

Description

Field of the invention

The present invention relates to novel magnetic materials and permanent magnets based on rare earth elements and iron without recourse to cobalt which is relatively rare and expensive. In the present disclosure, R denotes rare earth elements inclusive yttrium.

Background of the invention

Magnetic materials and permanent magnets 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 equipment, there has been an increasing demand for upgrading of permanent magnets and in general magnetic materials.

Now, referring to the permanent magnets, typical permanent magnet materials currently in use are alnico, hard ferrite and rare earth-cobalt magnets. With a recent unstable supply of cobalt, there has been a decreasing demand for alnico magnets containing 20—30 wt % of cobalt. Instead, inexpensive hard ferrite containing iron oxides as the main component has showed up as major magnet materials. Rare earth-cobalt magnets are very expensive, since they contain 50—65 wt % of cobalt and make use of Sm that is not much found in rare earth ores. However, such magnets have often been used primarily for miniaturized magnetic circuits of high added value, because they are by much superior to other magnets in magnetic properties.

If it could be possible to use, as the main component for the rare earth elements, light rare earth elements that occur abundantly in ores without recourse to 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-Fe₂ base compounds, wherein R is at least one of the rare earth metals, have been investigated. Regarding the following explanations, it is to be noted that the unit "1 G=10⁻⁴T", that the unit "1 Oe=0.0796 k · A/m" and that the unit "1 MGOe=7.96 kJ/m³". A. E. Clark has discovered that sputtered amorphous TbFe₂ has an energy product of 29.5 MGOe at 4.2°K, and shows a coercive force H_c=3.4 kOe and a maximum energy product (BH)_{max}=7 MGOe at room temperature upon heat-treatment at 300—500°C. Reportedly, similar investigations on SmFe₂ 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 for, e.g., speakers or motors. It has further been reported that melt-quenched ribbons of PrFe base alloys show a coercive force H_c as high as 2.8 kOe.

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 Fe₃B and R₅Fe₂₃ 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.

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.

These melt-quenched ribbons or sputtered thin films derived by the prior art, 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 magnetization 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.

Chaban et al (Deper. Akad. Nauk. UKSSR, Ser A (USSR), No. 10, pages 873 to 876 (1979)) reports on his investigations on (Nd, Sm, Gd)-Fe-B ternary systems. In the article (see diagram on page 874) no intermetallic magnetic compound is identifiable.

In JP—A—52-50598 rare earth cobalt magnets are disclosed which result from 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. All of these compounds contain Co.

Summary of the disclosure

5 An essential object of the present invention is to provide novel Co-free magnetic materials and permanent magnets.

Another object of the present invention is to provide practical permanent magnets from which the aforesaid disadvantages are removed.

10 A further object of the present invention is to provide magnetic materials and permanent magnets showing good magnetic properties at room temperature.

A still further object of the present invention is to provide permanent magnets capable of achieving such high magnetic properties that could not be achieved by R-Co permanent magnets.

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

15 A still further object of the present invention is to provide permanent magnets having magnetic anisotropy, good magnetic properties and excellent mechanical strength.

A still further object of the present invention is to provide magnetic materials and permanent magnets obtained by making effective use of light rare earth elements occurring abundantly in nature.

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

20 The present invention provides an alloy comprising Fe-B-R characterized by containing at least one stable compound of the ternary Fe-B-R type, which compound can be magnetized to become a permanent magnet at room temperature and above, wherein R stands for at least one rare earth element including yttrium.

25 The present invention further provides a process for preparing such alloys according to claim 13 and use of these alloys according to claim 17. Besides this, the invention provides a permanent magnet material according to claim 18 and a process of making same according to claim 30. Furthermore, the invention provides a magnetic material according to claim 36 comprising at least 50 vol. % of a phase comprising at least one Fe-B-R type compound having a tetragonal structure, wherein R is at least one rare earth element including Y, a sintered magnetic material of a special composition according to claim 48, and a process of 30 making a magnetic material powder showing a tetragonal structure according to claim 49 as well as permanent magnets according to claims 51 and 55, sintered permanent magnets according to claim 68 and a process for preparing same according to claim 87.

The novel magnetic materials and permanent magnets according to the present invention are essentially comprised of alloys essentially formed of novel intermetallic compounds and are substantially 35 crystalline, said intermetallic compounds being at least characterized by their novel Curie points Tc.

According to the first embodiment of the present invention, there is provided a magnetic material which comprises as indispensable components Fe, B and R (at least one of rare earth elements inclusive of Y), and in which a major phase is formed of an intermetallic compound(s) of the Fe-B-R type having a 40 crystal structure of the substantially tetragonal system.

40 According to the second embodiment of the present invention, there is provided a sintered magnetic material having a major phase formed of an intermetallic compound(s) consisting essentially of, by atomic percent, 8—30% R (at least one of rare earth elements inclusive of Y), 2—28% B and the balance being Fe with impurities.

45 According to the third embodiment of the present invention, there is provided a sintered magnetic material having the same composition as the second embodiment, and having a major phase formed of an intermetallic compound(s) of the substantially tetragonal system.

According to the fourth embodiment thereof, there is provided a sintered anisotropic permanent magnet consisting essentially of, by atomic percent, 8—30% R (at least one of rare earth elements inclusive of Y), 2—28% B and the balance being Fe with impurities.

50 The fifth embodiment thereof provides a sintered anisotropic permanent magnet having a major phase formed of an intermetallic compound(s) of the Fe-B-R type having a crystal structure of the substantially tetragonal system, and consisting essentially of, by atomic percent 8—30% R (at least one of rare earth elements inclusive of Y), 2—28% B and the balance being Fe with impurities.

"%" denotes atomic % in the present disclosure if not otherwise specified.

55 The magnetic materials of the 1st to 3rd embodiments according to the present invention may contain as additional components at least one of elements M selected from the group given below in the amounts of no more than the values specified below, provided that 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:

60	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
65	5.5% Hf.		

These constitute the 6th—8th embodiments (Fe-B-R-M type) of the present invention, respectively.

The permanent magnets (the 4th and 5th embodiments) of the present invention may further contain at least one of said additional elements M selected from the group given hereinabove in the amounts of no more than the values specified hereinabove, provided that the amount of M is not zero and the sum of M is no more than the maximum value among the values specified above of said elements M actually added.

These embodiments constitute the 9th and 10th embodiments (Fe-B-R-M type) of the present invention.

With respect to the inventive permanent magnets, practically useful magnetic properties are obtained when the mean crystal grain size of the intermetallic compounds is 1 to 80 μm for the Fe-B-R type, and 1 to 90 μm for the Fe-B-R-M type.

Furthermore, the inventive permanent magnets can exhibit good magnet 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 a sintered mass, and applied to magnetic recording media (such as magnetic recording tapes) as well as magnetic paints, temperature-sensitive materials and the like. Besides the inventive magnetic materials are useful as the intermediaries for the production of permanent magnets.

Brief description of the drawings

Fig. 1 is a graph showing magnetization change characteristics, depending upon temperature, of a block cut out of an ingot of an Fe-B-R alloy (66Fe-14B-20Nd) having a composition within the present invention (magnetization $4\pi I_0$ (kG) versus temperature $^{\circ}\text{C}$);

Fig. 2 is a graph showing an initial magnetization curve 1 and demagnetization curve 2 of a sintered 68Fe-17B-15Nd magnet (magnetization $4\pi I$ (kG) versus magnetic field H (kOe));

Fig. 3 is a graph showing the relation of iH_c (kOe) and Br (kG) versus the B content (at %) for sintered permanent magnets of an Fe-xB-15Nd system.

Fig. 4 is a graph showing the relation of iH_c (kOe) and Br (kG) versus the Nd content (at %) for sintered permanent magnets of an Fe-8B-xNd system;

Fig. 5 is a Fe-B-Nd ternary system diagram showing compositional ranges corresponding to the maximum energy product $(BH)_{\text{max}}$ (MGOe);

Fig. 6 is a graph depicting the relation between iH_c (kOe) and the mean crystal grain size D (μm) for examples according to the present invention;

Fig. 7 is a graph showing the change of the demagnetization curves depending upon the mean crystal grain size, as observed in the example of a typical composition according to the present invention;

Fig. 8 is a flow chart illustrative of the experimental procedures of powder X-ray analysis and demagnetization curve measurements;

Fig. 9 is an X-ray diffraction pattern of the results measured of a typical Fe-B-R sintered body according to the present invention with an X-ray diffractometer;

Figs. 10—12 are graphs showing the relation of Br (kG) versus the amounts of the additional elements M (at %) for sintered Fe-8B-15Nd-xM systems; and

Fig. 13 is a graph showing magnetization-demagnetization curves for typical embodiments of the present invention.

Detailed description of the preferred embodiments

It has been noted that R-Fe base compounds provide Co-free permanent magnet materials showing large magnetic anisotropies and magnetic moments. However, it has been found that the R-Fe base compounds containing as R light rare earth elements have extremely low Curie temperatures, and cannot occur in a stable state. For example, PrFe_2 , is unstable and difficulty is involved in the preparation thereof since a large amount of Pr is required. Thus, studies have been made with a view to preparing novel compounds which are stable at room or elevated temperatures and have high Curie points on the basis of R and Fe.

Based on the available results of researches, considerations have been made of the relationship between the magnetic properties and the structures of R-Fe base compounds. As a consequence, the following facts have been revealed:

(1) The interatomic distance between Fe atoms and the environment around the Fe atoms such as the number and kind of the vicinal-most atoms would play a very important role in the magnetic properties of R-Fe base compounds.

(2) With only combinations of R with Fe, no compound suitable for permanent magnets in a crystalline state would occur.

Fe-B-R Alloys

In view of these facts, the conclusion has been arrived at that, in the R-Fe base compounds, the presence of a third element is indispensable to alter the environment around Fe atoms and thereby attain the properties suitable for permanent magnets. With this in mind, close examinations have been made of the magnetic properties of R-Fe-X ternary compounds to which various elements were applied. As a result, R-Fe-B compounds (referred to "Fe-B-R type compounds" hereinafter) containing B as X have been

discovered. It follows that the Fe-B-R type compounds are unknown compounds, and can provide excellent permanent magnet materials, since they have higher Curie points and large anisotropy constants than the conventional R-Fe compounds.

Based on this view point, a number of R-Fe base systems have been prepared to seek out novel alloys. As a result, the presence of novel Fe-B-R base compounds showing Curie points of about 300°C has been confirmed, as illustrated in Table 1. Further, as a result of the measurement of the magnetization curves of these alloys with a superconductive magnet, it has been found that the anisotropic magnetic field reaches 100 kOe or higher. Thus, the Fe-B-R base compounds have turned out to be greatly promising for permanent magnet materials.

The Fe-B-R base alloys have been found to have a high crystal magnetic anisotropy constant K_u and an anisotropy field H_a standing comparison with that of the conventional SmCo type magnet.

Preparation of permanent magnets

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.

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 the end 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 usually applied to conventional magnets.

Noteworthy in this respect is that, as is the case with Fe_2B , Fe_2P , etc., there are a number of compounds incapable of being made into permanent magnets among those having a macro anisotropy constant, although not elucidatable. In view of the fact that any good properties suitable for the permanent magnets are not obtained until alloys have macro magnetic anisotropy and acquire a suitable microstructure, it has been found that practical permanent magnets are obtained by powdering of cast alloys followed by forming (pressing) and sintering.

Since the permanent magnets according to the present invention are based on the Fe-B-R system, they need not contain Co. In addition, the starting materials are not expensive, since it is possible to use as R light rare earth elements that occur abundantly in view of the natural resource, whereas it is not necessarily required to use Sm or to use Sm as the main component. In this respect, the invented magnets are prominently useful.

Crystal grain size of permanent magnets

According to the theory of the single domain particles, magnetic substances having high anisotropy field H_a 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, have 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 H_c . 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 H_c . The critical size defining the single magnetic domain varies depending upon diverse materials, and has been thought to be about 0.01 μm for iron, about 1 μm for hard ferrite, and about 4 μm for SmCo.

The H_c of various materials increases around their critical size. In the Fe-B-R base permanent magnets of the present embodiment, H_c of 1 kOe or higher is obtained when the mean crystal grain size ranges from 1 to 80 μm , while H_c of 4 kOe or higher is obtained in a range of 2 to 40 μm .

The permanent magnets according to the present invention are obtained as a sintered body, which enables production with any desired shape and size. 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 H_c of the sintered compact to exceed 1 kOe, the mean crystal grain size should be no less than about 1 μm , preferably 1.5 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 H_c of the sintered bodies decrease considerably, since the fine powders of the Fe-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 80 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 H_c . A grain size of no more than 80 μm is required to obtain H_c of no less than 1 kOe. Refer to Fig. 6.

5 With the systems incorporated with additional elements M (to be described in detail later), the compounds should have mean crystal grain size ranging from 1 to 90 μm (preferably 1.5 to 80 μm , more preferably 2 to 40 μm). Beyond this range, H_c of below 1 kOe will result.

10 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 H_c is then obtained. To this end, the presence of 1 vol % or higher of nonmagnetic phases contributes to the high H_c . In order that H_c is no less than 1 kOe, the nonmagnetic phases should be present in a volume ratio of at least 1%. However, the presence of 45% or higher of the nonmagnetic phases is not preferable. A preferable range is thus 2 to 10 vol %. The nonmagnetic phases are mainly comprised of intermetallic compound phases containing much of R, while the presence of a partial oxide phase serves effectively as the nonmagnetic phases.

15 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
20 tetragonal system crystal structure, which are then finely ground into fine powders.

As the magnetic 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 FeB and a reducing agent (Ca, etc.) for direct reduction. The resultant powder alloys show a tetragonal system as well.

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

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 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
30 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
35 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 ferroboration, and those containing as impurities Al, Si, C etc. may be used.

40 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 %. 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 an effect upon increases in Curie point, its amount is preferably about 5 at % or less, since iH_c 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.

45 Having an as-sintered composition of 8—30 at % R, 2—28 at % B and the balance Fe with the substantially tetragonal crystal system structure and a mean crystal grain size of 1—80 μm , the permanent magnets according to the present invention have magnetic properties such as coercive force H_c of ≥ 1 kOe, and residual magnetic flux density B_r of ≥ 4 kG, and provide a maximum energy product $(BH)_{\text{max}}$ value which is at least equivalent or superior to the hard ferrite (on the order of up to 4 MGOe).

50 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 at % R, 3—27 at % B with the balance being Fe, maximum energy product $(BH)_{\text{max}}$ of ≥ 7 MGOe is attained. A more preferable as-sintered composition of 12—20 at % R, 4—24 at % B with the balance being Fe, wherein Nd plus Pr amounts to 50% or higher of R provides maximum energy product $(BH)_{\text{max}}$ of ≥ 10 MGOe, and even reaches the highest value of
55 MGOe or higher. As shown in Fig. 5 as an embodiment, compositional ranges each corresponding to the $(BH)_{\text{max}}$ values of ≥ 10 , ≥ 20 , ≥ 30 and ≥ 35 MGOe are given in the Fe-B-R ternary system.

After sintering, the permanent magnet according to the present invention may be subjected to aging and other heat treatments ordinarily applied to conventional permanent magnets, which is understood to be within the concept of the present invention.

60 The embodiments and effects of the present invention will now be explained with reference to the results of experiments; however, the present invention is not limited to the experiments, examples and the manner of description given hereinbelow. The present invention should be understood to encompass any modifications within the concept derivable from the entire disclosure.

65 Table 1 shows the magnetization $4\pi I_{16K}$, as measured at the normal temperature and 16 kOe, and Curie points T_c , as measured at 10 kOe, of various Fe-B-R type alloys. These alloys were prepared by

high-frequency melting. After cooling, an ingot was cut into blocks weighing about 0.1 gram. Changes depending on temperature in $4\pi I_{10k}$ (magnetization at 10 kOe) of those blocks was measured on a vibrating sample type magnetometer (VSM) to determine their Curie points. Fig. 1 is a graphical view showing the change depending on temperature in magnetization of the ingot of 66Fe-14B-20Nd (sample 7 in Table 1), from which T_c is found to be 310°C.

Heretofore, there has been found no compound having T_c as shown in Table 1 among the R-Fe alloys. It has thus been found that new stable Fe-B-R type ternary compounds are obtained by adding B to the R-Fe system, and have T_c as shown in Table 1, which varies depending upon the individual R. As shown in Table 1, such new Fe-B-R type ternary compounds occur regardless of the type of R. With most of R, the new compounds have T_c on the order of about 300°C except Ce. It is understood that the known R-Fe alloys are much lower in T_c than the Fe-B-R type ternary compounds of the present invention.

Although, in Table 1, the measured $4\pi I_{16k}$ does not show saturated magnetization due to the fact that the samples are polycrystalline, the samples all exhibit high values above 6 kOe, and are found to be effective for permanent magnet materials having increased magnetic flux densities.

TABLE 1

	Samples	Composition in atomic percent	$4\pi I_{16k}(\text{kG})^{**}$	$T_c(^{\circ}\text{C})$
20	1	73Fe-17B-10La	11.8	320
	2	73Fe-17B-10Ce	7.4	160
	3	73Fe-17B-10Pr	7.5	300
25	4	73Fe-17B-10Sm	9.2	340
	5	73Fe-17B-10Gd	7.5	330
30	6	73Fe-17B-10Tb	6.0	370
	7	66Fe-14B-20Nd	6.2	310
	8	65Fe-25B-10Nd	6.8	260
35	9	73Fe-17B-5La-5Tb	6.0	330

($4\pi I_{16k}$: $4\pi I$ measured at 16 kOe**, T_c : measured at 10 kOe)

**1 kOe=79.6 kA/m 1 kG= 10^{-1} Tesla.

In what follows, explanation will be made to the fact that the novel compounds found in Table 1 provide high-performance permanent magnets by powder metallurgical sintering. Table 2 shows the characteristics of the permanent magnets consisting of various Fe-B-R type compounds prepared by the following steps. For the purpose of comparison, control magnets departing from the scope of the present invention are also described.

(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.

(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/cm²).

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

As seen from Table 2, the B-free compounds have a coercive force close to zero or of so small a value that high H_c measuring meters could not be applied, and thus provide no permanent magnets. However, the addition of 4 at % or only 0.64 wt % of B raises H_c to 2.8 kOe (sample No. 4), and there is a sharp increase in H_c with an increase in the amount of B. Incidentally, $(BH)_{\text{max}}$ increases to 7—20 MGOe and even reaches 35 MGOe or higher. Thus, the presently invented magnets exhibit high magnetic properties exceeding those of SmCo magnets currently known to be the highest grade magnets. Table 2 mainly shows Nd- and Pr-containing compounds but, as shown in the lower part of Table 2, the Fe-B-R type compounds

wherein R stands for other rare earth elements or various combinations of rare earth elements also exhibit good permanent magnet properties.

As is the case with the samples shown in Table 2, Fe-xB-15Nd and Fe-8B-xNd systems were measured for Br and iHc. The results are summarized in Figs. 3 and 4. Furthermore, Fig. 5 illustrates the relationship between (BH)max measured in a similar manner and the Fe-B-Nd composition in the Fe-B-R ternary system.

The Fe-B-R type compounds exhibit good permanent magnet properties when the amounts of B and R are in a suitable range. With the Fe-B-R system, Hc increases as B increases from zero as shown in Fig. 3. On the other hand, the residual magnetic flux density Br increases rather steeply, and peaks in the vicinity of 5—7 at % B. A further increase in the amount of B causes Br to decrease.

TABLE 2-1

No.	Composition	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
*1	85Fe-15Nd	0	0	0
2	83Fe-2B-15Nd	1.3	7.5	4.1
3	82Fe-3B-15Nd	1.8	10.4	7.0
4	81Fe-4B-15Nd	2.8	10.8	13.4
5	79Fe-6B-15Nd	8.0	13.0	36.5
6	78Fe-7B-15Nd	8.2	12.9	36.0
7	77Fe-8B-15Nd	7.3	12.1	32.1
8	75Fe-10B-15Nd	8.0	11.9	31.9
9	73Fe-12B-15Nd	8.2	10.5	25.2
10	68Fe-17B-15Nd	7.6	8.7	17.6
11	62Fe-23B-15Nd	11.3	6.8	10.9
12	55Fe-30B-15Nd	10.7	4.2	4.0
*13	53Fe-32B-15Nd	10.2	3.0	1.8
14	70Fe-17B-13Nd	5.5	8.9	11.0
15	63Fe-17B-20Nd	12.8	6.6	10.5
16	53Fe-17B-30Nd	14.8	4.5	4.2
*17	48Fe-17B-35Nd	>15	1.4	<1
18	86Fe-8B-6Nd	0	0	0
19	79Fe-8B-13Nd	4.8	13.1	29.3
20	78Fe-8B-14Nd	7.8	12.8	36.5
21	75Fe-8B-17Nd	9.2	11.6	31.1
22	73Fe-8B-19Nd	11.4	10.9	28.0

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³.

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TABLE 2-2

	No.	Composition	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	23	67Fe-8B-25Nd	12.6	5.8	8.6
	24	57Fe-8B-35Nd	14.6	1.9	≤1
	25	78Fe-10B-12Nd	2.4	8.3	6.3
10	*26	85Fe-15Pr	0	0	0
	27	73Fe-12B-15Pr	6.8	9.5	20.3
15	28	65Fe-15B-20Pr	12.5	7.1	10.2
	*29	76Fe-19B-5Pr	0	0	0
	30	76Fe-9B-15Pr	9.0	11.4	26.9
20	31	77Fe-8B-8Nd-7Pr	9.2	11.8	31.5
	32	66Fe-19B-8Nd-7Ce	5.5	7.1	10.0
25	33	74Fe-11B-2Sm-13Pr	6.8	9.5	17.2
	34	66Fe-19B-8Pr-7Y	6.1	7.7	10.5
	35	68Fe-17B-7Nd-3Pr-5La	7.1	7.9	13.9
30	36	68Fe-20B-12Tb	4.1	6.5	8.2
	37	72Fe-20B-8Tb	1.8	6.8	4.1
35	38	70Fe-10B-20Dy	5.3	6.4	8.0
	39	75Fe-10B-15Ho	4.5	6.4	7.8
	40	79Fe-8B-7Er-6Tb	4.8	7.1	8.1
40	41	74Fe-11B-10Nd-5Ho	10.3	10.1	23.9
	42	68Fe-17B-8Nd-7Gd	5.5	7.3	10.2
45	43	68Fe-17B-8Nd-7Tb	5.7	7.4	10.8
	44	77Fe-8B-10Nd-5Er	5.4	10.6	25.8

Mark * stands for comparative samples.

50 ** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³.

In order to meet the requirement for permanent magnets (materials) to have Hc of at least 1 kOe, the amount of B should be at least 2 at % (preferably at least 3 at %).

55 The instantly invented permanent magnets are characterized by possessing high Br after sintering, and often suitable for uses where high magnetic flux densities are needed. In order to be equivalent or superior to the hard ferrite's Br of about 4 kG, the Fe-B-R type compounds should contain at most 28 at % B. It is understood that B ranges of 3—27 at % and 4—24 at % are preferable, or the optimum, ranges for attaining (BH)max of ≥7 MGOe and ≥10 MGOe, respectively.

60 The optimum amount range for R will now be considered. As shown in Table 2 and Fig. 4, the more the amount of R, the higher Hc will be. Since it is required that permanent magnet materials have Hc of no less than 1 kOe as mentioned in the foregoing, the amount of R should be 8 at % or higher for that purpose. However, the increase in the amount of R is favourable to increase Hc, but incurs a handling problem since the powders of alloys having a high R content are easy to burn owing to the fact that R is very susceptible to
65 oxidation. In consideration of mass production, it is thus desired that the amount of R be no more than 30 at %.

When the amount of R exceeds the upper limit, difficulties would be involved in mass production since alloy powders are easy to burn.

It is also desired to decrease the amount of R as much as possible, since R is more expensive than Fe. It is understood that R ranges of 12—24 at % and 12—20 at % are preferable, or the optimum, ranges for making (BH)_{max} be ≥ 7 MGOe and ≥ 10 MGOe, respectively. Further compositional ranges for higher (BH)_{max} values are also presented, e.g., according to Fig. 5.

The amounts of B and R to be applied should be selected from the aforesaid ranges in such a manner that the magnetic properties as aimed at in the present invention are obtained. With the presently invented magnets, the most preferable magnetic properties are obtained when they are composed of about 8% B, about 15% R and the balance being Fe with impurities, as illustrated in Figs. 3—5 as an embodiment.

As a typical embodiment of the sintered, magnetic anisotropic magnets of the Fe-B-R system, Fig. 2 shows an initial magnetization curve 1, and a demagnetization curve 2 running through the first to the second quadrant, for 68Fe17B15Nd (having the same composition as sample No. 10 of Table 2).

The initial magnetization curve 1 rises steeply in a low magnetic field, and reaches saturation. The demagnetization curve 2 shows very high loop rectangularity. 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.

Among the compounds given in Table 2, the compounds falling under the scope of the present invention, except those marked *, did all show such a tendency as illustrated in Fig. 2, viz., steep rising of the initial magnetization curve and the high rectangularity of the demagnetization curve, such high permanent magnet properties are by no means obtained by crystallization of the Fe-R or Fe-B-R type amorphous ribbons which are known in the art. There is also not known at all any conventional permanent magnet materials which possess such high properties in the absence of cobalt.

Crystal grain size:

Pulverization (2) in the experimental procedures as aforementioned 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 , as measured with a sub-sieve-sizer manufactured by Fisher. 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 sintering 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 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 $\times 100$ to $\times 1000$. 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. *1, *3, *5 and *11 all depart from the scope of the composition of the magnets according to the present invention.

From *6, *7 and *17, it is found that H_c drops to 1 kOe or less when the crystal grain size departs from the scope as defined in the present invention.

TABLE 3

5	No.	Composition	Mean crystal grain size D (μm)	Magnetic properties		
				iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
	*1	80Fe-20Nd	15	0	0	0
	2	65Fe-15B-20Nd	17	11.4	7.2	11.0
	*3	53Fe-32B-15Nd	10	11.0	2.5	1.3
10	4	77Fe-8B-15Nd	33	5.2	11.0	22.0
	*5	48Fe-17B-35Nd	4	≥15	1.4	≤1
	*6	73Fe-10B-17Nd	0.7	<1	5.0	<1
15	*7	82Fe-5B-13Nd	140	<1	6.3	2.2
	8	79Fe-6B-15Nd	5	8.0	13.0	36.5
	9	68Fe-17B-15Pr	22	5.8	11.7	21.3
20	10	77Fe-8B-15Pr	4	9.0	11.4	26.9
	*11	78Fe-17B-5Pr	3.5	0	0	0
	12	75Fe-12B-13Pr	7	5.4	7.8	13.5
25	13	79Fe-6B-10Nd-5Pr	4	6.6	10.7	20.1
	14	71Fe-12B-12Nd-5Gd	8	4.8	7.8	11.5
	15	75Fe-9B-10Nd-6Pr	3	8.2	12.0	31.5
30	16	77Fe-8B-9Nd-6Ce	6	5.7	10.7	22.4
	*17	74Fe-11B-7Sm-8Pr	93	≤1	4.8	≤1
	18	74Fe-11B-5Ho-10Nd	4	10.3	10.1	23.9

(*): reference samples

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³.

A sample having the same composition as No. 4 given in Table 3 and other 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. 6, 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-B-R system magnets are the single domain-particulate type magnets.

Apart from the foregoing samples, an alloy having the same composition as Sample No. 8 of Table 3 was prepared by high-frequency melting and casting in a water cooled copper mold. 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 3 and Figs. 3, 4 and 6, it is evident that, in order for the Fe-B-R system 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 1—80 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 2—40 μm .

Fig. 7 shows demagnetization characteristic curves of sample No. 4—77Fe-8B-15Nd—given in Table 3 and Fig. 6 in respect of its typical mean crystal grain sizes (D=0.8, 5 and 65 μm). From this, it is found that the magnets having mean crystal grain size belonging to the scope as defined in the present invention possess high Hc and excellent rectangularity in the second quadrant.

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.

Crystal structure

It is believed that the magnetic material and permanent magnets based on the Fe-B-R alloy 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-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-B-R type contributes to the exhibition of magnetic properties. The Fe-B-R base 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.

The crystal structure of the Fe-B-R type alloys according to the present invention will now be elucidated with reference to the following experiments.

Experimental procedures

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

Fe: Electrolytic iron 99.9%

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

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

(2) The experimental procedures are shown in Fig. 8

The experimental results obtained are illustrated as below:

(1) Fig. 9 illustrates a typical X-ray diffractometric pattern of the Fe-B-Nd (77Fe-15Nd-8B 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, B and R, the second phase is a R-concentrated phase having an 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. 9, the sharp peaks included in this pattern may all be explained as the tetragonal crystals of $a_0=0.88$ nm (8.80 Å) and $c_0=1.223$ nm (12.23 Å).

In Fig. 9, indices are given at the respective X-ray peaks. The major phase simultaneously containing Fe, 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-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 and B and has lattice constants a_0 of about 0.8 nm (8 Å) and c_0 of about 1.2 nm (12 Å), good properties suitable for permanent magnets are obtained. Table 4 shows the lattice constants of tetragonal system compounds which constitute the major phase of typical Fe-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.

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

(iii) The said Fe-B-R tetragonal system compounds are present in a wide compositional range, and may be present in a stable state upon addition of certain elements other than R, Fe and B.

The said Fe-B-R intermetallic compounds have an angle of 90° between a , b and c axes within the tolerance of measurement in most cases, wherein $a_0=b_0 \neq c_0$, thus these compounds being tetragonal.

In the present invention, the Fe-B-R type tetragonal crystal may be substantially tetragonal for producing the desired magnetic properties. The term "substantially tetragonal" encompasses ones that have a slightly deflected angle between a , b and c axes, i.e., within 1° , or ones that have a_0 slightly different from b_0 , e.g., within 1%.

The Fe-B-R type permanent magnets of the tetragonal system according to the present invention will now be explained with reference to the following non-restrictive examples.

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TABLE 4
Crystal structure of various Fe-B-R type compounds

5	No.	Alloy composition	Structure of major phase (system)	Lattice constants of major phase	
				a_0 (Å)**	c_0 (Å)**
	1	Fe-15Ce-8B	tetragonal	8.77	12.16
10	2	Fe-15Pr-8B	"	8.84	12.30
	3	Fe-15Nd-8B	"	8.80	12.23
	4	Fe-15Sm-8B	"	8.83	12.25
15	5	Fe-10Nd-5Dy-8B	"	8.82	12.22
	6	Fe-10Nd-5Gd-8B	"	8.81	12.20
20	7	Fe-10Nd-5Er-8B	"	8.80	12.16
	8	Fe-10Nd-5Ho-8B	"	8.82	12.17
	9	Fe-15Nd-3B	"	8.81	12.30
25	10	Fe-15Nd-17B	"	8.80	12.28
	11	Fe-12Nd-8B	"	8.82	12.26
30	12	Fe-20Nd-8B	"	8.81	12.24
	13	Fe-15Nd-8B-1Ti	"	8.80	12.24
	14	Fe-15Nd-8B-2Mo	"	8.82	12.25
35	15	Fe-15Nd-8B-1Cr	"	8.80	12.23
	16	Fe-15Nd-8B-3Si	"	8.79	12.22
40	17	Fe-15Nd-8B-2Al	"	8.79	12.22
	18	Fe-15Nd-8B-1Nb	"	8.82	12.25
	19	Fe-15Nd-8B-1Sb	"	8.81	12.23
45	20	Fe-15Nd-8B-1Bi	"	8.82	12.25
	21	Fe-15Nd-8B-1Sn	"	8.80	12.23
50	22	Fe-6Nd-6B	body-centered cubic	2.87	—
	23	Fe-15Nd-2B	rhombohedral	8.60*	12.50*

N.B.: (*) indicated as hexagonal.

55 ** 1 Å = 10^{-1} nm, Fe = balance Fe.

Example 1

60 An alloy of 8 at % B, 16 at % Pr and the balance Fe was pulverized to prepare powders having an average particle size of 15 μ m. The powders were compacted under a pressure of 19.62×10^7 Pa (2 t/cm²) and in a magnetic field of 10 kOe, and the resultant compact was sintered at 1090°C for 1 hour in argon of 26.6 Pa (2×10^{-1} Torr).

65 X-ray diffraction has indicated that the major phase of the sintered body is a tetragonal system compound with lattice constants $a_0 = 0.885$ nm (8.85 Å) and $c_0 = 1.226$ nm (12.26 Å). As a consequence of XMA and optical microscopy, it has been found that the major phase contains simultaneously Fe, B and Pr, which amount to 90 vol % thereof. Nonmagnetic compound phases having a R content of no less than 80%

assumed 3% of the overall material with the remainder being oxides and pores. The mean crystal grain size was 25 μm .

The magnetic properties measured are: $B_r=9.9$ kG, $iH_c=6.5$ kOe, and $(BH)_{\text{max}}=18$ MGOe, and are by far higher than those of the conventional amorphous ribbon.

Example 2

An alloy of 8 at % B, 15 at % Nd and the balance Fe was pulverized to prepare powders having an average particle size of 3 μm . The powders were compacted in a magnetic field of 10 kOe under a pressure of 19.62×10^7 Pa (2 t/cm²), and sintered at 1100°C for 1 hour in argon of 2666 Pa (2×10 Torr).

X-ray diffraction has indicated that the major phase of the sintered compact is a tetragonal compound with lattice constants $a_0=0.880$ nm (8.80 Å) and $c_0=1.223$ nm (12.23 Å). As a consequence of XMA and optical microscopy, it has been found that the major phase contains simultaneously Fe, B and Nd, which amount to 90.5 vol % thereof. Nonmagnetic compound phases having a R content of no less than 80% were 4% with the remainder being virtually oxides and pores. The mean crystal grain size was 15 μm .

The magnetic properties measured are: $B_r=12.1$ kG, $iH_c=7.8$ kOe and $(BH)_{\text{max}}=34$ MGOe, and are much higher than those of the conventional amorphous ribbon.

Fe-B-R-M Type alloys containing additional elements M

According to the present invention, additional elements M can be applied to the magnetic materials and permanent magnets of the Fe-B-R type, the additional elements M including Ti, Ni, Bi, V, Nb, Ta, Cr, Mo, W, Mn, Al, Sb, Ge, Sn, Zr and Hf, which provides further magnetic materials and permanent magnets of the Fe-B-R-M system. Limitation is of course imposed upon the amount of these elements. The addition of these elements contribute to the increase in H_c compared with the Fe-R-B ternary system compounds. Among others, W, Mo, V, Al and Nb have a great effect in this respect. However, the addition of these elements incurs a reduction of B_r and, hence, their total amounts should be controlled depending upon the requisite properties.

In accordance with the present invention, the amounts of these elements are 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 shall be no more than the maximum value among the values specified hereinabove of the M actually added.

With respect to the permanent magnets, an increase in iH_c due to the addition of M results in increased stability and wide applicability of the magnets. However, the greater the amount of M, the lower the B_r and $(BH)_{\text{max}}$ will be, due to the fact that they are nonmagnetic elements (except Ni). For this reason, the addition of M is useful provided that $(BH)_{\text{max}}$ is at least 4 MGOe.

To ascertain the effect of M upon B_r , B_r was measured in varied amounts of M. The results are summarized in Figs. 10 to 12. As seen from Figs. 10 to 12, 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 B_r is at least equivalent to about 4 kG of hard ferrite. A preferable range in view of B_r should be appreciated from Figs. 10 to 12 by defining the B_r 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 have been put upon the aforesaid values at or below which $(BH)_{\text{max}}$ is at least equivalent or superior to about 4 MGOe of hard ferrite.

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. 10 to 12. Thus the amounts of the individual elements M are within the aforesaid ranges, and the total amount thereof is no more than the maximum values allowed for the individual elements which are added and present. For example, if Ti and V are present, the total amount of Ti plus V allowed is 9.5 at %, wherein no more than 4.5 at % Ti and no more than 9.5 at % of V can be used.

A composition comprised of 12—24% R, 3—27% B and the balance being (Fe+M) is preferred for providing $(BH)_{\text{max}} \geq 7$ MGOe.

More preferred is a composition comprised of 12—20% R, 4—24% B and the balance being (Fe+M) for providing $(BH)_{\text{max}} \geq 10$ MGOe wherein $(BH)_{\text{max}}$ achieves maximum values of 35 MGOe or higher. Still more preferred compositional ranges are defined principally on the same basis as is the case in the Fe-B-R ternary system.

In general, the more the amount of M, the lower the B_r ; however, most elements of M serve to increase iH_c . Thus, $(BH)_{\text{max}}$ 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. 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 a large amount of Mn and Ni are incorporated, iH_c will decrease; there is only slight decrease in Br due to the fact that Ni is a ferromagnetic element. Therefore, the upper limit of Ni is 8%, preferably 4.5%, 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 3.5%, in view of iH_c .

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.

In what follows, Fe-B-R-M alloys containing various additional elements M will be explained in detail with reference to their experiments and examples.

Permanent magnet materials were prepared in the following manner.

(1) Alloys were prepared by high-frequency melting and cast in a copper mold cooled with water. As the starting Fe, B and R, use was made of electrolytic iron having a purity of 99.9% (by weight % so far as the purity is concerned), ferroboron alloys or 99% pure boron, and a rare earth element(s) having a purity of no less than 99.7% (and containing impurities mainly comprising other rare earth metals). The additional elements applied were Ti, Mo, Bi, Mn, Sb, Ni and Ta, those having a purity of 99%, W having a purity of 98%, Al having a purity of 99.9%, Hf having a purity of 95%, and Cu having a purity of 99.9%. 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.

(2) The resultant as-cast alloys were coarsely ground in a stamp mill until they passed through a 0.42 mm (35-mesh) sieve and, subsequently, finely pulverized to 3–10 μ m for 3 hours in a ball mill.

(3) The resultant particles were oriented in a magnetic field (10 kOe) and compacted under a pressure of 14.71×10^7 Pa (1.5 t/cm²).

(4) The resultant compacted bodies were sintered at 1000–1200°C for 1 hour in argon and, thereafter, allowed to cool.

The thus sintered compacts were measured on their iH_c , Br and (BH)_{max}, and the results of typical compacts out of these are shown in Table 5 and Table 6. The samples marked * in Table 6 represent comparative samples. In Tables 5 and 6, Fe is of course the remainder, although not specified quantitatively.

The results have revealed the following facts. Table 5-1 elucidates the effect of the additional elements M in the Fe-8B-15Nd system wherein neodymium is employed, Nd being a typical light-rare earth element. As a result, all the samples (Nos. 1 to 36 inclusive) according to the present embodiment are found to exhibit high coercive force (iH_c greater than about 8.0 kOe), compared with sample 1 (iH_c = 7.3 kOe) given in Table 6. Among others, samples Nos. 31 and 36 possess coercive force of 15 kOe or higher. On the other hand, the samples containing a small amount of M are found to be substantially equivalent to those containing no M with respect to Br see Table 6, sample 1 (12.1 kG). It is found that there is a gradual decrease in Br with the increase in the amount of M. However, all the samples given in Table 5 have a residual magnetic flux density considerably higher than about 4 kG of the conventional hard ferrite.

In the permanent magnets of the present invention, the additional elements M are found to be effective for all the Fe-B-R ternary systems wherein R ranges from 8 to 30 at %, B ranges from 2 to 28 at %, with the balance being Fe. When B and R depart from the aforesaid ranges, the elements M are ineffective (*12, *13—R is too low—, *14—B is in excess—, *15—R is in excess, and *8—*11—is without B—).

To elucidate the effect of the addition of the additional elements M, changes in Br were measured in varied amounts of M according to the same testing manner as hereinabove mentioned. The results are summarized in Figs. 10–12 which illustrate that the upper limits of the amounts of the additional elements M are defined as aforementioned.

As apparent from Figs. 10 to 12, in most cases, the greater the amounts of the additional elements M, the lower the Br resulting in the lower (BH)_{max}, as illustrated in Table 5. However, increases in iH_c are vital for such permanent magnets as to be exposed to a very high reversed magnetic field or severe environmental conditions such as high temperature, and provide technical advantages as well as in the case of those with the high (BH)_{max} type. Typically, Fig. 13 illustrates three initial magnetization curves and demagnetization curves 1–3 of (1) Fe-8B-15Nd, (2) Fe-8B-15Nd-1Nb, and (3) Fe-8B-15Nd-2Al (Fe=balance Fe).

Samples 1, 2 and 3 (curves 1, 2 and 3) were obtained based on the samples identical with sample No. 1 (Table 6), sample No. 5 and sample No. 21 (Table 5), respectively. The curves 2 and 3 also show the rectangularity or loop squareness in the second quadrant useful for permanent magnets.

In Table 5, for samples Nos. 37–42, 51 and 52 Pr as R was used, samples Nos. 48–50 were based on 67Fe-12B-20Nd-1M, and samples Nos. 51 and 52 based on 67Fe-12B-20Pr-1M. Samples Nos. 40, 42–47, 53–58 and 60–65 indicate that even the addition of two or more elements M gives good results.

Increased iH_c of samples Nos. 5 and 6 of Table 6 are due to high Nd contents. However, the effect of M addition is apparent from samples 48–50, 53–55, 63 and 64, respectively.

Samples No. 56 shows iH_c of 4.3 kOe, which is higher than 2.8 kOe of *16, and sample No. 59 shows iH_c of 7.3 kOe which is higher than 5.1 kOe of No. 7. Thus, the addition of M is effective on both samples.

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As samples Nos. 1 and 4, it is also possible to obtain a high coercive force while maintaining a high (BH)_{max}.

The Fe-B-R-M base permanent magnets may contain, in addition to Fe, B, R and M, impurities which are entrained in the process of industrial production.

TABLE 5-1

No.	Composition in atomic percent	iH _c (kOe)**	Br (kG)**	(BH) _{max} (MGoe)**
1	Fe-8B-15Nd-1Ti	9.0	12.3	35.1
2	Fe-8B-15Nd-1V	8.1	11.5	30.0
3	Fe-8B-15Nd-5V	8.3	9.2	15.5
4	Fe-8B-15Nd-0.5Nb	8.5	12.4	35.7
5	Fe-8B-15Nd-1Nb	9.1	11.9	32.9
6	Fe-8B-15Nd-5Nb	10.2	10.5	25.9
7	Fe-8B-15Nd-0.5Ta	9.0	11.7	31.5
8	Fe-8B-15Nd-1Ta	9.2	11.6	30.7
9	Fe-8B-15Nd-0.5Cr	9.5	11.4	30.0
10	Fe-8B-15Nd-1Cr	9.9	11.3	29.9
11	Fe-8B-15Nd-5Cr	10.4	8.6	17.4
12	Fe-8B-15Nd-0.5Mo	8.0	11.6	30.5
13	Fe-8B-15Nd-1Mo	8.1	11.7	31.0
14	Fe-8B-15Nd-5Mo	9.9	9.2	18.9
15	Fe-8B-15Nd-0.5W	9.4	11.8	32.9
16	Fe-8B-15Nd-1Mn	8.0	10.6	25.3
17	Fe-8B-15Nd-3Mn	7.6	9.5	19.7
18	Fe-8B-15Nd-0.5Ni	8.1	11.8	29.5
19	Fe-8B-15Nd-4Ni	7.4	11.2	20.5
20	Fe-8B-15Nd-0.5Al	9.3	12.0	33.0

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGoe=7.96 kJ/m³
Fe=balance Fe.

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TABLE 5-2

	No.	Composition in atomic percent	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	21	Fe-8B-15Nd-2Al	10.7	11.3	29.0
	22	Fe-8B-15Nd-5Al	11.2	9.0	19.2
	23	Fe-8B-15Nd-0.5Ge	8.1	11.3	25.3
10	24	Fe-8B-15Nd-1Sn	14.2	9.8	20.1
	25	Fe-8B-15Nd-1Sb	10.5	9.1	15.2
15	26	Fe-8B-15Nd-1Bi	11.0	11.8	31.8
	27	Fe-17B-15Nd-3.5Ti	8.9	9.7	20.8
	28	Fe-17B-15Nd-1Mo	9.5	8.5	16.4
20	29	Fe-17B-15Nd-5Mo	13.1	7.8	14.4
	30	Fe-17B-15Nd-2Al	12.3	7.9	14.3
25	31	Fe-17B-15Nd-5Al	>15	6.5	10.2
	32	Fe-17B-15Nd-1.5Zr	11.3	8.4	16.5
	33	Fe-17B-15Nd-4Zr	13.6	7.8	14.5
30	34	Fe-17B-15Nd-0.5Hf	8.9	8.6	17.6
	35	Fe-17B-15Nd-4Hf	13.6	7.9	14.6
35	36	Fe-17B-15Nd-6V	>15	7.4	12.8
	37	Fe-8B-15Pr-3Al	9.6	9.8	20.2
	38	Fe-8B-15Pr-2Mo	8.1	9.8	20.3
40	39	Fe-14B-15Pr-2Zr	10.3	6.9	10.9
	40	Fe-17B-15Pr-1Hf-1Al	9.2	6.8	10.2

45 ** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

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TABLE 5-3

	No.	Composition in atomic percent	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	41	Fe-15B-15Pr-3Nb	10.1	6.9	10.8
	42	Fe-16B-15Pr-0.5W-1Cr	10.3	6.7	10.2
	43	Fe-8B-14Nd-1Al-2W	10.0	10.7	24.7
10	44	Fe-6B-16Nd-1Mo-0.5Ta	8.6	10.5	23.7
	45	Fe-8B-10Nd-5Pr-2Nb-3V	11.6	9.4	20.2
15	46	Fe-8B-10Nd-5Ce-0.5Hf-2Cr	8.5	9.0	19.3
	47	Fe-12B-15Pr-5Nd-2Zr-1Al	10.1	8.7	15.1
	48	Fe-12B-20Nd-1Al	14.1	8.1	14.4
20	49	Fe-12B-20Nd-1W	14.2	7.9	14.5
	50	Fe-12B-20Nd-1Nb	13.9	8.2	14.3
25	51	Fe-12B-20Pr-1Cr	13.4	7.0	11.2
	52	Fe-12B-20Pr-1Bi	14.1	7.3	11.6
	53	Fe-8B-20Nd-0.5Nb-0.5Mo-1W	>15	7.3	11.5
30	54	Fe-8B-20Nd-1Ta-0.5Ti-2V	>15	7.4	11.7
	55	Fe-8B-20Nd-1Mn-1Cr-1Al	>15	7.0	10.9
35	56	Fe-4B-15Nd-0.5Mo-0.5W	4.3	10.8	20.7
	57	Fe-18B-14Nd-0.5Cr-0.5Nb	8.5	7.9	14.3
	58	Fe-17B-13Nd-0.5Al-1Ta	8.0	8.2	14.7
40	59	Fe-8B-10Nd-5Ce-2V	7.3	9.5	20.0
	60	Fe-8B-10Nd-5Tb-1Sn-0.5W	9.3	8.4	15.7

45 ** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

TABLE 5-4

	No.	Composition in atomic percent	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
50	61	Fe-8B-10Nd-5Dy-0.5Ge-1Al	8.9	8.3	15.2
	62	Fe-8B-13Nd-2Sm-0.5Nb-0.5Ti	8.5	8.9	15.4
55	63	Fe-8B-25Nd-1Mo-0.3Ti	>15	7.1	11.0
	64	Fe-8B-25Nd-1V-0.3Nb	>15	7.1	10.9
60	65	Fe-8B-25Pr-1Ni-0.3W	>15	6.7	10.3

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

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TABLE 6

	No.	Composition in atomic percent	iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	1	Fe-8B-15Nd	7.3	12.1	32.1
	2	Fe-8B-15Pr	6.6	11.0	26.5
	3	Fe-17B-15Nd	7.6	8.7	17.6
10	4	Fe-17B-15Pr	7.2	7.9	14.8
	5	Fe-12B-20Nd	12.4	8.5	15.1
15	6	Fe-12B-25Nd	13.9	6.8	9.4
	7	Fe-8B-10Nd-5Ce	5.1	9.8	17.8
	*8	Fe-15Nd-5Al	<1	<1	<1
20	*9	Fe-15Pr-3W	<1	<1	<1
	*10	Fe-15Pr-2Nb	<1	<1	<1
25	*11	Fe-15Pr-2Cr	<1	<1	<1
	*12	Fe-19B-5Nd-2W	<1	<1	<1
	*13	Fe-19B-5Nd-3V	<1	<1	<1
30	*14	Fe-30B-15Nd-5Al	<1	<1	<1
	*15	Fe-8B-35Nd-5Cr	>15	<1	<1
35	16	Fe-4B-15Nd	2.8	10.8	13.4

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

Crystal grain size (Fe-B-R-M system)

Pulverization in the experimental procedures as aforementioned was carried out for varied periods of time selected in such a manner that the measured average particle sizes of the powder ranges from 0.5 to 100 μ m, as measured with a sub-sieve-sizer manufactured by Fisher. In this manner, various samples having the compositions as specified in Tables 7 and 8 were obtained.

Comparative Examples: To obtain a crystal grain size of 100 μ m 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 (Table 7, No. *11).

From the thus prepared samples having the compositions as specified in Tables 7 and 8 were obtained magnets which were studied to determine their magnetic properties and the mean crystal grain sizes. The results are set forth in Tables 7 and 8. The measurements of the mean crystal grain size were done substantially in the same manner as for the Fe-B-R system aforementioned.

In Table 7, the samples marked * represent Comparative Examples. Nos. *1—*4, *6 and *8—*10 depart from the scope of the composition of the magnets according to the present invention. Nos. *5, *7, *11 and *12 have the mean crystal grain size outside of the present invention.

From Nos. *11 and *12, it is found that Hc drops to less 1 kOe when the crystal grain size departs from the scope as defined in the present invention.

Samples having the same composition as Nos. 9 and 21 given in Table 8 were studied in detail in respect of the relationship between their mean crystal grain size D and Hc. The results are illustrated in Fig. 6, from which it is found that Hc peaks when D is approximately in a range of 3—10 μ m, 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 mean crystal grain size D and Hc is substantially maintained. This indicates that the Fe-B-R-M system magnets are the single domain fine particle type magnets as in the case of the Fe-B-R system.

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TABLE 7

	No.	Composition	Mean crystal grain size D (μm)	Magnetic properties		
				iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	*1	80Fe-20Nd	15	0	0	0
	*2	53Fe-32B-15Nd	7	10.2	3.0	1.8
10	*3	48Fe-17B-35Nd	4	>15	1.4	<1
	*4	73Fe-10B-17Nd	0.4	<1	5.0	<1
15	*5	82Fe-5B-13Nd	140	<1	6.3	2.0
	*6	78Fe-17B-5Pr	3.5	0	0	0
	*7	74Fe-11B-7Sm-8Pr	93	<1	4.8	<1
20	*8	74Fe-19B-5Nd-2W	8.8	<1	<1	1
	*9	83Fe-15Pr-2Nd	33	<1	<1	<1
25	*10	51Fe-6B-35Nd-8Cr	12.1	<1	<1	<1
	*11	76Fe-8B-15Nd-1Mn	105	<1	3.2	<1
	*12	74Fe-8B-15Nd-3Cr	0.3	<1	<1	<1

30 ** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³.

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TABLE 8-1

	No.	Composition	Mean crystal grain size D (μm)	Magnetic properties		
				iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	1	Fe-8B-15Nd-1Ti	5.6	9.0	12.6	36.5
	2	Fe-8B-15Nd-1V	3.5	9.0	11.0	26.8
10	3	Fe-8B-15Nd-2Nb	7.8	9.4	11.7	30.4
	4	Fe-8B-15Nd-1Ta	10.2	8.6	11.6	28.0
	5	Fe-8B-15Nd-2Cr	4.8	9.9	11.2	29.6
15	6	Fe-8B-15Nd-0.5Mo	5.6	8.4	12.0	33.1
	7	Fe-8B-15Nd-1Mo	4.9	8.3	11.7	30.8
20	8	Fe-8B-15Nd-5Mo	8.5	8.8	9.0	17.5
	9	Fe-8B-15Nd-1W	6.3	9.6	12.1	33.6
	10	Fe-8B-15Nd-1Nb	6.6	9.6	12.3	35.3
25	11	Fe-8B-15Nd-1Mn	8.2	8.0	10.6	25.3
	12	Fe-8B-15Nd-1Mn	20.2	6.8	10.2	18.4
30	13	Fe-8B-15Nd-2Ni	12.0	7.3	11.4	22.7
	14	Fe-8B-15Nd-1Al	9.6	9.9	11.2	29.0
	15	Fe-8B-15Nd-0.5Ge	4.6	8.1	11.3	25.3
35	16	Fe-8B-15Nd-1Sn	6.4	14.2	9.8	20.1
	17	Fe-8B-15Nd-1Sb	7.7	10.5	9.1	15.2
40	18	Fe-8B-15Nd-1Bi	5.1	11.0	11.8	31.8
	19	Fe-14B-15Nd-2Zr	8.9	10.8	8.2	16.3
	20	Fe-14B-15Nd-4Hf	9.5	11.4	7.7	13.3

**1 kOe=79.6 kA/m 1 kG=10⁻¹ Tesla
1 MGOe=7.96 kJ/m³
Fe=balance Fe

TABLE 8-2

5	No.	Composition	Mean crystal grain size D (μm)	Magnetic properties		
				iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
	21	Fe-8B-15Nd-5Al	4.4	11.2	9.3	20.0
10	22	Fe-15B-15Pr-3Nb	2.2	10.1	7.4	11.6
	23	Fe-10B-14Nd-1Al-2W	6.5	10.8	10.6	24.4
	24	Fe-8B-10Nd-5Pr-2Nb-2Ge	7.1	11.2	9.6	21.2
15	25	Fe-8B-20Nd-1Ti-1Nb-1Cr	4.4	>15	7.1	10.8
	26	Fe-8B-20Nd-1Ta-1Hf-1W	5.9	>15	7.0	11.3
20	27	Fe-8B-10Nd-5Ho-1Al-1Nb	8.5	13.3	9.2	20.2
	28	Fe-8B-20Pr-1Ti-1Mn	6.8	14.0	6.8	9.8
	29	Fe-8B-25Nd-1Mo-1Zr	3.6	>15	6.6	9.2
25	30	Fe-17B-15Pr-1Nb-1V	7.8	9.6	7.0	10.4
	31	Fe-10B-13Nd-2Dy-1La	8.8	7.4	10.2	21.8
30	32	Fe-9B-10Nd-5Pr-1Sn-0.5Gd	6.3	7.2	9.4	18.2
	33	Fe-9B-16Nd-1Ce	13.7	6.8	9.1	16.6

** 1 kOe=79.6 kA/m, 1 kG= 10^{-1} Tesla, 1 MGO=7.96 kJ/m³
Fe=balance Fe.

From the results given in Tables 7 and 8 and Fig. 6, it is apparent that, in order for the Fe-B-R-M system 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 embodiment and the mean crystal grain size is 1—90 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 2—40 μm .

The three curves shown in Fig. 13 for the magnetization and demagnetization were obtained based on the mean crystal grain size of 5—10 μm .

The Fe-B-R-M system magnetic materials and permanent magnets have basically the same crystal structure as the Fe-B-R system as shown in Table 4, Nos. 13—21, and permit substantially the same impurities as in the case of the Fe-B-R system (see Table 10).

For the purpose of comparison, Table 9 shows the magnetic and physical properties of the typical example according to the present invention and the prior art permanent magnets.

Accordingly, the present invention provides Co-free, Fe base inexpensive alloys, magnetic materials having high magnetic properties, and sintered, magnetic anisotropic permanent magnets having high remanence, high coercive force, high energy product and high mechanical strength, and thus present a technical breakthrough.

It should be understood that the present invention is not limited to the disclosure of the experiments examples and embodiments herein-mentioned and any modifications apparent in the art may be done without departing from the concept and Claims as set forth hereinbelow.

TABLE 9

	Magnetic properties				Physical properties			
	Residual magnetic flux density Br (KG)**	bHc (kOe)**	Coercive force iHc (kOe)**	Maximum energy product (BH)max (MGOe)**	Specific gravity g/cm ³	Resistivity $\mu\Omega \cdot \text{cm}$	Hardness Hv	Bending strength kg/mm ²
FeBR Magnet Fe-8B-14Nd	12.5	10.9	11.1	36.0	7.4	144	600	25
Rare earth cobalt magnet Sm ₂ Co ₁₇	11.2	6.7	6.9	31.0	8.4	85	550	12
Ferrite magnet SrO,6Fe ₂ O ₃	4.4	2.8	2.9	4.6	5.0	>10 ⁴	530	13

** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

TABLE 10

		iHc (kOe)**	Br (kG)**	(BH)max (MGOe)**
5	Fe-8B-15Nd-2Cu	2.6	9.2	8.2
	Fe-8B-15Nd-1S	6.4	7.1	11.0
10	Fe-8B-15Nd-1C	6.6	11.7	21.9
	Fe-8B-15Nd-5Ca	9.3	11.6	25.8
	Fe-8B-15Nd-5Mg	7.8	11.5	22.6
15	Fe-8B-15Nd-5Si	6.8	10.6	25.2
	Fe-8B-15Nd-0.7O	8.0	11.6	30.1
20	Fe-8B-15Nd-1.5P	10.6	9.4	19.7
	Fe-8B-15Nd-2W-2Mg	8.5	10.8	21.8
	Fe-8B-15Nd-1Nb-1Cu	5.5	10.9	16.7

25 ** 1 kOe=79.6 kA/m, 1 kG=10⁻¹ Tesla, 1 MGOe=7.96 kJ/m³
Fe=balance Fe.

Preferred embodiments of the invention are now described in condensed language:

30 1. A magnetic material comprising Fe, B and R wherein R is at least one rare earth element including Y, and in which a major phase is formed of at least one intermetallic compound of the Fe-B-R type having a crystal structure of the substantially tetragonal system.

2. A sintered magnetic material having a major phase formed of at least one intermetallic compound consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one of rare earth element including Y, 2—28 percent B and the balance being Fe with impurities.

35 3. A sintered magnetic material having a major phase formed of at least one intermetallic compound of the substantially tetragonal system, and consisting essentially of, by atomic percent, 8—30 percent R, wherein R is at least one rare earth element including Y, 2—28 percent B and the balance being Fe with impurities.

40 4. A sintered anisotropic permanent magnet consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B and the balance being Fe with impurities.

5. A sintered anisotropic permanent magnet having a major phase formed of at least one intermetallic compound of the Fe-B-R type having a crystal structure of the substantially tetragonal system, and consisting essentially of, by atomic percent 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B and the balance being Fe with impurities.

45 6. A magnetic material as defined in embodiment 1 or 3, in which the substantially tetragonal system amounts to no less than 50 vol. %.

7. A permanent magnet as defined in embodiment 5, in which the substantially tetragonal system amounts to no less than 50 vol. %.

50 8. A permanent magnet as defined in embodiment 7, which contains no less than 1 vol % of nonmagnetic intermetallic compound phases.

9. A permanent magnet as defined in embodiment 4 or 5, in which the mean crystal grain size is 1 to 80 μ m.

55 10. A permanent magnet as defined in embodiment 9, in which the mean crystal grain size is 2 to 40 μ m.

11. A permanent magnet as defined in embodiment 4 or 5, in which R is 12—24%, and B is 3—27%.

12. A permanent magnet as defined in embodiment 11, in which R is 12—20%, and B is 4—24%.

13. A permanent magnet as defined in embodiment 4 or 5, in which, the light-rare earth element(s) amounts to no less than 50 at % of the overall rare earth elements R.

60 14. A permanent magnet as defined in embodiment 13, in which the sum of Nd plus Pr amounts to no less than 50 at % of the overall rare earth elements R.

15. A permanent magnet as defined in embodiment 13 or 14, in which R is about 15%, and B is about 8%.

65 16. A permanent magnet as defined in embodiment 4 or 5, in which the maximum energy product (BH)max is no less than 32 kJ/m³ (4 MGOe).

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17. A permanent magnet as defined in embodiment 11, in which the maximum energy product (BH)_{max} is no less than 56 kJ/m³ (7 MGOe).

18. A permanent magnet as defined in embodiment 12, in which the maximum energy product (BH)_{max} is no less than 80 kJ/m³ (10 MGOe).

19. A permanent magnet as defined in embodiment 18, in which the maximum energy product (BH)_{max} is no less than 160 kJ/m³ (20 MGOe).

20. A permanent magnet as defined in embodiment 19, in which the maximum energy product (BH)_{max} is no less than 240 kJ/m³ (30 MGOe).

21. A permanent magnet as defined in embodiment 20, in which the maximum energy product (BH)_{max} is no less than 280 kJ/m³ (35 MGOe).

22. A magnetic material which comprises Fe, B and R wherein R is at least one rare earth element including Y, and at least one element M selected from the group given below in the amounts of no more than the values specified below, wherein when more than one element comprises M, 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, and in which a major phase is formed of at least one intermetallic compound of the Fe-B-R type having a crystal structure of the substantially tetragonal system:

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.		

23. A sintered magnetic material having a major phase formed of at least one intermetallic compound consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B, at least one additional element M selected from the group given below in the amounts of no more than the values specified below wherein when more than one element comprises M, 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, and the balance being Fe with impurities:

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.		

24. A sintered magnetic material having a major phase formed of at least one intermetallic compound of the substantially tetragonal system, and consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B, at least one additional element M selected from the group given below in the amounts of no more than the values specified below wherein when more than one element comprises M, 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, and the balance being Fe with impurities:

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.		

25. A sintered anisotropic permanent magnet consisting essentially of, by atomic percent, 8—30 percent R, wherein R is at least one rare earth element including Y, 2—28 percent B, at least one additional element M selected from the group given below in the amounts of no more than the values specified below, wherein the amount of M is not zero and wherein when more than one element comprises M, the sum of M is no more than the maximum value among the values specified below of said elements M actually added, and the balance being Fe with impurities:

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.		

26. A sintered anisotropic permanent magnet having a major phase formed of at least one intermetallic compound of the Fe-B-R type having a crystal structure of the substantially tetragonal system and consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B, at least one additional element M selected from the group given below in the amounts no more than the values specified below, wherein the amount of M is not zero and wherein when more than one element comprises M, the sum of M is no more than the maximum value among the values specified below of said elements M actually added, and the balance being Fe with impurities:

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.		

27. A magnetic material as defined in embodiment 22 or 24, in which the substantially tetragonal system amounts to no less than 50 vol %.

28. A permanent magnet as defined in embodiment 26, in which the substantially tetragonal system amounts to no less than 50 vol %.

29. A permanent magnet as defined in embodiment 28, which contains no less than 1 vol % of nonmagnetic intermetallic compound phases.

30. A permanent magnet as defined in embodiment 25 or 26, in which the mean crystal grain size is 1 to 90 μm .

31. A permanent magnet as defined in embodiment 20, in which the mean crystal grain size is 2 to 40 μm .

32. A permanent magnet as defined in embodiment 25 or 26, in which R is 12 to 24%, and B is 3 to 27%.

33. A permanent magnet as defined in embodiment 32, in which R is 12 to 20%, and B is 4 to 24%.

34. A permanent magnet as defined in embodiment 28 or 29, in which the light rare earth element(s) amounts to no less than 50 at % of the overall rare earth elements R.

35. A permanent magnet as defined in embodiment 34, in which the sum of Nd plus Pr amounts to no less than 50 at % of the overall rare earth elements R.

36. A permanent magnet as defined in embodiment 34 or 35, in which R is about 15%, and B is about 8%.

37. A permanent magnet as defined in embodiment 25 or 26, in which the maximum energy product (BH)_{max} is no less than 32 kJ/m³ (4 MGOe).

38. A permanent magnet as defined in embodiment 32, in which the maximum energy product (BH)_{max} is no less than 56 kJ/m³ (7 MGOe).

39. A permanent magnet as defined in embodiment 33, in which the maximum energy product (BH)_{max} is no less than 80 kJ/m³ (10 MGOe).

40. A permanent magnet as defined in embodiment 39, in which the maximum energy product (BH)_{max} is no less than 160 kJ/m³ (20 MGOe).

41. A permanent magnet as defined in embodiment 40, in which the maximum energy product (BH)_{max} is no less than 240 kJ/m³ (30 MGOe).

42. A permanent magnet as defined in embodiment 41, in which the maximum energy product (BH)_{max} is no less than 280 kJ/m³ (35 MGOe).

Claims

1. An alloy comprising Fe-B-R characterized by containing at least one stable compound of the ternary Fe-B-R type, which compound can be magnetized to become a permanent magnet at room temperature and above, where R stands for at least one rare earth element inclusive yttrium.

2. The alloy of claim 1 wherein said compound has a tetragonal structure.

3. The alloy of claim 2 wherein the C_4 axis of the tetragonal structure is about 1.2 nm (12 Å).

4. The alloy of claim 2 or 3 wherein the a_0 axis of the tetragonal structure is about 0.8 nm (8 Å).

5. The alloy of one of the preceding claims, characterized by Curie points of 160 to 370°C, preferably of about 300°C.

6. The alloy of one of the preceding claims having crystals with a mean grain size of 1 μm to 80 μm .

7. The alloy of claim 6 having crystals with a mean grain size of 2 μm to 40 μm .

8. The alloy of one of the preceding claims wherein the light rare earth elements amount to no less than 50 at % of the overall rare earth elements R.

9. The alloy of claim 8 wherein Nd and/or Pr amounts to no less than 50 at % of the overall R.

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



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26. A sintered anisotropic permanent magnet having a major phase formed of at least one intermetallic compound of the Fe-B-R type having a crystal structure of the substantially tetragonal system and consisting essentially of, by atomic percent, 8—30 percent R wherein R is at least one rare earth element including Y, 2—28 percent B, at least one additional element M selected from the group given below in the amounts no more than the values specified below, wherein the amount of M is not zero and wherein when more than one element comprises M, the sum of M is no more than the maximum value among the values specified below of said elements M actually added, and the balance being Fe with impurities:

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.		

27. A magnetic material as defined in embodiment 22 or 24, in which the substantially tetragonal system amounts to no less than 50 vol %.

28. A permanent magnet as defined in embodiment 26, in which the substantially tetragonal system amounts to no less than 50 vol %.

29. A permanent magnet as defined in embodiment 28, which contains no less than 1 vol % of nonmagnetic intermetallic compound phases.

30. A permanent magnet as defined in embodiment 25 or 26, in which the mean crystal grain size is 1 to 90 μm .

31. A permanent magnet as defined in embodiment 20, in which the mean crystal grain size is 2 to 40 μm .

32. A permanent magnet as defined in embodiment 25 or 26, in which R is 12 to 24%, and B is 3 to 27%.

33. A permanent magnet as defined in embodiment 32, in which R is 12 to 20%, and B is 4 to 24%.

34. A permanent magnet as defined in embodiment 28 or 29, in which the light rare earth element(s) amounts to no less than 50 at % of the overall rare earth elements R.

35. A permanent magnet as defined in embodiment 34, in which the sum of Nd plus Pr amounts to no less than 50 at % of the overall rare earth elements R.

36. A permanent magnet as defined in embodiment 34 or 35, in which R is about 15%, and B is about 8%.

37. A permanent magnet as defined in embodiment 25 or 26, in which the maximum energy product (BH)max is no less than 32 kJ/m³ (4 MGOe).

38. A permanent magnet as defined in embodiment 32, in which the maximum energy product (BH)max is no less than 56 kJ/m³ (7 MGOe).

39. A permanent magnet as defined in embodiment 33, in which the maximum energy product (BH)max is no less than 80 kJ/m³ (10 MGOe).

40. A permanent magnet as defined in embodiment 39, in which the maximum energy product (BH)max is no less than 160 kJ/m³ (20 MGOe).

41. A permanent magnet as defined in embodiment 40, in which the maximum energy product (BH)max is no less than 240 kJ/m³ (30 MGOe).

42. A permanent magnet as defined in embodiment 41, in which the maximum energy product (BH)max is no less than 280 kJ/m³ (35 MGOe).

Claims

1. An alloy comprising Fe-B-R characterized by containing at least one stable compound of the ternary Fe-B-R type, which compound can be magnetized to become a permanent magnet at room temperature and above, where R stands for at least one rare earth element inclusive yttrium.

2. The alloy of claim 1 wherein said compound has a tetragonal structure.

3. The alloy of claim 2 wherein the c_0 axis of the tetragonal structure is about 1.2 nm (12 Å).

4. The alloy of claim 2 or 3 wherein the a_0 axis of the tetragonal structure is about 0.8 nm (8 Å).

5. The alloy of one of the preceding claims, characterized by Curie points of 160 to 370°C, preferably of about 300°C.

6. The alloy of one of the preceding claims having crystals with a mean grain size of 1 μm to 80 μm .

7. The alloy of claim 6 having crystals with a mean grain size of 2 μm to 40 μm .

8. The alloy of one of the preceding claims wherein the light rare earth elements amount to no less than 50 at % of the overall rare earth elements R.

9. The alloy of claim 8 wherein Nd and/or Pr amounts to no less than 50 at % of the overall R.

10. The alloy of one of the preceding claims further comprising additional elements M evident from the below list, 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 metals M added.

11. The alloy of claim 10 having a mean crystal grain size of 1—90 μm , preferably 2—40 μm .
12. An alloy as defined in one of the preceding claims wherein R is 15 at % and B is 8 at %.
13. A process of preparing an alloy according to one of the preceding claims by melting and casting a composition containing 2—28 at % B, 8—30 at % R, where R stands for at least one rare earth element including yttrium and the balance being iron.
14. The process of claim 13 wherein as the starting materials iron, a ferroboration alloy for B and rare earth elements are used.
15. The process of claim 13 or 14 wherein the castings are pulverized.
16. The process of claim 15 wherein pulverization is effected to 3—10 μm .
17. Use of the alloys of one of claims 1 to 12 for being applied to magnetic recording media, as magnetic paints, temperature-sensitive materials and intermediaries for the production of permanent magnets.
18. A permanent magnet material comprising 8—30 at % of 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 to 28 at % of B and the balance Fe.
19. A permanent magnet material of claim 18 comprising 12—20 at % R and 4—24 at % B.
20. The permanent magnet material of claim 18 or 19 which contains more than 50% of a phase containing at least one stable Fe-B-R compound having a tetragonal structure.
21. The permanent magnet material of claim 20 wherein the C_4 axis of the tetragonal structure is about 1,2 nm (12 Å).
22. The permanent magnet material of claim 20 or 21 wherein the a_0 axis of the tetragonal structure is about 0,8 nm (8 Å).
23. The permanent magnet material of one of claims 20 to 22 having a mean crystal grain size of 1—80 μm .
24. The permanent magnet material of claim 23 having a mean crystal grain size of 2—40 μm .
25. The permanent magnet material of one of claims 20 to 22 wherein the fine particles of the phase containing at least one stable Fe-B-R compound are separated from one another by nonmagnetic phases.
26. The permanent magnet material of claim 25 wherein the nonmagnetic phases have a high content of R of 1 to 45 vol %.
27. A permanent magnet material of one of claims 18 to 26 further comprising additional elements M evident from the below list, 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 shall be no more than the maximum value among the values specified hereinabove of the M actually added.

28. The permanent magnet material of claim 27 having a mean crystal grain size of 1 to 90 μm , preferably 2 to 40 μm .
29. The permanent magnet material of one of the preceding claims wherein R is 15 at % and B 8 at %.
30. A process for making a 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, cooling the melt to crystallize and powderizing the crystalline product.
31. The process of claim 30 wherein the balance is Fe and one or more of the following specified elements in amounts 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 metals M added.

32. The process of claims 30 or 31 wherein the crystalline product is pulverized to 3—10 μm .

33. The process of one of claims 30 or 32 wherein the pulverized product is sintered.

5 34. The process of claim 33 wherein the sintering is effected at a temperature of 1000 to 1200°C.

35. The process of claim 34 wherein the sintering is effected in an argon atmosphere.

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

37. The magnetic material of claim 36 wherein the C_4 axis of the tetragonal structure is about 1,2 nm (12 Å).

38. The magnetic material of claim 36 or 37 wherein the a_0 axis of the tetragonal structure is about 0,8 nm (8 Å).

39. The magnetic material of one of claims 36 to 38 comprising 2—28% of B, 8—30% of R, and the balance being Fe.

40. The magnetic material of one of claims 36 to 38 wherein the mean crystal grain size ranges, preferably from 1.0 μm to 80 μm .

41. The magnetic material of claim 40 wherein the mean crystal grain size ranges from 2 μm to 40 μm .

42. The magnetic material of one of claims 36 to 41 wherein the particles of the phase comprising at least one Fe-B-R type compound having tetragonal structure are separated individually by nonmagnetic phases.

43. The magnetic material of one of claims 36 to 42 comprising nonmagnetic phases of 1 vol % to 45 vol % containing much of R.

44. The magnetic material of one of claims 36 to 43 comprising 2—28% of B, 8 to 30% of R and the balance being Fe and M, M being one or more of the elements specified hereinbelow, the amounts of these elements being 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 metals M added.

45. The magnetic material of claim 44, wherein the mean crystal grain size ranges from 1 to 90 μm , preferably 1.5 to 80 μm .

46. The magnetic material of one of claims 36 to 43 wherein the light rare earth elements are used for the rare earth element R.

47. The magnetic material of claim 46 wherein Nd and/or Pr are used for the rare earth elements R.

48. A sintered magnetic material consisting of a magnetic material powder 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.

49. A process of making a magnetic material powder showing a tetragonal structure 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, by heating a powdery rare earth oxide R_2O_3 as raw material for R, with powdery Fe, powdery FeB and a reducing agent for direct reduction.

50. The process of claim 49 including a further step of sintering the powder alloys.

51. A permanent magnet comprising at least one stable ternary compound of the Fe-B-R type where R stands for at least one of the rare earth elements including Y.

52. The permanent magnet of claim 51 comprising 8—30 at % R, R being one or more of the rare earth elements including Y, 2—28 at % of B and the balance being Fe.

53. The permanent magnet of claim 52 comprising 12—20 at % R and 4—24 at % B, the balance being Fe.

54. The permanent magnet of one of claims 51 to 53, having anisotropic properties obtainable by sintering a powder of said material.

55. A permanent magnet comprising 8—30 at % R, R being one or more of the rare earth elements including Y, 2—28 at % of B and the balance being Fe, obtainable by sintering a powder of said material.

56. The permanent magnet of claim 54 or 55 having anisotropic properties obtainable by additional alignment in a magnetic field.

57. The permanent magnet of one of claims 51 to 56 wherein the light rare earth elements amount to no less than 50 at % of the overall rare earth elements R.

58. The permanent magnet of claim 57 wherein Nd and/or Pr amounts to no less than 50 at % of the overall R.

59. The permanent magnet of one of claims 54 to 58 wherein the mean crystal grain size is 1—80 μm , preferably 2—40 μm .



60. The permanent magnet of one of claims 52 to 58 further comprising additional elements M evident from the below list, the amounts of these elements being respectively limited to no more than the values specified hereinbelow by atomic percent

5	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,
10	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 metals M added.

61. The permanent magnet of claim 60 having a mean crystal grain size of 1—90 μm , preferably 2—40 μm .

62. The permanent magnet of claims 52 to 61 wherein R is 15 at % and B 8 at %.

63. The permanent magnet of one of claims 51 to 62 wherein the at least one stable ternary compound has a tetragonal structure.

64. The permanent magnet of claim 63 wherein the c_0 axis of the tetragonal structure is about 1,2 nm (12 Å).

65. The permanent magnet of claim 63 or 64 wherein the a_0 axis of the tetragonal structure is about 0,8 nm (8 Å).

66. The permanent magnet of one of claims 54 to 65 comprising nonmagnetic phases separating the fine particles of the at least one stable ternary compound from one another.

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

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

69. The sintered permanent magnet of claim 68 containing nonmagnetic phases of 1—45 vol % containing much of R.

70. The sintered permanent magnet of claim 69 wherein the nonmagnetic phases are present in 2—10 vol %.

71. The sintered permanent magnet of one of claims 68 to 70 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.

72. The sintered permanent magnet of claim 71 wherein R is 12—20 at % and B is 4—24 at %.

73. The sintered permanent magnet of one of claims 68 to 72 wherein the light rare earth element(s) amounts to no less than 50 at % of the overall rare earth elements R.

74. The sintered permanent magnet of claim 73 wherein Nd and/or Pr amounts to no less than 50 at % of the overall rare earth elements R.

75. The sintered permanent magnet of one of claims 71 to 74 wherein R amounts to about 15 at % and B amounts to about 8 at %.

76. The sintered permanent magnet of one of claims 68 to 75 wherein the mean crystal grain size is 1—80 μm .

77. The sintered permanent magnet of claim 76 wherein the mean crystal grain size is 2 to 40 μm .

78. The sintered permanent magnet of one of claims 68 to 75 containing at least one additional element M selected from the group given below in the amounts of no more than the values specified below,

50	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 metals M added.

79. The sintered permanent magnet of claim 78 wherein the mean crystal grain size is 1—90 μm .

80. The sintered permanent magnet of claim 79 wherein the mean crystal grain size is 2 to 40 μm .

81. The permanent magnet of claim 52 or 71 wherein the maximum energy product (BH)_{max} is no less than 32 kJ/m³ (4 MGOe).

82. The permanent magnet of claim 53 or 72 wherein the maximum energy product (BH)_{max} is no less than 80 kJ/m³ (10 MGOe).

83. The permanent magnet of claim 82 wherein the maximum energy product (BH)_{max} is no less than 160 kJ/m³ (20 MGOe).



84. The permanent magnet of claim 82 wherein the maximum energy product (BH)_{max} is no less than 240 kJ/m³ (30 MGOe).

85. The permanent magnet of claim 82 wherein the maximum energy product (BH)_{max} is no less than 280 kJ/m³ (35 MGOe).

5 86. The permanent magnet of one of claims 51 to 85 obtainable by a powder metallurgical process.

87. 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, cooling the melt to crystallize, powdering the crystallized product, pressing and sintering the powdered product.

10 88. The process for 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 and M, M being at least one additional element selected from the group given below in the amounts of no more than the values specified below,

15	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		

20 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 metals M added, cooling the melt to crystallize, powdering the crystallized product, pressing and sintering the powdered alloy.

89. The process of claim 87 or 88 wherein the pressed powdered product is oriented in a magnetic field.

25 90. The process of one of claims 87 to 89 wherein the compacts are sintered at 1000 to 1200°C.

91. The process of claim 90 wherein the sintering is effected in an argon atmosphere.

92. The process of one of claims 88 to 91 wherein a step of aging is effected after sintering.

Patentansprüche

30 1. Legierung mit einem Gehalt an Fe-B-R, dadurch gekennzeichnet, daß sie mindestens eine stabile Verbindung des ternären Typs Fe-B-R enthält, die magnetisiert werden kann, um bei Raumtemperatur und darüber ein Permanentmagnet zu werden, wobei R mindestens ein Seltenerdelement einschließlich Yttrium bedeutet.

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

3. Legierung nach Anspruch 2, worin die c₀-Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

4. Legierung nach Anspruch 2 oder 3, worin die a₀-Achse der tetragonalen Struktur etwa 0,8 nm (8 Å) beträgt.

40 5. Legierung nach einem der vorstehenden Ansprüche, gekennzeichnet durch Curie-Punkte von 160 bis 370°C, vorzugsweise von etwa 300°C.

6. Legierung nach einem der vorstehenden Ansprüche, mit Kristallen, deren mittlere Korngröße 1 bis 80 µm beträgt.

7. Legierung nach Anspruch 6, mit Kristallen, deren mittlere Korngröße 2 bis 40 µm beträgt.

45 8. Legierung nach einem der vorstehenden Ansprüche, worin die leichten Seltenerdelemente nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R betragen.

9. Legierung nach Anspruch 8, worin Nd und/oder Pr nicht weniger als 50 Atom-% der gesamten Komponente R betragen.

50 10. Legierung nach einem der vorstehenden Ansprüche, die außerdem zusätzliche Elemente M gemäß der nachfolgenden Liste enthält, deren Menge jeweils nicht mehr als die nachstehenden Werte in Atomprozent betragen,

55	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,		

60 wobei beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist.

11. Legierung nach Anspruch 10, mit einer mittleren Kristallkorngröße von 1 bis 90 µm, vorzugsweise 2 bis 40 µm.

12. Legierung nach einem der vorstehenden Ansprüche, worin R einen Wert von 15 Atom-% und B einen Wert von 8 Atom-% aufweisen.

65 13. Verfahren zum Herstellen einer Legierung nach einem der vorstehenden Ansprüche, durch



Schmelzen und Gießen einer Zusammensetzung, die aus 2 bis 28 Atom-% B, 8 bis 30 Atom-% R, wobei R mindestens ein Seltenerdelement einschließlich Yttrium bedeutet, und als Rest Eisen besteht.

14. Verfahren nach Anspruch 13, worin als Ausgangsstoffe Eisen, eine Eisen-Bor-Legierung für B und Seltenerdelemente eingesetzt werden.

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

16. Verfahren nach Anspruch 15, worin das Pulverisieren bis auf 3 bis 10 µm durchgeführt wird.

17. Verwendung der Legierungen nach einem der Ansprüche 1 bis 12 für magnetische Aufzeichnungsmaterialien, als magnetische Anstrichmittel, temperaturempfindliche Materialien und Zwischenprodukte zur Herstellung von Permanentmagneten.

18. Permanentmagnetmaterial, enthaltend 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y, Nd und/oder Pr bedeutet und in einer Menge von nicht weniger als 50 Atom-% von R vorliegt, 2 bis 28 Atom-% B und als Rest Fe.

19. Permanentmagnetmaterial nach Anspruch 18, enthaltend 2 bis 20 Atom-% R und 4 bis 24 Atom-% B.

20. Permanentmagnetmaterial nach Anspruch 18 oder 19, das mehr als 50% einer Phase enthält, die mindestens eine stabile Fe-B-R-Verbindung mit einer tetragonalen Struktur aufweist.

21. Permanentmagnetmaterial nach Anspruch 20, worin die c_0 -Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

22. Permanentmagnetmaterial nach Anspruch 20 oder 21, worin die a_0 -Achse der tetragonalen Struktur etwa 0,8 nm (8 Å) beträgt.

23. Permanentmagnetmaterial nach einem der Ansprüche 20 bis 22, mit einer mittleren Kristallkorngröße von 1 bis 80 µm.

24. Permanentmagnetmaterial nach Anspruch 23, mit einer mittleren Kristallkorngröße von 2 bis 40 µm.

25. Permanentmagnetmaterial nach einem der Ansprüche 20 bis 22, worin die Feinteilchen der Phase, die mindestens eine stabile Fe-B-R-Verbindung enthält, durch nichtmagnetische Phasen voneinander getrennt sind.

26. Permanentmagnetmaterial nach Anspruch 25, worin die nichtmagnetischen Phasen einen hohen Gehalt an R von 1 bis 45 Vol-% aufweisen.

27. Permanentmagnetmaterial nach einem der Ansprüche 18 bis 26, das weiterhin zusätzliche Elemente M gemäß der nachfolgenden Liste enthält, wobei die Mengen dieser Elemente jeweils nicht mehr als die nachstehend in Atomprozent angegebenen Werte betragen,

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 beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge nicht mehr als der maximale Wert der vorstehend angegebenen Werte der zugegebenen Elemente M beträgt.

28. Permanentmagnetmaterial nach Anspruch 27, mit einer mittleren Kristallkorngröße von 1 bis 90 µm, vorzugsweise 2 bis 40 µm.

29. Permanentmagnetmaterial nach einem der vorstehenden Ansprüche, worin R einen Wert von 15 Atom-% und B einen Wert von 8 Atom-% aufweist.

30. Verfahren zum Herstellen eines Permanentmagnetmaterials durch Bereitstellen einer Schmelze mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% Bor und als Rest Fe, Abkühlen der Schmelze bis zum Kristallisieren und Pulverisieren des kristallinen Produkts.

31. Verfahren nach Anspruch 30, worin der Rest Fe und ein oder mehrere der nachfolgend angegebenen Elemente in Mengen, die auf nicht mehr als die nachfolgend angegebenen Werte in Atomprozent begrenzt sind,

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 beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist.

32. Verfahren nach Anspruch 30 oder 31, worin das kristalline Produkt bis auf 3 bis 10 µm pulverisiert wird.

33. Verfahren nach einem der Ansprüche 30 oder 32, worin das pulverisierte Produkt gesintert wird.



34. Verfahren nach Anspruch 33, worin das Sintern bei einer Temperatur von 1000 bis 1200°C durchgeführt wird.

35. Verfahren nach Anspruch 34, worin das Sintern in einer Argonatmosphäre durchgeführt wird.

36. Magnetisches Material mit einem Gehalt an mindestens 50 Vol-% einer Phase, die mindestens eine Verbindung des Typs Fe-B-R mit einer tetragonalen Struktur aufweist, wobei R mindestens ein Seltenerdelement einschließlich Y bedeutet.

37. Magnetisches Material nach Anspruch 36, worin die c_0 -Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

38. Magnetisches Material nach Anspruch 36 oder 37, worin die a_0 -Achse der tetragonalen Struktur etwa 0,8 nm (8 Å) beträgt.

39. Magnetisches Material nach einem der Ansprüche 36 bis 38, enthaltend 2 bis 28% B, 8 bis 30% R und als Rest Fe.

40. Magnetisches Material nach einem der Ansprüche 36 bis 38, worin die mittlere Kristallkorngröße vorzugsweise im Bereich von 1,0 bis 80 µm liegt.

41. Magnetisches Material nach Anspruch 40, worin die mittlere Kristallkorngröße im Bereich von 2 bis 40 µm liegt.

42. Magnetisches Material nach einem der Ansprüche 36 bis 41, worin die Teilchen der Phase, die mindestens eine Verbindung des Typs Fe-B-R mit einer tetragonalen Struktur enthält, durch nichtmagnetische Phasen voneinander getrennt sind.

43. Magnetisches Material nach einem der Ansprüche 36 bis 42, das 1 bis 45 Vol-% nichtmagnetische Phasen mit einem hohen Gehalt an R aufweist.

44. Magnetisches Material nach einem der Ansprüche 36 bis 43, enthaltend 2 bis 28% B, 8 bis 30% R sowie als Rest Fe und M, wobei M ein oder mehrere der nachfolgend angegebenen Elemente bedeutet, deren Mengen nicht mehr als die nachstehend in Atomprozent angegebenen Werte betragen,

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 beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist.

45. Magnetisches Material nach Anspruch 44, worin die mittlere Kristallkorngröße im Bereich von 1 bis 90 µm, vorzugsweise 1,5 bis 80 µm, liegt.

46. Magnetisches Material nach einem der Ansprüche 36 bis 43, worin die leichten Seltenerdelemente als Seltenerdelement R eingesetzt werden.

47. Magnetisches Material nach Anspruch 46, worin Nd und/oder Pr als Seltenerdelemente R eingesetzt werden.

48. Gesintertes magnetisches Material, bestehend aus einem magnetischen Pulver mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe.

49. Verfahren zum Herstellen eines Pulvers eines magnetischen Materials mit einer tetragonalen Struktur, enthaltend 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe, durch Erhitzen eines pulverförmigen Seltenerdeelementoxids R_2O_3 als Ausgangsstoff für R mit pulverförmigem Fe, pulverförmigem FeB und einem Reduktionsmittel für direkte Reduktion.

50. Verfahren nach Anspruch 49, das eine weitere Stufe des Sinterns der Pulverlegierungen umfaßt.

51. Permanentmagnet mit einem Gehalt an mindestens einer stabilen ternären Verbindung des Typs Fe-B-R, worin R mindestens ein Seltenerdelement einschließlich Y bedeutet.

52. Permanentmagnet nach Anspruch 51, enthaltend 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe.

53. Permanentmagnet nach Anspruch 52, enthaltend 12 bis 20 Atom-% R, 4 bis 24 Atom-% B und als Rest Fe.

54. Permanentmagnet nach einem der Ansprüche 51 bis 53, mit anisotropen Eigenschaften, die durch Sintern eines Pulvers des genannten Materials erhältlich sind.

55. Permanentmagnet, enthaltend 8 bis 30 Atom-% R, wobei R ein oder mehrere der Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe, erhältlich durch Sintern eines Pulvers des genannten Materials.

56. Permanentmagnet nach Anspruch 54 oder 55, mit anisotropen Eigenschaften, erhältlich durch zusätzliches Ausrichten in einem Magnetfeld.

57. Permanentmagnet nach einem der Ansprüche 51 bis 56, worin die leichten Seltenerdelemente in einer Menge von nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R vorliegen.



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58. Permanentmagnet nach Anspruch 57, worin Nd und/oder Pr in einer Menge von nicht weniger als 50 Atom-% der gesamten Komponente R vorliegen.

59. Permanentmagnet nach einem der Ansprüche 54 bis 58, worin die mittlere Kristallkorngröße 1 bis 80 μm , vorzugsweise 2 bis 40 μm , beträgt.

5 60. Permanentmagnet nach einem der Ansprüche 52 bis 58, der weiterhin zusätzliche Elemente M gemäß der nachfolgenden Liste enthält, deren Mengen jeweils auf die nachfolgend angegebenen Werte in Atomprozent begrenzt sind,

	4,5% Ti,	8,0% Ni,	5,0% Bi,
10	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,		

15 wobei beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist.

61. Permanentmagnet nach Anspruch 60 mit einer mittleren Kristallkorngröße von 1 bis 90 μm , vorzugsweise 2 bis 40 μm .

20 62. Permanentmagnet nach den Ansprüchen 52 bis 61, worin R einen Wert von 15 Atom-% und B einen Wert von 8 Atom-% aufweist.

63. Permanentmagnet nach einem der Ansprüche 51 bis 62, worin die mindestens eine vorliegende stabile ternäre Verbindung eine tetragonale Struktur aufweist.

64. Permanentmagnet nach Anspruch 63, worin die c_0 -Achse der tetragonalen Struktur etwa 1,2 nm (12 Å) beträgt.

25 65. Permanentmagnet nach Anspruch 63 oder 64, worin die a_0 -Achse der tetragonalen Struktur etwa 0,8 nm (8 Å) beträgt.

66. Permanentmagnet nach einem der Ansprüche 54 bis 65, enthaltend nichtmagnetische Phasen, welche die Feinteilchen der mindestens einen stabilen ternären Verbindung voneinander trennt.

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

68. Gesinterter Permanentmagnet, enthaltend mindestens 50 Vol-% einer Phase, die mindestens eine Verbindung des Typs Fe-B-R mit einer tetragonalen Struktur aufweist, wobei R mindestens ein Seltenerdelement einschließlich Y bedeutet.

35 69. Gesinterter Permanentmagnet nach Anspruch 68, enthaltend nichtmagnetische Phasen in einer Menge von 1 bis 45 Vol-%, die viel R aufweisen.

70. Gesinterter Permanentmagnet nach Anspruch 69, worin die nichtmagnetischen Phasen in einer Menge von 2 bis 10 Vol-% vorliegen.

71. Gesinterter Permanentmagnet nach einem der Ansprüche 68 bis 70, enthaltend 8 bis 30 Atom-% R, worin R mindestens ein Seltenerdelement einschließlich Y bedeutet, 2 bis 28 Atom-% B und als Rest Fe.

40 72. Gesinterter Permanentmagnet nach Anspruch 71, worin R einen Wert von 12 bis 20 Atom-% und B einen Wert von 4 bis 24 Atom-% aufweist.

73. Gesinterter Permanentmagnet nach einem der Ansprüche 68 bis 72, worin das leichte Seltenerdelement oder die leichten Seltenerdelemente in einer Menge von nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R vorliegen.

45 74. Gesinterter Permanentmagnet nach Anspruch 73, worin Nd und/oder Pr in einer Menge von nicht weniger als 50 Atom-% der gesamten Seltenerdelemente R vorliegen.

75. Gesinterter Permanentmagnet nach einem der Ansprüche 71 bis 74, worin R in einer Menge von etwa 15 Atom-% und B in einer Menge von etwa 8 Atom-% vorliegt.

50 76. Gesinterter Permanentmagnet nach einem der Ansprüche 68 bis 75, worin die mittlere Kristallkorngröße 1 bis 80 μm beträgt.

77. Gesinterter Permanentmagnet nach Anspruch 76, worin die mittlere Kristallkorngröße 2 bis 40 μm beträgt.

55 78. Gesinterter Permanentmagnet nach einem der Ansprüche 68 bis 75, enthaltend mindestens ein zusätzliches Element M, ausgewählt aus der nachfolgend angegebenen Gruppe, in Mengen, welche die unten angeführten Werte nicht übersteigen,

	4,5% Ti,	8,0% Ni,	5,0% Bi,
	9,5% V,	12,5% Nb,	10,5% Ta,
60	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,		

65 wobei beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist.



79. Gesinterter Permanentmagnet nach Anspruch 78, worin die mittlere Kristallkorngröße 1 bis 90 μm beträgt.

80. Gesinterter Permanentmagnet nach Anspruch 79, worin die mittlere Kristallkorngröße 2 bis 40 μm beträgt.

5 81. Permanentmagnet nach Anspruch 52 oder 71, worin das Maximalenergieprodukt (BH)_{max} nicht weniger als 32 kJ/m³ (4 MGOe) beträgt.

82. Permanentmagnet nach Anspruch 53 oder 72, worin das Maximalenergieprodukt (BH)_{max} nicht weniger als 80 kJ/m³ (10 MGOe) beträgt.

10 83. Permanentmagnet nach Anspruch 82, worin das Maximalenergieprodukt (BH)_{max} nicht weniger als 160 kJ/m³ (20 MGOe) beträgt.

84. Permanentmagnet nach Anspruch 82, worin das Maximalenergieprodukt (BH)_{max} nicht weniger als 240 kJ/m³ (30 MGOe) beträgt.

85. Permanentmagnet nach Anspruch 82, worin das Maximalenergieprodukt (BH)_{max} nicht weniger als 280 kJ/m³ (35 MGOe) beträgt.

15 86. Permanentmagnet nach einem der Ansprüche 51 bis 85, erhältlich durch ein pulvermetallurgisches Verfahren.

87. Verfahren zum Herstellen eines Permanentmagneten durch Bereitstellen einer Schmelze mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% Bor und als Rest Fe, Abkühlen der Schmelze bis zum Kristallisieren, Pulverisieren des kristallisierten Produkts sowie Pressen und Sintern des gepulverten Produkts.

20 88. Verfahren zum Herstellen eines Permanentmagneten durch Bereitstellen einer Schmelze mit einem Gehalt an 8 bis 30 Atom-% R, wobei R ein oder mehrere Seltenerdelemente einschließlich Y bedeutet, 2 bis 28 Atom-% Bor sowie als Rest Fe und M, wobei M mindestens ein zusätzliches Element bedeutet, das aus der nachfolgend angegebenen Gruppe in Mengen, welche nicht über den unten angegebenen Werten liegen, ausgewählt ist,

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,		

30 wobei beim Einsatz von zwei oder mehr der Elemente M deren Gesamtmenge auf den höchsten Wert eines der einzelnen zugegebenen Metalle M begrenzt ist, Abkühlen der Schmelze bis zum Kristallisieren, Pulverisieren des kristallisierten Produkts sowie Pressen und Sintern der gepulverten Legierung.

89. Verfahren nach Anspruch 87 oder 88, worin das gepreßte, gepulverte Produkt in einem Magnetfeld ausgerichtet wird.

40 90. Verfahren nach einem der Ansprüche 87 bis 89, worin die verdichteten Körper bei 1000 bis 1200°C gesintert werden.

91. Verfahren nach Anspruch 90, worin das Sintern in einer Argonatmosphäre durchgeführt wird.

92. Verfahren nach einem der Ansprüche 88 bis 91, worin nach dem Sintern eine Alterungsstufe durchlaufen wird.

45 Revendications

1. Alliage comprenant Fe-B-R, caractérisé par le fait qu'il contient au moins un composé stable du type ternaire Fe-B-R, composé qui peut être magnétisé en devenant un aimant permanent à la température ambiante et au-dessus, R représentant au moins un élément des terres rares, y compris l'yttrium.

50 2. Alliage suivant la revendication 1, dans lequel ledit composé a une structure tétragonale.

3. Alliage suivant la revendication 2, dans lequel l'axe C de la structure tétragonale est d'environ 1,2 nm (12 Å).

4. Alliage suivant la revendication 2 ou 3, dans lequel l'axe a₀ de la structure tétragonale est d'environ 0,8 nm (8 Å).

55 5. Alliage suivant l'une des revendications précédentes, caractérisé par des points de Curie de 160 à 370°C, de préférence d'environ 300°C.

6. Alliage suivant l'une des revendications précédentes, ayant des cristaux avec une dimension moyenne de grain de 1 μm à 80 μm .

60 7. Alliage suivant la revendication 6, ayant des cristaux avec une dimension moyenne de grain de 2 μm à 40 μm .

8. Alliage suivant l'une des revendications précédentes, dans lequel les éléments légers des terres rares ne constituent pas moins de 50% en atomes de l'ensemble des éléments R des terres rares.

9. Alliage suivant la revendication 8, dans lequel les éléments Nd et/ou Pr ne représentent pas moins de 50% en atomes de l'ensemble de R.

65 10. Alliage suivant l'une des revendications précédentes, comprenant en outre d'autres éléments M



ressortant de la liste ci-dessous, les quantités de ces éléments étant respectivement limitées à des valeurs ne dépassant pas celles qui sont précisées ci-dessous, en pourcentages atomiques

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

auquel cas, lorsque deux ou plus de deux éléments M sont impliqués, la quantité totale de M est limitée à la valeur maximale de l'un des métaux individuels M ajoutés.

11. Alliage suivant la revendication 10, ayant une dimension moyenne du grain des cristaux de 1 à 90 μm , de préférence de 2 à 40 μm .

12. Alliage tel que défini dans l'une des revendications précédentes, dans lequel le pourcentage atomique de R est égal à 15 et le pourcentage atomique de B est égal à 8.

13. Procédé de préparation d'un alliage suivant l'une des revendications précédentes par fusion et coulée d'une composition contenant 2 à 28% en atomes de B, 8 à 30% en atomes de R, R représentant au moins un élément des terres rares y compris l'yttrium et le reste étant du fer.

14. Procédé suivant la revendication 13, dans lequel on utilise comme matières de départ du fer, un alliage ferro-bore pour B, et des éléments des terres rares.

15. Procédé suivant la revendication 13 ou 14, dans lequel les masses coulées sont pulvérisées.

16. Procédé suivant la revendication 15, dans lequel la pulvérisation est effectuée jusqu'à 3—10 μm .

17. Utilisation des alliages suivant l'une des revendications 1 à 12 par application à des supports magnétiques d'enregistrement, comme peintures magnétiques, comme matériaux thermosensibles et comme produits intermédiaires pour l'obtention d'aimants permanents.

18. Matériau pour aimant permanent, comprenant 8 à 30 atomes % de R, R représentant un ou plusieurs éléments des terres rares comprenant Y, Nd et/ou Pr en quantité non inférieure à 50% en atomes de R, 2 à 28% en atomes de B, le reste étant du fer.

19. Matériau pour aimant permanent suivant la revendication 18, comprenant 12 à 20% en atomes de R et 4 à 24% en atomes de B.

20. Matériau pour aimant permanent suivant la revendication 18 ou 19, qui contient plus de 50% d'une phase renfermant au moins un composé Fe-B-R stable à structure tétragonale.

21. Matériau pour aimant permanent suivant la revendication 20, dans lequel l'axe C_0 de la structure tétragonale est d'environ 1,2 nm (12 Å).

22. Matériau pour aimant permanent suivant la revendication 20 ou 21, dans lequel l'axe a_0 de la structure tétragonale est d'environ 0,8 nm (8 Å).

23. Matériau pour aimant permanent suivant l'une des revendications 20 à 22, ayant une dimension moyenne du grain des cristaux de 1 à 80 μm .

24. Matériau pour aimant permanent suivant la revendication 23, ayant une dimension moyenne du grain des cristaux de 2 à 40 μm .

25. Matériau pour aimant permanent suivant l'une des revendications 20 à 22, dans lequel les fines particules de la phase contenant au moins un composé Fe-B-R stable sont séparées les unes des autres par des phases non magnétiques.

26. Matériau pour aimant permanent suivant la revendication 25, dans lequel les phases non magnétiques ont une haute teneur en R de 1 à 45% en volume.

27. Matériau pour aimant permanent suivant l'une des revendications 18 à 26, comprenant en outre des éléments additionnels M ressortant de la liste ci-dessous, les quantités de ces éléments étant respectivement limitées à des valeurs ne dépassant pas celles qui sont spécifiées ci-dessous, en pourcentages atomiques

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

où lorsque deux ou plus de deux éléments M sont impliqués, la quantité totale d'éléments M ne doit pas dépasser la valeur maximale parmi les valeurs spécifiées ci-dessus des éléments M réellement ajoutés.

28. Matériau pour aimant permanent suivant la revendication 27, ayant une dimension moyenne du grain des cristaux de 1 à 90 μm , de préférence de 2 à 40 μm .

29. Matériau pour aimant permanent suivant l'une des revendications précédentes, dans lequel le pourcentage atomique de R est égal à 15, et le pourcentage atomique de B est égal à 8.

30. Procédé de préparation d'un matériau magnétique permanent par formation d'une masse fondue



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comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de bore, le reste étant du fer, refroidissement de la masse fondue jusqu'à cristallisation, et transformation en poudre du produit cristallisé.

31. Procédé suivant la revendication 30, dans lequel le reste consiste en fer et un ou plusieurs des éléments spécifiés ci-après en quantités limitées à des valeurs ne dépassant pas les valeurs précisées ci-dessous, en pourcentages atomiques

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

où, lorsque deux ou plus de deux éléments M sont impliqués, la quantité totale de M est limitée à la valeur maximale de l'un des métaux individuels M ajoutés.

32. Procédé suivant la revendication 30 ou 31, dans lequel le produit cristallin est pulvérisé jusqu'à 3—10 μm .

33. Procédé suivant l'une des revendications 30 ou 32, dans lequel le produit pulvérisé est fritté.

34. Procédé suivant la revendication 33, dans lequel le frittage est effectué à une température de 1000 à 1200°C.

35. Procédé suivant la revendication 34, dans lequel le frittage est effectué dans une atmosphère d'argon.

36. Matériau magnétique comprenant au moins 50% en volume d'une phase constituée d'au moins un composé du type Fe-B-R ayant une structure tétragonale, où R représente au moins un élément des terres rares y compris l'yttrium.

37. Matériau magnétique suivant la revendication 36, dans lequel l'axe C_0 de la structure tétragonale est d'environ 1,2 nm (12 Å).

38. Matériau magnétique suivant la revendication 36 ou 37, dans lequel l'axe a_0 de la structure tétragonale est d'environ 0,8 nm (8 Å).

39. Matériau magnétique suivant l'une des revendications 36 à 38, comprenant 2 à 28% de B, 8 à 30% de R, le reste étant du fer.

40. Matériau magnétique suivant l'une des revendications 36 à 38, dans lequel la dimension moyenne du grain des cristaux se situe de préférence dans l'intervalle de 1,0 μm à 80 μm .

41. Matériau magnétique suivant la revendication 40, dans lequel la dimension moyenne du grain des cristaux va de 2 à 40 μm .

42. Matériau magnétique suivant l'une des revendications 36 à 41, dans lequel les particules de la phase comprenant au moins un composé du type Fe-B-R à structure tétragonale sont séparées individuellement par des phases non magnétiques.

43. Matériau magnétique suivant l'une des revendications 36 à 42, comprenant des phases non magnétiques de 1% en volume à 45% en volume contenant beaucoup de R.

44. Matériau magnétique suivant l'une des revendications 36 à 43, comprenant 2 à 28% de B, 8 à 30% de R, le reste étant Fe et M, M représentant un ou plusieurs des éléments spécifiés ci-dessous, les quantités de ces éléments étant limitées à une valeur ne dépassant pas les valeurs précisées ci-dessous en pourcentages atomiques

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

où, lorsque deux ou plus de deux M sont impliqués, la quantité totale de M est limitée à la valeur maximale de l'un des métaux individuels M ajoutés.

45. Matériau magnétique suivant la revendication 44, dans lequel la dimension moyenne du grain des cristaux va de 1 à 90 μm , de préférence de 1,5 à 80 μm .

46. Matériau magnétique suivant l'une des revendications 36 à 43, dans lequel les éléments légers des terres rares sont utilisés comme élément R des terres rares.

47. Matériau magnétique suivant la revendication 46, dans lequel on utilise du Nd et/ou du Pr comme éléments R des terres rares.

48. Matériau magnétique fritté constitué d'un matériau magnétique en poudre comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs des éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de B, le reste étant du fer.

49. Procédé de préparation d'un matériau magnétique en poudre à structure tétragonale, comprenant



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8 à 30% en atomes de R, R représentant un ou plusieurs des éléments des terres rares y compris Y, 2 à 28% en atomes de B, le reste étant du fer, par chauffage d'un oxyde de terre rare R_2O_3 en poudre en tant que matière première pour R, avec du fer en poudre, du FeB en poudre et un agent réducteur en vue d'une réduction directe.

5 50. Procédé suivant la revendication 49, comprenant une étape additionnelle de frittage des alliages en poudre.

51. Aimant permanent comprenant au moins un composé ternaire stable du type Fe-B-R où R représente au moins l'un des éléments des terres rares y compris l'yttrium.

10 52. Aimant permanent suivant la revendication 51, comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de B, le reste étant du fer.

53. Aimant permanent suivant la revendication 52, comprenant 12 à 20% en atomes de R et 4 à 24% en atomes de B, le reste étant du fer.

15 54. Aimant permanent suivant une ou plusieurs des revendications 51 à 53, doué de propriétés anisotropes, pouvant être obtenu par frittage d'une poudre dudit matériau.

55. Aimant permanent comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs des éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de B, le reste étant du fer, pouvant être obtenu par frittage d'une poudre dudit matériau.

20 56. Aimant permanent suivant la revendication 54 ou 55, doué de propriétés anisotropes, pouvant être obtenu par alignement additionnel dans un champ magnétique.

57. Aimant permanent suivant l'une des revendications 51 à 56, dans lequel les éléments légers des terres rares représentent une quantité non inférieure à 50% en atomes de l'ensemble des éléments R des terres rares.

25 58. Aimant permanent suivant la revendication 57, dans lequel les quantités de Nd et/ou de Pr ne sont pas inférieures à 50% en atomes du total des éléments R.

59. Aimant permanent suivant l'une des revendications 54 à 58, dans lequel la dimension moyenne du grain des cristaux va de 1 à 80 μm , de préférence de 2 à 40 μm .

30 60. Aimant permanent suivant l'une des revendications 52 à 58, comprenant en outre des éléments additionnels M qui ressortent de la liste ci-dessous, les quantités de ces éléments étant respectivement limitées à des valeurs ne dépassant pas les valeurs précisées ci-dessous en pourcentages atomiques

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

où, lorsque deux ou plus de deux éléments M sont impliqués, la quantité totale de M est limitée à la valeur maximale de l'un des métaux individuels M ajoutés.

40 61. Aimant permanent suivant la revendication 60, présentant une dimension moyenne du grain des cristaux de 1 à 90 μm , de préférence de 2 à 40 μm .

62. Aimant permanent suivant les revendications 52 à 61, dans lequel le pourcentage atomique de R est égal à 15 et le pourcentage atomique de B est égal à 8.

45 63. Aimant permanent suivant l'une des revendications 51 à 62, dans lequel le composé ternaire stable dont il existe au moins un représentant a une structure tétragonale.

64. Aimant permanent suivant la revendication 63, dans lequel l'axe C_0 de la structure tétragonale est d'environ 1,2 nm (12 Å).

50 65. Aimant permanent suivant la revendication 63 ou 64, dans lequel l'axe a_0 de la structure tétragonale est d'environ 0,8 nm (8 Å).

66. Aimant permanent suivant l'une des revendications 54 à 65, comprenant des phases non magnétiques qui séparent les unes des autres les fines particules du composé ternaire stable dont il existe au moins un représentant.

55 67. Aimant permanent suivant la revendication 66, dans lequel les phases non magnétiques contiennent beaucoup de R et sont présentes en proportions de 1 à 45% en volume.

68. Aimant permanent fritté comprenant au moins 50% en volume d'une phase renfermant au moins un composé de Fe-B-R ayant une structure tétragonale, R représentant au moins un élément des terres rares y compris l'yttrium.

60 69. Aimant permanent fritté suivant la revendication 68, contenant des phases non magnétiques en proportions de 1 à 45% en volume renfermant beaucoup de R.

70. Aimant permanent fritté suivant la revendication 69, dans lequel les phases non magnétiques sont présentes en proportions de 2 à 10% en volume.

65 71. Aimant permanent fritté suivant l'une des revendications 68 à 70, comprenant 8 à 30% en atomes de R, où R représente au moins un éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de B, le reste étant du fer.



72. Aimant permanent fritté suivant la revendication 71, dans lequel R est présent en proportions de 12 à 20% en atomes et B est présent en proportions de 4 à 24% en atomes.

73. Aimant permanent fritté suivant l'une des revendications 68 à 72, dans lequel le ou les éléments légers des terres rares représentent une proportion qui n'est pas inférieure à 50% en atomes du total des éléments R des terres rares.

74. Aimant permanent fritté suivant la revendication 73, dans lequel le néodyme et/ou le prazéodyme représentent une proportion non inférieure à 50% en atomes du total des éléments R des terres rares.

75. Aimant permanent fritté suivant l'une des revendications 71 à 74, dans lequel la proportion de R est d'environ 15% en atomes et la proportion de B est d'environ 8% en atomes.

76. Aimant permanent fritté suivant l'une des revendications 68 à 75, dans lequel la dimension moyenne du grain des cristaux est de 1 à 80 μm .

77. Aimant permanent fritté suivant la revendication 76, dans lequel la dimension moyenne du grain des cristaux est de 2 à 40 μm .

78. Aimant permanent fritté suivant l'une des revendications 68 à 75, contenant au moins un élément M additionnel choisi dans le groupe indiqué ci-dessous, en quantités ne dépassant pas les valeurs spécifiées ci-dessous,

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

où, lorsque deux ou plus de deux métaux M sont impliqués, la quantité totale de M est limitée à la valeur maximale de l'un des métaux M individuels ajoutés.

79. Aimant permanent fritté suivant la revendication 78, dans lequel la dimension moyenne du grain des cristaux est de 1 à 90 μm .

80. Aimant permanent suivant la revendication 79, dans lequel la dimension moyenne du grain des cristaux est de 2 à 40 μm .

81. Aimant permanent suivant la revendication 52 ou 71, dans lequel le facteur maximal d'énergie (BH)max n'est pas inférieur à 32 kJ/m³ (4 MGOe).

82. Aimant permanent suivant la revendication 53 ou 72, dans lequel le facteur maximal d'énergie (BH)max n'est pas inférieur à 80 kJ/m³ (10 MGOe).

83. Aimant permanent suivant la revendication 82, dans lequel le facteur maximal d'énergie (BH)max n'est pas inférieur à 160 kJ/m³ (20 MGOe).

84. Aimant permanent suivant la revendication 82, dans lequel le facteur maximal d'énergie (BH)max n'est pas inférieur à 240 kJ/m³ (30 MGOe).

85. Aimant permanent suivant la revendication 82, dans lequel le facteur maximal d'énergie (BH)max n'est pas inférieur à 280 kJ/m³ (35 MGOe).

86. Aimant permanent suivant l'une des revendications 51 à 85, pouvant être obtenu par un procédé de la métallurgie des poudres.

87. Procédé de production d'un aimant permanent par préparation d'une masse fondue comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs des éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de bore, le reste étant du fer, refroidissement jusqu'à cristallisation de la masse fondue, pulvérisation du produit cristallisé, pressage et frittage du produit en poudre.

88. Procédé de production d'un aimant permanent par préparation d'une masse fondue comprenant 8 à 30% en atomes de R, R représentant un ou plusieurs éléments des terres rares y compris l'yttrium, 2 à 28% en atomes de bore, le reste étant du fer et M, M représentant au moins un élément additionnel choisi dans le groupe indiqué ci-dessous en quantités ne dépassant pas les valeurs spécifiées ci-après,

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

où, lorsque deux ou plus de deux métaux M sont impliqués, la quantité totale de métaux M est limitée à la valeur maximale de l'un des métaux M individuels ajoutés, refroidissement de la masse fondue jusqu'à cristallisation, transformation en poudre du produit cristallisé, pressage et frittage de l'alliage pulvérisé.

89. Procédé suivant la revendication 87 ou 88, dans lequel le produit en poudre pressé est orienté dans un champ magnétique.

90. Procédé suivant l'une des revendications 87 à 89, dans lequel les masses compactes sont frittées à une température de 1000 à 1200°C.



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91. Procédé suivant la revendication 90, dans lequel le frittage est effectué en atmosphère d'argon.
92. Procédé suivant l'une des revendications 88 à 91, dans lequel une opération de vieillissement est effectuée après le frittage.

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