

"METHOD OF MAKING A PERMANENT MAGNET"

The present invention relates to a method of making a permanent magnet from an alloy comprising a rare earth, iron and boron (R-Fe-B).

5 The term "rare earth", as used in this specification is to be understood to include yttrium (Y).

At present, the following three methods are in practice used for manufacturing a magnet from such an alloy:-

- (1) A sintering method based upon a powder metallurgy technique (Reference No. 1);
- 10 (2) A method in which rapidly quenched ribbon fragments having a thickness of about 30 microns are prepared by a melt spinning apparatus and are used for producing an amorphous alloy, the magnet being made from the ribbon fragments by a resin-bonding technique (Reference No. 2); and
- 15 (3) A method in which a mechanical alignment treatment is performed on the fragments prepared by the above method (2) by a 2-step hot pressing technique (Reference No. 2).

Reference No. 1: M. Sagawa, S. Fujimura, N. Togawa,
H. Yamamoto and Y. Matsuura; Japan
20 Applied Physics Vol. 55(6), 15 March
1984, p2083.

Reference No. 2: R.W. Lee; Applied Physics Letters,
Vol 46 (8), 15 April 1985, p790.

The prior art techniques mentioned above are explained
25 below.

In the sintering method (1), an alloy ingot is made by melting and casting, and then the ingot is pulverized to a fine powder whose particle diameter is about 3 microns. The powder is then kneaded with a binder which serves as a moulding additive and is press-moulded in a magnetic field to obtain a moulded body. The moulded body is sintered in an argon atmosphere for 1 hour at about 1100°C and thereafter quenched to room temperature. After sintering, the body is heat-treated at about 600°C, thereby increasing its intrinsic coercivity.

In the method (2), quenched ribbon fragments of R-Fe-B alloy are prepared by a melt spinning apparatus which spins at an optimum substrate velocity. The obtained fragments are ribbon-shaped, and have a thickness of 30 microns, and consist of an aggregation of grains whose diameter is 1000 Angstroms or less. These fragments are fragile and are magnetically isotropic since the grains are distributed isotropically. The fragments are crushed to form particles of suitable size and these particles are kneaded with resin and are press-moulded. At this time, the density of the material is 85 volume percent under a pressure of about 7 tons/cm².

In the method (3), the rapidly quenched ribbons or fragments are passed into a graphite or other suitable high-temperature die which has been pre-heated in a vacuum or in an inert gas atmosphere to about 700°C. When the

temperature of the ribbons rises to the predetermined temperature, the ribbons are subjected to a unidirectional pressure. The temperature and the time are not limited although it is desirable that the temperature should be $725 \pm 250^{\circ}\text{C}$ and that the pressure should be $P \sim 1.4\text{ton/cm}^2$ so as to achieve sufficient plasticity. At this time, the grains of the magnet are slightly aligned in the pressing direction but are isotropic as a whole.

A further hot pressing process is performed using a larger cross-section die. As a rule, the hot pressing is effected at a temperature of 700°C and at a pressure of 0.7 ton/cm^2 for a period of several seconds. Then the thickness of the material is reduced by half of the initial thickness and a magnetic alignment is introduced parallel to the direction of pressing so that the alloy becomes anisotropic.

The above process is called a "two-stage hot-press procedure". By using this procedure an anisotropic R-Fe-B series magnet of high density is produced.

It is preferable to make the particle diameter of the grains of the ribbon fragments initially prepared by the melt spinning method slightly smaller than the grain diameter at which the maximum intrinsic coercivity is produced. This is because, since the grains become coarse to some degree during the hot-press procedure, if the grain diameter of the crystals before the hot-press procedure are a little smaller than the optimum diameter, they will be the optimum size after the

procedure.

The prior art techniques mentioned above, however, have some disadvantages.

5 In the sintering method (1), the alloy must be ground to a fine powder. However, a R-Fe-B series alloy is extremely easily oxidized and so a R-Fe-B series alloy powder is all the more easily oxidized. Accordingly, the oxygen concentration of the sintered body is inevitably high.

10 Furthermore, when moulding the powder, an additive such as, for example, zinc stearate is necessary. Although such an additive is eliminated prior to the sintering process, some of the additive remains in the final magnet in the form of carbon. Such carbon greatly deteriorates the magnetic performance of a R-Fe-B magnet.

15 The moulded body, after the moulding with the moulding additive has been effected, is called the "green body" and this is easily breakable and very difficult to handle. Therefore, it is very difficult to place the green bodies in the sintering furnace in good order, which is a big disadvantage.

20 Because of the above disadvantages, in order to manufacture R-Fe-B series sintered magnets, expensive equipment has been necessary. Moreover, productivity has been extremely low, which has resulted in high manufacturing costs for this type of magnet.

25 Thus, the sintering method (1) is not a satisfactory method for making good use of the advantage of the cheap

raw material cost of an R-Fe-B series magnet.

In methods (2) and (3), a vacuum melt spinning apparatus is used. At present, however, this apparatus has a low output and is expensive.

In method (2), the crystals of the resulting magnet are isotropic and so the energy production is low and the squareness of the hysteresis loop thereof is not good. Therefore, the magnet produced by the method (2) has bad temperature coefficients and is unsatisfactory in practical use.

The method (3) is performed in two stages and is therefore very inefficient.

According, therefore, to the present invention, there is provided a method of making a permanent magnet comprising melting and casting an alloy whose constituents comprise at least one rare earth, iron and boron; hot working the cast alloy ingot at a hot working temperature of at least 500°C and at a strain rate $d\varepsilon/dt$ in the range of 10^{-4} to 1 per second, where ε is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.

The logarithmic strain $\varepsilon = \ln \cdot l_2/l_1$, where l_1 is the length of the cast alloy prior to the said hot working, and l_2 is its length after the said hot working, $\ln$ being the natural logarithm $\log_e$.

The permanent magnet is preferably annealed at a temperature of at least 250°C.

The hot worked alloy may be pulverized to form a powder,

the powder being kneaded with an organic binder.

The said hot working temperature is preferably in the range of 800°C to 1050°C.

5 The hot working preferably effects a reduction ratio of at least 60% in the thickness, cross-sectional area or diameter of the cast alloy ingot. Thus if the reduction is a reduction in the thickness, the reduction ratio may be represented as $\frac{d_1 - d_2}{d_1} \times 100$ (%), where d_1 is the thickness
10 of the cast alloy prior to the said hot working and d_2 is its thickness after the said hot working.

The alloy may contain a total of 8 to 30 atomic percent of one or more rare earths.

The alloy may contain 2 to 28 atomic percent of boron.
15 Thus the alloy may, for example, contain 8 to 30 atomic percent of R, 2 to 28 atomic percent of B, 50 or less atomic percent of Co, 15 or less atomic percent of Al, the balance being iron and impurities which are inevitably included during the preparation process.

20 The invention also comprises a method of making a permanent magnet comprising melting and casting a $\text{Ce}_3\text{Pr}_{10}\text{Nd}_{10}\text{Fe}_{73}\text{B}_4$ alloy; hot working the cast alloy ingot at a hot working temperature of at least 500°C, and a strain rate $d\varepsilon/dt$ in the range of 10^{-4} to 10 per second
25 where ε is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.

The present invention further comprises a method of making a permanent magnet comprising melting and casting an alloy whose constituents comprise at least one rare earth, iron and boron; hot working the cast alloy ingot at a hot
5 working temperature of 1000°C , and at a strain rate $d\varepsilon/dt$ in the range of 10^{-4} to 10 per second where ε is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.

As described before, the known methods for preparing a
10 rare earth-iron series permanent magnet, i.e. the sintering method and the quenching method, have the respective disadvantages that handling of the powder is difficult and that productivity is poor.

It has been found, however, that if the alloy has the preferred composition referred to in the previous paragraph, the alloy will be made fine and anisotropic by the hot working. The hot working on the cast ingot at the temperature of 500°C or higher may be such as to produce fine crystal grains whose grain axis is aligned in a specific direction, thereby making the cast alloy magnetically anisotropic.

In order to improve the magnetic properties and especially to increase the intrinsic coercivity of the resulting magnet, the alloy may consist of 8 to 25 atomic percent of R, 2 to 8 atomic percent of B, 40 or less atomic percent of Co, 15 or less atomic percent of Al, the balance being iron and impurities which are inevitably included during the preparation process, the resulting magnet being magnetically hardened by heat-treatment at a temperature of 250°C or more. In this case, sufficient intrinsic coercivity is obtained merely by the hot working.

For resin-bonded magnets, an alloy of the above composition may be pulverized to a fine powder by utilizing its property of easily producing a hydrogenated compound, the said fine powder being kneaded with an organic binder and then cured to obtain a resin-bonded magnet.

To obtain a resin-bonded magnet by the usual pulverization, the powder may be such that, by utilizing the property that the grains are easily made fine by the hot working, each grain of the powder includes a plurality of magnetic $R_2Fe_{14}B$ grains

even after the pulverization has been effected, and the powder is kneaded with the organic binder and cured to obtain the resin-bonded magnet.

In the method of the present invention, the hot working, which may be effected to make the ingot anisotropic, may be only a one-stage process and not a two-stage process as in the quenching method disclosed in Reference No. 2. Moreover, the intrinsic coercivity of the product will be substantially increased because the grains are made fine. Furthermore, since it is not essential to pulverize the cast ingot, it is not necessary to strictly control the atmosphere for sintering and so on, thereby greatly reducing the equipment cost.

It is another advantage of the present invention that the resin-bonded magnet which can be obtained by the method of the present invention is not originally isotropic as is the magnet obtained by the usual quenching method and that an anisotropic resin-bonded magnet can easily be obtained. Thus the advantages of R-Fe-B magnet of high-performance and low cost can be achieved.

A report on the magnetization of an alloy in the bulk state has been presented by Hiroaki Miho et al. (The Lecture Meeting of The Japanese Institute of Metals, Autumn 1985, Lecture No. 544). However, this report refers to small alloy samples having a composition of $\text{Nd}_{16.2}\text{Fe}_{50.7}\text{Co}_{22.6}\text{V}_{1.3}\text{B}_{9.2}$ which are melted in air, exposed to an argon gas spray

and then extracted for sampling. Accordingly, it is considered that, in the study of this report, the fine grains obtained by quenching occurred because of the small-quantity sampling.

We have found, however, that, in the composition disclosed in this report, the grains of the main phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ thereof become coarse when they are cast by the usual casting method. Although it is possible to make an alloy of the composition $\text{Nd}_{16.2}\text{Fe}_{50.7}\text{Co}_{22.6}\text{V}_{1.3}\text{B}_{9.2}$ anisotropic by hot working, it is very difficult to obtain sufficient intrinsic coercivity as a permanent magnet for the resulting body.

Also, we have found that, in order to obtain a magnet of sufficient intrinsic coercivity even by the usual casting method, the composition of the starting material should have a B-poor composition of 8 to 25 atomic percent of R, 2 to 8 atomic percent of B, 50 or less atomic percent of Co, 15 or less atomic percent of Al, the balance being Fe and impurities.

A typical optimum composition for a R-Fe-B series magnet of the prior art is believed to be $\text{R}_{15}\text{Fe}_{77}\text{B}_8$ as shown in Reference No. 1. In this composition, R and B are richer than in the composition $\text{R}_{11.7}\text{Fe}_{82.4}\text{B}_{5.9}$ which is equivalent in atomic percentage to the main phase $\text{R}_2\text{Fe}_{14}\text{B}$ compound. This is because, in order to obtain sufficient intrinsic coercivity, not only the main phase but also the non-magnetic phase of R-rich phase and B-rich phase are necessary.

In the composition B-poor region referred to in the preceding paragraph but one, the intrinsic coercivity becomes a maximum when B is poorer than in the usual composition. Generally, such a B-poor composition shows a great decrease in intrinsic coercivity when the sintering method is applied and therefore this composition region has not been considered very carefully in the past. However, if the usual casting method is employed, an high intrinsic coercivity is obtained only in the said composition region and, in the B-rich composition which is the main composition region for the sintering method, the intrinsic coercivity is not sufficient.

The reason for the above is considered to be as follows. Primarily, by employing either a sintering method or the casting method of the present invention, the intrinsic coercivity mechanism of the magnet itself is in accordance with a nucleation model. This is proved by the fact that the initial magnetization curve of the magnets by both methods shows a steep rise similar for example, to that of SmCo_5 . A magnet of this type has the intrinsic coercivity according to the single domain model. Namely, if the grains of $\text{R}_2\text{Fe}_{14}\text{B}$ compound having a large crystal magnetic anisotropy are too large, magnetic domain walls are introduced into the grains and accordingly movement of the magnetic domain walls causes the reverse magnetization

to be easily inverted, thereby decreasing the intrinsic coercivity. Whereas, if the grains of $R_2Fe_{14}B$ compound are smaller than a specific size, the magnetic walls disappear from the grains. In this case, since the reversal of the magnetization is caused only by the rotation of the magnetization, the intrinsic coercivity decreases.

Thus, in order to obtain sufficient coercivity, the $R_2Fe_{14}B$ phase is required to have adequate grain diameter, i.e. about 10 microns. When the sintering method is applied, the grain diameter can be suitably adjusted by the adjustment of the powder diameter before sintering. However, by the casting method, the grains diameter of the $R_2Fe_{14}B$ compound is determined when the liquid material is solidified. Accordingly, it is necessary to control the composition and the solidification process with great care.

The composition is especially important. If the B content of the alloy is more than 8 atomic percent, it is very likely that the grains of the $R_2Fe_{14}B$ phase in the magnet after casting are larger than 100 microns. Accordingly, in this case, sufficient intrinsic coercivity is difficult to obtain in the cast state without using a quenching device as used in Reference 2. On the contrary, in the said B-poor composition region, the diameter of the grains of the magnet is easily reduced by adjusting the kind of mould, the moulding temperature and so on. However, in either case, the

grains of the main phase $R_2Fe_{14}B$ are made finer by performing the hot working and so the intrinsic coercivity of the magnet increases after the hot working.

The composition region in which there is sufficient intrinsic coercivity in the cast state, i.e. the said B-poor composition, can also be called a Fe-rich composition. At the solidifying state, Fe first appears as the primary phase and then the $R_2Fe_{14}B$ phase appears by peritectic reaction. At this time, since the cooling speed is much higher than the speed of equilibrium reaction, the sample is solidified in such a way that the $R_2Fe_{14}B$ phase surrounds the primary phase Fe. Since this composition region is B-poor, the B-rich phase as seen in a $R_{15}Fe_{77}B_8$ magnet which is the typical composition suitable for use in the sintering method is necessarily so small in quantity that the B-rich phase can almost be neglected. The heat treatment employed for the said B-poor composition is used to diffuse the primary phase Fe and to attain an equilibrium state, so that the intrinsic coercivity of the resulting magnet greatly depends on the diffusion of Fe.

A resin-bonded magnet is actually prepared by the quenching method of Reference No. 2. However, since the powder obtained by the quenching method consists of isotropic aggregation of polycrystals whose diameter is 1000 Angstroms or less, the powder is magnetically isotropic. Thus, an anisotropic magnet cannot be obtained and the advantages of a R-Fe-B series magnet,

i.e. low cost and high performance, are not achieved according to the quenching method. When a R-Fe-B series magnet is to be prepared, the intrinsic coercivity of the magnet is kept sufficiently high by a pulverizing step comprising hydrogen decrepitation which causes little mechanical distortion, and accordingly the resin-bonding can be achieved. The greatest merit of this method is that an anisotropic magnet can be prepared otherwise than by the method of Reference No.2.

There are two reasons why a resin-bonded R-Fe-B series magnet can be prepared by pulverizing the alloy by using its property of easily producing an hydrogenated compound, kneading the resulting powder with an organic binder, and curing the alloy to obtain a resin-bonded magnet.

First, attention should be given to the fact that the critical radius of the single domain of the $R_2Fe_{14}B$ compound is much smaller than that of $SmCo_5$ and so on and is of the order of submicrons. It is extremely difficult to pulverize material to such a small grain diameter by the usual mechanical pulverization. Moreover, the obtained powder is too highly activated and consequently is oxidized and ignited very easily, and therefore the intrinsic coercivity of the resulting magnet is very low for its grain diameter. As a result of a study of the relationship between the grain diameter and the resulting intrinsic coercivity, however, we have found that the intrinsic coercivity was at most some kOe and did not increase even by performing surface

treatment on the magnet.

Another problem is a distortion caused by mechanical working. For example, if a magnet having an intrinsic coercivity of 10kOe in the sintered state is mechanically pulverized, the resulting powder of a grain diameter of 20 to 30 microns possesses a coercivity as low as less than 1 kOe. If a SmCo magnet, which is considered to have a similar nucleation model, is mechanically pulverized, such a decrease of the intrinsic coercivity does not occur and a powder having sufficient coercivity is easily prepared. The reason for such a phenomenon is assumed to be that the effect of the distortion and so on caused by pulverization and working on a R-Fe-B series magnet is considerable. This effect is a critical problem when a small magnet such as a rotor magnet of a step motor for a watch, is cut from a sintered magnet block.

For the above reasons, namely, that the critical radius is small and that the effect of mechanical distortion is considerable, a resin-bonded magnet cannot be obtained by the usual pulverization. In order to obtain a powder having sufficient intrinsic coercivity, a powder whose grains include a proportion of $R_2Fe_{14}B$ grains as disclosed in Reference No. 2 should be prepared. However, the quenching method of Reference No. 2 has low productivity. Furthermore, it is actually impossible to prepare a powder of this kind

by pulverization of a sintered body because the grains grow larger to some degree during sintering and it is necessary to make the grain diameter before sintering smaller than the diameter finally desired. However, if the grain diameter of the powder is so small, the oxygen concentration thereof is extremely high and the performance of the magnet is far from satisfactory.

Thus, at present, the allowable grain diameter of the $R_2Fe_{14}B$ compound after sintering is about 10 microns, but the intrinsic coercivity is reduced to almost zero after pulverization.

We have also considered the matter of the fining of grains by hot working. It is relatively easy to make a $R_2Fe_{14}B$ compound in the moulded state of about the same size as the grains prepared by sintering. So, by performing hot working on a cast block having a RFeB phase of that grain size, the grains are made finer and aligned, and are pulverized thereafter. By such a method, since the grain diameter of a powder for a resin-bonded magnet is between 20 and 30 microns, it is possible to include a plurality of $R_2Fe_{14}B$ grains in the powder, so that a powder having sufficient intrinsic coercivity is obtained. Moreover, these obtained powders are not isotropic as they are when obtained by the quenching method of Reference No. 2 but can be aligned in the magnetic field, and accordingly, an anisotropic magnet can be prepared from the powder of this type. Of course, if the grains are

pulverized by hydrogen decrepitation, the intrinsic coercivity is maintained better.

The reason for the particular composition of the alloy used in the present invention is explained below.

5 As the rare earth elements used in the said alloy, one may employ one of more of the elements Y, La, Ce, Pr, Ho, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Lu. The highest magnetic performance is obtained when Pr is selected either alone or in combination with other rare earth elements. Accordingly, for the practical use, a Pr alloy, a Pr-Nd alloy,
10 a Ce-Pr-Nd alloy and so on are used.

A small amount of an additive consisting of heavy rare earth elements such as Dy, Tb etc., may be employed in the alloy. Moreover, Al, Mo, Si and so on are sometimes desired in the alloy in order to enhance the intrinsic coercivity.

15 The main phase of the R-Fe-B series magnet is $R_2Fe_{14}B$. If R is less than 8 atomic percent, the above compound is not present but a body centered cubic compound of the same structure as α -iron is present and consequently high magnetic properties are not obtained. If, on the contrary, R is more
20 than 30 atomic percent, the quantity of the non-magnetic R-rich phase increases and the magnetic properties are extremely reduced. Thus, the amount of R is preferably between 8 and 30 atomic percent. However, the range of R which is more satisfactory for a cast magnet is between 8 and 25 atomic
25 percent.

B is an essential element to produce the $R_2Fe_{14}B$ phase. If B is less than 2 atomic percent, the rhombohedral R-Fe series is present and so high intrinsic coercivity is not obtained. However, as in the case of a magnet produced by the sintering method of the prior art, if B is included in an amount in excess of 28 atomic percent, the non-magnetic B-rich phase increases and the residual magnetic flux density is substantially reduced. The preferred upper limit of the amount of B for a moulded magnet is therefore 8 atomic percent. If B is more than 8 atomic percent, the fine $R_2Fe_{14}B$ phase is not obtained unless a specific cooling is performed, and the intrinsic coercivity is low.

Co is an element which is effective to enhance the Currie point and has the effect basically to substitute the site of the Fe element so as to produce $R_2Co_{14}B$. However, this $R_2Co_{14}B$ compound has a small crystalline anisotropy field, and the more the compound $C_2Co_{14}B$ increases, the less is the intrinsic coercivity of the magnet. Accordingly, in order to obtain a coercivity of at least 1kOe, which is considered to be sufficient for a permanent magnet, Co should be 50 atomic percent or less.

Al has the effect of increasing the intrinsic coercivity as described in Reference No 4; Shang Maocai et al. Proceedings of the 8th International Workshop on Rare-Earth Magnets, 1985, P541. This reference No 4 refers only to the effect of Al in the case of a sintered magnet, although the same effect is

present in case of a cast magnet.

However, since Al is a non-magnetic element, if the amount of Al is large, the residual magnetic flux density decreases and if more than 15 atomic percent thereof is present, the residual magnetic flux density is reduced to the level of hard ferrite. Such a magnet does not achieve the high performance of a rare earth magnet. Therefore, the amount of Al is preferably 15 atomic percent or less.

The invention is illustrated, merely by way of example, in the accompanying drawings, in which:-

Figure 1 illustrates alternative steps in a method of producing a magnet in accordance with the present invention;

Figure 2 illustrates the alignment of the grains of a magnetic alloy by extrusion hot working,

1 being a hydraulic press,

2 being a die,

3 being a magnetic alloy,

4 being an arrow showing pressure, and

5 being arrows showing the direction of the easy magnetization of the magnetic alloy;

Figure 3 shows the alignment of the grains of the magnetic alloy by rolling hot working,

6 being rollers,

7 being a magnetic alloy,

8 being arrows showing the direction of rotation of the rollers,

9 being an arrow showing the direction of the movement of the magnetic alloy, and

5 10 being arrows showing the directions of easy magnetization; and

Figure 4 shows the alignment of the grains of the magnetic alloy by stamping hot working,

11 being a stamp,

10 12 being a magnetic alloy,

13 being a base plate,

14 being arrows showing the direction of easy magnetization,

15 being an arrow showing the vertical movement of the stamp 11, and

15 16 being an arrow showing the direction of movement of the base plate 13.

Example 1

Reference is made to Figure 1 which is a flow diagram illustrating a method of making a permanent magnet in accordance with the present invention.

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First, an alloy of the desired composition is melted in an induction furnace and is cast into a die to form a cast alloy ingot. Then, in order to give anisotropy to the magnet, various kinds of hot workings are performed on the ingot. In this example, use was made not of a general

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moulding method but of a specific moulding method, that is, the Liquid Dynamic Compaction method (Reference No. 5; T.S. Chin et al, J. Appl. Phys, 59(4), 15 February 1986, P. 1297) which has a substantial effect in producing fine
 5 crystal grains by quenching.

The hot working method used in this example is one of the following:- (1) extrusion-type (Figure 2), (2) rolling-type (Figure 3) and (3) stamping-type (Figure 4) each being performed at a temperature of 1000°C . In each
 10 case, the strain rate is from 10^{-3} to 10^{-2} per second and the reduction ratio is 80%.

In the case of the extrusion-type, in order to apply an isostatic pressure to the sample, a means to apply pressure to the sample from the side of the die was also provided. In the case of the rolling-and the stamping-types, the speed
 15 of rolling or stamping was adjusted so as to minimize the strain rate. Whichever type thereof is used, the axis of easy magnetization of the grains is substantially parallel to the direction into which the alloy is urged.

Alloys Nos 1 to 14 of the compositions indicated in
 20 Table 1 were melted and made into magnets by the process shown in Figure 1. The hot working applied to each sample is shown in the Table.

The annealing after the hot working was performed at a temperature of 1000°C for 24 hours.

TABLE 1

Alloy No	Composition	hot working
1	Nd ₈ Fe ₈₄ B ₈	extrusion
2	Nd ₁₅ Fe ₇₇ B ₈	rolling
3	Nd ₂₂ Fe ₇₀ B ₈	stamping
4	Nd ₃₀ Fe ₅₈ B ₁₂	extrusion
5	Ce _{3.4} Nd _{8.5} Pr _{7.1} Fe ₇₅ B ₆	rolling
6	Nd ₁₇ Fe ₆₀ Co ₁₇ B ₆	stamping
7	Nd ₁₇ Fe ₆₀ Co ₁₅ V ₂ B ₆	extrusion
8	Ce ₄ Nd ₉ Pr ₆ Fe ₅₅ Co ₁₅ Al ₅ B ₆	rolling
9	Ce ₃ Nd ₁₀ Pr ₈ Fe ₅₂ Co ₁₅ Mo ₄ B ₈	stamping
10	Ce ₃ Nd ₁₀ Pr ₈ Fe ₅₂ Co ₁₇ Nb ₂ B ₈	extrusion
11	Ce ₃ Nd ₆ Pr ₁₀ Fe ₅₄ Co ₁₇ Ta ₂ B ₈	rolling
12	Ce ₃ Nd ₆ Pr ₈ Fe ₅₀ Co ₁₉ Ti ₂ B ₁₂	stamping
13	Ce ₃ Nd ₁₀ Pr ₆ Fe ₅₀ Co ₁₅ Zr ₂ B ₁₄	extrusion
14	Ce ₃ Nd ₁₀ Pr ₆ Fe ₅₆ Co ₁₅ Hf ₂ B ₈	rolling

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The properties of the resulting magnets are shown in Table 2.

For the purposes of comparison, the residual magnetic flux density of a sample "after casting", i.e. a sample on which the hot working has not been performed, is also shown.

TABLE 2

Alloy No	after hot working			after casting		
	Br (KG)	bHc(MGOe)	(BH) _{max} (MGOe)	Br (KG)	(BH) _{max} (MGOe)	
5	1	9.3	2.6	5.7	0.8	0.1
	2	9.7	3.4	4.9	1.3	0.3
	3	8.5	2.9	6.4	1.7	0.5
	4	6.4	4.5	5.1	1.3	0.2
	5	10.6	3.8	5.6	1.2	0.3
10	6	11.3	3.9	5.8	1.4	0.4
	7	11.9	10.7	30.1	6.1	2.3
	8	11.3	10.7	27.5	6.1	1.9
	9	11.5	10.2	28.3	6.0	1.6
	10	9.2	6.9	15.3	5.5	2.5
15	11	9.6	7.1	13.2	4.7	3.2
	12	9.1	6.0	11.3	4.9	2.1
	13	7.7	5.6	8.2	5.1	1.9
	14	8.7	7.1	15.1	6.2	3.1

From Table 2, it is obvious that, irrespective of whether the hot working is by extrusion rolling or stamping, the residual magnetic flux density increases, and thereby the samples are made magnetically anisotropic.

5 Example 2

The present example employs a general casting method.

First alloys Nos 15 to 31 of the composition indicated in Table 3 were melted in an induction furnace and cast into a die to form columnar zones. Hot working was effected at 1000°C using hot pressing, the strain rate being maintained between 10^{-3} and 10^{-2} per second, the reduction ratio being 80%. An annealing treatment was performed on the ingot at 1000°C for 24 hours to magnetically harden the same. After the annealing, the mean grain diameter of the sample was about 15 microns.

15 In contrast, in the case of a cast magnet of the desired shape which has been made without hot working, a plane anisotropic magnet utilizing the anisotropy of the columnar zone is obtained. In order to produce a resin-bonded magnet in a 18-8 stainless steel container at room temperature, hydrogen absorption in an hydrogen atmosphere of about 10 atmospheric pressure and hydrogen desorption at a pressure of 10^{-5} torr were repeated and the samples were pulverized, and 4 weight percent of epoxy resin was kneaded thereafter. Then the compacts were
20 moulded in a magnetic field of 10kOe which was applied
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perpendicularly to the pressing direction.

The properties of the resulting magnets are shown in

Table 4.

TABLE 3

Alloy No.	composition			
15	Pr ₁₀	Fe ₈₆	B ₄	
16	Pr ₁₆	Fe ₈₀	B ₄	
17	Pr ₂₂	Fe ₇₄	B ₄	
18	Pr ₂₆	Fe ₇₀	B ₄	
19	Pr ₁₃	Fe ₈₅	B ₂	
20	Pr ₁₃	Fe ₈₁	B ₆	
21	Pr ₁₃	Fe ₇₉	B ₈	
22	Pr ₁₂	Fe ₇₄	Co ₁₀	B ₄
23	Pr ₁₂	Fe ₅₉	Co ₂₅	B ₄
24	Pr ₁₃	Fe ₄₃	Co ₄₀	B ₄
25	Pr ₁₃	Dy ₃	Fe ₈₀	B ₄
26	Pr ₁₆	Fe ₇₈	B ₄	Si ₂
27	Pr ₁₆	Fe ₇₆	Al ₄	B ₄
28	Pr ₁₆	Fe ₇₆	Mo ₄	B ₄
29	Nd ₁₄	Fe ₇₈	P ₄	B ₄
30	Ce ₃	Nd ₃	Pr ₁₀	Fe ₈₀ B ₄
31	Nd ₁₂	Fe ₈₀	Al ₄	B ₄

TABLE 4

Alloy No.	hot working type		resin-bonded type	
	1Hc(KOe)	(BH) _{max} (MGOe)	1Hc(KOe)	(BH) _{max} (MGOe)
15	6.1	9.8	4.9	5.9
16	15.3	27.1	12.0	17.6
17	11.7	17.5	9.4	9.8
18	10.2	11.0	8.2	5.6
19	4.1	3.0	3.0	1.8
20	12.0	21.5	9.0	14.2
21	6.1	2.2	4.7	11.3
22	13.1	25.8	10.5	16.8
23	7.5	16.2	6.2	9.7
24	3.6	12.8	2.9	7.7
25	18.0	26.8	13.4	17.4
26	15.9	24.5	12.5	16.2
27	16.4	25.4	13.0	16.5
28	16.6	25.1	13.3	17.1
29	9.6	12.5	7.5	10.3
30	11.6	15.0	9.3	13.5
31	16.7	21.1	13.5	14.9

As will be seen, (BH)max and iHc are greatly increased by the hot working. This is because the grains are aligned by the hot working and the squareness of the BH curve is very much improved. In the quenching method of Reference No. 2, on the other hand, iHc tends to be lowered by the hot working. Accordingly, it is one of the major advantages of the present invention that the intrinsic coercivity is generally improved.

TABLE 5

10

strain rate (dε/dt/ second)	Pr ₁₅ Fe ₈₁ B ₄		Ce ₃ Pr ₁₀ Nd ₁₀ Fe ₇₃ B ₄	
	iHc (KOe)	Br (KG)	iHc (KOe)	Br (KG)
10 ⁻⁵ ~ 10 ⁻⁴ /s	10.6	10.9	9.0	10.7
10 ⁻⁴ ~ 10 ⁻³ /s	14.3	10.8	10.4	10.6
15 10 ⁻³ ~ 10 ⁻² /s	15.1	9.5	12.0	10.6
10 ⁻² ~ 10 ⁻¹ /s	16.0	8.8	13.8	8.9
10 ⁻¹ ~ 1/s	16.6	7.0	15.9	7.1
1 ~ 10/s	X	X	15.9	6.8
20 10 ~ 10 ² /s	X	X	X	X
10 ² ~ 10 ³ /s	X	X	X	X

X : the sample was cracked.

Table 5 above shows the relationship between the strain rate and the magnetic properties of two alloys whose composition is indicated in Table 5. These alloys, which constitute representative examples, are melted in an induction furnace and are cast in a die made of iron, and then they are subjected to hot pressing at various speeds. The results are shown in Table 5. In this case, the temperature is controlled at 1000°C , and the ratio of reduction is 80%. After the hot pressing, an annealing treatment is performed at 1000°C for 24 hours.

As shown in Table 5, when the strain rate is smaller than 10^{-4} per second, the intrinsic coercivity is decreased extremely. The reason for this is considered to be that the growth of crystal grains is hastened by the heat and that they are too bulky. On the other hand, the strain rate is too small, the productivity is decreased and thus the manufacturing cost is increased. When the strain rate is bigger than 1 per second, some samples are cracked due to the composition thereof, and such samples cannot be manufactured. Therefore, the desirable strain rate is from 10^{-4} to 1 per second, and that from 10^{-3} to 10^{-1} per second is desirable in order to get excellent magnetic properties.

TABLE 6

composition	property	plastic processing temperature (°C)										
		room temperature	250	500	700	800	900	950	1000	1050	1100	1150
Pr ₁₇ Fe ₇₉ B ₄	iHc(KOe)	Δ	Δ	10.8	11.8	10.6	8.4	9.0	8.6	7.8	6.2	2.1
	C axis orientation rate	Δ	Δ	82	80	85	85	95	96	97	95	70
Nd ₃₀ Fe ₅₅ B ₁₅	iHc(KOe)	X	X	15.0	13.6	12.6	12.6	12.0	12.4	9.2	5.8	1.5
	C axis orientation rate	X	X	72	71	82	98	96	98	97	97	73
Ce ₃ Nd ₁₀ Pr ₁₀ Fe ₅₀ Co ₁₇ Zr ₂ B ₈	iHc(KOe)	X	Δ	20.0	19.0	14.4	16.8	14.2	17.2	15.6	11.4	2.5
	C axis orientation rate	X	Δ	63	75	81	89	96	95	97	95	69

X : the sample cannot be manufactured

Δ : the sample is cracked and cannot be measured.

The alloys of the three compositions indicated in Table 6 as representative examples, are melted in an induction furnace and are cast in a die made of iron. Then hot working is effected by extrusion at the various temperatures shown, and an annealing treatment at 1000°C for 24 hours is performed. The relationship of the manufacturing temperature, the intrinsic coercivity and the C axis orientation rate are shown in Table 6. The strain rate is arranged to be from 10^{-3} to 10^{-2} per second, and the reduction ratio is arranged to be 80%.

Further, the C axis orientation rate represents the rate (volume %) of the easy magnetization axis of the crystal grains (corresponding to the C axis of the permanent magnet of the present invention) which are aligned in the same direction. The bigger this rate is, the finer the anisotropic magnet which can be obtained.

As shown in Table 6, if the manufacturing temperature is less than 500°C, the sample is cracked and thus cannot be manufactured. The C axis orientation rate of 80% is desirable to obtain excellent magnetic properties. In this case, the manufacturing temperature should be from 800°C to 1100°C. However, if the temperature is 1100°C, the intrinsic coercivity is substantially decreased. Therefore, the best manufacturing temperature is from 800°C to 1050°C.

TABLE 7

ratio of reduction (%)	Pr ₁₇ Fe ₇₉ B ₄		Nd ₃₀ Fe ₅₅ B ₁₅	
	(KOe)	C axis orientation rate (%)	(KOe)	C axis orientation rate %
0	4.3	58.	5.5	60
20	4.7	68	6.7	66
40	4.9	71	7.4	70
60	6.9	80	9.0	81
70	7.7	90	10.8	93
80	8.6	96	12.4	98
90	9.4	95	12.8	98

The alloys of the compositions indicated in Table 7 are melted and cast by the same method as those of Table 6. Then hot working is effected by an extrusion method in this case at a temperature of 1000°C, the reduction ratio being varied. Then an annealing treatment at a temperature of 1000°C for 24 hours is performed. The relationship of the reduction ratio, the intrinsic coercivity and the C axis orientation rate are shown in Table 7. Further, the strain rate is arranged to be from 10^{-3} to 10^{-2} per second. As shown in Table 7, if the C axis orientation rate is required to be 80% or higher, the reduction ratio should be 60% or higher.

The present invention thus enables a permanent magnet of sufficient intrinsic coercivity to be provided merely by carrying out a hot working without pulverizing the ingot as in the usual sintering method.

5 Furthermore, the hot working is only a one-stage process and is not a two-stage process as in the quenching method. Moreover, the hot working not only makes the magnet anisotropic but also increases the intrinsic coercivity.

10 Thus the present invention provides a method of making a permanent magnet which is much simpler than the sintering method or the quenching method in the prior art.

15 Moreover, by hydrogen decrepitation or pulverization of the samples after the hot working, an anisotropic resin-bonded magnet can also be provided in accordance with the present invention.

CLAIMS

1. A method of making a permanent magnet comprising melting and casting an alloy whose constituents comprise at least one rare earth, iron and boron; hot working the cast alloy ingot at a hot working temperature of at least 500°C, and at a strain rate $d\epsilon/dt$ in the range of 10^{-4} to 1 per second where ϵ is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.
2. A method as claimed in claim 1 in which the permanent magnet is annealed at a temperature of at least 250°C.
3. A method as claimed in claim 1 or 2 in which the hot worked alloy ingot is pulverized to form a powder, the powder being kneaded with an organic binder.
4. A method as claimed in any preceding claim in which the said hot working temperature is in the range of 800°C to 1050°C.
5. A method as claimed in any preceding claim in which the hot working effects a reduction ratio of at least 60% in the thickness, cross-sectional area or diameter of the cast alloy ingot.
6. A method as claimed in any preceding claim in which the alloy contains a total of 8 to 30 atomic percent of one or more rare earths.



7. A method as claimed in any preceding claim in which the alloy contains 2 to 28 atomic percent of boron.
8. A method as claimed in any preceding claim in which the alloy contains at least 50 atomic percent of iron.
- 5 9. A method as claimed in any preceding claim in which the alloy contains praseodymium.
10. A method as claimed in any preceding claim in which the alloy contains one or more of the elements Al, Mo and Si.
- 10 11. A method as claimed in any preceding claim in which the alloy contains 50 or less atomic percent of Co.
12. A method as claimed in any of claims 1-6 in which the composition of the alloy is substantially that of any of Alloys Nos 1-31.
- 15 13. A method of making a permanent magnet comprising melting and casting a $\text{Ce}_3\text{Pr}_{10}\text{Nd}_{10}\text{Fe}_{73}\text{B}_4$ alloy; hot working the cast alloy ingot at a hot working temperature of at least 500°C , and at a strain rate $d\varepsilon/dt$ in the range of 10^{-4} to 10 per second where ε is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.
- 20 14. A method of making a permanent magnet comprising melting and casting an alloy whose constituents comprise at least one rare earth, iron and boron; hot working the cast alloy ingot at a hot working temperature of 1000°C and a strain rate of $d\varepsilon/dt$ in the range of 10^{-4} to 10 per second where ε is the logarithmic strain and t is time; and forming the hot worked alloy ingot into a permanent magnet.
- 25 15. A method of making a permanent magnet substantially as described in any of the Examples.
16. A permanent magnet when made by the method claimed in any preceding claim.