmosphere such as argon.

56. A permanent magnet comprising 8—30 at% R, R being one or more of the rare earth elements including Y, 2—28 at% B and the balance being Fe substituted by Co, wherein the Co amounts to no more than 50% of the whole material, obtainable by sintering a powder of said material.

57. The permanent magnet of claim 56 comprising 4—24 at% of B and 12—20 at% of R.

58. The permanent magnet of claim 56 or 57 having anisotropic properties obtainable by additional alignment in a magnetic field.

59. The permanent magnet of one of claims 56 to 59 wherein the light rare earth elements amount to no less than 50 at% of the overall rare earth elements R.

60. The permanent magnet of claim 59 wherein Nd and/or Pr amounts to no less than 50 at% of the overall R.

61. The permanent magnet of one of claims 56 to 60 wherein the mean crystal grain size is 1 to 100 µm, preferably 1.5 to 50 µm.

62. The permanent magnet of one of claims 56 to 61 further comprising additional elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	17.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added.

63. The permanent magnet of one of claims 56 to 62 comprising at least one Fe—Co—B—R-type compound having a tetragonal structure.

64. The permanent magnet of claim 63 wherein the Co axis of the tetragonal structure is about 1.2 nm (12 Å).

65. The permanent magnet of claim 63 or 64 wherein the ao axis of the tetragonal structure is about 0.9 nm (9 Å).

66. The permanent magnet of one of claims 56 to 65 comprising nonmagnetic phases separating the fine particles of the at least one Fe—Co—B—R-type compound from one another.

67. The permanent magnet of claim 66 wherein the nonmagnetic phases are present between 1—45 vol.%.

68. The permanent magnet of claim 67 wherein the nonmagnetic phases contain much of R.

69. The permanent magnet of one of claims 56 to 68 wherein Co is 5—45 at%, preferably 5—25 at%.

70. The permanent magnet of one of claims 56 to 69 in which R is about 15 at% and B is about 8 at%.

71. A sintered permanent magnet comprising at least one Fe—Co—B—R-type compound having a tetragonal structure, where R is at least one rare earth element including Y.

72. A sintered permanent magnet according to claim 70 containing nonmagnetic phases with much R of 1 vol.% to 45 vol.%.

73. A sintered permanent magnet of claim 72 wherein the nonmagnetic phases are present in 2—10 vol.%.

74. The sintered permanent magnet of one of claims 71 to 73 comprising 8—30 at% R, wherein R is at least one rare earth element including Y, 2—28 at% B, and the balance being Fe substituted by Co, wherein the Co amounts to no more than 50 at% of the whole material.

75. The sintered permanent magnet of claim 74 wherein R is 12—20 at% and B is 4—24 at%.

76. The sintered permanent magnet of one of claims 71 to 75 wherein the light rare earth elements amount to no less than 50 at% of the overall rare earth elements R.

77. The sintered permanent magnet of claim 76 wherein Nd and/or Pr amounts to no less than 50 at% of the overall rare earth elements R.

78. The sintered permanent magnet of one of claims 71 to 77 wherein R amounts to about 15 at% and B amounts to about 8 at%.

79. The sintered permanent magnet of one of claims 71 to 78 wherein the mean crystal grain size is 1 to 100 µm, preferably 1.5 to 50 µm.

80. An anisotropic permanent magnet of claim 57 or 75 characterized by a maximum energy product of at least 80 kJ/m^3 (10 MGOe).

81. The magnet of claim 80 characterized in that the maximum energy product is no less than 160 kJ/m^3 (20 MGOe).

82. The permanent magnet as defined in claim 81 characterized in that the maximum energy product is no less than 240 kJ/m^3 (30 MGOe).

83. The permanent magnet as defined in claim 82 characterized in that the maximum energy product is no less than 260 kJ/m^3 (33 MGOe).

84. The permanent magnet of one of claims 56 to 83 obtainable by a powder metallurgical process.

85. A process of making a permanent magnet by providing a melt comprising 8—30 at% R, R being one or more rare earth element including Y, 2—28 at% of boron, the balance being Fe substituted by Co, wherein Co amounts to no more than 50 at% of the whole material, cooling the melt to crystallize, powdering the crystallized product, pressing and sintering the powdered product.

86. The process of claim 85 wherein the melt further comprises additional elements M evident from the list below, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

4.5% Ti,	8.0% Ni,	5.0% Bi,
9.5% V,	12.5% Nb,	10.5% Ta,
8.5% Cr,	9.5% Mo,	9.5% W,
8.0% Mn,	9.5% Al,	2.5% Sb,
7.0% Ge,	3.5% Sn,	5.5% Zr,
and 5.5% Hf.		

wherein, when two or more of M are applied, the total amount of M is limited to the highest value of one of the individual elements M added, cooling the melt to crystallize, powdering the crystallized product, pressing and sintering the powdered alloy.

87. The process of claim 85 or 86 wherein the powdered product is oriented in a magnetic field.

88. The process of one of claims 85 to 87 wherein the compacts are sintered at 1000 to 1200°C.

Patentansprüche

1. Legierung mit einem Gehalt an Fe—B—R, dadurch gekennzeichnet, daß sie mindestens eine stabile Verbindung des Typs Fe—Co—B—R enthält, die bei Raumtemperatur oder einer höheren Temperatur zu einem Permanentmagneten magnetisierbar ist, wobei R die Elemente Nd und/oder Pr bedeutet.

2. Legierung nach Anspruch 1, worin die Verbindung eine tetragonale Struktur aufweist.

3. Legierung des Typs Fe—B—R, gekennzeichnet durch einen Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und dem Rest Fe, der durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials ausmacht, das mindestens eine Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Kristallstruktur enthält.

4. Legierung nach Anspruch 2 oder 3, worin die co-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

5. Legierung nach Anspruch 2, 3 oder 4, worin die ao-Achse etwa 0,9 nm (9 Å) beträgt.

6. Legierung nach einem der Ansprüche 3 bis 5, worin mindestens 50% des Gesamtgehalts an R aus Nd und/oder Pr bestehen.

7. Legierung nach einem der vorstehenden Ansprüche mit einer Curie-Temperatur T_c zwischen 310 und 750°C.

8. Legierung nach einem der vorstehenden Ansprüche mit Kristallen, deren mittlere Korngröße 1 bis 100 µm, vorzugsweise 1,5 bis 50 µm, beträgt.

9. Legierung nach einem der vorstehenden Ansprüche, die zusätzliche Elemente M gemäß der nachstehenden Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachstehend angegebenen Werte in Atom-%,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

wobei im Falle des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge an M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

10. Legierung nach einem der vorstehenden Ansprüche, worin das System Fe—Co—B—R 4 bis 24 Atom-% B und 12 bis 24 Atom-% R enthält.

11. Legierung nach einem der Ansprüche 1 bis 10, worin Co 5 bis 45 Atom-%, vorzugsweise 5 bis 25 Atom-%, beträgt.

12. Verfahren zum Herstellen einer Legierung, die mindestens eine stabile Verbindung des Typs Fe—Co—B—R enthält, die bei Raumtemperatur oder einer höheren Temperatur zu einem Permanentmagneten magnetisierbar ist, durch Schmelzen und Gießen eines Gemisches mit einem Gehalt an 2 bis 28 Atom-% B, 8 bis 30 Atom-% R, wobei R mindestens ein Seltenerdelement einschließlich Yttrium bedeutet, und als Rest Eisen, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt.

13. Verfahren nach Anspruch 12, worin die Ausgangsstoffe Eisen, Co, Ferroborlegierungen für B und Seltenerdelemente eingesetzt werden.

14. Verfahren nach Anspruch 12 oder 13, worin die Gießlinge pulverisiert werden.

15. Verfahren nach Anspruch 14, worin das Pulverisieren bis zu 0,5 bis 100 µm, vorzugsweise bis zu 3 bis 10 µm, durchgeführt wird.

16. Verfahren nach einem der Ansprüche 12 bis 15, bei dem die Legierung zusätzlich ein oder mehrere Elemente aus der nachstehenden Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin für den Fall des Einsatzes von zwei oder mehr Elementen M die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

17. Verwendung der Legierungen gemäß einem der vorstehenden Ansprüche in magnetischen Aufzeichnungsmaterialien, magnetischen Anstrichmitteln, wärmeempfindlichen Materialien und Zwischenprodukten zur Herstellung von Permanentmagneten.

18. Magnetisches Material mit einem Gehalt an 8 bis 30 Atom-% R, worin R mindestens ein Seltenerdelement einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt, und wobei mindestens 50 Vol-% einer Phase vorliegen, die mindestens eine Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur enthält.

19. Magnetisches Material nach Anspruch 18, worin die co-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

20. Magnetisches Material nach Anspruch 18 oder 19, worin die ao-Achse der tetragonalen Struktur etwa 0,9 nm (9 Å) beträgt.

21. Magnetisches Material nach einem der Ansprüche 18 bis 20, worin die mittlere Kristallkorngröße im Bereich von 1,0 bis 100 µm, vorzugsweise von 1,5 bis 50 µm, liegt.

22. Magnetisches Material nach einem der Ansprüche 18 bis 21, das zusätzlich ein oder mehrere Elemente gemäß nachstehender Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als der nachfolgend angegebene Wert in Atom-%,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falle des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge von M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist.

23. Magnetisches Material nach einem der Ansprüche 18 bis 22, worin für die Seltenerdelemente R die leichten Saltenerdelemente eingesetzt sind.

24. Magnetisches Material nach Anspruch 23, worin für die Seltenerdelemente R die Element Nd und/oder Pr eingesetzt sind.

25. Gesintertes magnetisches Material, bestehend aus einem Pulver eines magnetischen Materials mit Kristellen einer tetragonalen Struktur und enthaltend 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% der gesamten Zusammensetzung beträgt.

26. Verfahren zum Herstellen eines Pulvers eines magnetischen Materials mit einer tetragonalen Struktur und einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y ist, 2 bis 28 Atom-% B und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% der gesamten Zusammensetzung beträgt, durch Erhitzen eines pulverförmigen Oxids eines Seltenerdelements der Formel R_2O_3 als Ausgangsstoff für R, mit pulverförmigem Fe, pulverförmigem Co, pulverförmigem Fe—B und einem für direkte Reduktion geeigneten Reduktionsmittel.

27. Verfahren nach Anspruch 26, das zusätzlich die Stufe des Sinterns der pulverförmigen Legierungen umfaßt.

28. Permanentmagnetmaterial mit einem Gehalt von 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y, Nd und/oder Pr ist, die nicht weniger als 50 Atom-% von R betragen, 2 bis 28 Atom-% B und als Rest Eisen, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt.

29. Permanentmagnetmaterial nach Anspruch 28, worin R in einer Menge von 11 bis 24 Atom-% und B in einer Menge von 4 bis 24 Atom-% vorliegen.

30. Permanentmagnetmaterial nach Anspruch 28 oder 29 mit einem Gehalt von 12 bis 20 Atom-% R und 4 bis 24 Atom-% B.

31. Permanentmagnetmaterial nach einem der Ansprüche 28 bis 30 mit einem Gehalt von mehr als 50 Vol-% einer Phase, die mindestens eine stabile Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur enthält.

32. Permanentmagnetmaterial, das mindestens 50 Vol-% einer Phase enthält, in der mindestens eine Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur vorliegt, wobei R mindestens ein Seltenerdelement einschließlich Y bedeutet.

33. Permanentmagnetmaterial nach Anspruch 31 oder 32, worin die co-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

34. Permanentmagnetmaterial nach einem der Ansprüche 31 bis 33, worin die ao-Achse der tetragonalen Struktur etwa 0,9 nm (9 Å) beträgt.

35. Permanentmagnetmaterial nach einem der Ansprüche 28 bis 34 mit einer mittleren Kristallkorngröße von 1 bis 100 µm, vorzugsweise 1,5 bis 50 µm.

36. Permanentmagnetmaterial nach einem der Ansprüche 28 bis 35, worin die feinen Teilchen der Phase mit einem Gehalt an mindestens einer stabilen Verbindung des Typs Fe—Co—B—R voneinander durch nichtmagnetische Phasen getrennt sind.

37. Permanentmagnetmaterial nach Anspruch 36, worin die nichtmagnetischen Phasen mit einem Volumen von 1 bis 45 Vol-% vorliegen.

38. Permanentmagnetmaterial nach Anspruch 37, worin die nichtmagnetischen Phasen viel an R enthalten.

39. Permanentmagnetmaterial nach einem der Ansprüche 28 bis 38, das zusätzliche Elemente M gemäß der nachstehenden Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte,

4,5% Ti,	8,0% Ni,	5,0% Si,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falle des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge von M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist.

40. Anisotropes Permanentmagnetmaterial mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y ist, 2 bis 28 Atom-% Bor und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt.

41. Anisotropes Permanentmagnetmaterial nach Anspruch 40, mit einem Gehalt an 12 bis 20 Atom-% R und 4 bis 24 Atom-% B.

42. Anisotropes Permanentmagnetmaterial nach Anspruch 40 oder 41 mit einem Gehalt von mehr als

50 Vol-% einer Phase, die mindestens eine stabile Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur enthält.

43. Anisotropes Permanentmagnetmaterial nach Anspruch 42, wobei die co-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

44. Anisotropes Permanentmagnetmaterial nach Anspruch 42 oder 43, worin die ao-Achse der tetragonalen Struktur etwa 0,9 nm (9 Å) beträgt.

45. Anisotropes Permanentmagnetmaterial nach einem der Ansprüche 40 bis 44 mit einer mittleren Kristallkorngröße von 1 bis 100 µm, vorzugsweise 1,5 bis 50 µm.

46. Anisotropes Permanentmagnetmaterial nach einem der Ansprüche 40 bis 45, worin die feinen Teilchen der Phase, die mindestens eine stabile Verbindung des Typs Fe—Co—B—R enthält, durch nichtmagnetische Phasen voneinander getrennt sind.

47. Anisotropes Permanentmagnetmaterial nach Anspruch 46, worin die nichtmagnetischen Phasen mit einem Volumen von 1 bis 45 Vol-% vorliegen.

48. Anisotropes Permanentmagnetmaterial nach Anspruch 47, worin die nichtmagnetischen Phasen viel R enthalten.

49. Anisotropes Permanentmagnetmaterial nach einem der Ansprüche 40 bis 48, das weiterhin zusätzliche Elemente M gemäß der nachstehenden Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falle des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge an M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist.

50. Verfahren zum Herstellen eines anisotropen Permanentmagnetmaterials durch Bilden einer Schmelze mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y ist, 2 bis 28 Atom-% Bor und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% der gesamten Zusammensetzung beträgt, Abkühlen der Schmelze bis zur Kristallisation und Pulverisieren des kristallinen Produkts.

51. Verfahren zum Herstellen eines anisotropen Permanentmagnetmaterials nach Anspruch 50, worin der Rest aus Fe, das durch Co ersetzt ist, und einem oder mehreren Elementen M gemäß der nachfolgenden Liste gebildet wird, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falle des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge von M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist.

52. Verfahren nach Anspruch 50 oder 51, worin das kristalline Produkt auf 3 bis 10 µm pulverisiert wird.

53. Verfahren nach einem der Ansprüche 50 bis 52, worin das pulverisierte Produkt gesintert wird.

54. Verfahren nach Anspruch 53, worin das Sintern bei einer Temperatur von 1000 bis 1200°C durchgeführt wird.

55. Verfahren nach Anspruch 54, worin das Sintern in einer Inertgasatmosphäre, wie Argon, durchgeführt wird.

56. Permanentmagnet mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y ist, 2 bis 28 Atom-% B und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50% des gesamten Materials beträgt, erhältlich durch Sintern eines Pulvers dieses Materials.

57. Permanentmagnet nach Anspruch 56 mit einem Gehalt an 4 bis 24 Atom-% B und 12 bis 20 Atom-% R.

58. Permanentmagnet nach Anspruch 56 oder 57 mit anisotropen Eigenschaften, erhältlich durch zusätzliches Ausrichten in einem Magnetfeld.

59. Permanentmagnet nach einem der Ansprüche 56 bis 59, worin die leichten Seltenerdmetallelemente nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R betragen.

60. Permanentmagnet nach Anspruch 59, worin Nd und/oder Pr nicht weniger als 50 Atom-% der Gesamtmenge an R betragen.

61. Permanentmagnet nach einem der Ansprüche 56 bis 60, worin die mittlere Kristallkorngröße 1 bis 100 µm, vorzugsweise 1,5 bis 50 µm, beträgt.

62. Permanentmagnet nach einem der Ansprüche 56 bis 61 mit einem weiteren Gehalt zu zusätzlichen Elementen M gemäß der unten angegebenen Liste, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falle des Einsetzes von mehr als zwei der Elemente M die Gesamtmenge von M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist.

63. Permanentmagnet nach einem der Ansprüche 56 bis 62 mit einem Gehalt an mindestens einer Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur.

64. Permanentmagnet nach Anspruch 63, worin die co-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

65. Permanentmagnet nach Anspruch 63 oder 64, worin die ao-Achse der tetragonalen Struktur etwa 0,9 nm (9 Å) beträgt.

66. Permanentmagnet nach einem der Ansprüche 56 bis 65 mit einem Gehalt an nichtmagnetischen Phasen, welche die feinen Teilchen der Verbindung des Typs Fe—Co—B—R, von der mindestens eine vorliegt, voneinander trennen.

67. Permanentmagnet nach Anspruch 66, worin die nichtmagnetischen Phasen in einer Menge von 1 bis 45 Vol-% vorliegen.

68. Permanentmagnet nach Anspruch 67, worin die nichtmagnetischen Phasen viel R enthalten.

69. Permanentmagnet nach einem der Ansprüche 56 bis 68, worin Co 5 bis 45 Atom-%, vorzugsweise 5 bis 25 Atom-%, beträgt.

70. Permanentmagnet nach einem der Ansprüche 56 bis 69, worin R etwa 15 Atom-% und B etwa 8 Atom-% betragen.

71. Gesinterter Permanentmagnet mit einem Gehalt an mindestens einer Verbindung des Typs Fe—Co—B—R mit einer tetragonalen Struktur, wobei R mindestens ein Seltenerdelement einschließlich Y ist.

72. Gesinterter Permanentmagnet nach Anspruch 70 mit einem Gehalt an nichtmagnetischen Phasen, die viel R aufweisen, in einer Menge von 1 bis 45 Vol-%.

73. Gesinterter Permanentmagnet nach Anspruch 72, worin die nichtmagnetischen Phasen in einer Menge von 2 bis 10 Vol-% vorliegen.

74. Gesinterter Permanentmagnet nach einem der Ansprüche 71 bis 73 mit einem Gehalt an 8 bis 30 Atom-% R, wobei R mindestens ein Seltenerdelement einschließlich Y ist, 2 bis 28 Atom-% B und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt.

75. Gesinterter Permanentmagnet nach Anspruch 74, worin R 12 bis 20 Atom-% und B 4 bis 24 Atom-% betragen.

76. Gesinterter Permanentmagnet nach einem der Ansprüche 71 bis 75, worin die leichten Seltenerdelemente nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R betragen.

77. Gesinterter Permanentmagnet nach Anspruch 76, worin Nd und/oder Pr in einer Menge von nicht weniger als 50 Atom-% der Gesamtmenge der Seitenerdelemente R betragen.

78. Gesinterter Permanentmagnet nach einem der Ansprüche 71 bis 77, worin R etwa 15 Atom-% und B etwa 8 Atom-% betragen.

79. Gesinterter Permanentmagnet nach einem der Ansprüche 71 bis 78 mit einer mittleren Kristallkorngröße von 1 bis 100 µm, vorzugsweise 1,5 bis 50 µm.

80. Anisotroper Permanentmagnet nach Anspruch 57 oder 75, gekennzeichnet durch ein Maximalenergieprodukt von mindestens 80 kJ/m^3 (10 MGOe).

81. Magnet nach Anspruch 80, gekennzeichnet durch ein Maximalenergieprodukt von nicht weniger als 160 kJ/m^3 (20 MGOe).

82. Permanentmagnet nach Anspruch 81, dadurch gekennzeichnet, daß das Maximalenergieprodukt nicht weniger als 240 kJ/m^3 (30 MGOe) beträgt.

83. Permanentmagnet nach Anspruch 82, dadurch gekennzeichnet, daß das Maximalenergieprodukt nicht weniger als 260 kJ/m^3 (33 MGOe) beträgt.

84. Permanentmagnet nach einem der Ansprüche 56 bis 83, erhältlich durch ein pulvermetallurgisches Verfahren.

85. Verfahren zum Herstellen eines Permanentmagneten durch Bilden einer Schmelze mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y ist, 2 bis 28

Atom-% Bor und als Rest Fe, das durch Co ersetzt ist, wobei Co nicht mehr als 50 Atom-% des gesamten Materials beträgt, Abkühlen der Schmelze bis zur Kristallisation, Pulverisieren des kristallisierten Produkts sowie Pressen und Sintern des gepulverten Produkts.

86. Verfahren nach Anspruch 85, worin die Schmelze weiterhin zusätzliche Elemente M gemäß der nachstehenden Liste enthält, wobei die Mengen dieser Elemente jeweils auf einen Wert begrenzt sind, der nicht größer ist als die nachfolgend in Atom-% angegebenen Werte,

4,5% Ti,	8,0% Ni,	5,0% Bi,
9,5% V,	12,5% Nb,	10,5% Ta,
8,5% Cr,	9,5% Mo,	9,5% W,
8,0% Mn,	9,5% Al,	2,5% Sb,
7,0% Ge,	3,5% Sn,	5,5% Zr
und 5,5% Hf,		

worin im Falls des Einsatzes von zwei oder mehr der Elemente M die Gesamtmenge an M auf den höchsten Wert eines der eingesetzten einzelnen Elemente M begrenzt ist, Abkühlen der Schmelze bis zum Kristallisieren, Pulverisieren des kristallisierten Produkts sowie Pressen und Sintern der gepulverten Legierung.

87. Verfahren nach Anspruch 85 oder 86, worin das gepulverte Produkt in einem Magnetfeld ausgerichtet wird.

88. Verfahren nach einem der Ansprüche 85 bis 87, worin die verdichteten Körper bei 1000 bis 1200°C gesintert werden.

Revendications

1. Alliage comprenant Fe—B—R, caractérisé en ce qu'il contient au moins un composé stable du type Fe—Co—B—R, composé qui peut être aimanté pour devenir un aimant permanent à température ambiante et à une température supérieure à la température ambiante, R représentant Nd et/ou Pr.

2. Alliage suivant la revendication 1, dans lequel le composé possède une structure tétragonale.

3. Alliage du type Fe—B—R, caractérisé en ce qu'il contient 8 à 30% de R, R représentant un ou plusieurs éléments faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co ne s'élève pas à plus de 50% de la quantité de matière totale contenant au moins un composé du type Fe—Co—B—R ayant une structure cristalline tétragonale.

4. Alliage suivant la revendication 2 ou 3, dans lequel l'axe Co de la structure tétragonale est égal à environ 1,2 nm (12 Å).

5. Alliage suivant la revendication 2, 3 ou 4, dans lequel l'axe ao est égal à environ 0,9 nm (9 Å).

6. Alliage suivant l'une quelconque des revendications 3 à 5, dans lequel au moins 50% de la quantité totale de R sont constitués de Nd et/ou Pr.

7. Alliage suivant l'une des revendications précédentes, ayant un point de Curie T_c compris dans l'intervalle de 310°C à 750°C.

8. Alliage suivant l'une des revendications précédentes, présentant des cristaux ayant un diamètre moyen de grains de 1 µm à 100 µm, de préférence de 1,5 µm à 50 µm.

9. Alliage suivant l'une des revendications précédentes, comprenant en outre des éléments supplémentaires M choisis dans la liste ci-dessous, les quantités de ces éléments étant limitées respectivement à des valeurs non supérieures aux valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni,	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

alliage dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

10. Alliage suivant l'une des revendications précédentes, dans lequel le système Fe—Co—B—R comprend 4 à 24% de R.

11. Alliage suivant l'une des revendications 1 à 10, dans lequel Co est présent en une quantité de 5 à 45%, de préférence de 5 à 25%.

12. Procédé de préparation d'un alliage contenant au moins un composé stable du type Fe—Co—B—R, composé qui peut être aimanté pour devenir un aimant permanent à température ambiante et à une température supérieure à la température ambiante, par fusion et coulée d'une composition contenant 2 à 28% de B, 8 à 30% de R, R représentant au moins un élément faisant partie des terres rares, y compris

l'yttrium, le reste étant du fer substitué avec du Co, la quantité de Co étant non supérieure à 50% de la matière totale.

13. Procédé suivant la revendication 12, dans lequel le fer, Co, des alliages de ferro-bore pour B et des éléments faisant partie des terres rares sont utilisée comme matières de départ.

14. Procédé suivant la revendication 12 ou 13, dans lequel les pièces coulées sont pulvérisées.

15. Procédé suivant la revendication 14, dans lequel la pulvérisation est effectuée à des dimensions de 0,5 à 100 µm, de préférence de 3 à 10 µm.

16. Procédé suivant l'une des revendications 12 à 15, dans lequel l'alliage comprend en outre un ou plusieurs des éléments choisis dans la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à une quantité non supérieure à la valeur mentionnée ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

procédé dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur le plus élevée de l'un des différents éléments M ajoutés.

17. Utilisation des alliages suivant l'une des revendications précédentes pour l'application à des supports d'enregistrement magnétique, des peintures magnétiques, des matières thermosensibles et des matières intermédiaires pour la production d'aimants permanents.

18. Matériau magnétique comprenant 8 à 30% de R, R étant au moins un élément faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant de Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la matière totale, et comprenant au moins 50% en volume d'une phase renfermant au moins un composé du type Fe—Co—B—R ayant une structure tétragonale.

19. Matériau magnétique suivant la revendication 18, dans lequel l'axe Co de la structure tétragonale est égal à environ 1,2 nm (12 Å).

20. Matériau magnétique suivant la revendication 18 ou 19, dans lequel l'axe ao de la structure tétragonale est égal à environ 0,9 nm (9 Å).

21. Matériau magnétique suivant l'une des revendications 18 à 20, dans lequel le diamètre moyen des grains cristallins est compris dans l'intervalle de 1,0 à 100 µm, de préférence de 1,5 à 50 µm.

22. Matériau magnétique suivant l'une des revendications 18 à 21, comprenant en outre un ou plusieurs des éléments choisis parmi la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités non supérieures à la valeur mentionnée ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

matériau dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

23. Matériau magnétique suivant l'une des revendications 18 à 22, dans lequel les éléments faisant partie des terres rares légères sont utilisés comme éléments R faisant partie des terres rares.

24. Matériau magnétique suivant la revendication 23, dans lequel Nd et/ou Pr sont utilisés comme éléments R faisant partie des terres rares.

25. Matériau magnétique fritté consistant en une poudre de matière magnétique présentant des cristaux de structure tétragonale et comprenant 8 à 30% de R, R représentant un ou plusieurs des éléments faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la composition totale.

26. Procédé de production d'une poudre de matériau magnétique présentant une structure tétragonale et comprenant 8 à 30% de R, R représentant un ou plusieurs éléments faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la composition totale, par chauffage d'un oxyde de terres rares R_2O_3 pulverulent servant de matière première pour R, avec du Fe pulvérulent, du Co pulvérulent, un mélange Fe—B pulvérulent et un agent réducteur destiné à une réduction directe.

27. Procédé suivant la revendication 26, comprenant une étage supplémentaire de frittage des alliages en poudre.

28. Matériau magnétique permanent comprenant 8 à 30% de R, R représentant un ou plusieurs

éléments faisant partie des terres rares, y compris Y, Nd et/ou Pr en des quantités non inférieures à 50% de R, 2 à 28% de B, le reste étant de fer substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la matière totale.

29. Matériau magnétique permanent suivant la revendication 28, dans lequel la quantité de R est comprise dans l'intervalle de 11 à 24% en le quantité de R est comprise dans l'intervalle de 4 à 24%.

30. Matériau magnétique permanent suivant la revendication 28 ou 29, comprenant 12 à 20% de R et 4 à 24% de B.

31. Matériau magnétique permanent suivant l'une des revendications 28 à 30, qui contient plus de 50% en volume d'une phase renfermant au moins un composé Fe—Co—B—R stable ayant une structure tétragonale.

32. Matériau magnétique permanent comprenant au moins 50% en volume d'une phase renfermant au moins un composé de type Fe—Co—B—R ayant une structure tétragonale, dans lequel R représente au moins un élément faisant partie des terres rares, y compris Y.

33. Matériau magnétique permanent suivant la revendication 31 ou 32, dans lequel l'axe Co de la structure tétragonale est égal à environ 1,2 nm (12 Å).

34. Matériau magnétique permament suivant l'une des revendications 31 à 33, dans lequel l'axe ao de la structure tétragonale est égal à environ 0,9 nm (9 Å).

35. Matériau magnétique permanent suivant l'une des revendications 28 à 34, ayant un diamètre moyen des grains cristallins de 1 à 100 µm, de préférence de 1,5 à 50 µm.

36. Matériau magnétique permanent suivant l'une des revendications 28 à 35, dans leque les particules fines de la phase contenant au moins un composé Fe—Co—B—R stable sont séparées les unes des autres par des phases non magnétiques.

37. Matériau magnétique permanent suivant la revendication 36, dans lequel les phases non magnétiques sont présentes en un volume de 1 à 45% en volume.

38. Matériau magnétique permanent suivant la revendication 37, dans lequel les phases non magnétiques contiennent une forte proportion de R.

39. Matériau magnétique permanent suivant l'une des revendications 28 à 38, comprenant en outre des éléments M supplémentaires choisis dans la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités n'excédant pas les valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

matériau dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

40. Matériau magnétique permanent anisotrope comprenant 8 à 30% de R, R représentant un ou plusieurs éléments faisant partie des terres rares, y compris Y, 2 à 28% de bore, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la matière totale.

41. Matériau magnétique permanent anisotrope suivant la revendication 40, comprenant 12 à 20% de R et 4 à 24% de B.

42. Matériau magnétique permanent anisotrope suivant la revendication 40 ou 41, qui contient plus de 50% en volume d'une phase renfermant au moins en composé Fe—Co—B—R stable ayant une structure tétragonale.

43. Matériau magnétique permanent anisotrope suivant la revendication 42, dans lequel l'axe Co de la structure tétragonale est égal à environ 1,2 nm (12 Å).

44. Matériau magnétique permanent anisotrope suivant la revendication 42 ou 43, dans lequel l'axe ao de la structure tétragonale est égal à environ 0,9 nm (9 Å).

45. Matériau magnétique permanent anisotrope suivant l'une des revendications 40 à 44, ayant un diamètre moyen des grains cristallins de 1 à 100 µm, de préférence de 1,5 à 50 µm.

46. Matériau magnétique permanent anisotrope suivant l'une des revendications 40 à 45, dans lequel les particules fines de la phase contenant au moins un composé Fe—Co—B—R stable sont séparées les unes des autres par des phases non magnétiques.

47. Matériau magnétique permanent anisotrope suivant la revendication 46, dans lequel les phases non magnétiques sont présentes en un volume de 1 à 45% en volume.

48. Matériau magnétique permanent anisotrope suivant la revendication 47, dans lequel les phases non magnétiques contiennent une forte proportion de R.

49. Matériau magnétique permanent anisotrope suivant l'une des revendications 40 à 48, comprenant en outre des éléments supplémentaires M choisis dans la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités non supérieures aux valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

matériau dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

50. Procédé de production d'un matériau magnétique permanent anisotrope consistant à préparer une masse fondue comprenant 8 à 30% de R, R représentant un ou plusieurs éléments faisant partie des terres rares, y compris Y, 2 à 28% de bore, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co s'excède pas 50% de la composition totale, à refroidir la masse fondue pour provoquer une cristallisation et à pulvériser le produit cristallin.

51. Procédé de production d'un matériau magnétique permanent anisotrope suivant la revendication 50, dans lequel la quantité restante est représentée par du Fe substitué avec du Co, et un ou plusieurs des éléments M choisis dans la liste mentionnée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités non supérieures aux valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

procédé dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

52. Procédé suivant la revendication 50 ou 51, dans lequel le produit cristallin est pulvérisé à des dimensions de 3 à 10 µm.

53. Procédé suivant l'une des revendications 50 à 52, dans lequel le produit pulvérisé est fritté.

54. Procédé suivant la revendication 53, dans lequel le frittage est effectué à une température de 1000 à 1200°C.

55. Procédé suivant la revendication 54, dans lequel le frittage est effectué sous atmosphère d'un gaz inerte tel que l'argon.

56. Aimant permanent comprenant 8 à 30% de R, R étant un ou plusieurs des éléments faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% du matériau total, pouvant être obtenu par frittage d'une poudre dudit matériau.

57. Aimant permanent suivant la revendication 56, comprenant 4 à 24% de B et 12 à 20% de R.

58. Aimant permanent suivant la revendication 56 ou 57, présentant des propriétés anisotropes pouvant être obtenues par une opération supplémentaire d'alignement dans un champ magnétique.

59. Aimant permanent suivant l'une des revendications 56 à 58, dans lequel la quantité d'éléments faisant partie des terres rares légères est non inférieure à 50% de la quantité totale des éléments R faisant partie des terres rares.

60 Aimant permanent suivant la revendication 59, dans lequel la quantité de Nd et/ou Pr n'est pas inférieure à 50% de la quantité totale de R.

61. Aimant permanent suivant l'une des revendications 56 à 60, dans lequel le diamètre moyen des grains cristallins est compris dans l'intervalle de 1 à 100 µm, de préférence de 1,5 à 50 µm.

62. Aimant permanent suivant l'une des revendications 56 à 61, comprenant en outre des éléments M choisis dans la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités non supérieures aux valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

aimant dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés.

63. Aimant permanent suivant l'une des revendications 56 à 62, comprenant au moins un composé du type Fe—Co—B—R ayant une structure tétragonale.

64. Aimant permanent suivant la revendication 63, dans lequel l'axe Co de la structure tétragonale est égal à environ 1,2 nm (12 Å).

65. Aimant permanent suivant la revendication 63 ou 64, dans lequel l'axe ao de la structure tétragonale est égal à environ 0,9 nm (9 Å).

66. Aimant permanent suivant l'une des revendications 56 à 65, comprenant des phases non magnétiques séparant les particules fines d'au moins un composé de type Fe—Co—B—R d'un autre composé.

67. Aimant permanent suivant la revendication 66, dans lequel les phases non magnétiques sont présentes en une proportion de 1 à 45% en volume.

68. Aimant permanent suivant la revendication 67, dans lequel les phases non magnétiques contiennent une forte proportion de R.

69. Aimant permanent suivant l'une des revendications 56 à 68, dans lequel Co est présent en une quantité de 5 à 45%, de préférence de 5 à 25%.

70. Aimant permanent suivant l'une des revendications 56 à 69, dans lequel R est présent en une quantité d'environ 15% et B est présent en une quantité d'environ 8%.

71. Aimant permanent fritté comprenant au moins un composé de type Fe—Co—B—R ayant une structure rétragonale, dans lequel R représente au moins un élément faisant partie des terres rares, y compris Y.

72. Aimant permanent fritté suivant la revendication 70, contenant des phases non magnétiques avec une forte proportion de R comprise dans l'intervalle de 1 à 45% en volume.

73. Aimant permanent fritté suivant la revendication 72, dans lequel les phases non magnétiques sont présentes en une proportion de 2 à 10% en volume.

74. Aimant permanent fritté suivant l'une des revendications 71 à 73, comprenant 8 à 30% de R, R représentant au moins un élément faisant partie des terres rares, y compris Y, 2 à 28% de B, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la matière totale.

75. Aimant permanent fritté suivant la revendication 74, dans lequel R est présent en une proportion de 12 à 20% et B est présent en une proportion de 4 à 24%.

76. Aimant permanent fritté suivant l'une des revendications 71 à 75, dans lequel la quantité d'éléments faisant partie des terres rares légères est non inférieure à 50% de la quantité totale d'éléments R faisant partie des terres rares.

77. Aimant permanent fritté suivant la revendication 76, dans lequel la quantité de Nd et/ou Pr n'est pas inférieure à 50% de la quantité totale d'éléments R faisant partie des terres rares.

78. Aimant permanent fritté suivant l'une des revendications 71 à 77, dans lequel R est présent en une quantité d'environ 15% et B est présent en une quantité d'environ 8%.

79. Aimant permanent fritté suivant l'une des revendications 71 à 78, dans lequel le diamètre moyen des grains cristallins est compris dans l'intervalle de 1 à 100 µm, de préférence de 1,5 à 50 µm.

80 Aimant permanent anisotrope suivant la revendication 57 ou 75, caractérisé par un facteur d'énergie maximal d'au moins 80 kJ/m³ (10 MGOe).

81. Aimant suivant la revendication 80, caractérisé en ce que le facteur d'énergie maximal est non inférieur à 160 kJ/m³ (20 MGOe).

82. Aimant permanent suivant la revendication 81, caractérisé en ce que le facteur d'énergie maximal est non inférieur à 240 kJ/m³ (30 MGOe).

83. Aimant permanent suivant la revendication 82, caractérisé en ce que le facteur d'énergie maximal est non inférieur à 260 kJ/m³ (33 MGOe).

84. Aimant permanent suivant l'une des revendications 56 à 83, pouvant être obtenu par mise en oeuvre d'un procédé de métallurgie des poudres.

85. Procédé de production d'un aimant permanent par préparation d'une masse fondue comprenant 8 à 30% de R, R représentant en ou plusieurs éléments faisant partie des terres rares, y compris Y, 2 à 28% de bore, le reste étant du Fe substitué avec du Co, dans lequel la quantité de Co n'excède pas 50% de la matière totale, refroidissement de la masse fondue pour provoquer sa cristallisation, pulvérisation de produit cristallisé, passage à la presse et frittage du produit pulvérisé.

86. Procédé suivant la revendication 85, dans lequel la masse fondue comprend en outre des éléments supplémentaires M choisis dans la liste présentée ci-dessous, les quantités de ces éléments étant limitées respectivement à des quantités non supérieures aux valeurs mentionnées ci-dessous, en pourcentages atomiques:

4,5% Ti	8,0% Ni	5,0% Bi
9,5% V	12,5% Nb	10,5% Ta
8,5% Cr	9,5% Mo	9,5% W
8,0% Mn	9,5% Al	2,5% Sb
7,0% Ge	3,5% Sn	5,5% Zr
et 5,5% Hf		

procédé dans lequel, lorsque deux ou plus de deux éléments M sont introduits, la quantité totale de M est limitée à la valeur la plus élevée de l'un des différents éléments M ajoutés, la masse fondue est refroidie

pour provoquer sa cristallisation, le produit cristallisé est pulvérisé et l'alliage pulvérisé est passé à la presse et fritté.

87. Procédé suivant la revendication 85 ou 86, dans lequel le produit pulvérisé est soumis à une orientation dans un champ magnétique.

88. Procédé suivant l'une des revendications 85 à 87, dans lequel les comprisés sont frittés à une température de 1000 à 1200°C.

FIG. 1

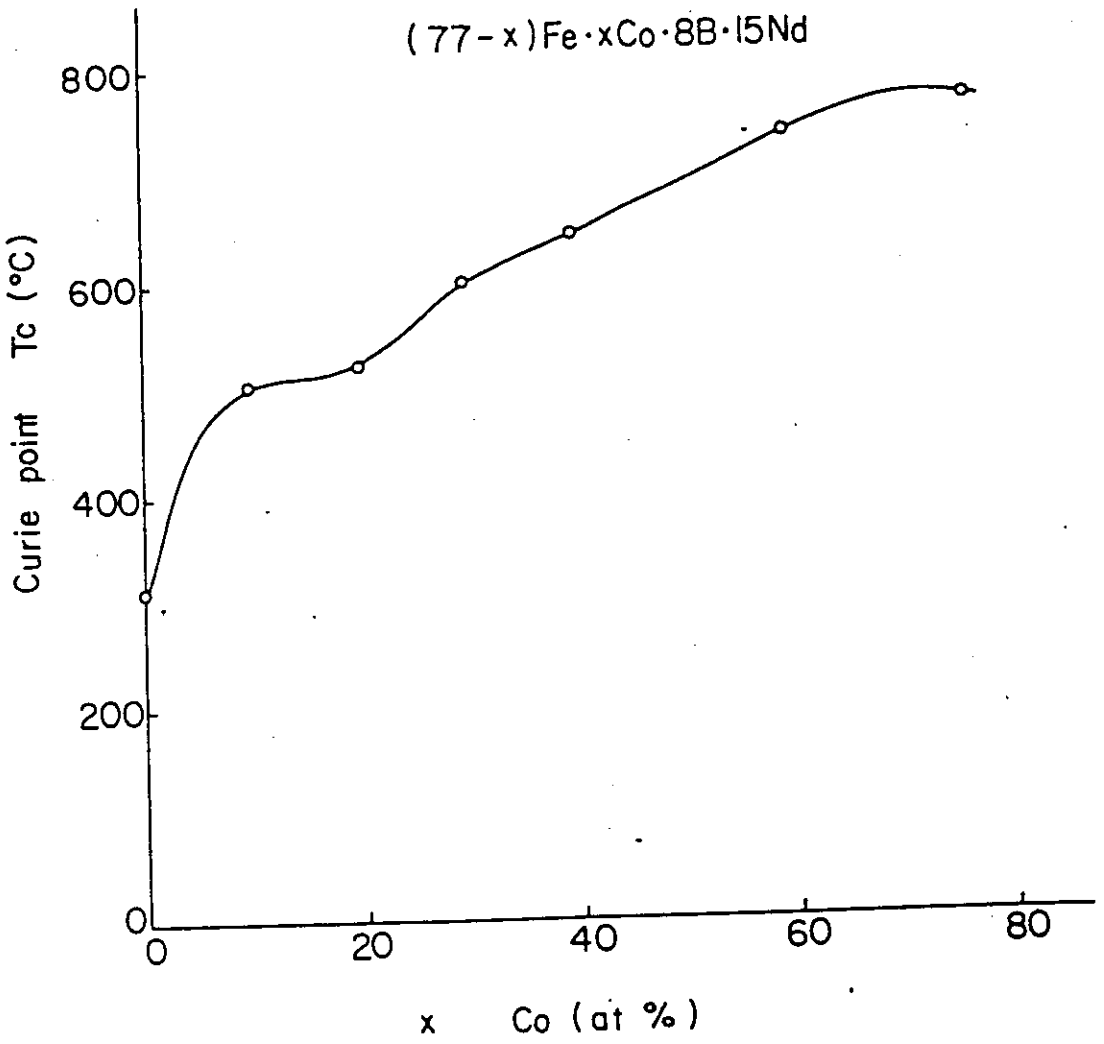

(77-x)Fe·xCo·8B·15Nd
Curie point Tc (°C)
800
600
400
200
0
0
20
40
60
80
x Co (at %)

FIG. 2

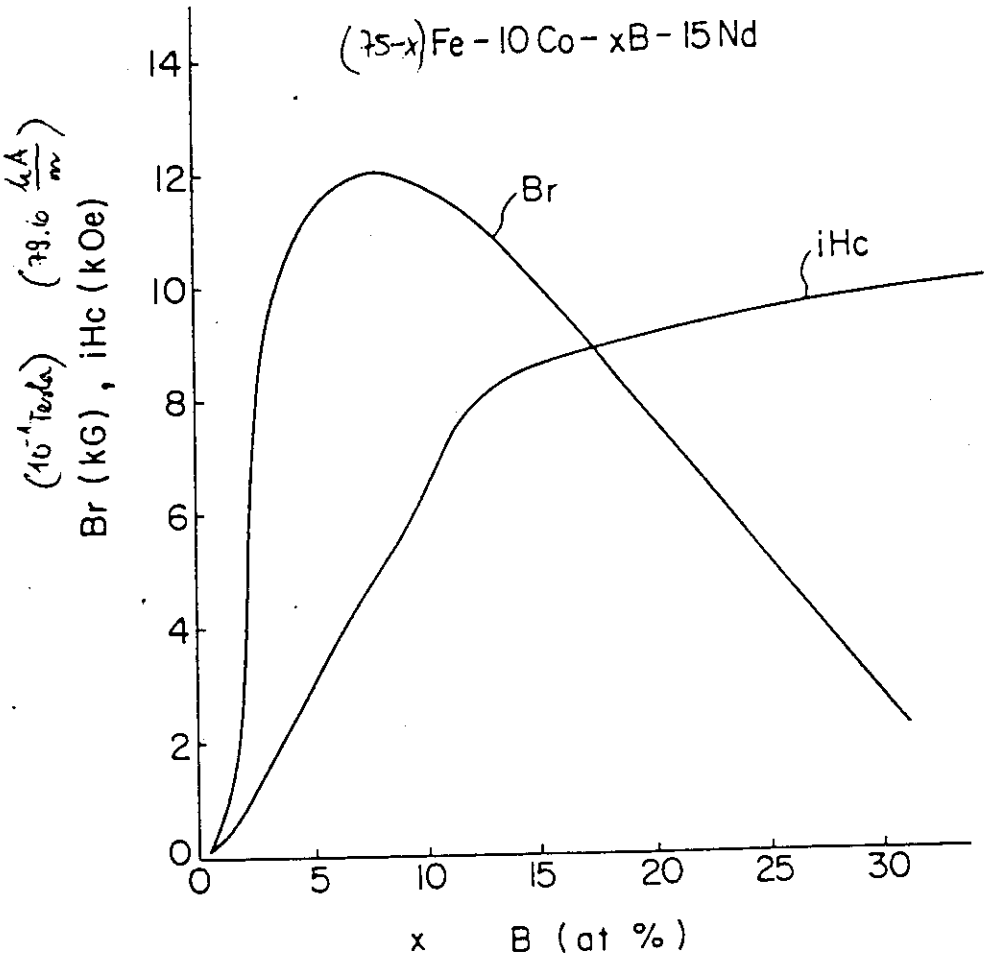

(75-x) Fe - 10 Co - xB - 15 Nd
Br (kG), iHc (kOe)
(10⁻⁴ Tesla) (79.6 kA/m)
Br
iHc
0
2
4
6
8
10
12
14
0
5
10
15
20
25
30
x B (at %)

FIG. 3

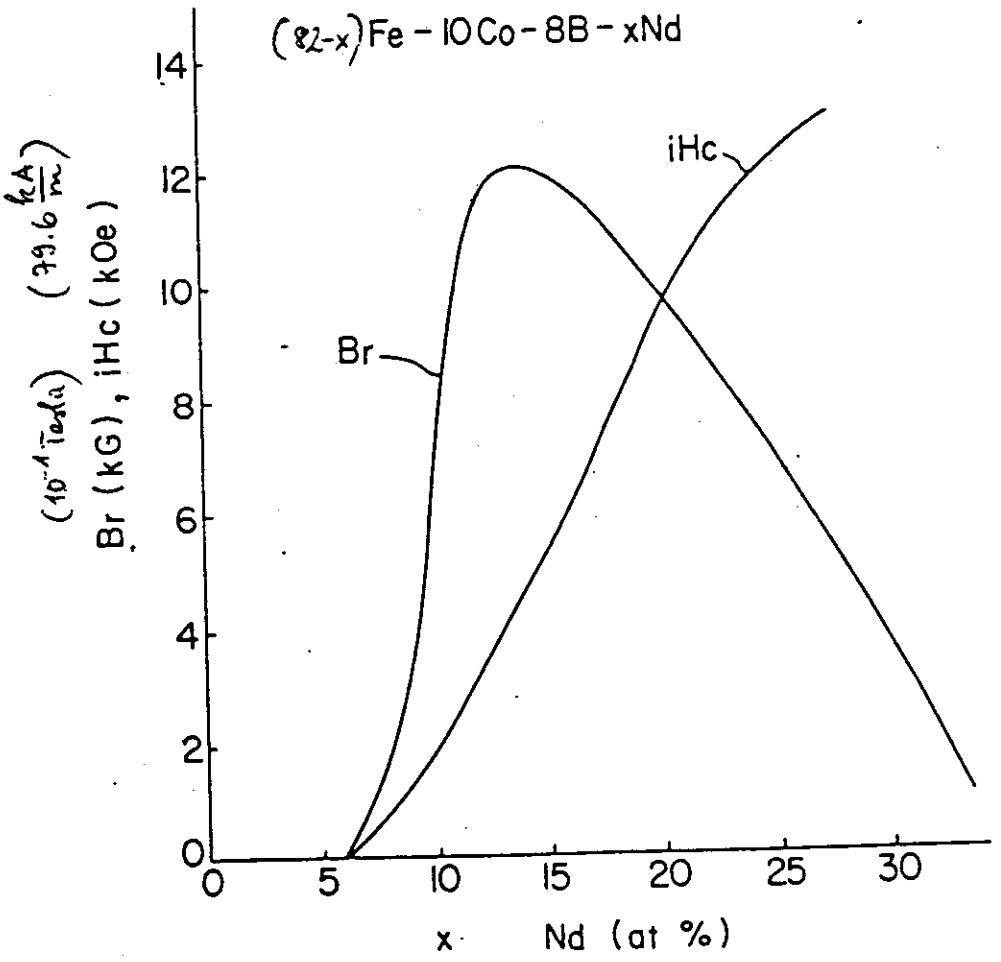

(82-x)Fe - 10Co - 8B - xNd
Br (kG), iHc (kOe)
(10⁻¹ Tesla) (79.6 kA/m)
Br
iHc
0
2
4
6
8
10
12
14
0
5
10
15
20
25
30
x Nd (at %)

FIG. 4

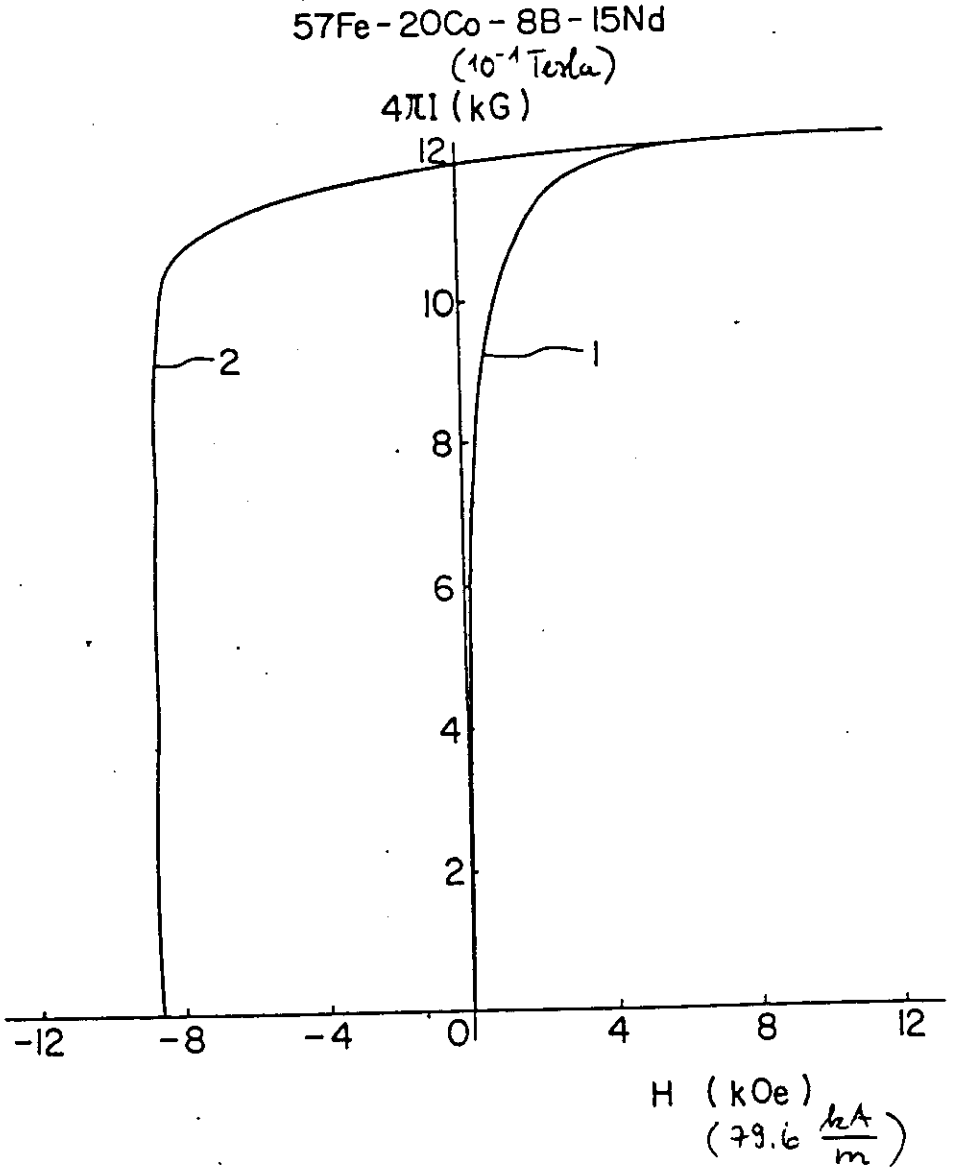

57Fe - 20Co - 8B - 15Nd
(10⁻¹ Tesla)
4πI (kG)
12
10
8
6
4
2
1
2
-12
-8
-4
0
4
8
12
H (kOe)
(79.6 kA/m)

FIG. 5

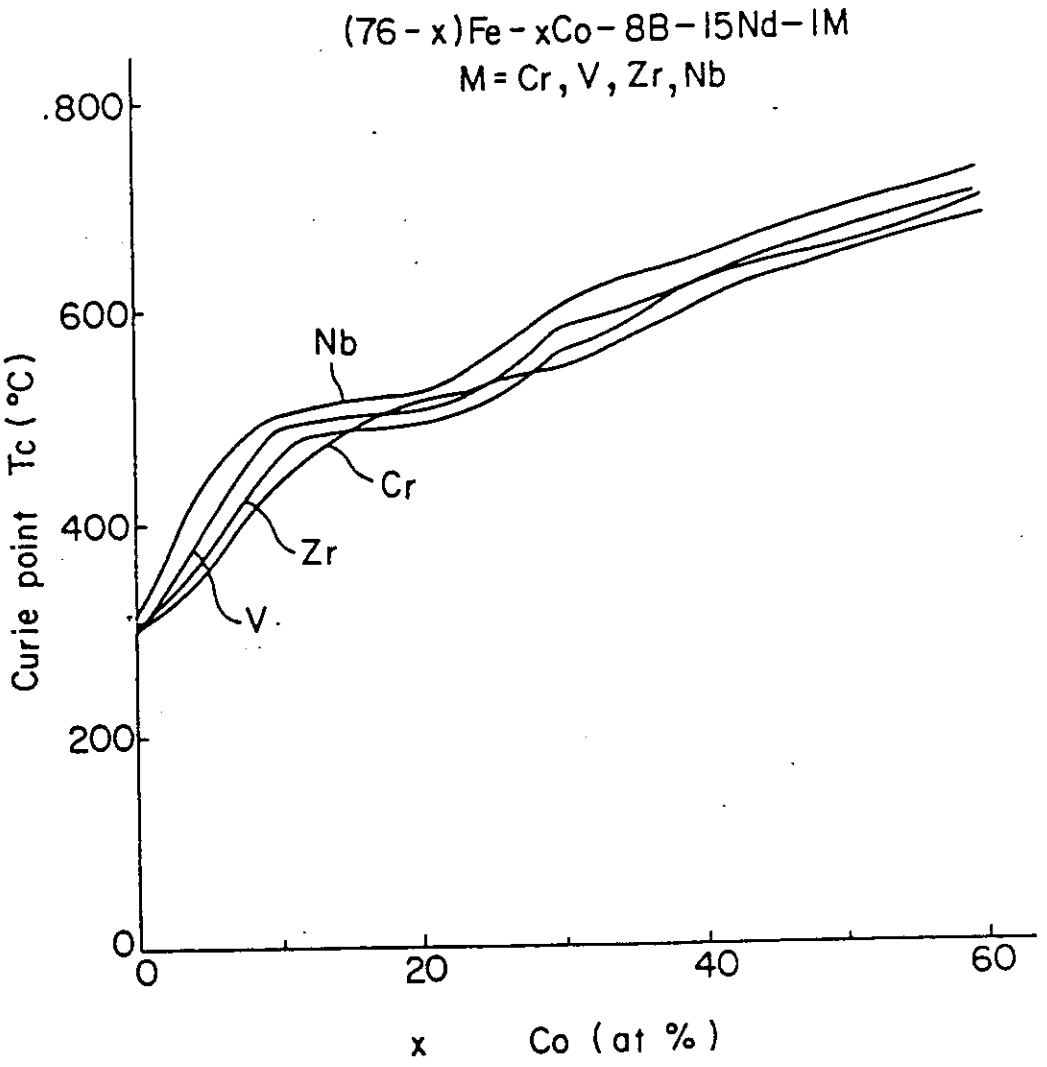

(76 - x) Fe - xCo - 8B - 15Nd - 1M
M = Cr, V, Zr, Nb
800
600
400
200
0
Curie point Tc (°C)
Nb
Cr
Zr
V
0
20
40
60
x Co (at %)

FIG. 6

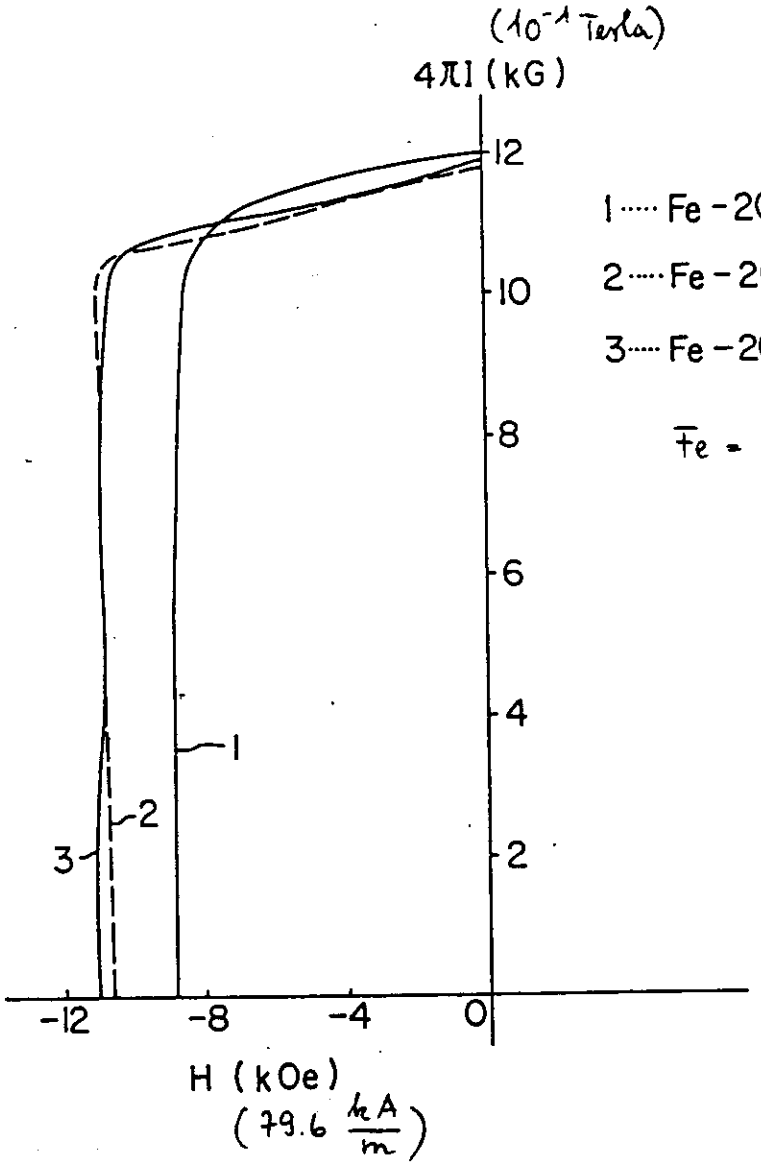

(10⁻¹ Tesla)
4πI (kG)
12
10
8
6
4
2
1
2
3
-12
-8
-4
0
H (kOe)
(79.6 kA/m)
1 ····· Fe - 20Co - 8B - 15Nd
2 ····· Fe - 20 Co - 8B - 15Nd - 1Nb
3 ····· Fe - 20 Co - 8B - 15Nd - 1W
Fe = balance Fe

FIG. 7

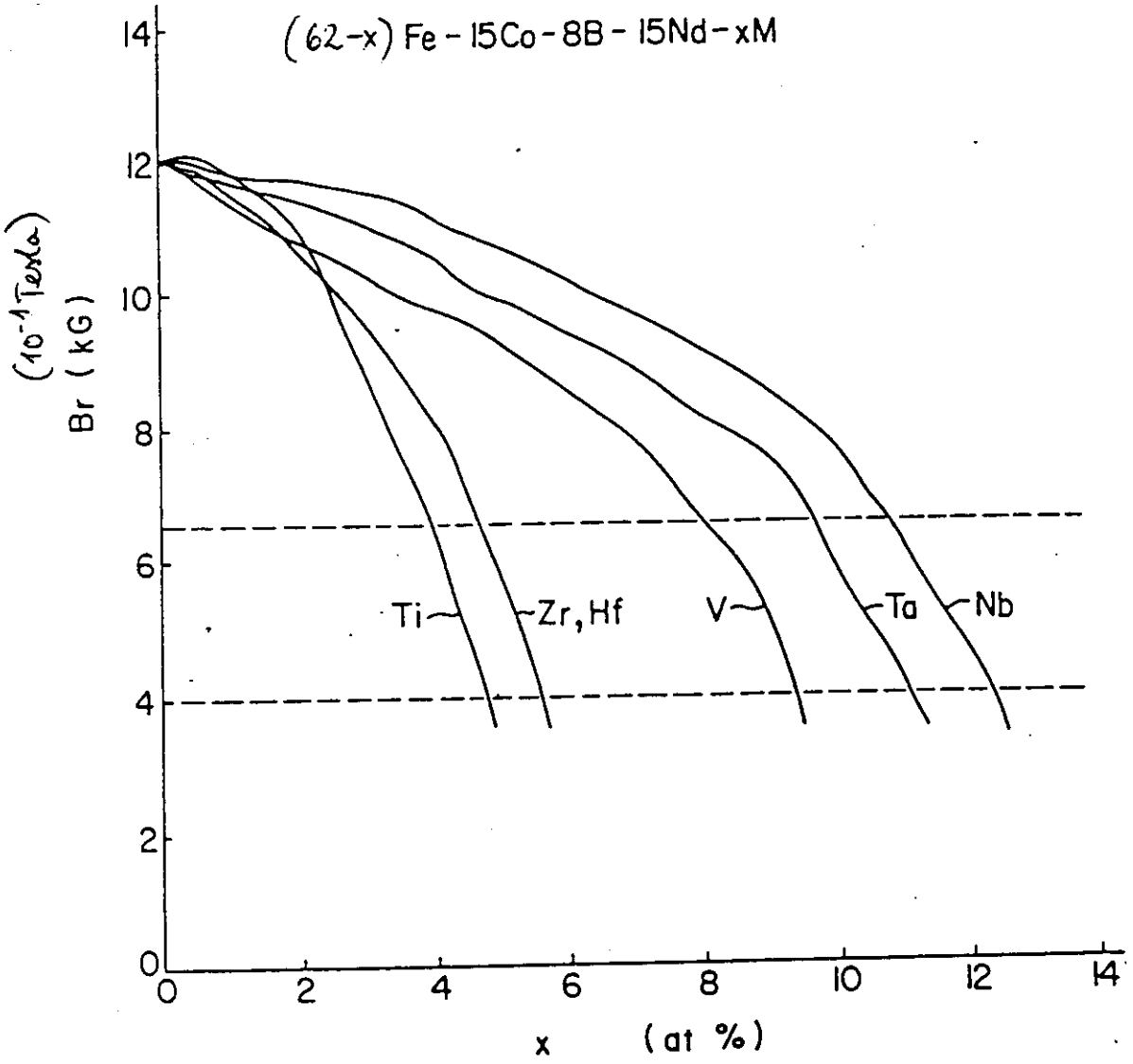

(62-x) Fe - 15Co - 8B - 15Nd - xM
Br (kG)
(10⁻¹ Tesla)
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
x (at %)
Ti
Zr, Hf
V
Ta
Nb

FIG. 8

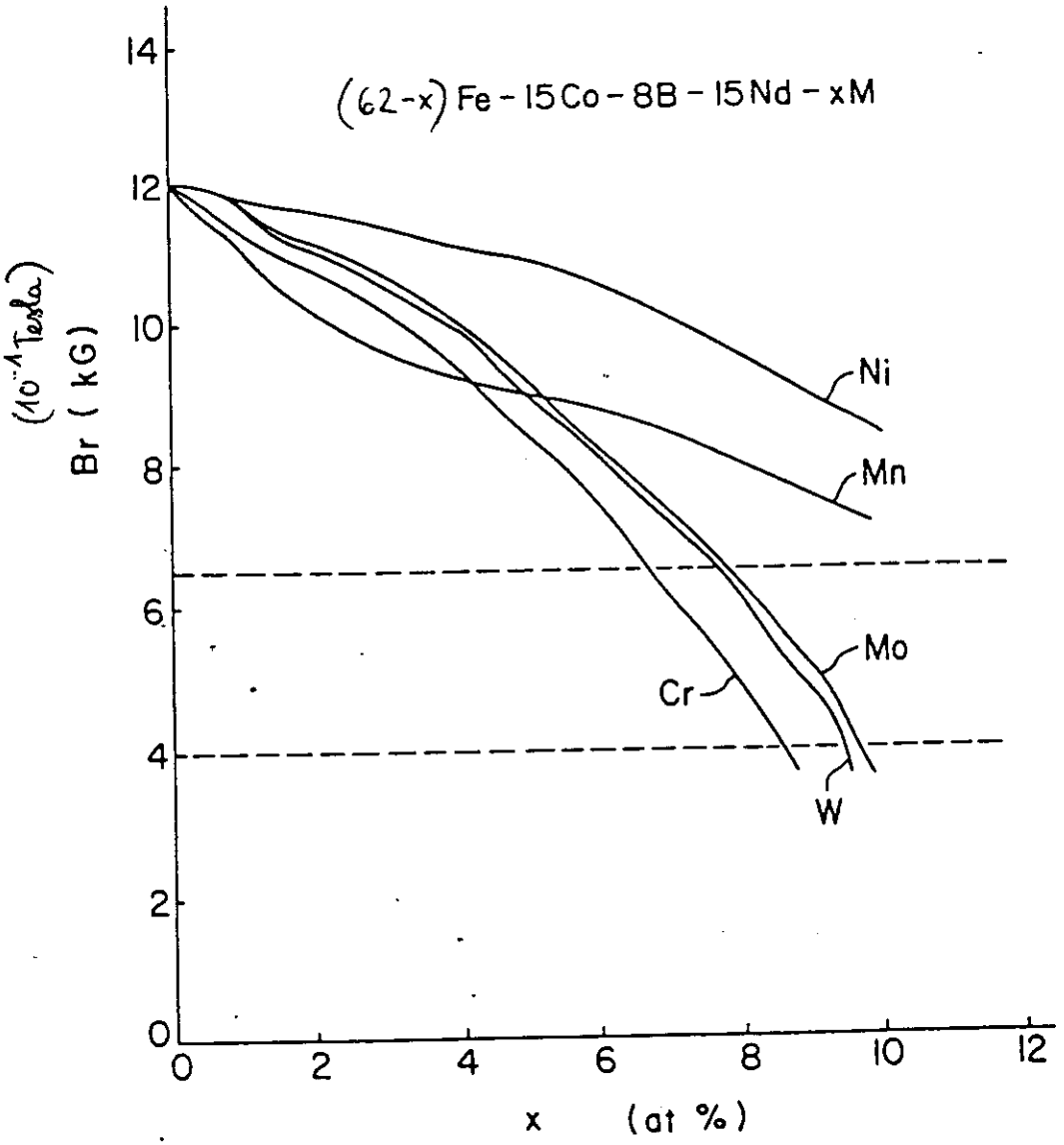

(62-x) Fe - 15 Co - 8B - 15 Nd - xM
Br (kG) (10⁻¹ Tesla)
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
x (at %)
Ni
Mn
Mo
Cr
W

FIG. 9

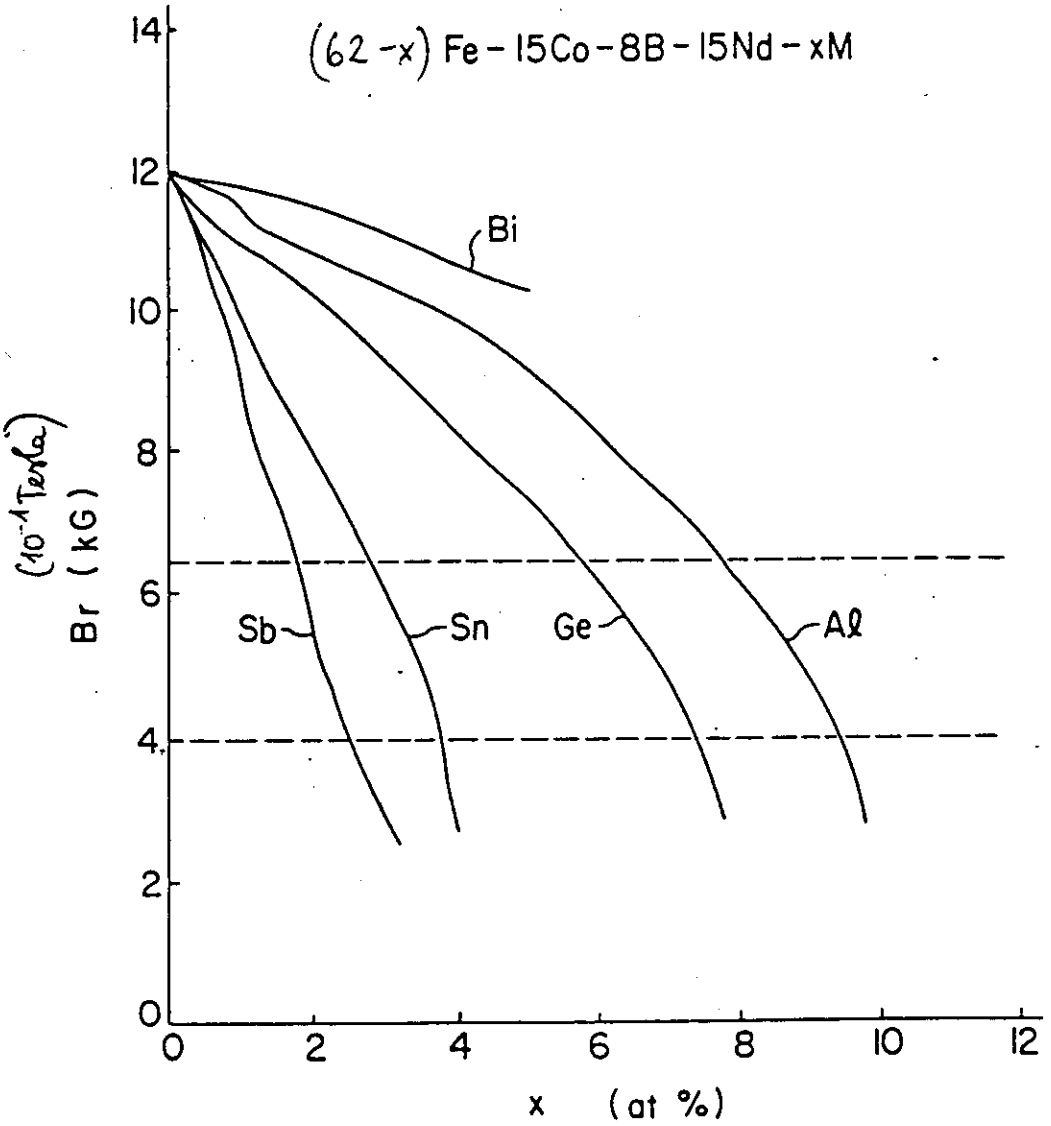

(62-x) Fe-15Co-8B-15Nd-xM
Br (kG)
(10⁻¹ Tesla)
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
x (at %)
Bi
Sb
Sn
Ge
Al

FIG. 10

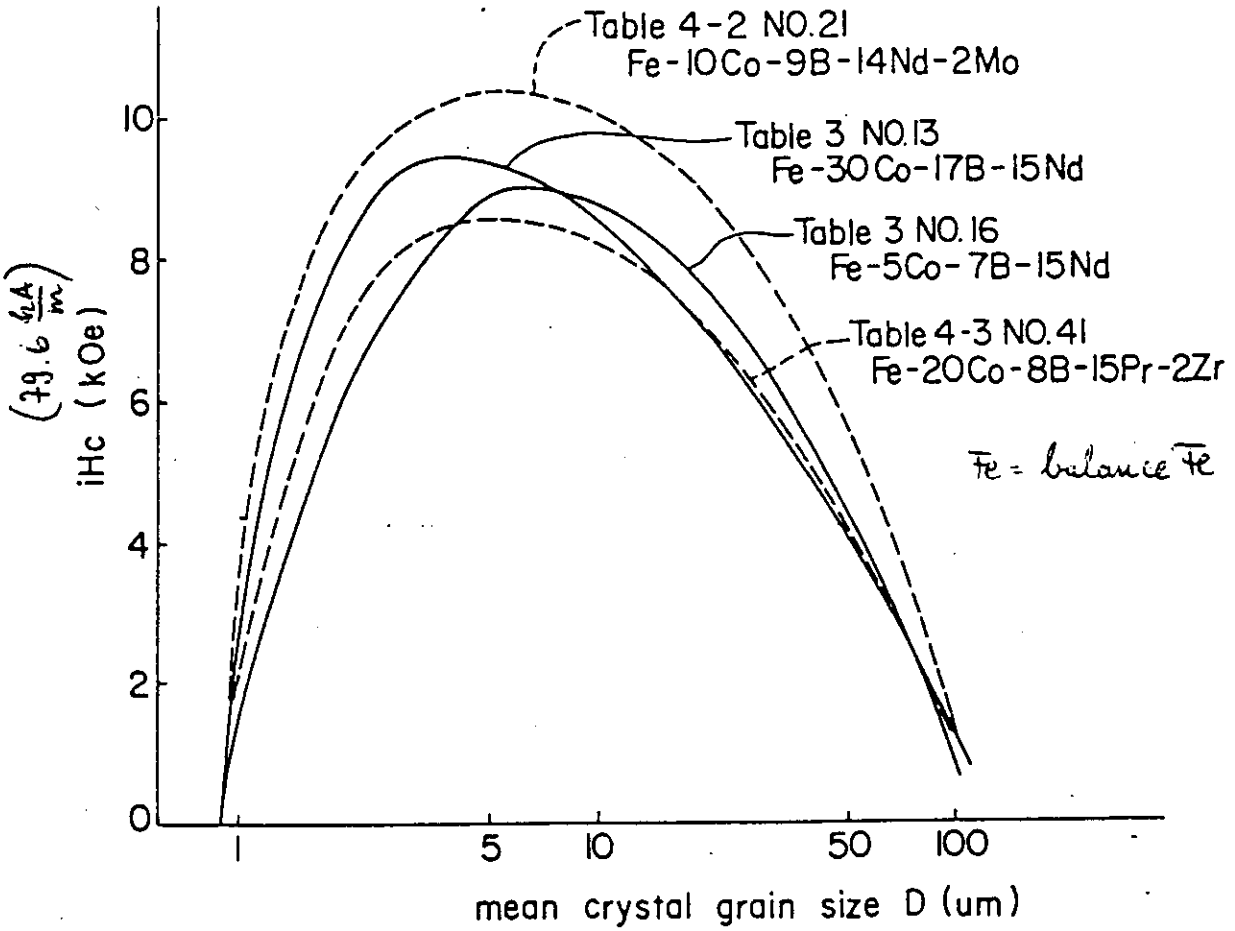


Table 4-2 NO.21
Fe-10Co-9B-14Nd-2Mo
Table 3 NO.13
Fe-30Co-17B-15Nd
Table 3 NO.16
Fe-5Co-7B-15Nd
Table 4-3 NO.41
Fe-20Co-8B-15Pr-2Zr
Fe = balance Fe
iHc (kOe)
(79.6 kA/m)
0
2
4
6
8
10
1
5
10
50
100
mean crystal grain size D (um)

FIG. 11

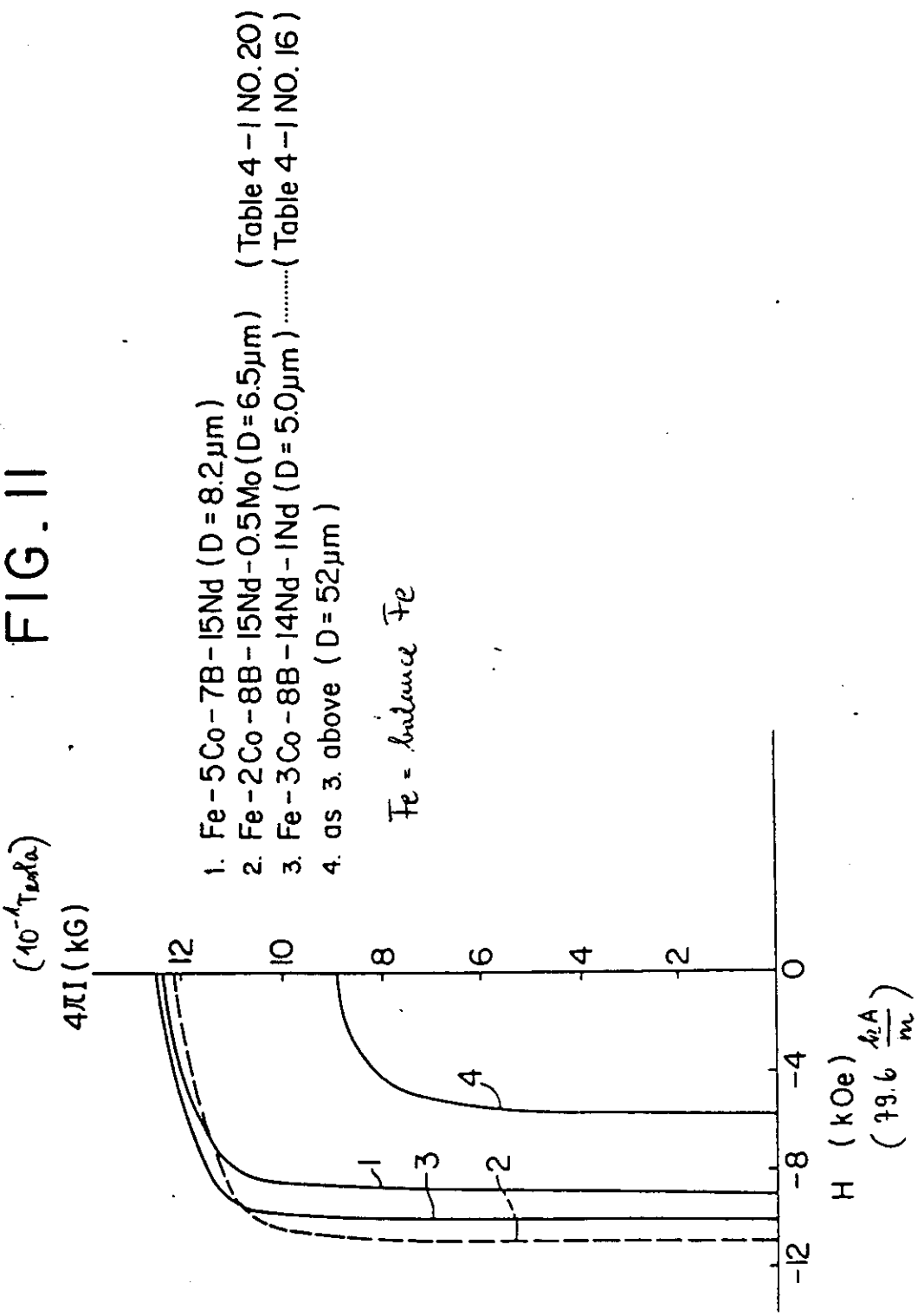

1. Fe-5Co-7B-15Nd (D=8.2μm)
2. Fe-2Co-8B-15Nd-0.5Mo (D=6.5μm) (Table 4-1 NO. 20)
3. Fe-3Co-8B-14Nd-1Nd (D=5.0μm) ..... (Table 4-1 NO. 16)
4. as 3. above (D=52μm)
Fe = balance Fe
4πI (kG)
(10⁻⁴Tesla)
12
10
8
6
4
2
0
-4
-8
-12
H (kOe)
(79.6 kA/m)
1
2
3
4

FIG. 12

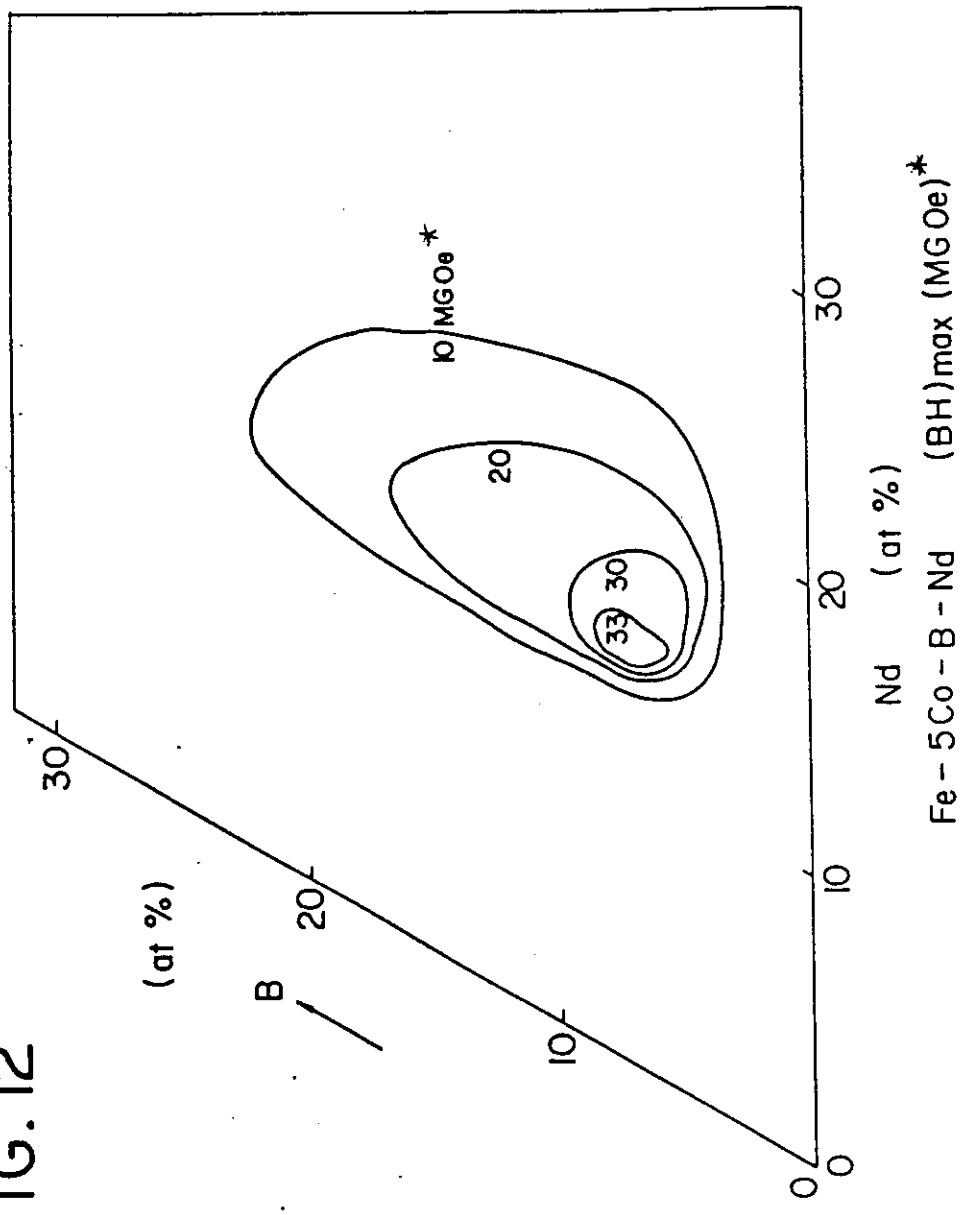
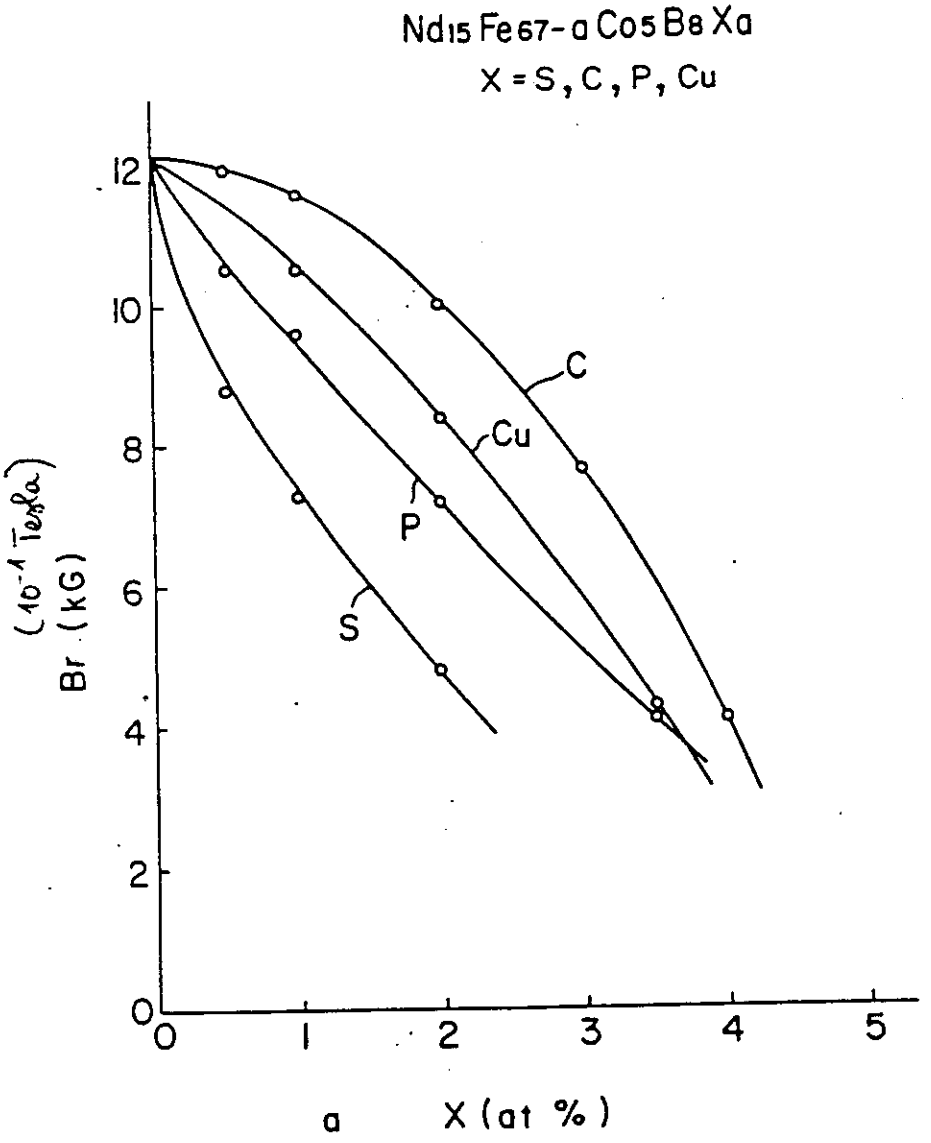

10 MGOe*
20
30
33
0
10
20
30
B (at %)
Nd (at %)
Fe - 5Co - B - Nd (BH)max (MGOe)*
* 1 MGOe = 7.96 kJ/m³
Fe = balance Fe

FIG. 13


Nd15 Fe67-a Co5 B8 Xa
X = S, C, P, Cu
12
10
8
6
4
2
0
0
1
2
3
4
5
C
Cu
P
S
(10⁻¹ Tesla)
Br (kG)
a
X (at %)

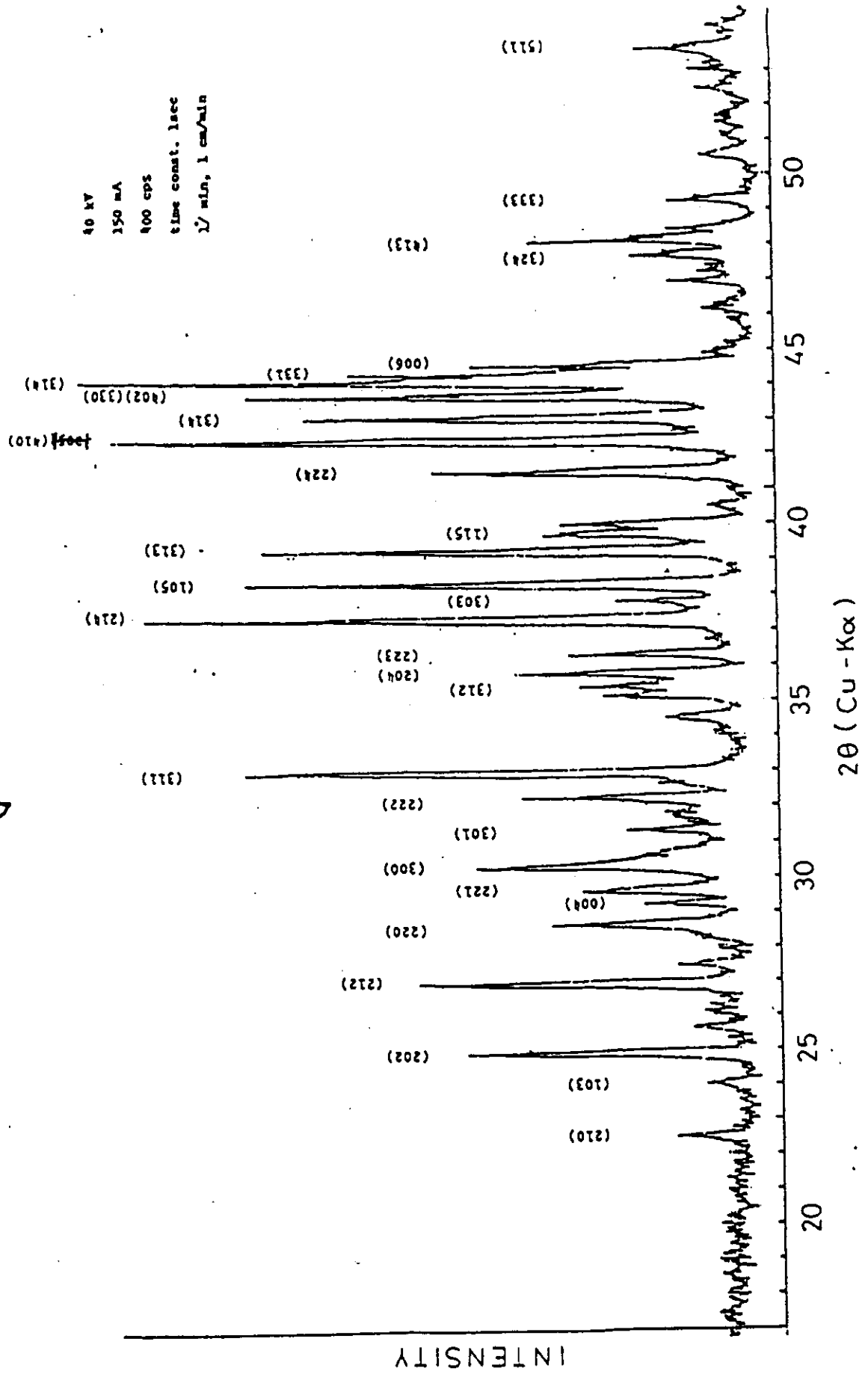
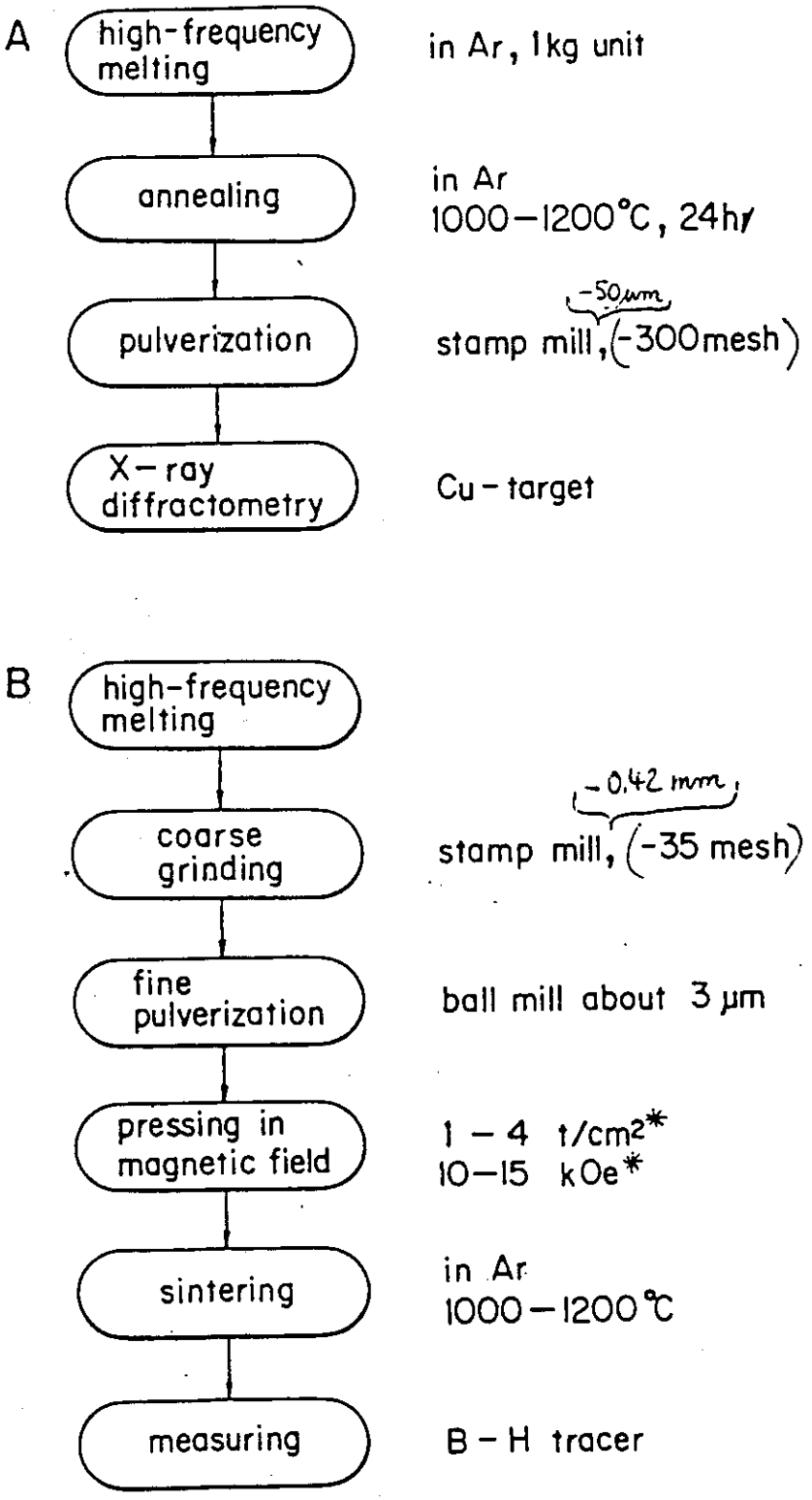

40 kV
150 mA
400 cps
time const. 1sec
1° min, 1 cm/min
(511)
(333)
(413)
(324)
(006)
(331)
(314)
(402)(330)
(314)
(410)
(224)
(115)
(313)
(105)
(303)
(214)
(223)
(204)
(312)
(311)
(222)
(301)
(300)
(221)
(004)
(220)
(212)
(202)
(103)
(210)
INTENSITY
20
25
30
35
40
45
50
2θ (Cu - Kα)

Fig. 14

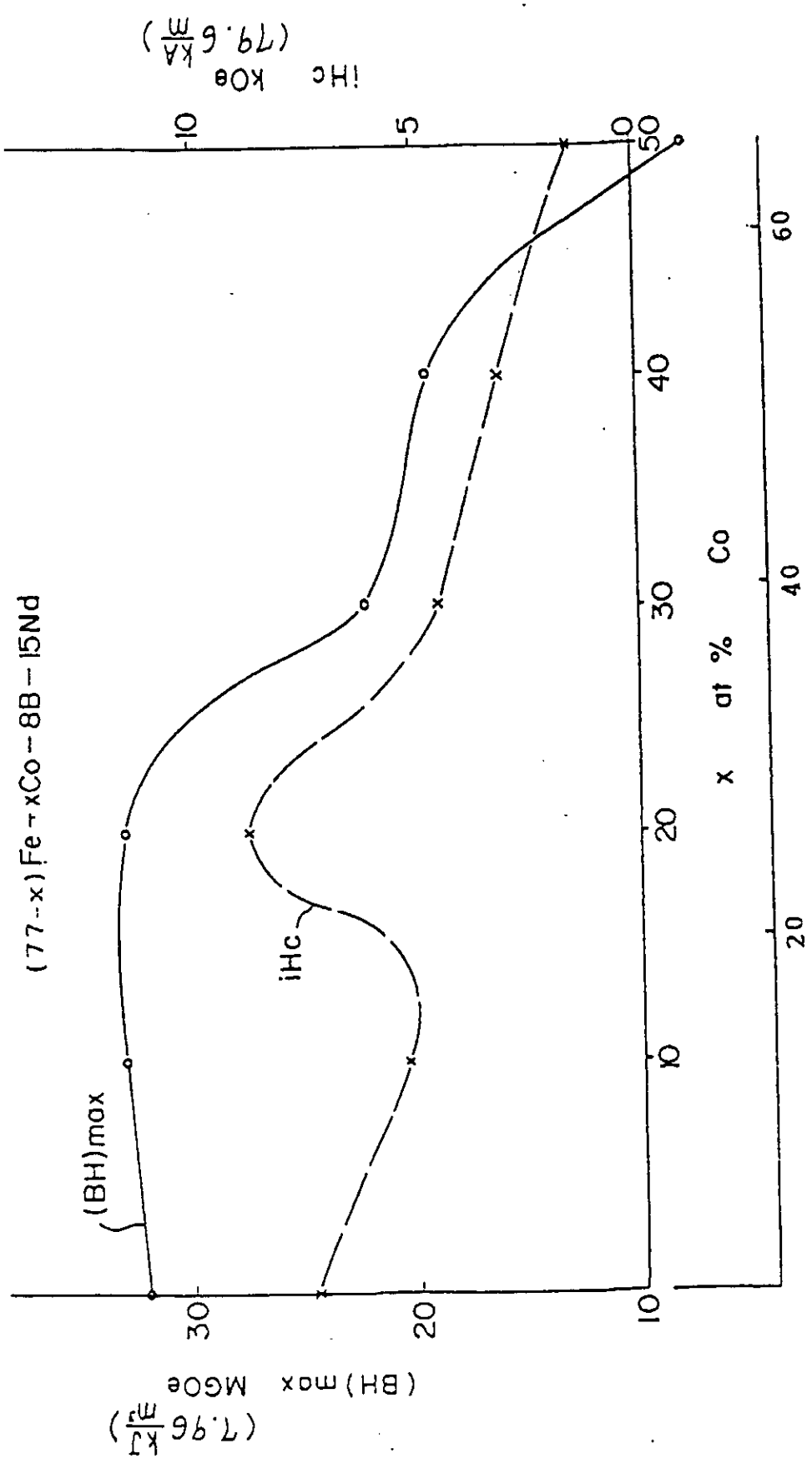
FIG. 15



*. $1\ t/cm^2 = 9.81 \times 10^7\ Pa$

$1\ kOe = 79.6\ \frac{kA}{m}$

FIG. 16


(77-x) Fe-xCo-8B-15Nd
(BH)max
iHc
(BH)max MGOe
(7.96 kJ/m³)
iHc kOe
(79.6 kA/m)
x at % Co
x/77 · 100 (%)

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14.05.1983 in Japan - doc: 05848608
31.05.1983 in Japan - doc: 05948768
27.09.1982 in Japan - doc: 051666638

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Title MAGNETIC MATERIALS AND PERMANENT MAGNETS

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Classified to
C1A U1S
H01F

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Examination requested 26.07.1983

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12.03.1985 EPO: Search report published on 13.03.1985
Entry Type 25.11 Staff ID. Auth ID. EPT

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Entry Type 8.11 Staff ID. BW2 Auth ID. AA

17.10.1989 Notification of change of Applicant/Proprietor address of SUMITOMO SPECIAL METALS CO., LTD., 22, Kitahama 5-chome Higashi-ku, Osaka-shi Osaka 541, Japan [ADP No. 507227500011]
to
SUMITOMO SPECIAL METALS CO LTD, 4-7-19 KITAHAMA, CHUO-KU, OSAKA, Japan [ADP No. 043874110011]
dated 07.08.1989. Official evidence filed on EP0134305
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**** END OF REGISTER ENTRY ****