

Description

The present invention relates to a process for producing rare earth-iron base permanent magnets according to claim 1, in which expensive and resourceless cobalt is not used at all or contained in a reduced amount. Further features of the process of the present invention are given in the dependent claims.

Permanent magnet materials are one of the very important electrical and electronic materials which are used in an extensive range covering from various electrical appliances for domestic use to the peripheral devices of large-scaled computers. With recent demands for electrical and electronic devices to reduce in size and increase in efficiency, it has increasingly been desired to improve the efficiency of the permanent magnet materials, correspondingly.

Typical permanent magnet materials currently in use are alnico, hard ferrite and rare earth-cobalt magnets. Recent uncertainty of supply of the raw material for cobalt has caused decreasing demand for the alnico magnets containing 20—30% by weight of cobalt. Instead, rather inexpensive hard ferrite is now taking that position for magnet materials. On the other hand, the rare earth-cobalt magnets are very expensive, since they contain as high as 50—65% by weight of cobalt and, in addition thereto, Sm that does not abundantly occur in rare earth ores. However, such magnets are mainly used for small magnetic circuits of high added value due to their much higher magnetic properties over those of other magnets. In order that the rare earth magnets are employed at low price as well as in wider ranges and amounts, it is required that they be freed of expensive cobalt or they contain only a reduced amount of cobalt, and their main rare earth metal components be light rare earth which abounds with ores. There have been attempts to obtain such permanent magnets. For instance, A. E. Clark found out that sputtered amorphous $TbFe_2$ had an energy product of 29.5 MGOe at 4.2°K, and showed a coercive force iH_c of 3.4 kOe and a maximum energy product $(BH)_{max}$ of 7 MGOe at room temperature upon heat-treated at 300—500°C. Similar studies were made of $SmFe_2$, and it was reported that an energy product of as high as 9.2 MGOe was reached at 77°K. However, these materials are all thin films prepared by sputtering, from which any practical magnets are not obtained whatsoever. It was also reported that the ribbons prepared by melt-quenching of PrFe base alloys showed a coercive force iH_c of 2.8 kOe. Furthermore, Koon et al found out that, with melt-quenched amorphous ribbons of $(FeB)_{0.9}Tb_{0.05}La_{0.05}$, the coercive force iH_c reached as high as 9 kOe upon annealed at 627°C, and the residual magnetic flux density B_r was 5 kG. However, the $(BH)_{max}$ of the obtained ribbons is then low because of the unsatisfactory loop rectangularity of the demagnetization curves thereof (N. C. Koon et al, Appl. Phys. Lett. 39(10), 1981, 840—842 pages). L. Kabacoff et al have reported that a coercive force on the kOe level is attained at room temperature with respect to the FePr binary system ribbons obtained by melt-quenching of $(FeB)_{1-x}Pr_x$ compositions ($x=0-0.3$ in atomic ratio). However, these melt-quenched ribbons or sputtered thin films are not any practical permanent magnets (bodies) that can be used as such, and it would be impossible to obtain therefrom any practical permanent magnets. It comes to this that it is impossible to obtain bulk permanent magnets of any desired shape and size from the conventional melt-quenched ribbons based on FeBR and the sputtered thin films based on RFe. Due to the unsatisfactory loop rectangularity of the magnetization curves, the FeBR base ribbons heretofore reported are not taken as being any practical permanent magnets comparable to the conventionally available magnets. Since both the sputtered thin films and the melt-quenched ribbons are magnetically isotropic by nature, it is virtually almost impossible to obtain therefrom any magnetically anisotropic permanent magnets of high performance for the practical purpose.

In order to transfer the values for kG, kOe and MGOe, as given above and below, into the proper SI units, the following equations must be used:

$$\begin{aligned} 1 \text{ MGOe} &= 7.96 \text{ kJ/m}^3 \\ 1 \text{ kOe} &= 79.6 \text{ kA/m} \\ 1 \text{ kG} &= 10^{-1} \text{ T} \end{aligned}$$

"R" generally represents rare earth elements which include Y.

One object of the present invention is to provide a novel and practical process for producing permanent magnet materials or magnets in which any expensive material such as Co is not used, and from which the disadvantages of the prior art are eliminated.

Another object of the present invention is to provide a process for producing novel and practical permanent magnets which have favorable magnetic properties at room or higher temperatures, can be formed into any desired shape and practical size, show high loop rectangularity of the magnetization curves, and can effectively use resourceful light rare earth elements with no substantial need of using rare resources such as Sm.

It is a further object of the present invention to provide a novel process for producing permanent magnet materials or magnets which contain only a reduced amount of cobalt and still have good magnetic properties.

It is a further object of the present invention to provide a process for manufacturing Fe-B-R base magnetic materials and magnets showing an improvement (i.e., reduction) in the temperature dependency.

It is still a further object of the present invention to provide a process for manufacturing a permanent magnet materials or magnets with a high performance such that has not been ever reported.

Other objects will become apparent in the entire disclosure.

In consequence of intensive studies made by the present inventors to achieve these objects, it has been found that the magnetic properties, after sintering, of Fe-B-R alloys within a certain composition range, inter alia, the coercive force and the loop rectangularity of demagnetization curves, are significantly improved by forming (compacting) a powder having a specified particle size, sintering the formed body, and, thereafter, subjecting the sintered body to a heat treatment or a so-called aging treatment under the specific conditions as mentioned in EP-A-126802. However, more detailed studies have led to findings that, by applying a two-stage heat treatment under more specific conditions than in the aforesaid heat treatment, the coercive force and the loop rectangularity of demagnetization curves are further improved and, hence, variations in the magnetic properties are reduced.

More specifically the present invention provides a process for producing a permanent magnet material comprising the steps of:

forming an alloy powder having a mean particle size of 0.3 to 80 μm and composed of, in atomic percentage, 8—30% R (provided that R is at least one of rare earth elements including Y), 2—28% B, and the balance being Fe and inevitable impurities (hereinbelow referred to as "FeBR base alloy"), sintering the formed body at 900—1200°C, subjecting the sintered body to a primary heat treatment at a temperature of 750—1000°C, then cooling the resultant body to a temperature of no higher than 680°C at a cooling rate of 3—2000°C/min, and further subjecting the thus cooled body to a secondary heat treatment at a temperature of 480—700°C.

The percentage hereinbelow refers to the atomic percent if not otherwise specified.

The FeBR base alloy further contains no more than 50% of cobalt partially substituted for Fe of the FeBR base alloy, whereby the Curie temperature of the resultant magnet material is increased resulting in the improved dependency on temperature.

The FeBR base alloy may further contain no more than the given percentage of at least one of the additional elements M (except for 0% M):

no more than 9.5% V,	no more than 12.5% Nb,
no more than 10.5% Ta,	no more than 9.5% Mo,
no more than 9.5% W,	no more than 8.5% Cr,
no more than 9.5% Al,	no more than 4.5% Ti,
no more than 5.5% Zr,	no more than 5.5% Hf,
no more than 8.0% Mn,	no more than 8.0% Ni,
no more than 7.0% Ge,	no more than 3.5% Sn,
no more than 5.0% Bi,	no more than 2.5% Sb,
no more than 5.0% Si,	and no more than 2.0% Zn,

provided that in the case where two or more of M are contained the sum thereof is no more than the largest value among the specified values of the additional elements M as contained.

Most of the additional elements M serve to improvement in the coercivity.

The FeBR base alloy may further contain cobalt in the specific amount as mentioned above, and may contain the additional elements M in the specific amount as mentioned above.

The foregoing and other objects and features of the present invention will become apparent from the following detailed description with reference to the accompanying drawing, which is given for the purpose of illustration alone, and in which:

Fig. 1 is a graph showing the relation between the amount of Co and the Curie point T_c (°C) in an FeCoBR base alloy.

The present invention will now be explained in further detail.

In the permanent magnet materials manufactured in accordance with the present invention, the amount of B should be no less than 2% ("%" shall hereinafter stand for the atomic percentage in the alloys) to meet a coercive force iH_c of no less than 3 kOe, and should be no more than 28% to attain a residual magnetic flux density B_r of no less than about 6 kG which is far superior to hard ferrite. The amount of R should be no less than 8% so as to attain a coercive force of no less than 3 kOe. However, it is required that the amount of R be no higher than 30%, since R is so apt to burn that difficulties are involved in the technical handling and production, and is expensive too.

The raw materials are inexpensive, and so the present invention is very useful, since resourceful rare earth may be used as R without necessarily using Sm, and without using Sm as the main component.

The rare earth elements R used in the present invention include Y, and embrace light rare earth, and at least one thereof may be used. In other words, R embraces one of Nd, Pr, Dy, Tb, Ho, preferably Nd and Pr or the like as R, but, practically, use is made of mixtures of two or more elements (mischmetal, didymium, etc.) due to easiness in availability, etc. Sm, Y, La, Ce, Gd, etc. may be used in the form of mixtures with other R, especially Nd, Pr, Dy, Tb, Ho, etc. It is noted that R may not be pure rare earth elements, and may contain impurities, other rare earth elements, Ca, Mg, Fe, Ti, C, O, etc. which are to be inevitably entrained from the process of production, as long as they are industrially available. To obtain the most preferable effect upon an increase in coercive force, a combination of R_1 , one or more selected from the group consisting of Dy, Tb, Gd, Ho, Er, Tm and Yb, with R_2 consisting of at least 80% (per total R_2) of Nd and Pr and the balance being one or more rare earth elements including Y, except for R_1 , is used as R. It is preferred to

contain no Sm or as little as Sm, and La should not be present much, too, preferably each below 2% (more preferably below 1%).

The boron B used may be pure boron or ferrobaboron, and may contain as the impurities Al, Si, C, etc. In the magnet materials of the present invention, the balance is constituted by Fe, save B and R, but may contain impurities to be inevitably entrained from the process of production.

Composed of 8—30% R, 2—28% B and the balance being Fe, the permanent magnet materials of the present invention show magnetic properties expressed in terms of a maximum energy product (BH)_{max} exceeding largely 4 MGOe of hard ferrite.

So far as R is concerned, it is preferred that the sum of Nd and Pr is at least 50% (most preferred 80% or more) in the entire R in order to attain high magnetic properties with sureness and less expense.

Preferred is a composition range in which light rare earth (Nd, Pr) accounts for 50% or more of the overall R, and which is composed of 12—24% R, 3—27% B and the balance of Fe, since (BH)_{max} exceeds 10 MGOe. Very preferred is a composition range in which the sum of Nd and Pr accounts for 50% or more of the overall R and which is composed of 12—20% R, 5—24% B and the balance of Fe, since the resulting magnetic properties are then expressed in terms of (BH)_{max} exceeding 15 MGOe and reaching a high of 35 MGOe. If R₁ is 0.05—5%, R is 12.5—20%, B is 5—20% and the balance is Fe, then the maximum energy product (BH)_{max} is maintained at no lower than 20 MGOe with iH_c of no lower than 10 kOe. However, the aging treatment of the present invention brings about an additional effect. Furthermore, a composition of 0.2—3% R₁, 13—19% R, 5—11% B and the balance being Fe gives rise to a maximum energy product (BH)_{max} of no lower than 30 MGOe.

A further preferable FeBR range is given at 12.5—20% R, 5—15% B and 65—82.5% Fe, wherein an energy product of 20 MGOe or more is attainable. Above 20% R or below 65% Fe, Br will decrease. iH_c will decrease above 82.5% Fe.

A still further preferable FeBR range is at 13—18% R, 5—15% B, and 67—82% Fe, wherein the energy product can exceed 20 MGOe while at 5—11% B can 30 MGOe.

It is surprising that the energy product of 40 MGOe or higher up to 44 MGOe can be achieved, i.e., approximately at 6—7% B, 13—14.5% R, and the balance of Fe (or with certain amount of Co and/or M). Co may be up to 10% and M may be up to about 1%.

In a little wider range, the energy product can be 35 MGOe or more, i.e., 6—11% B, 13—16% R and the balance of Fe. M may be up to 2% and Co may be up to 15%.

It should be noted that in the subsequent aspects containing Co or M, these amounts should be included in the Fe amounts hereinabove discussed, since Fe is defined as the balance in every composition.

The permanent magnet materials produced according to the present invention are obtained by pulverizing, forming (compacting), sintering, and further heat-treating the alloys having the aforesaid compositions.

The present invention will now be explained with reference to the preferred embodiment of the process for producing magnetically anisotropic FeBR permanent magnet materials.

As the starting materials use may be made of electrolytic iron as Fe, pure boron or ferrobaboron as B, and rare earth R of 95% or more purity. Within the aforesaid range, these materials are weighed and formulated, and melted into alloys, e.g., by means of high-frequency melting, arc melting, etc. in vacuo or in an inert gas atmosphere, followed by cooling. The thus obtained alloys are roughly pulverized by means of a stamp mill, a jaw crusher, etc. and are subsequently finely pulverized by means of a jet mill, a ball mill, etc. Fine pulverization may be carried out in the dry manner to be effected in an inert gas atmosphere, or alternatively in the wet manner to be effected in an organic solvent such as acetone, toluene, etc. The alloy powders obtained by fine pulverization are adjusted to a mean particle size of 0.3—80 μm. In a mean particle size below 0.3 μm, considerable oxidation of the powders takes place during fine pulverization or in the later steps of production, resulting in no density increase and low magnet properties. (A further slight reduction in the particle size might be possible under particular conditions. However, it would be difficult and require considerable expense in the preparation and apparatus.) A mean particle size exceeding 80 μm makes it impossible to obtain higher magnet properties, inter alia, make coercive force high. To obtain excellent magnet properties, the mean particle size of fine powders is preferably 1—40 μm, most preferably 2—20 μm.

The powders having a mean particle size of 0.3—80 μm are pressed and formed in a magnetic field (of e.g., no less than 5 kOe). A forming pressure is preferably 500—3000 kg/cm². For pressing and forming the powders in a magnetic field, they may be formed per se, or may alternatively be formed in an organic solvent such as acetone, toluene, etc. The formed body is sintered at a temperature of 900—1200°C for a given period of time in an reducing or non-oxidizing atmosphere, for example, in vacuum of no higher than $1.33 \cdot 10^{-2}$ mbar or in an inert or reducing gas atmosphere, preferably inert gas of 99.9% or higher (purity) under a pressure of 1.33—1000 mbar. At a sintering temperature below 900°C, no sufficient sintering density is obtained. Nor is high residual magnetic flux density obtained. At a temperature of higher than 1200°C, the sintered body deforms and misalignment of the crystal grains occurs, so that there are drops of the residual magnetic flux density and the loop rectangularity of demagnetization curves. On the other hand, a sintering period may be 5 minutes or longer, but, too long a period poses a problem with respect to mass-productivity. Thus a sintering period of 0.5—4 hours is preferred with respect to the acquisition of magnet properties, etc. in mind. It is noted that it is preferred that the inert or reducing gas atmosphere

used as the sintering atmosphere is maintained at a high level, since one component R is very susceptible to oxidation at high temperatures. When using the inert gas atmosphere, sintering may be effected under a reduced pressure of 1,33 mbar to less than 1 bar to obtain a high sintering density.

While no particular limitation is placed upon the rate of temperature rise during sintering, it is desired that, in the aforesaid wet forming, a rate of temperature rise of no more than 40°C/min is applied to remove the organic solvents, or a temperature range of 200—800°C is maintained for 0.5 hours or longer in the course of heating for the removal of the organic solvents. In cooling after sintering, it is preferred that a cooling rate of no less than 20°C/min is applied to limit variations in the product (quality). To enhance the magnet properties by the subsequent heat treatment or aging treatment, a cooling rate of no less than 100°C/min is preferably applied after sintering. (However, it is noted that the heat treatment may be applied just subsequent to sintering too.)

The heat treatment to be effected after sintering comprises the following stages. First of all, the sintered body is subjected to a first-stage heat treatment at a temperature of 750—1000°C and, thereafter, is cooled to a temperature of no higher than 680°C at a cooling rate of 3—2000°C/min. Thereafter, the thus cooled body is subjected to a second-stage heat treatment at a temperature of 480—700°C.

Referring to the first-stage heat treatment temperature, the first-stage heat treatment is so ineffective at a temperature of less than 750°C that the enhanced amount of the coercive force is low. At a temperature exceeding 1000°C, the sintered body undergoes crystal grain growth, so that the coercive force drops.

To enhance the coercive force of magnet properties and the loop rectangularity of demagnetization curves, and to reduce variations therein, the first-stage heat treatment temperature is preferably 770—950°C, most preferably 790—920°C.

Referring to the cooling rate to be applied following the first-stage heat treatment, the coercive force and the loop rectangularity of demagnetization curves drop at a cooling rate of less than 3°C/min, while micro-cracks occur in the sintered body at a cooling rate of higher than 2000°C/min, so that the coercive force drops. The temperature range in which the given cooling rate should be maintained is limited to ranging from the first-stage heat treatment temperature to a temperature of no higher than 680°C. Within a temperature range of no higher than 680°C, cooling may be effected either gradually or rapidly. If the lower limit of a cooling temperature range at the given cooling rate is higher than 680°C, there is then a marked lowering of coercive force. To reduce variations in magnet properties without lowering them, it is desired that the lower limit of a cooling temperature range at the given rate is no higher than 650°C. In order to enhance the coercive force and the loop rectangularity of demagnetization curves as well as to reduce variations in the magnet properties and suppress the occurrence of micro-cracks, the cooling rate is preferably 10—1500°C/min, most preferably 20—1000°C/min.

One characteristic feature of the two-stage heat treatment of the present invention is that, after the primary heat treatment has been applied at a temperature of 750—1000°C, cooling to a temperature of no higher than 680°C is applied, whereby rapid cooling is applied to the range between 750°C and 700°C, and, thereafter, the secondary heat treatment is applied in a low temperature zone of 480—700°C. The point to be noted in this regard is, however, that, if the secondary heat treatment is effected immediately subsequent to cooling such as cooling in the furnace etc. after the primary heat treatment has been applied, then the improvement in the resulting magnet properties are limited. In other words, it is inferred that there would be between 750°C and 700°C an unknown unstable region of a crystal structure or a metal phase, which gives rise to deterioration of the magnet properties; however, the influence thereof is eliminated by rapid cooling. It is understood that the secondary heat treatment may be effected immediately, or after some delay, subsequent to the predetermined cooling following the primary heat treatment.

The temperature for the secondary heat treatment is limited to 480—700°C. At a temperature of less than 480°C or higher than 700°C, there are reduced improvements in the coercive force and the loop rectangularity of demagnetization curves. To enhance the coercive force and the loop rectangularity of demagnetization curves as well as to reduce variations in the magnet properties, the temperature range of the secondary heat treatment is preferably 520—670°C, most preferably 550—650°C.

While no particular limitation is imposed upon the first-stage heat treatment time, a preferred period of time is 0.5 to 8.0 hours, since temperature control is difficult in too short a time, whereas industrial merits diminish in too long a period.

While no particular limitation is also placed upon the second-stage heat treatment time, a preferred period of time is 0.5 to 12.0 hours, since, like the foregoing, temperature control is difficult in too short a time, whereas industrial merits diminish in too long a time.

Reference is now made to the atmosphere for the aging treatment. Since R, one component of the alloy composition, reacts violently with oxygen or moisture at high temperatures, the vacuum to be used should be no higher than 1,33 μ bar in the degree of vacuum. Or alternatively the inert or reducing gas atmosphere to be used should be of 99.99% or higher purity. The sintering temperature is selected from within the aforesaid range depending upon the composition of the permanent magnet materials, whereas the aging temperature is selected from a range of no higher than the respective sintering temperature.

It is noted that the aging treatment including the 1st and 2nd-stage heat treatments may be carried out subsequent to sintering, or after cooling to room temperature and re-heating have been applied upon completion of sintering. In either case, equivalent magnet properties are obtained.

The present invention is not exclusively limited to the manufacturing of magnetically anisotropic

permanent magnets, but is applicable to the manufacturing of magnetically isotropic permanent magnets in a substantially similar manner, provided that no magnetic field is impressed during forming, whereby excellent magnet properties are attained.

Composed of 10—25% R, 3—23% B, and the balance being Fe and inevitable impurities, the isotropic magnets show (BH)max of no less than 3 MGOe. Although the isotropic magnets have originally their magnet properties lower than those of the anisotropic magnets by a factor of 1/4—1/6, yet the magnets according to the present invention show so high properties relative to isotropy. As the amount of R increases, iHc increase, but Br decreases after reaching the maximum value. Thus, the amount of R should be no less than 10% and no higher than 25% to meet (BH)max of no less than 3 MGOe.

As the amount of B increases, iHc increases, but Br decreases after reaching the maximum value. Thus, the amount of B should be between 3% and 23% to obtain (BH)max of no less than 3 MGOe.

Preferably, high magnetic properties expressed in terms of (BH)max of no less than 4 MGOe is obtained in a composition in which the main component of R is light rare earth such as Nd and/or Pr (accounting for 50% or higher of the overall R) and which is composed of 12—20% R, 5—18% B and the balance being Fe. Most preferable is a composition in which the main component of R is light rare earth such as Nd, Pr, etc., and which is composed of 12—16% R, 6—18% B and the balance being Fe, since the resulting isotropic permanent magnets show magnetic properties represented in terms of (BH)max of no less than 7 MGOe that has not ever been achieved in the prior art isotropic magnets.

In the case of anisotropic magnets, any binders and lubricants are not generally used, since they interfere with orientation in forming. In the case of isotropic magnets, however, the incorporation of binders, lubricants, etc. may lead to improvements in pressing efficiency, increases in the strength of the formed bodies, etc.

The permanent magnets produced according to the present invention may also permit the presence of impurities which are to be inevitably entrained from the industrial production. Namely, they may contain within the given ranges Ca, Mg, O, C, P, S, Cu, etc. No more than 4% of Ca, Mg and/or C, no more than 3.5% Cu and/or P, no more than 2.5% S, and no more than 2% of O may be present, provided that the total amount thereof should be no higher than 4%. C may originate from the organic binders used, while Ca, Mg, S, P, Cu, etc. may result from the raw materials, the process of production, etc. The effect of C, P, S and Cu upon the Br is substantially similar with the case without aging since the aging primarily affects the coercivity. In this connection our earlier EP application now published as EPA 101552 is referred to, wherein such impurities may be defined to a certain level depending upon any desired Br level.

As detailed above, the present invention realizes inexpensive, Fe-base permanent magnet materials in which Co is not used at all, and which show high residual magnetization, coercive force and energy product, and is thus of industrially high value.

The FeBR base magnetic materials and magnets hereinabove disclosed has a main (at least 50 vol. %: preferably at least 80 vol. %) magnetic phase of an FeBR type tetragonal crystal structure and generally of the crystalline nature that is far different from the melt-quenched ribbons or any magnet derived therefrom. The central chemical composition thereof is believed to be $R_2Fe_{14}B$ and the lattice parameters are a of about 88 nm and c of about 122 nm. The crystal grain size in the finished magnetic materials usually ranges 1—80 μ m (note for FeCoBR, FeBRM or FeCoBRM magnet materials 1—90 μ m) preferably 2—40 μ m. With respect to the crystal structure EPA 101552 may be referred to for reference.

The FeBR base magnetic materials include a secondary nonmagnetic phase, which is primarily composed of R rich (metal) phase and surrounds the grains of the main magnetic phase. This nonmagnetic phase is effective even at a very small amount, e.g., 1 vol. % is sufficient.

The Curie temperature of the FeBR base magnetic materials ranges from 160°C (for Ce) to 370°C (for Tb), typically around 300°C or more (for Pr, Nd etc).

The permanent magnetic materials produced according to the present invention may further contain cobalt Co in a certain amount (50% or less) so that the Curie temperature of the resultant FeCoBR magnet materials will be enhanced. Namely a part of Fe in the FeBR base magnet material is substituted with Co. A post-sintering heat treatment (aging) thereof improves the coercivity and the rectangularity of the demagnetization curves, which fact was disclosed in the Japanese Patent Application No. 58—90802, corresponding to European application now EPA 126802.

A further improvement can be realized through the two-stage heat treatment as set forth hereinabove. For the FeCoBR magnet materials the heat treatment, as well as forming and sintering procedures, are substantially the same as the FeBR base magnet materials.

In general, it is appreciated that some Fe alloys increase in Curie points T_c with increases in the amount of Co to be added, while another decrease, thus giving rise to complicated results which are difficult to anticipate, as shown in Fig. 1. According to this aspect, it has turned out that, as a result of the substitution of a part of Fe of the FeBR systems T_c rises gradually with increases in the amount of Co to be added. A parallel tendency has been confirmed regardless of the type of R in the FeBR base alloys. Co is effective for increasing T_c in a slight amount (of, for instance, barely 0.1 to 1%). As exemplified by (77-x)Fe_xCo₈B₁₅Nd in Fig. 1, alloys having any T_c between ca. 300°C and ca. 670°C may be obtained depending upon the amount of Co.

In these FeCoBR base permanent magnets aspect, the amounts of the respective components B, R and (Fe+Co) are basically the same as in the FeBR base magnets.

The amount of Co should be no more than 50% due to its expensiveness and in view of Tc improvements and Br. In general, the incorporation of Co in an amount of 5 to 25%, in particular 5 to 15% brings about preferred results.

Composed of 8—30% R, 2—28% B, no more than 50% Co and the balance being substantially Fe, the permanent magnet materials according to this aspect show magnetic properties represented in terms of a coercive force of no less than 3 kOe and a residual magnetic flux density Br of no less than 6 kG, and exhibit a maximum energy product (BH)max exceeding by far that of hard ferrite.

Preferred is a compositional range in which the main components of R are light rare earth (Nd, Pr) accounting for 50% or higher of the overall R, and which is composed of 12—24% R, 3—27% B, no more than 50% Co, and the balance being substantially Fe, since the resulting (BH)max reaches or exceeds 10 MGOe. More preferably is a compositional range in which the overall R contain 50% or higher of Nd+Pr, and which is composed of 12—20% R, 5—24% B, no more than 25% Co, and the balance being substantially Fe, since it is possible to obtain magnetic properties represented in terms of (BH)max exceeding 15 MGOe and reaching 35 MGOe or more. When Co is no less than 5%, the temperature coefficient (α) of Br is no higher than 0.1%/°C, which means that the temperature dependence is favorable. In an amount of no higher than 25%, Co contributes to increases in Tc without deteriorating other magnetic properties (equal or more improved properties being obtained in an amount of no higher than 23%). A composition of 0.05—5% R₁, 12.5—20% R, 5—20% B, no more than 35% Co and the balance being Fe allows a maximum energy product (BH)max to be maintained at no less than 20 MGOe and iHc to exceed 10 kOe. To such a composition, however, the effect of the aging treatment according to the present invention is further added. Moreover, a composition of 0.2—3% R₁, 13—19% R, 5—11% B, no more than 23% Co and the balance being Fe shows a maximum energy product (BH)max exceeding 30 MGOe.

Over the FeBR systems free from Co, the invented FeCoBR base magnet bodies do not only have better temperature dependence, but are further improved in respect of the rectangularity of demagnetization curves by the addition of Co, whereby the maximum energy product can be improved. In addition, since Co is more corrosion-resistant than Fe, it is possible to afford corrosion resistance to those bodies by the addition of Co.

With 50% or less Co inclusion substituting for Fe, almost the same applies as the FeBR base isotropic magnets, particularly with respect to the R and B amounts. The preferred composition for (BH)max of at least 4 MGOe allows 35% or less Co, while the most preferred composition for (BH)max of at least 17 MGOe allows 23% or less Co.

Substantially the same level of the impurities as the FeBR base magnet materials applies to the FeCoBR magnet materials.

According to the present invention, the certain additional elements M may be incorporated in the FeBR base magnet materials or the FeCoBR magnet materials as mentioned above. The additional elements M comprises at least one selected from the group consisting of V, Nb, Ta, Mo, W, Cr, Al, Ti, Zr, Hf, Mn, Ni, Ge, Sn, Bi, Sb, Si and Zn in the given amount as set forth below. The incorporation of M serves, in most cases, to improvements in coercivity and loop squareness particularly for the anisotropic magnet materials.

In this case, the heat treatment as well as the other preparation, e.g., forming, sintering etc. are substantially the same as mentioned above.

The amount and role of Co, R and B are also substantially the same as given above.

Now, referring to the additional elements M in the permanent magnet materials, they serve to increase the coercive force. Especially, they serve to increase that coercive force in the maximum region of Br, thereby improving the rectangularity of demagnetization curves. The increase in the coercive force leads to an increase in the stability of magnets and enlargement of their use. However, Br drops with increases in the amount of M. For that reason, there is a decrease in the maximum energy product (BH)max. The M-containing alloys are very useful esp., in a (BH)max range of no less than 6 MGOe, since there are recently increasing applications where high coercive force is needed at the price of slight reductions in (BH)max.

To ascertain the effect of the additional elements M upon Br, Br was measured in varied amounts of M to measure Br changes. In order to allow Br to exceed by far about 4 kG of hard ferrite and (BH)max to exceed by far about 4 MGOe of hard ferrite, the upper limits of the amounts of M to be added are fixed as follows:

9.5% V,	12.5% Nb,	10.5% Ta,
9.5% Mo,	9.5% W,	8.5% Cr,
9.5% Al,	4.5% Ti,	5.5% Zr,
5.5% Hf,	8.0% Mn,	8.0% Ni,
7.0% Ge,	3.5% Sn,	5.0% Bi,
2.5% Sb,	5.0% Si,	2.0% Zn.

Except for 0% M, one or two or more of M may be used. When two or more of M are contained, the resulting properties are generally represented in terms of the intermediate values lying between the characteristic values of the individual elements added, and the respective amounts thereof should be within the aforesaid % ranges, while the combined amount thereof should be no more than the maximum values given with respect to the respective elements as actually contained.

In the aforesaid FeBRM compositions, the permanent magnet materials produced according to the present invention have a maximum energy product (BH)_{max} far exceeding that of hard ferrite (up to 4 MGOe).

Preferred is a compositional range in which the overall R contains 50% or higher of light rare earth elements (Nd, Pr), and which is composed of 12—24% R, 3—27% B, one or more of the additional elements M—no more than 8.0% V, no more than 10.5% Nb, no more than 9.5% Ta, no more than 7.5% Mo, no more than 7.5% W, no more than 6.5% Cr, no more than 7.5% Al, no more than 4.0% Ti, no more than 4.5% Zr, no more than 4.5% Hf, no more than 6.0% Mn, no more than 3.5% Ni, no more than 5.5% Ge, no more than 2.5% Sn, no more than 4.0% Bi, no more than 1.5% Sb, no more than 4.5% Si and no more than 1.5% Zn—provided that the sum thereof is no more than the maximum given atomic percentage among the additional elements M as contained, and the balance being substantially Fe, since (BH)_{max} preferably exceeds 10 MGOe. More preferable is a compositional range in which the overall R contains 50% or higher of light rare earth elements (Nd, Pr), and which is composed of 12—20% R, 5—24% B, one or more of the additional elements M—no more than 6.5% V, no more than 8.5% Nb, no more than 8.5% Ta, no more than 5.5% Mo, no more than 5.5% W, no more than 4.5% Cr, no more than 5.5% Al, no more than 3.5% Ti, no more than 3.5% Zr, no more than 3.5% Hf, no more than 4.0% Mn, no more than 2.0% Ni, no more than 4.0% Ge, no more than 1.0% Sn, no more than 3.0% Bi, no more than 0.5% Sb, no more than 4.0% Si and no more than 1.0% Zn—provided that the sum thereof is no more than the maximum given atomic percentage among the additional elements M as contained, and the balance being substantially Fe, since it is possible to achieve (BH)_{max} of no lower than 15 MGOe and a high of 35 MGOe or higher.

A composition of 0.05% R₁, 12.5—20% R, 5—20% B, no more than 35% Co, and the balance being Fe allows a maximum energy product (BH)_{max} to be maintained at no less than 20 MGOe and iH_c to exceed 10 kOe. To such a composition, however, the effect of the aging treatment according to the present invention is further added. Furthermore, a composition of 0.2—3% R₁, 13—19% R, 5—11% B and the balance being Fe shows a maximum energy product (BH)_{max} exceeding 30 MGOe. Particularly useful M is V, Nb, Ta, Mo, W, Cr and Al. The amount of M is preferably no less than 0.1% and no more than 3% (most preferable up to 1%) in view of its effect.

With respect to the effect of the additional elements M the earlier application EPA 101552 may be referred to for reference to understand how the amount of M affects the Br. Thus it can be appreciated to define the M amount depending upon any desired Br level.

Referring to the isotropic magnets, substantially the same as the foregoing aspects will apply except for those mentioned hereinbelow. The amount of the additional elements M should be the same as the above mentioned anisotropic magnet materials provided that

no more than 10.5% V, no more than 8.8% W,
no more than 4.7% Ti, no more than 4.7% Ni, and
no more than 6.0% Ge.

In the case of the isotropic magnets generally certain amount of impurities are permitted, e.g., C, Ca, Mg (each no more than 4%); P (no more than 3.3%), S (no more than 2.5%), Cu (no more than 3.3%), etc. provided that the sum is no more than the maximum thereof.

In what follows, the inventive embodiments and the effect of the present invention will be explained with reference to the examples. It is understood, however, that the present invention is not limited by the examples and the manner of description.

Tables 1 to 20 inclusive show the properties of the FeBR base permanent magnets prepared by the following steps. Namely, Tables 1 to 5, Tables 6 to 10, Tables 11 to 15 and Tables 16 to 20 enumerate the properties of the permanent magnet bodies of the compositions based on FeBR, FeCoBR, FeBRM and FeCoBRM, respectively.

(1) Referring to the starting materials, electrolytic iron of 99.9% purity (given by weight %, the same shall hereinafter apply to the purity of the raw materials) was used as Fe, a ferroboration alloy (19.38% B, 5.32% Al, 0.74% Si, 0.03% C and the balance of Fe) was used as B, and rare earth elements of 99% or more purity (impurities being mainly other rare earth metals) was used as R.

Electrolytic Co of 99.9% purity was used as Co.

The M used was Ta, Ti, Bi, Mn, Sb, Ni, Sn, Zn and Ge, each of 99% purity, W of 98% purity, Al of 99.9% purity and Hf of 95% purity. Ferrozirconium containing 77.5% Zr, ferrovanadium containing 81.2% V, ferroniobium containing 67.6% Nb and ferrochromium containing 61.9% Cr were used as Zr, V, Nb and Cr, respectively.

(2) The raw magnet materials were melted by means of high-frequency induction. An aluminium crucible was then used as the crucible, and casting was effected in a water-cooled copper mold to obtain ingots.

(3) The ingots obtained by melting were crushed to -35 mesh, and pulverized in a ball mill in such a manner that the given mean particle size was obtained.

(4) The powders were formed under the given pressure in a magnetic field. (In the production of isotropic magnets, however, forming was effected without application of any magnetic field.)

(5) The formed bodies were sintered at the given temperature within a range of 900—1200°C in the given atmosphere and, thereafter, were subjected to the given heat treatments.

Example 1

An alloy having a composition of 77Fe9B14Nd in atomic percentage was obtained by high-frequency melting in an argon gas and casting with a water-cooled copper mold. The obtained alloy was roughly pulverized to no more than 40 mesh by means of stamp mill, and was then finely pulverized to a mean particle size of 8 μm by means of a ball mill in an argon atmosphere. The obtained powders were pressed and formed at a pressure of 2200 kg/cm² in a magnetic field of 10 kOe, and were sintered at 1120°C for 2 hours in 1 bar argon of 99.99% purity. After sintering, the sintered body was cooled down to room temperature at a cooling rate of 500°C/min. Subsequently, the aging treatment was effected at 820°C for various periods in an argon atmosphere, following cooling to no higher than 650°C at a cooling rate of 250°C/min, and the aging treatment was further carried out at 600°C for 2 hours to obtain the magnets of the present invention.

The resulting magnet properties are set forth in Table 1 along with those of the comparison example wherein a single-stage heat treatment was applied 820°C.

TABLE 1

1st stage aging temp. (°C)	Aging time (hr)	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Comparative (After 1st stage aging)		10.6	6.2	24.1
820	0.75	11.2	10.8	29.2
820	1.0	11.2	11.9	29.4
820	4.0	11.2	12.4	29.6
820	8.0	11.2	10.9	29.1

Example 2

An alloy having a composition of 70Fe13B9Nd8Pr in atomic percentage was obtained by melting in argon gas arc and casting with a water-cooled copper mold. The obtained alloy was roughly pulverized to no more than 40 mesh by a ball mill, and was finely pulverized to a mean particle size of 3 μm in an organic solvent by means of a ball mill. The thus obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 15 kOe, and were sintered at 1140°C for 2 hours in 0.33 bar argon of 99.999% purity. After sintering, the sintered body was cooled down to room temperature at a cooling rate of 150°C/min. Subsequently, the first-stage aging treatment was effected for 2 hours at various temperatures as specified in Table 2, followed by cooling to no higher than 600°C at a cooling rate of 300°C/min, and the second-stage aging treatment was further effected at 640°C for 8 hours to obtain the magnets of the present invention. The resulting magnet properties are set forth in Table 2 along with those of the comparison example (after a single-stage aging treatment).

TABLE 2

1st stage aging temp. (°C)	Aging time (min)	Br (kG)	iHc (kOe)	(BH)max (MGOe)
800	120	8.9	11.8	19.5
850	120	8.9	11.7	19.9
900	120	8.9	11.8	19.5
950	120	8.7	8.3	17.2
720 Comparative	120	8.6	6.3	15.3
Comparative (after 1st stage aging)		8.4	6.2	15.4

Example 3

Fe-B-R alloys of the compositions in atomic percentage, as specified in Table 3, were obtained by melting in Ar gas arc and casting with a water-cooled copper mold. The alloys were roughly pulverized to no more than 50 mesh by means of a stamp mill, and were finely pulverized to a mean particle size of 5 μm in an organic solvent by means of a ball mill. The powders were pressed and formed at a pressure of 2000 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0.2 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 600°C/min. Subsequently, the first-stage aging treatment was effected at 800°C for 2 hours in 0.65 bar Ar of high purity, followed by cooling to no higher than 630°C at a cooling rate of 300°C/min, and the second-stage aging treatment was conducted at 620°C for 4 hr to obtain the invented alloy magnets. The results of the magnet properties are set forth in Table 3 along with those of the comparison examples (after the first-stage aging treatment).

TABLE 3

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
78Fe9B13Nd	11.4	14.3	27.1
69Fe15B14Pr2Nd	8.5	12.4	15.8
71Fe14B10Nd5Gd	8.9	10.9	17.3
66Fe19B8Nd7Tb	8.1	12.4	15.2
69Fe14B10Nd5Gd (after 1st stage aging)	8.5	6.9	14.2
66Fe19B8Nd7Tb (after 1st stage aging)	7.9	7.4	11.9

Example 4

Fe-B-R alloys of the following compositions in atomic percentage were obtained by melting in Ar gas arc and casting with a water-cooled copper mold. The alloys were roughly pulverized to no more than 35 mesh by means of a stamp mill, and were finely pulverized to a mean particle size of 4 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in the absence of any magnetic field, and were sintered at 1090°C for 2 hours in 180 Torr of 99.99% purity, followed by rapid cooling to room temperature at a cooling rate of 400°C/min. Subsequently, the first-stage aging treatment was effected at 840°C for 3 hours in 0.85 bar Ar of high purity, followed by cooling to no higher than 600°C at a cooling rate of 180°C/min, and the second-stage aging treatment was conducted at 630°C×2 hr to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 4 along with those of the samples subjected to the first-stage aging treatment alone (comparison examples).

TABLE 4

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
76Fe9B15Nd	5.4	12.4	6.0
79Fe7B14Nd	5.6	13.0	6.2
78Fe8B12Nd2Gd	5.6	12.3	5.9
76Fe9B15Nd (after 1st stage aging)	5.2	6.9	5.2
79Fe7B14Nd (after 1st stage aging)	5.3	7.4	5.1

Example 5

Fe-B-R alloys of the following compositions in atomic percentage were obtained by high-frequency melting in an Ar gas and casting with a water-cooled copper mold.

The alloys were roughly pulverized to no more than 35 mesh by means of a stamp mill, and were finely pulverized to a mean particle size of 3 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0,26 bar Ar of 99.99% purity, followed by rapid cooling to room temperature at a cooling rate of 500°C/min.

Subsequently, the aging treatment was effected at 800°C for 1 hour in 1 bar Ar, followed by cooling to room temperature at a cooling rate of 300°C/min, and the aging treatment was further conducted at 620°C for 3 hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 5 along with those of the comparison example (after sintering).

TABLE 5

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
79.5Fe6.5B14Nd	13.7	10.2	44.2
79.5Fe6.5B14Nd (Comparative, as-sintered)	13.6	7.2	41.4

Example 6

An alloy of a composition of 62Fe6B16Nd16Co in atomic percentage was obtained by high-frequency melting in an argon gas and casting with a water-cooled copper mold. The alloy was roughly pulverized to no more than 35 mesh by a stamp mill, and was finely pulverized to a mean particle size of 3 μm in an argon atmosphere by means of a ball mill. The obtained powders were pressed and formed at a pressure of 2000 kg/cm² in a magnetic field of 15 kOe, were sintered at 1100°C for 2 hours in 1 bar argon of 99.99% purity, and were thereafter cooled down to room temperature at a cooling rate of 500°C/min. Further, the aging treatment was carried out at 800°C for various times in an argon atmosphere. After cooling to 500°C had been carried out at a cooling rate of 400°C/min., the aging treatment was further conducted at 580°C for 2 hours to obtain the magnets according to the present invention. The results of the magnet properties of the obtained magnets are set forth in Table 6 along with those of the comparison example wherein one-stage aging was applied at 800°C for 1 hour. Table 6 also shows the temperature coefficient α (%/°C) of the residual magnetic flux density (Br) of the invented alloy magnets together with that of the comparison example wherein only one-stage aging was applied.

TABLE 6

Aging temp. (°C)	Aging time (hr)	Br (kG)	iHc (kOe)	(BH)max (MGOe)	α
Comparative (after 1st stage aging)		11.0	6.9	19.6	0.085
800	0.75	11.3	9.3	26.4	0.085
800	1.0	11.4	13.8	32.9	0.084
800	4.0	11.4	13.6	32.4	0.084
800	8.0	10.3	13.4	32.0	0.085

Example 7

An alloy of a composition of 60Fe12B15Nd3Y10Co in atomic percentage was obtained by melting an argon gas arc and casting with a water-cooled copper mold. The obtained alloy was roughly pulverized to no more than 50 mesh by a stamp mill, and was finely pulverized to a mean particle size of 2 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 2000 kg/cm² in a magnetic field of 10 kOe, were sintered at 1150°C for 2 hours in 0,26 bar argon of 99.99% purity, and were thereafter cooled to room temperature at a cooling rate of 150°C/min. The first-stage aging was at the respective temperatures as specified in Table 7 in $2,66 \cdot 10^{-5}$ mbar vacuum, followed by cooling to 350°C at a cooling rate of 350°C/min. Subsequently, the second-stage aging was applied at 620°C for 4 hours to obtain the magnets according to the present invention. The results of the magnet properties and the temperature coefficient α (%/°C) of the residual magnetic flux density (Br) of the magnets according to the present invention are set forth in Table 7 along with those of the comparison example (after the application of one stage aging).

TABLE 7

Aging temp. (°C)	Aging time (min)	Br (kG)	iHc (kOe)	(BH)max (MGOe)	α
700	120	10.6	8.1	17.3	0.084
800	120	11.8	10.9	28.1	0.082
850	120	11.9	12.4	33.4	0.083
900	120	11.9	13.0	33.6	0.083
950	120	11.9	13.2	33.9	0.083
Comparative (after 1st stage aging)		10.6	6.4	20.4	0.083

Example 8

FeBRCo alloys of the compositions in atomic percentage, as specified in Table 8, were obtained by melting in argon gas arc, and casting with a water-cooled copper mold. The obtained alloys were roughly pulverized to no more than 40 mesh by a stamp mill, and were finely pulverized to a mean particle size of 4 μ m in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 15 kOe, were sintered at 1080°C for 2 hours in 0.26 bar argon of 99.99% purity, and were thereafter rapidly cooled down to room temperature at a cooling rate of 400°C/min. The first-stage aging was then effected at 850°C for 2 hours in 0.79 bar argon, followed by cooling to 350°C at a cooling rate of 200°C/min. Subsequently, the second-stage heat treatment was carried out at 650°C for 2 hours to obtain the magnets according to the present invention. The resulting magnet properties and the temperature coefficient α (%/°C) of Br were set forth in Table 8 together with those of the comparison example subjected to one-stage aging alone.

TABLE 8

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)	α (%/°C)
59Fe10B17Nd14Co	12.3	9.4	34.0	0.08
58Fe8B14Pr20Co	12.2	12.4	32.5	0.07
62Fe8B13Nd2Tb15Co	11.8	10.9	24.8	0.08
46Fe6B14Nd2La32Co	12.2	13.5	27.6	0.06
60Fe6B12Nd2Ho20Co	11.2	8.4	22.8	0.07
60Fe6B12Nd2Ho20Co (Comparative; after 1st stage aging)	11.0	6.3	20.3	0.07

Example 9

FeBRCo alloys of the following compositions in atomic percentage were obtained by melting argon gas arc and casting with a water-cooled copper mold. The alloys were roughly pulverized to no more than 25 mesh by a stamp mill, and were finely pulverized to a mean particle size of 3 μ m in an organic solvent by means of a ball mill. The thus obtained powders were pressed and formed at a pressure of 1500 kg/cm² in the absence of any magnetic field, and were sintered at 1030°C for 2 hours in 0.33 bar argon of 99.99% purity. After sintering, rapid cooling to room temperature was applied at a cooling rate of 300°C/min. The primary aging treatment was then carried out at 840°C for 4 hours in 0.85 bar argon, followed by cooling to 450°C at a cooling rate of 350°C/min. Subsequently, the secondary aging treatment was conducted at 650°C for 2 hours to obtain the magnets according to the present invention. The results of the magnet properties are set forth in Table 9 along with those of the sample (comparison example) wherein only the primary aging treatment was applied.

TABLE 9

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
65Fe9B16Nd10Co	5.2	13.4	5.8
61Fe10B17Nd12Co	5.4	13.6	6.0
62Fe8B13Nd2Gd15Co	5.6	12.7	5.7
65Fe9B16Nd10Co (after 1st stage aging)	5.2	8.6	5.1
61Fe10B17Nd12Co (after 1st stage aging)	5.3	8.3	5.0

Example 10

FeCoBR alloys of the following compositions in atomic percentage were obtained by melting in argon gas arc and casting with a water-cooled copper mold.

The obtained alloys were roughly pulverized to no more than 35 mesh by a stamp mill, and were finely pulverized to a mean particle size of 3 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0,26 bar argon of 99.99% purity, followed by rapid cooling to room temperature at a cooling rate of 500°C/min.

The aging treatment was effected at 800°C for 1 hour 1 bar Ar, followed by cooling to room temperature at a cooling rate of 300°C/min. Subsequently, the aging treatment was conducted at 580°C for 3 hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 10 along with those of the comparison example (after sintering).

TABLE 10

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
73.5Fe6.5B14Nd6Co	13.6	9.7	41.8
73.5Fe6.5B14Nd6Co (Comparative, as-sintered)	13.4	6.8	39.1

Example 11

Alloy powders having a mean particle size of 1.8 μm and a composition BaFe-8B-16Nd-2Ta-1Sb in atomic percentage were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 15 kOe, and were sintered at 1080°C for 2 hours in 0,33 bar argon of 99.99% purity, followed by cooling to room temperature at a cooling rate of 600°C/min. The aging treatment was conducted at 780°C for various times in an argon atmosphere, followed by cooling to 480°C at a cooling rate of 360°C/min. Subsequently, the aging treatment was conducted at 560°C for 2 hours to obtain the magnets according to the present invention. The results of the magnet properties are set forth in Table 11 along with those of the comparison example wherein only the one-stage aging treatment was conducted at 780°C for 1 hour.

TABLE 11

Aging temp. (°C)	Aging time (hr)	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Comparative (after 1st stage aging)		12.4	10.3	33.1
780	0.75	12.6	12.4	35.8
780	1.0	12.6	12.6	36.2
780	4.0	12.6	12.8	36.3
780	8.0	12.7	12.9	36.1

Example 12

The alloy powders of the following composition $\text{BaFe-10B-13Nd-3Pr-2W-1Mn}$ alloys in atomic percentage and a mean particle size of $2.8 \mu\text{m}$ were pressed and formed at a pressure of 1500 kg/cm^2 in a magnetic field of 10 kOe, and were sintered at 1120°C for 2 hours in 0.37 bar Ar of 99.999% purity, followed by cooling down to room temperature at a cooling rate of 500°C/min . Subsequent to the first-stage aging treatment at the various temperatures as specified in Table 12 for 2 hours in $5.33 \cdot 10^{-6}$ mbar vacuum, cooling to no more than 600°C was applied at a cooling rate of 320°C/min , and the second-stage aging treatment was then effected at 620°C for 8 hours to obtain the permanent magnets according to the present invention. The results of the magnet properties are set forth in Table 12 along with those of the comparison example (after the first-stage aging treatment).

TABLE 12

Aging Temp. (°C)	Aging time (min)	Br (kG)	iHc (kOe)	(BH)max (MGOe)
800	120	10.6	10.3	23.7
850	120	10.7	11.4	23.9
900	120	10.7	11.0	23.5
950	120	10.8	10.8	23.3
720 Comparative	120	10.4	8.6	21.3
Comparative (after 1st stage aging)		10.1	8.8	21.2

Example 13

The powders of Fe-B-R-M alloys having the compositions in atomic percentage as specified in Table 13 and a mean particle size of 1 to $6 \mu\text{m}$ were pressed and formed at a pressure of 1200 kg/cm^2 in a magnetic field of 15 kOe, and were sintered at 1080°C for 2 hours in 0.24 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 650°C/min . Further, the aging treatment was carried out at 775°C for 2 hours in 0.72 bar Ar of high purity, followed by cooling to no higher than 550°C at a cooling rate of 280°C/min . Thereafter, the second-stage aging treatment was conducted at 640°C for 3 hours to obtain the permanent magnets of the present invention. The results of the magnet properties are set forth in Table 13 along with those of the comparison example (after the single-stage aging treatment).

TABLE 13

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe8B14Nd1Mo1Si	12.5	10.3	34.6
Fe10B14Nd4Pr1Nb1Hf	11.8	12.4	32.0
Fe12B10Nd5Gd2V	10.5	11.0	24.1
Fe8B8Nd8Ho1Nb1Ge	9.9	13.2	22.4
Fe11B15Nd1Mo2Al	7.9	12.8	13.6
Fe9B15Nd2Cr1Ti	11.6	11.6	33.4
Fe9B15Nd2Cr1Ti (Comparative)	11.4	8.1	30.8
Fe16B10Nd5Gd2V (Comparative)	10.3	7.6	22.4
Fe14B15Nd1Mo2Al (Comparative)	7.8	6.4	12.4

Example 14

The powders of Fe-B-R-M alloys of the following compositions in atomic percentage and a mean particle size of 2 to 8 μm were pressed and formed at a pressure of 1000 kg/cm² in the absence of any magnetic field, and were sintered at 1080°C for 2 hours in 0,24 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 630°C/min. Further, the first-stage aging treatment was effected at 630°C for 4 hours in 0,46 bar Ar, followed by cooling to no higher than 550°C at a cooling rate of 220°C/min, and the second-stage heat treatment was subsequently conducted at 580°C for 2 hours to obtain the permanent magnets of the present invention. The results of the magnet properties are set forth in Table 14 along with those of the sample (comparison example) wherein only the first-stage aging treatment was applied).

TABLE 14

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe8B14Nd1Ta1Zn	6.3	13.0	6.4
Fe8B16Nd2Ho2W	6.4	12.7	6.6
Fe8B12Nd2Ce1Nb1Mo	6.6	11.4	6.9
Fe8B14Nd1Ta1Zn (Comparative)	6.2	10.6	6.0
Fe8B16Nd2Ho2W (Comparative)	6.3	10.1	5.8
Fe6B18Nd1Cr1Zr	5.8	12.0	6.1
Fe6B18Nd1Cr1Zr (Comparative)	5.7	8.9	5.4

Example 15

The Fe-B-R-M alloys of the following compositions in atomic percentage were obtained by high-frequency melting in an Ar gas and casting with a water-cooled copper mold.

The obtained alloys were roughly pulverized to no more than 35 mesh by a stamp mill, and were finely

done to a mean particle size of 2.7 μm in an organic solvent by means of a ball mill. The thus obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0,26 bar Ar of 99.99% purity, followed by rapid cooling to room temperature at a cooling rate of 500°C/min.

Subsequently, the aging treatment was effected at 800°C for 1 hour in 1 bar Ar, followed by cooling to room temperature at a cooling rate of 300°C/min, and the aging treatment was done at 620°C for further 3 hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 15 along with those of the comparison example (after sintering).

TABLE 15

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe7B14Nd1Mo	13.3	11.6	42.2
Fe6.5B14Nd1Nb	13.4	11.3	42.5
Fe7B14Nd1Mo (Comparative, as-sintered)	13.2	8.8	41.1
Fe6.5B14Nd1Nb (Comparative, as-sintered)	13.3	8.2	41.8

Example 16

The powders of an alloy of the composition BalFe-12Co-9B-14Nd-1Mo in atomic percentage and a mean particle size of 35 μm were pressed and formed at a pressure of 1300 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1120°C for 2 hours in 0,26 bar Ar of 99.99% purity, followed by cooling to room temperature at a cooling rate of 650°C/min. Subsequently, the aging treatment was effected at 820°C at various temperatures in an argon atmosphere, followed by cooling to 480°C at a cooling rate of 350°C/min., and the aging treatment was conducted at 600°C for 2 hours to obtain the magnets according to the present invention. The results of the magnet properties and the temperature coefficient α (%/°C) of the residual magnetic flux density (Br) of the invented alloy magnets are set forth in Table 16 along with those of the magnets subjected to only the single-stage aging treatment of 820°C×1 hour.

TABLE 16

Aging temp. (°C)	Aging time (hr)	Br (kG)	iHc (kOe)	(BH)max (MGOe)	α (%/°C)
Comparative		12.0	10.3	28.0	0.086
820	0.75	12.2	12.4	31.2	0.086
820	1.0	12.3	12.9	32.4	0.087
820	4.0	12.3	13.0	32.8	0.086
820	8.0	12.2	13.2	32.9	0.086

Example 17

The powders of an alloy of the composition BalFe-18Co-10B-14Nd-1Y-2Nd-1Ge in atomic percentage and a mean particle size of 2.8 μm were pressed and formed at a pressure of 1200 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1140°C for 2 hours in 0,66 bar Ar of 99.999% purity, followed by cooling to room temperature at a cooling rate of 400°C/min. Subsequently, the first-stage aging treatment was effected at the various temperatures as specified in Table 17 for 2 hours in $6,66 \cdot 10^{-5}$ mbar vacuum, followed by cooling to 420°C at a cooling rate of 400°C/min, and the second-stage aging treatment was done at 580°C for 3 hours to obtain the magnets of the present invention. The results of the magnet properties and the temperature coefficient α (%/°C) of the residual magnetic flux density (Br) are shown in Table 17 along with those of the comparison example (after the first-stage aging treatment).

TABLE 17

Aging temp. (°C)	Aging time (min)	Br (KG)	iHc (kOe)	(BH)max (MGOe)	α (%/°C)
700	120	11.2	11.4	28.7	0.081
800	120	11.7	11.8	28.9	0.082
850	120	11.6	11.7	29.3	0.081
900	120	11.6	11.7	29.4	0.081
950	120	11.5	11.6	29.2	0.081
Comparative (after 1st stage aging)		11.3	9.3	24.5	0.081

Example 18

The powders of alloys of the Fe-Co-B-R-M compositions in atomic percentage as specified in Table 18 and a mean particle size of 2 to 8 μm were pressed and formed at a pressure of 1200 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1100°C for 2 hours in 0,26 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 750°C/min. The primary aging treatment was conducted at 820°C for 2 hours in 0,59 bar Ar, followed by cooling to 380°C at a cooling rate of 250°C/min, and the secondary aging treatment was then effected at 600°C for 2 hours to obtain the magnets of the present invention. The figures of the magnets properties and the temperature coefficient α (%/°C) of Br are set forth in Table 18 along with those of the comparison example wherein the first aging treatment alone was applied.

TABLE 18

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)	α (%/°C)
Fe5Co10B16Nd1Ta1Mn	12.6	10.4	35.4	0.06
Fe20Co7B9Nd5Pr2W	11.3	9.8	27.5	0.03
Fe8Co7B12Nd4Tb1V	12.4	11.2	31.7	0.06
Fe10Co7B16Nd1Al1Bi	12.8	13.8	33.4	0.05
Fe5Co8B12Nd2Ho1Al	10.9	10.6	26.4	0.08
Fe5Co8B12Nd2Ho1Al (Comparative)	10.8	7.3	23.6	0.09
Fe8Co6B20Nd1Cr	11.2	11.4	28.8	0.08
Fe8Co6B20Nd1Cr (Comparative)	11.1	9.3	26.2	0.09

Example 19

The powders of Fe-Co-B-R-M alloys of the following compositions and a mean particle size of 1 to 6 μm were pressed and formed at a pressure of 1200 kg/cm² in the absence of any magnetic field, and were sintered at 1080°C for 2 hours in 0,24 bar Ar of 99.999% purity, followed by rapid cooling at room temperature at a cooling rate of 630°C/min. The primary aging treatment was conducted at 850°C for 4 hours in 0,92 bar Ar, followed by cooling to 420°C at a cooling rate of 380°C/min., and the secondary aging treatment was then effected at 620°C for 3 hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 19 along with those of the sample (comparison example) not subjected to the secondary aging treatment.

TABLE 19

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe15Co10B16Nd1Ta	6.3	11.2	8.6
Fe10Co8B13Nd2Ho2Al1Sb	5.9	10.4	8.3
Fe25Co8B12Nd4Gd2V	5.3	11.7	8.2
Fe15Co10B16Nd1Ta (Comparative)	5.4	9.3	8.3
Fe10Co10B20Nd1Cr1Zr	4.9	13.4	5.2
Fe10Co10B20Nd1Cr1Zr (Comparative)	4.6	10.1	4.8

Example 20

Fe-Co-B-R-M alloys of the following compositions in atomic percentage were obtained by high-frequency melting in an Ar gas and casting with a water-cooled copper mold.

The alloys were roughly pulverized to no more than 35 mesh by means of a stamp mill, and were finely pulverized to a mean particle size of 2.6 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0.26 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 500°C/min.

The aging treatment was effected at 800°C for one hour in 1 bar Ar, followed by cooling down to room temperature at a cooling rate of 300°C/min., and the aging treatment was conducted at 580°C for further three hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 20 along with those of the comparison example (after sintering).

TABLE 20

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe6Co6.5B14Nd1Nb	13.6	11.7	41.5
Fe6Co6.5B14Nd1Nb (Comparative, as-sintered)	13.5	7.8	40.0

Claims

1. A process for producing permanent magnets of the Fe-B-R type comprising:
 providing a sintered body having a composition comprising, by atomic percent, 8—30% R, wherein R is at least one rare earth element including Y, 2—28% boron (B) and the balance being iron (Fe), and
 subjecting said sintered body to a primary heat treatment at a temperature of 750—1000°C,
 then cooling the resultant body to a temperature of no higher than 680°C at a cooling rate of 3—2000°C/min, and
 further subjecting the thus cooled material to a secondary heat treatment at a temperature of 480—700°C.

2. A process according to Claim 1, wherein a part of Fe is substituted by Co such that the formed body comprises no more than 50 at-% of Co.

3. A process according to Claim 1 or 2, wherein the formed body optionally comprises at least one additional element M of no more than the values, in at-%, specified below:

TABLE 19

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe15Co10B16Nd1Ta	6.3	11.2	8.6
Fe10Co8B13Nd2Ho2Al1Sb	5.9	10.4	8.3
Fe25Co8B12Nd4Gd2V	5.3	11.7	8.2
Fe15Co10B16Nd1Ta (Comparative)	5.4	9.3	8.3
Fe10Co10B20Nd1Cr1Zr	4.9	13.4	5.2
Fe10Co10B20Nd1Cr1Zr (Comparative)	4.6	10.1	4.8

Example 20

Fe-Co-B-R-M alloys of the following compositions in atomic percentage were obtained by high-frequency melting in an Ar gas and casting with a water-cooled copper mold.

The alloys were roughly pulverized to no more than 35 mesh by means of a stamp mill, and were finely pulverized to a mean particle size of 2.6 μm in an organic solvent by means of a ball mill. The obtained powders were pressed and formed at a pressure of 1500 kg/cm² in a magnetic field of 12 kOe, and were sintered at 1080°C for 2 hours in 0,26 bar Ar of 99.999% purity, followed by rapid cooling to room temperature at a cooling rate of 500°C/min.

The aging treatment was effected at 800°C for one hour in 1 bar Ar, followed by cooling down to room temperature at a cooling rate of 300°C/min., and the aging treatment was conducted at 580°C for further three hours to obtain the magnets of the present invention. The results of the magnet properties are set forth in Table 20 along with those of the comparison example (after sintering).

TABLE 20

Composition	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Fe6Co6.5B14Nd1Nb	13.6	11.7	41.5
Fe6Co6.5B14Nd1Nb (Comparative, as-sintered)	13.5	7.8	40.0

Claims

1. A process for producing permanent magnets of the Fe-B-R type comprising:
providing a sintered body having a composition comprising, by atomic percent, 8—30% R, wherein R is at least one rare earth element including Y, 2—28% boron (B) and the balance being iron (Fe), and
subjecting said sintered body to a primary heat treatment at a temperature of 750—1000°C,
then cooling the resultant body to a temperature of no higher than 680°C at a cooling rate of 3—2000°C/min, and

further subjecting the thus cooled material to a secondary heat treatment at a temperature of 480—700°C.

2. A process according to Claim 1, wherein a part of Fe is substituted by Co such that the formed body comprises no more than 50 at-% of Co.

3. A process according to Claim 1 or 2, wherein the formed body optionally comprises at least one additional element M of no more than the values, in at-%, specified below:



no more than 9.5% V,	no more than 12.5% Nb,
no more than 10.5% Ta,	no more than 9.5% Mo,
no more than 9.5% W,	no more than 8.5% Cr,
no more than 9.5% Al,	no more than 4.5% Ti,
no more than 5.5% Zr,	no more than 5.5% Hf,
no more than 8.0% Mn,	no more than 8.0% Ni,
no more than 7.0% Ge,	no more than 3.5% Sn,
no more than 5.0% Bi,	no more than 2.5% Sb,
no more than 5.0% Si, and	no more than 2.0% Zn,

provided that in the case where two or more of M are contained, the sum thereof is no more than the largest value among the specified values of the additional elements M as contained.

4. A process as defined in any of Claims 1—3, wherein the cooling after sintering is conducted at a cooling rate of at least 20°C/min.

5. A process as defined in Claim 4, wherein the primary heat treatment is conducted subsequent to the sintering, or by reheating starting from any temperature below 750°C after cooling.

6. A process as defined in Claim 4, wherein said cooling after sintering is conducted at a cooling rate of at least 100°C/min.

7. A process as defined in any of Claims 1—3, wherein the sintering is effected in a reducing or non-oxidizing atmosphere.

8. A process as defined in any of Claims 1—3, wherein the secondary heat treatment is conducted by reheating starting from any temperature of no higher than 680°C.

9. A process as defined in Claim 8, wherein the secondary heat treatment is conducted at any time after said cooling to a temperature of no higher than 680°C.

10. A process as defined in Claim 9, wherein the secondary heat treatment is conducted subsequent to said cooling to a temperature of no higher than 680°C.

11. A process as defined in any of Claims 1—3, wherein the primary heat treatment is conducted at a temperature between 770—950°C.

12. A process defined in Claim 7, wherein the primary heat treatment is conducted at a temperature between 790—920°C.

13. A process as defined in any of Claims 1—3, wherein said cooling after the primary heat treatment is conducted at a cooling rate of 10—1500°C/min.

14. A process as defined in Claim 13, wherein said cooling rate is 20—1000°C/min.

15. A process as defined in any of Claims 1—3, wherein the secondary heat treatment is conducted at a temperature between 520—670°C.

16. A process as defined in Claim 15, wherein the secondary heat treatment is conducted at a temperature between 550—650°C.

17. A process as defined in any of Claims 1—3, wherein the heat treatments are conducted in vacuum or in an atmosphere of inert or reducing gas.

18. A process as defined in Claim 17, wherein the vacuum is at 1.33×10^{-3} mbar or less.

19. A process as defined in Claim 17, wherein the atmosphere gas has a purity of at least 99.99%.

20. A process as defined in any of Claims 1—3, wherein the primary heat treatment is conducted at a temperature below the respective sintering temperature.

21. A process as defined in any of Claims 1—3, wherein R includes at least one selected from a group consisting of Nd, Pr, Dy, Tb and Ho.

22. A process as defined in Claim 21, wherein R includes at least one selected from a group consisting of Nd, Pr, Dy, Tb and Ho and at least one rare earth elements except for said group.

23. A process as defined in Claim 21, wherein at least 50% of the entire R is the sum of Nd and Pr.

24. A process as defined in any of Claims 1—3, wherein R is 12—24% and B is 3—27%.

25. A process as defined in Claim 24, wherein R is 12—20% and B is 5—24%.

26. A process as defined in Claim 25, wherein R is 12.5—20% and B is 5—15%.

27. A process as defined in Claim 26, wherein R is 13—18% and B is 5—15%.

28. A process as defined in Claim 27, wherein B is 5—11%.

29. A process as defined in Claim 28, wherein R is 13—16% and B is 6—11%.

30. A process as defined in Claim 29, wherein R is 13—14.5% and B is 6—7%.

31. A process as defined in Claim 26, wherein Fe, or the sum of Fe, Co and M is 65—82.5%.

32. A process as defined in Claim 27, wherein Fe, or the sum of Fe, Co and M is 67—82%, preferably 71%.

33. A process as defined in claim 23 or 29, wherein at least 50%, preferably 80%, of the entire R is the sum of Nd and/or Pr.

34. A process as defined in Claim 33, wherein R is Nd and/or Pr.

35. A process as defined in Claim 2 or 3, wherein Co is 0.1—35%.

36. A process as defined in Claim 35, wherein Co is 5—25%.

37. A process as defined in Claim 35, wherein Co is no more than 23%.

38. A process as defined in Claim 29, wherein Co is no more than 15% and M is no more than 2%.



39. A process as defined in Claim 30, wherein Co is no more than 10% and M is no more than 1%.

40. A process as defined in Claim 3, wherein M is at least 0.1%.

41. A process as defined in Claim 40, wherein M is no more than the following given percentage provided that the sum of M is no more than the maximum given percentage among the respective additional elements M contained where two or more M are contained:

8.0% V,	10.5% Nb,	9.5% Ta,	7.5% Mo,
7.5% W,	6.5% Cr,	7.5% Al,	4.0% Ti,
4.5% Zr,	4.5% Hf,	6.0% Mn,	3.5% Ni,
5.5% Ge,	2.5% Sn,	4.0% Bi,	1.5% Sb,
4.5% Si, and	1.5% Zn.		

10

42. A process as defined in Claim 41, wherein M is no more than the following given percentage provided that the sum of M is no more than the maximum given percentage among the respective additional elements M contained where two or more M are contained:

15

6.5% V,	8.5% Nb,	8.5% Ta,	5.5% Mo,
5.5% W,	4.5% Cr,	5.5% Al,	3.5% Ti,
3.5% Zr,	3.5% Hf,	4.0% Mn,	2.0% Ni,
4.0% Ge,	1.0% Sn,	3.0% Bi,	0.5% Sb,
4.0% Si, and	1.0% Zn		

20

43. A process as defined in Claim 42, wherein M is at least one selected from the group consisting of V, Nb, Ta, Mo, W, Cr and Al and the sum of M is no more than 3%.

25

44. A process as defined in any of Claims 1—3, wherein the forming is effected in a magnetic field under a condition to provide anisotropy.

45. A process as defined in any of Claims 1—3, wherein the forming is effected without applying a magnetic field provided that R is 10—25% and B is 3—23%.

46. A process as defined in Claim 45, wherein R is 12—20%, B is 5—18% and Co is no more than 35%.

30

47. A process as defined in Claim 46, wherein R is 12—16%, B is 6—18% and Co is no more than 25%.

48. A process as defined in Claim 3, provided that with respect to V, W, Ti, Ni and Ge, the given percentage is as follows:

35

no more than 10.5% V,	no more than 8.8% W,
no more than 4.7% Ti,	no more than 4.7% Ni,
and no more than 6.0% Ge.	

49. A process as defined in Claim 32, wherein $R=R_1+R_2$ provided that R_1 is 0.2—3% per the total material of at least one of Dy, Tb and Ho, and the balance being R_2 consisting of at least 80% per the entire R of the sum of Nd and/or Pr and other R than R_1 , Nd and Pr.

40

50. A process as defined in Claim 33, wherein R includes 0.2—3% per total magnet of at least one of Dy, Tb and Ho, the balance of R being at least one of Nd and Pr.

51. The process as defined in Claim 50, wherein the balance of R is Nd.

52. A process as defined in any of Claims 1 to 4 wherein R is 12.5 to 14.5% and B is 5—7%.

45

Patentansprüche

1. Verfahren zur Herstellung von Permanentmagneten vom Fe-B-R-Typ, das die Bereitstellung eines Sinterkörpers mit einer Zusammensetzung in Atom-% von 8 bis 30% R, worin R wenigstens ein Element der Seltenen Erden einschließlich Y darstellt, 2 bis 28% Bor (B) und Rest Eisen (Fe) und die Unterwerfung des Sinterkörpers einer ersten Hitzebehandlung bei einer Temperatur von 750 bis 1000°C,

50

dann die Abkühlung des erhaltenen Körpers auf eine Temperatur, die nicht höher als 680°C ist, mit einer Abkühlgeschwindigkeit von 3 bis 2000°C/min und anschließend die Unterwerfung des so abgekühlten Materials einer zweiten Hitzebehandlung bei einer Temperatur von 480 bis 700°C umfaßt.

55

2. Verfahren nach Anspruch 1, worin ein Teil des Fe durch Co ersetzt ist, so daß der gebildete Körper nicht mehr als 50 Atom-% Co enthält.

60

3. Verfahren nach Anspruch 1 oder 2, worin der gebildete Körper gegebenenfalls wenigstens ein zusätzliches Element M in einer Menge in Atom-% enthält, die nicht größer ist als die unten angegebene:

65



- 5 nicht mehr als 9,5% V,
nicht mehr als 10,5% Ta,
nicht mehr als 9,5% W,
nicht mehr als 9,5% Al,
nicht mehr als 5,5% Zr,
nicht mehr als 8,0% Mn,
nicht mehr als 7,0% Ge,
nicht mehr als 5,0% Bi,
nicht mehr als 5,0% Si, und
- 10 nicht mehr als 12,5% Nb,
nicht mehr als 9,5% Mo,
nicht mehr als 8,5% Cr,
nicht mehr als 4,5% Ti,
nicht mehr als 5,5% Hf,
nicht mehr als 8,0 Ni,
nicht mehr als 3,5% Sn,
nicht mehr als 2,5% Sb,
nicht mehr als 2,0% Zn,
- vorausgesetzt, daß, falls zwei oder mehr Elemente M enthalten sind, ihre Summe nicht größer ist als der größte Wert unter den angegebenen Werten der zusätzlich enthaltenen Elemente M.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Abkühlen nach dem Sintern mit einer Abkühlgeschwindigkeit von wenigstens 20°C/min durchgeführt wird.
- 15 5. Verfahren nach Anspruch 4, worin die erste Hitzebehandlung nach dem Sintern oder durch Wiedererhitzung, beginnend bei einer Temperatur von unter 750°C nach dem Abkühlen, durchgeführt wird.
6. Verfahren nach Anspruch 4, worin das Abkühlen nach dem Sintern mit einer Abkühlgeschwindigkeit von wenigstens 100°C/min durchgeführt wird.
7. Verfahren nach einem der Ansprüche 1 bis 3, worin das Sintern in einer reduzierenden oder
- 20 nicht-oxidierenden Atmosphäre erfolgt.
8. Verfahren nach einem der Ansprüche 1 bis 3, worin die zweite Hitzebehandlung durch Wiedererhitzung, beginnend bei einer Temperatur, die nicht höher als 680°C liegt, durchgeführt wird.
9. Verfahren nach Anspruch 8, worin die zweite Hitzebehandlung zu einem Zeitpunkt nach der Abkühlung auf eine Temperatur von nicht mehr als 680°C durchgeführt wird.
- 25 10. Verfahren nach Anspruch 9, worin die zweite Hitzebehandlung nach der Abkühlung auf eine Temperatur von nicht mehr als 680°C durchgeführt wird.
11. Verfahren nach einem der Ansprüche 1 bis 3, worin die erste Hitzebehandlung bei einer Temperatur von 770 bis 950°C durchgeführt wird.
12. Verfahren nach Anspruch 7, worin die erste Hitzebehandlung bei einer Temperatur von 790 bis
- 30 920°C durchgeführt wird.
13. Verfahren nach einem der Ansprüche 1 bis 3, worin das Abkühlen nach der ersten Hitzebehandlung mit einer Abkühlgeschwindigkeit von 10 bis 1500°C/min durchgeführt wird.
14. Verfahren nach Anspruch 13, worin die Abkühlrate 20 bis 1000°C beträgt.
15. Verfahren nach einem der Ansprüche 1 bis 3, worin die zweite Hitzebehandlung bei einer
- 35 Temperatur von 520 bis 670°C durchgeführt wird.
16. Verfahren nach Anspruch 15, worin die zweite Hitzebehandlung bei einer Temperatur von 550 bis 650°C durchgeführt wird.
17. Verfahren nach einem der Ansprüche 1 bis 3, worin die Hitzebehandlungen im Vakuum oder in einer Atmosphäre aus inertem oder reduzierendem Gas durchgeführt wird.
- 40 18. Verfahren nach Anspruch 17, worin das Vakuum $1,33 \times 10^{-3}$ mbar oder weniger beträgt.
19. Verfahren nach Anspruch 17, worin das Atmosphärendruckgas eine Reinheit von wenigstens 99,99% aufweist.
20. Verfahren nach einem der Ansprüche 1 bis 3, worin die erste Hitzebehandlung bei einer Temperatur durchgeführt wird, die unter der entsprechenden Sintertemperatur liegt.
- 45 21. Verfahren nach einem der Ansprüche 1 bis 3, worin R wenigstens ein Element aus der Gruppe Nd, Pr, Dy, Tb und Ho ist.
22. Verfahren nach Anspruch 21, worin R wenigstens ein Element aus der Gruppe Nd, Pr, Dy, Tb und Ho sowie wenigstens ein Element der Seltenen Erden umfaßt, das nicht in dieser Gruppe enthalten ist.
23. Verfahren nach Anspruch 21, worin wenigstens 50% des gesamten R aus der Summe von Nd und
- 50 Pr besteht.
24. Verfahren nach einem der Ansprüche 1 bis 3, worin R 12 bis 24% und B 3 bis 27% ist.
25. Verfahren nach Anspruch 24, worin R 12 bis 20% und B 5 bis 24% ist.
26. Verfahren nach Anspruch 25, worin R 12,5 bis 20% und B 5 bis 15% ist.
27. Verfahren nach Anspruch 26, worin R 13 bis 18% und B 5 bis 15% ist.
- 55 28. Verfahren nach Anspruch 27, worin B 5 bis 11% ist.
29. Verfahren nach Anspruch 28, worin R 13 bis 16% und B 6 bis 11% ist.
30. Verfahren nach Anspruch 29, worin R 13 bis 14,5% und B 6 bis 7% ist.
31. Verfahren nach Anspruch 26, worin Fe oder die Summe von Fe, Co und M 65 bis 82,5% ist.
32. Verfahren nach Anspruch 27, worin Fe oder die Summe von Fe, Co und M 67 bis 82%, bevorzugt
- 60 71%, ist.
33. Verfahren nach Anspruch 23 oder 29, worin wenigstens 50%, bevorzugt 80%, des gesamten R die Summe aus Nd und/oder Pr darstellt.
34. Verfahren nach Anspruch 33, worin R Nd und/oder Pr ist.
35. Verfahren nach Anspruch 2 oder 3, worin Co 0,1 bis 35% ist.
- 65 36. Verfahren nach Anspruch 35, worin Co 5 bis 25% ist.



37. Verfahren nach Anspruch 35, worin Co nicht mehr als 23% ausmacht.

38. Verfahren nach Anspruch 29, worin Co nicht mehr als 15% und M nicht mehr als 2% ausmacht.

39. Verfahren nach Anspruch 30, worin Co nicht mehr als 10% und M nicht mehr als 1% ist.

40. Verfahren nach Anspruch 3, worin M wenigstens 0,1% ist.

41. Verfahren nach Anspruch 40, worin M nicht mehr als die im folgenden angegebenen Prozentsätze ausmacht, mit der Maßgabe, daß die Summe von M nicht größer ist als der maximale angegebene Prozentsatz unter den entsprechenden zusätzlich enthaltenen Elementen M, wenn zwei oder mehr Elemente M enthalten sind:

8,0% V,	10,5% Nb,	9,5% Ta,	7,5% Mo,
7,5% W,	6,5% Cr,	7,5% Al,	4,0% Ti,
4,5% Zr,	4,5% Hf,	6,0% Mn,	3,5% Ni,
5,5% Ge,	2,5% Sn,	4,0% Bi,	1,5% Sb,
4,5% Si, und	1,5% Zn.		

42. Verfahren nach Anspruch 41, worin M nicht mehr als die im folgenden angegebenen Prozentsätze ausmacht, mit der Maßgabe, daß die Summe von M nicht größer ist als der maximale angegebene Prozentsatz unter den entsprechenden zusätzlich enthaltenen Elementen M, wenn zwei oder mehr Elemente M enthalten sind:

6,5% V,	8,5% Nb,	8,5% Ta,	5,5% Mo,
5,5% W,	4,5% Cr,	5,5% Al,	3,5% Ti,
3,5% Zr,	3,5% Hf,	4,0% Mn,	2,0% Ni,
4,0% Ge,	1,0% Sn,	3,0% Bi,	0,5% Sb,
4,0% Si, und	1,0% Zn.		

43. Verfahren nach Anspruch 42, worin M wenigstens ein Element aus der Gruppe V, Nb, Ta, Mo, W, Cr und Al und die Summe von M nicht größer als 3% ist.

44. Verfahren nach einem der Ansprüche 1 bis 3, worin das Formen in einem Magnetfeld unter Bedingungen zur Ausbildung einer Anisotropie führt.

45. Verfahren nach einem der Ansprüche 1 bis 3, worin das Formen ohne das Anlegen eines Magnetfelds erfolgt, mit der Maßgabe, daß R 10 bis 25% und B 3 bis 23% ist.

46. Verfahren nach Anspruch 45, worin R 12 bis 20%, B 5 bis 18% und Co nicht mehr als 35% ist.

47. Verfahren nach Anspruch 46, worin R 12 bis 16%, B 6 bis 18% und Co nicht mehr als 25% ist.

48. Verfahren nach Anspruch 3, mit der Maßgabe, daß im Hinblick auf V, W, Ti, Ni und Ge die Prozentsätze wie folgt sind:

nicht mehr als 10,5% V,	nicht mehr als 8,8% W,
nicht mehr als 4,7% Ti,	nicht mehr als 4,7% Ni,
und nicht mehr als 6,0% Ge.	

49. Verfahren nach Anspruch 32, worin $R=R_1+R_2$ ist, mit der Maßgabe, daß R_1 0,2 bis 3% des gesamten Materials aus wenigstens einem der Elemente Dy, Tb und Ho ausmacht und der Rest R_2 ist, der aus wenigstens 80% des gesamten R aus der Summe von Nd und/oder Pr und anderen Elementen R, die nicht R_1 , Nd und Pr sind, besteht.

50. Verfahren nach Anspruch 33, worin R 0,2 bis 3%, bezogen auf den gesamten Magneten, wenigstens eines der Elemente Dy, Tb und Ho enthält, wobei der Rest von R wenigstens eines der Elemente Nd oder Pr ist.

51. Verfahren nach Anspruch 50, worin der Rest von R Nd ist.

52. Verfahren nach einem der Ansprüche 1 bis 4, worin R 12,5 bis 14,5% und B 5 bis 7% ausmacht.

Revendications

1. Procédé de production d'aimants permanents du type Fe-B-R, qui consiste:
à former un corps fritté dont la composition comprend, en pourcentages atomiques, 8—30% de R, où R représente au moins un élément des terres rares y compris Y, 2—28% de bore (B), le reste étant du fer (Fe), et

à soumettre ledit corps fritté à un traitement thermique primaire à une température de 750—1000°C, à refroidir ensuite le corps résultant jusqu'à une température ne dépassant pas 680°C à une vitesse de refroidissement de 3—2000°C/min, et

à soumettre encore la matière ainsi refroidie à un traitement thermique secondaire à une température de 480—700°C.

2. Procédé suivant la revendication 1, dans lequel une partie du fer est remplacée par du cobalt, de manière que le corps mis en forme ne comporte pas plus de 50% de cobalt, en pourcentage atomique.

3. Procédé suivant la revendication 1 ou 2, dans lequel le corps mis en forme comprend à titre facultatif



EP 0 153 744 B1

au moins un autre élément M ne dépassant pas les valeurs, en pourcentages atomiques, indiquées ci-dessous:

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

à condition que lorsqu'il y a deux ou plus de deux éléments M, leur somme ne dépasse pas la valeur la plus grande parmi les valeurs spécifiées des éléments additionnels M tels qu'ils sont contenus.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le refroidissement après frittage est conduit à une vitesse de refroidissement d'au moins 20°C/min.

5. Procédé suivant la revendication 4, dans lequel le traitement thermique primaire est conduit à la suite du frittage, ou par un nouveau chauffage à partir de toute température au-dessous de 750°C après refroidissement.

6. Procédé suivant la revendication 4, dans lequel le refroidissement après frittage est conduit à une vitesse de refroidissement d'au moins 100°C/min.

7. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le frittage est effectué dans une atmosphère réductrice ou non oxydante.

8. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le traitement thermique secondaire est conduit par un nouveau chauffage à partir de n'importe quelle température ne dépassant pas 680°C.

9. Procédé suivant la revendication 8, dans lequel le traitement thermique secondaire est conduit à un moment quelconque après ledit refroidissement jusqu'à une température ne dépassant pas 680°C.

10. Procédé suivant la revendication 9, dans lequel le traitement thermique secondaire est conduit à la suite dudit refroidissement jusqu'à une température ne dépassant pas 680°C.

11. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le traitement thermique primaire est conduit à une température comprise entre 770 et 950°C.

12. Procédé suivant la revendication 7, dans lequel le traitement thermique primaire est conduit à une température comprise entre 790 et 920°C.

13. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le refroidissement après le traitement thermique primaire est conduit à une vitesse de refroidissement de 10 à 1500°C/min.

14. Procédé suivant la revendication 13, dans lequel la vitesse de refroidissement est de 20—1000°C/min.

15. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le traitement thermique secondaire est conduit à une température comprise entre 520 et 670°C.

16. Procédé suivant la revendication 15, dans lequel le traitement thermique secondaire est conduite à une température comprise entre 550 et 650°C.

17. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel les traitements thermiques sont conduits sous vide ou dans une atmosphère de gaz inerte ou de gaz réducteur.

18. Procédé suivant la revendication 17, dans lequel le vide est de $1,33 \times 10^{-3}$ mbar ou moins.

19. Procédé suivant la revendication 17, dans lequel l'atmosphère gazeuse a une pureté d'au moins 99,99%.

20. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le traitement thermique primaire est conduit à une température inférieure à la température respective de frittage.

21. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel R comprend au moins un élément choisi dans le groupe constitué de Nd, Pr, Dy, Tb et Ho.

22. Procédé suivant la revendication 21, dans lequel R comprend au moins un élément choisi dans le groupe constitué de Nd, Pr, Dy, Tb et Ho et au moins un élément des terres rares en dehors dudit groupe.

23. Procédé suivant la revendication 21, dans lequel au moins 50% du total de R constituent la somme de Nd et Pr.

24. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel la proportion de R est de 12 à 24% et la proportion de B est de 3 à 27%.

25. Procédé suivant la revendication 24, dans lequel la proportion de R est de 12 à 20% et la proportion de B est de 5 à 24%.

26. Procédé suivant la revendication 25, dans lequel la proportion de R est de 12,5 à 20% et la proportion de B est de 5 à 15%.

27. Procédé suivant la revendication 26, dans lequel la proportion de R est de 13 à 18% et la proportion de B est de 5 à 15%.

28. Procédé suivant la revendication 27, dans lequel la proportion de B est de 5 à 11%.



29. Procédé suivant la revendication 28, dans lequel la proportion de R est de 13 à 16% et la proportion de B est de 6 à 11%.

30. Procédé suivant la revendication 29, dans lequel la proportion de R est de 13 à 14,5% et la proportion de B est de 6 à 7%.

31. Procédé suivant la revendication 26, dans lequel la proportion de Fe ou de la somme de Fe, Co et M est de 65 à 82,5%.

32. Procédé suivant la revendication 27, dans lequel la proportion de Fe ou de la somme de Fe, Co et M est de 67 à 82%, de préférence 71%.

33. Procédé suivant la revendication 23 ou 29, dans lequel au moins 50%, de préférence au moins 80% du total de R représente la somme de Nd et/ou de Pr.

34. Procédé suivant la revendication 33, dans lequel R représente Nd et/ou Pr.

35. Procédé suivant la revendication 2 ou 3, dans lequel la proportion de Co est de 0,1 à 35%.

36. Procédé suivant la revendication 35, dans lequel la proportion de Co est de 5 à 25%.

37. Procédé suivant la revendication 35, dans lequel la proportion de Co ne dépasse pas 23%.

38. Procédé suivant la revendication 29, dans lequel la proportion de Co ne dépasse pas 15% et la proportion de M ne dépasse pas 2%.

39. Procédé suivant la revendication 30, dans lequel la proportion de Co ne dépasse pas 10% et la proportion de M ne dépasse pas 1%.

40. Procédé suivant la revendication 3, dans lequel la proportion de M est d'au moins 0,1%.

41. Procédé suivant la revendication 40, dans lequel la proportion de M ne dépasse pas les pourcentages indiqués ci-après, à condition que la somme de M ne soit pas supérieure au pourcentage maximal indiqué parmi les éléments additionnels respectifs M contenus, lorsqu'il y a deux ou plus de deux éléments M:

8,0% de V,	10,5% de Nb,	9,5% de Ta,	7,5% de Mo,
7,5% de W,	6,5% de Cr,	7,5% de Al,	4,0% de Ti,
4,5% de Zr,	4,5% de Hf,	6,0% de Mn,	3,5% de Ni,
5,5% de Ge,	2,5% de Sn,	4,0% de Bi,	1,5% de Sb,
4,5% de Si, et	1,5% de Zn.		

42. Procédé suivant la revendication 41, dans lequel la proportion de M n'est pas supérieure aux pourcentages indiqués ci-après à condition que la somme des éléments M ne dépasse pas le pourcentage maximal indiqué parmi les éléments additionnels respectifs M contenus, lorsqu'il y a deux ou plus de deux éléments M:

6,5% de V,	8,5% de Nb,	8,5% de Ta,	5,5% de Mo,
5,5% de W,	4,5% de Cr,	5,5% de Al,	3,5% de Ti,
3,5% de Zr,	3,5% de Hf,	4,0% de Mn,	2,0% de Ni,
4,0% de Ge,	1,0% de Sn,	3,0% de Bi,	0,5% de Sb,
4,0% de Si, et	1,0% de Zn.		

43. Procédé suivant la revendication 42, dans lequel M est l'un au moins des éléments choisis dans le groupe comprenant V, Nb, Ta, Mo, W, Cr et Al et la somme des éléments M n'est pas supérieure à 3%.

44. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel la mise en forme est effectuée dans un champ magnétique dans des conditions aptes à créer une anisotropie.

45. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel la mise en forme est effectuée sans application de champ magnétique, à condition que la proportion de R soit de 10 à 25% et que celle de B soit de 3 à 23%.

46. Procédé suivant la revendication 45, dans lequel la proportion de R est de 12 à 20%, la proportion de B est de 5 à 18% et la proportion de Co ne dépasse pas 35%.

47. Procédé suivant la revendication 46, dans lequel la proportion de R est de 12 à 16%, la proportion de B est de 6 à 18% et la proportion de Co ne dépasse pas 25%.

48. Procédé suivant la revendication 3, à condition que, en ce qui concerne les éléments V, W, Ti, Ni et Ge, les pourcentages indiqués soient les suivants:

pas plus de 10,5% de V,	pas plus de 8,8% de W,
pas plus de 4,7% de Ti,	pas plus de 4,7% de Ni,
et pas plus de 6,0% de Ge.	

49. Procédé suivant la revendication 32, dans lequel R est égal à la somme $R_1 + R_2$ à condition que R_1 représente 0,2 à 3%, par rapport à la matière totale, d'au moins l'un des éléments Dy, Tb et Ho, et que le reste, désigné par R_2 , consiste en au moins 80%, par rapport au total de R, de la somme Nd et/ou Pr et d'un élément R autre que R_1 , Nd et Pr.

50. Procédé suivant la revendication 33, dans lequel R comprend 0,2 à 3%, par rapport à la totalité de la



EP 0 153 744 B1

matière magnétique, d'au moins l'un des éléments Dy, Tb et Ho, le reste de R étant au moins l'un des éléments Nd et Pr.

51. Procédé suivant la revendication 50, dans lequel le reste de R est constitué de Nd.

52. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel la proportion de R est de 12,5 à 14,5% et la proportion de B est de 5 à 7%.

10

15

20

25

30

35

40

45

50

55



* C L M S *

60

65