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D-81925 München (DE)(54) **Permanent magnet material of high coercive force Pr-Co alloy and permanent magnet material of thin film and method of manufacturing the same.**

(57) The present invention relates to a permanent magnet material of an alloy and a thin film consisting essentially of Pr and Co and inevitable impurities, and further consisting at least one element selected from the group consisting of B, C, Fe, Cu, W, Ti, Ce and Sm as a secondary component and a method of manufacturing the permanent magnet comprising compacting or injection molding, then heating and sintering, and an object of the invention is to provide a small-sized and strong permanent magnet material having extremely large coercive force.

A permanent magnet material of a high coercive force Pr-Co alloy having coercive force of more than 80 kA/m, which alloy consists essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities and as a secondary component at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm, and a method of manufacturing the same, and a Pr-Co thin film magnet material and a method of manufacturing the same.

The present invention is to provide a method of manufacturing a permanent magnet having a high coercive force and consisting of the same component which comprises compacting or injection molding of same alloy powder, and then heating and sintering, so as to provide a small-sized and strong permanent magnet material having extremely high coercive force.

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Background of the InventionField of the Invention

5 The present invention relates to a permanent magnet material of an alloy prepared by compacting or injection molding a powder consisting essentially of Pr and Co and inevitable impurities, and further containing as a secondary component selected from the group consisting of B, C, Fe, Cu, W, Ti, Ce and Sm, and thereafter heating and sintering, and of a sputtered thin film consisting of the same components and concentration, and thereafter heating, and a method of manufacturing the same, and aims to provide a
 10 small and strong permanent magnet material having extremely large coercive force.

Related Art Statement

15 Recently, as highly efficient permanent magnet material, Fe-Pt, Nd-Fe-B and Sm-Fe-N alloys, compounds and the like have been discovered and remarkably developed.

On the other hand, with development of electronic technique, miniature and highly efficient electronic devices have successively been produced. Particularly, study of the above-described permanent magnet material and micromagnetic device having high properties has been active, and their excellent properties remarkably contribute to miniaturization and precision of apparatus. A small permanent magnet material
 20 having high coercive force according to the present invention is considered to be applied to magnetic recording media, and bias magnetic field supplying element of minute electromagnetic actuator or magneto-resistant head.

However, Pt magnet alloy limited to special use because of its expensive cost (Nippon Kinzoku Gakkaishi 56 (1992) 1495), Nd-Fe-B having a disadvantage in corrosion resistance (Nippon Oyo Jiki
 25 Gakkaishi 14 (1990) 189) or Sm-Fe-N compound which loses excellent properties caused by decomposition of nitrogen with a heat treatment at high temperature and has a limit in manufacturing method of material (Nippon Oyo Jiki Gakkaishi 17 (1993) 5) has a big problem, respectively.

PrCo₅ permanent magnet material has been discovered together with SmCo₅ magnet material substantially at the same time in the 1970's, and both crystalline structures belong to a CaCu₅ (hexagonal lattice)
 30 type. The latter SmCo₅ compound is extremely well-known by exhibiting excellent properties, while the PrCo₅ compound has an advantageous conditions such as high saturation magnetization, but is low in coercive force (J. MMM 94 (1991) 57) such as 590 kA/m at the highest (J. Less-Common Metals 148 (1989) 67) as a rare earth magnet and is not yet practically used. According to a study result so far, the cause of low coercive force, as understood from the equilibrium diagram of a Pr-Co alloy shown in Fig. 1, is
 35 considered that the compound (rhombohedral system) of Pr₅Co₁₉ adjacent to PrCo₅ has soft magnetic properties, which prevent high coercive force.

Therefore, in order to ascertain these results, the present invention has been studied over a wide composition range from 15 to 30 at% Pr in the Pr-Co system in which containing compounds of PrCo₅, Pr₅Co₁₉, Pr₂Co₇ and PrCo₃. As a result, it becomes clear that 2-10 times larger value than the conventional
 40 coercive force is obtained by finely grinding these compounds into 1-20 μm in a ball mill, compacting or injection molding as they are, and further heat treating the resulting molded products (Symposium summary of Nippon Kinzoku Gakkai (1993) 181), and from these results, the relationship between permanent magnet properties and compositions of a Pr-Co alloy is shown in Table 1 and Fig. 2.

In order to confirm that the present alloy can obtain high coercive force even by being thinned, a film
 45 was formed on a substrate at room temperature and thereafter heated to 300-800 °C or a film was formed on a substrate heated to 300-800 °C, and it was clarified that high coercive force can be obtained.

The relationship between permanent magnetic properties and compositions of the Pr-Co alloy thin films is shown in Table 2.

50

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Table 1

Composition at%		Heating temperature and time	Magnet properties		
Pr	Co		iHc (kA/m)	Br (T)	(BH) _{max} (KJ/m ³)
16.7	83.3	compacting	430	0.60	37
		850 °C 1 h	278	0.54	19
18.5	81.5	compacting	455	0.78	47
		850 °C 1 h	1220	0.82	110
19.5	80.5	compacting	450	0.70	42
		850 °C 1 h	1350	0.75	103
21.0	79.0	compacting	450	0.67	39
		850 °C 1 h	1300	0.70	85
23.0	77.0	compacting	445	0.63	36
		850 °C 1 h	1270	0.64	72
25.0	75.0	850 °C 1 h	955	0.48	27
27.0	73.0	900 °C 1 h	635	0.35	9

Table 2

Composition at%		Substrate temperature	Heating temperature and duration	Magnetic properties		
Pr	Co			iHc (kA/m)	Br (T)	(BH) _{max} (KJ/m ³)
18.4	81.6	R.T.*	500 °C 1h	376	0.81	88
		500 °C	(as deposit)	400	0.78	89
19.8	80.2	R.T.*	500 °C 1h	520	0.61	68
		500 °C	(as deposit)	496	0.58	63
24.0	76.0	R.T.*	500 °C 1h	328	0.46	24
		500 °C	(as deposit)	416	0.34	23

R.T.*: at room temperature

Summary of the Invention

The present invention is to provide a permanent magnet material having ultrahigh coercive force of higher than 1200 kA/m by compacting or injection molding an alloy powder having a composition from PrCo₅ to PrCo₃ and heating a thin film having the equal composition formed on a substrate or forming a film on a heated substrate.

As described above, the present invention is to provide a permanent magnet material having a high coercive force which cannot be obtained before, and characteristics of the present invention are as follows.

An object of the present invention is to provide a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy consists essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities, and have more than 80 kA/m of coercive force.

Another object of the present invention is to provide a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy consists essentially of 19.5-30 at% of Pr, the remainder Co and inevitable impurities, and have more than 80 kA/m of coercive force.

A further object of the present invention is to provide a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy consists essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities, and at least one element selected from the groups consisting of 0.1-8 at% of B, C, Si, Mn, Fe, Ni, Cu, Mo, W and Pt and 0.1-5 at% of O, Al, Ti, Y, Ph, Pd, La, Ce, Sm, Tb, Dy and Au as a secondary component, and have more than 80 kA/m of coercive force.

A still further object of the present invention is to provide a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy consists essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities, and at least one element selected from the groups consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and have more than 80 kA/m of coercive force.

Another object of the present invention is to provide a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy consists essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities, and at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and have more than 80 kA/m of coercive force.

A further object of the present invention is to provide a thin film magnet material of Pr-Co alloy having a high coercive force, wherein said thin film of Pr-Co alloy consists essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and has more than 80 kA/m of coercive force.

A still further object of the present invention is to provide a thin film magnet material of Pr-Co alloy having a high coercive force, wherein said thin film of Pr-Co alloy consists essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and at least one element of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and has more than 80 kA/m of coercive force.

Another object of the present invention is to provide a method of manufacturing a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy powder comprises finely grinding an alloy consisting essentially of 15-30 at% and the remainder Co and inevitable impurities into 1-20 μm in a ball mill for 5-30 hours, and comprises mechanical alloying a blend consisting of the equal components of metals coarse grain, finely powdering the thus ground powder, compacting or pressure molding in a magnetic field or injection molding it, and further heat treating or sintering at 300-1180 °C.

A further object of the present invention is to provide a method of manufacturing a permanent magnet material of Pr-Co alloy having a high coercive force, wherein said Pr-Co alloy powder comprises finely grinding an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities as main component, and as a secondary component, at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm into 1-20 μm in a ball mill for 5-30 hours, and comprises mechanical alloying a blend consisting of the equal components of metals coarse grain, finely powdering the thus ground powder, compacting or pressure molding in a magnetic field or injection molding it, and further heat treating and sintering at 300-1180 °C.

A still further object of the present invention is to provide a method of manufacturing a permanent magnet material of a high coercive force, wherein Pr-Co alloy comprising forming a film of an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities on a substrate at a room temperature in an atmosphere of at least one sputtering gas of nitrogen, oxygen, argon, krypton and xenon, heating the film to 300-800 °C or forming the film onto the substrate heated at 300-800 °C, and having more than 80 kA/m of coercive force.

Another object of the present invention is to provide a method of manufacturing a permanent magnet material of a high coercive force, wherein Pr-Co thin film comprises forming a film of an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, as a secondary component, at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% Ti, Ce and Sm on a substrate at room temperature in an atmosphere of at least one sputtering gas of nitrogen, oxygen, argon, krypton and xenon, heating the film to 300-800 °C or forming the film onto the substrate heated at 300-800 °C, and having more than 80 kA/m of coercive force.

In the present invention, "mechanical alloying" means a phenomenon that a blend consisting of coarse grain metallic elements are alloying and changing crystal structure to amorphous or other crystal structure by finely grinding for a long time of about 30-100 hours in a ball mill.

The present invention relates to a powder permanent magnet of a Pr-Co alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and this composition consists essentially of a compound having a crystal structure of hexagonal PrCo_5 or Pr_2Co_7 , to which a small amount of a rhombohedral $\text{Pr}_5\text{Co}_{19}$, PrCo_3 phase is added. Hitherto, PrCo_5 (16.7 at% Pr) does not exhibit high coercive force by mixing a small amount of $\text{Pr}_5\text{Co}_{19}$ with a PrCo_5 phase, but the present invention can obtain

superhigh coercive force in the above composition range including an alloy composition of $\text{Pr}_5\text{Co}_{19}$ (20.8 at% Pr). Moreover, in case of desiring to exhibit more larger coercive force, it is preferable to add at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and of 0.1-5 at% of Ti, Ce and Sm as a secondary component to a composition of 15-30 at% Pr-Co alloy.

These alloys formed by arc melting or high frequency induction melting is roughly ground, thereafter ground in a ball mill for more than 5 hours and finely ground into about 1-20 μm , or coarse powders of respective metals weighed in an alloy composition aimed at are finely powdered by mechanical alloying and the thus obtained fine powders are compacted under pressure of 1-10 t/cm^2 or injection molded in a magnetic field of more than 400 kA/m, or thereafter heated or sintered at 300-1180 °C for 10 minutes to 10 hours, thereby obtaining a superhigh coercive permanent magnet material.

In case of forming the permanent magnet material into a thin film according to use object of the present invention, an alloy thin film containing 15-30 at% of Pr and remainder Co and inevitable impurities, and a thin film of an alloy containing as a secondary element 0.1-8 at%, more preferably 0.1-5 at%, of at least one element selected from the group consisting of B, C, Fe, Cu and W or Ti, Ce and Sm and the remainder Co are preferably deposited onto a quartz or glass substrate at room temperature and heated at 300-800 °C, or deposited onto a substrate heated to 300-800 °C. It is possible to obtain a thin film of permanent magnet material having the same superhigh coercive force as that of alloy powder by sputter deposition in at least one sputtering gas selected from nitrogen, oxygen, argon, krypton and xenon.

Brief Description of the Drawings

For a better understanding of the invention, reference is made to the accompanying drawing, in which:

Fig. 1 is a phase diagram of a Pr-Co alloy system.

Fig. 2 is a graph showing the relationship between properties and compositions of permanent magnet of a Pr-Co alloy and compounds of PrCo_5 , $\text{Pr}_5\text{Co}_{19}$, Pr_2Co_7 and PrCo_3 .

Fig. 3 is a graph showing the relationship between the high coercive force of alloy obtained by Schweizer et al (1971) and the temperature of heat treatment and comparison with that of the present invention.

Fig. 4 is a graph showing the comparison of demagnetization curves of typical 18 at% Pr-2 at% Ti-80 at% Co, 17 at% Pr-3 at% Cu-80 at% Co and 17 at% Pr-3 at% Ce-80 at% Co permanent magnet materials adding 19.5 at% Pr-80.5 at% Co and secondary components thereto.

Fig. 5 is a graph showing the relationship between a secondary component X_x in case of (20-x) at% Pr-x at% X-80 at% Co and magnetic properties.

The embodiments of the present invention are explained next.

Example 1

In the present embodiment, there was examined the heat treatment effect of a permanent magnet material consisting of two kinds of compositions of a typical magnet (A) consisting of 19.5 at% of Pr and the remainder Co and a magnet (B) consisting of 23 at% of Pr and the remainder Co as shown in Fig. 3.

(1) First, as a raw material, use were made of electrolytic Co and reduced Pr of 99.9%. In order to manufacture a test sample, total weight 20 g of a raw material was weighed to a composition aimed at and arc melted. The sample was rotated several times by repeating arc melting and manufactured a homogeneous alloy.

(2) These alloys were further heated at 1080 °C for 1-10 hours to apply a homogenization treatment, thereafter ground to form coarse powder, thus obtained powder was charged into a ball mill sealed with argon gas, then finely ground into 1-20 μm , and compacted under a pressure of 5 t/cm^2 in a magnetic field of 800 kA/m. Moreover, in case of manufacturing an isotropic permanent magnet material, the alloy powder is compacted without applying any magnetic field. Measurement was carried out by a BH fluxmeter after magnetizing in a pulse magnetic field of 4000 kA/m.

(3) As understood from Fig. 3, a compacted magnet (A) as it is shows high coercive force iH_c of 450 kA/m and residual flux density B_r of 0.70 T, and if further heated in vacuo or argon atmosphere at 700-950 °C for 1 hour, there are obtained superhigh coercive force iH_c of 1350 kA/m at the highest and B_r of 0.75 T. This tendency is the same with respect to the magnet (B), and there are shown the superhigh coercive force of more than 1270 kA/m and the residual flux density B_r of 0.64 T.

(4) Moreover, when sintering treatment at 1000 °C-1100 °C was applied, the coercive force iH_c is decreased, but the residual flux density B_r is gradually increased together with the increase of a heating temperature.

These results are shown in Fig. 3. Typical examples of the thus obtained Pr-Co permanent magnet material are shown in Table 1.

Example 2

A permanent magnet material of the composition described in the present invention can easily be obtained by mechanical alloying, and this method does not require to be solubilized. Here is explained an example of the magnet (B) which is 23 at% Pr-Co alloy.

(1) First, coarse Co powder and Pr powder of about 100-200 mesh were weighed to necessary compositions in a non-oxidize atmosphere, these were charged into a ball mill, the argon gas was sealed therein to form fine powder by carrying out mechanical alloying for 50 hours, and compacted under a pressure of 5 t/cm² in a magnetic field of 800 kA/m.

(2) This product was low in coercive force iH_c, such as about 12 kA/m, but when it was placed in a vacuum furnace at 800 °C and heated for 1 hour, there were obtained the superhigh coercive force of more than 1400 kA/m and the residual flux density Br of 0.65 T, and the same properties were obtained as those in case of arc melting

Example 3

Pr-Co binary alloy as a main component and typical 18 at% Pr-2 at% Ti-80 at% Co, 17 at% Pr-3 at% Cu-80 at% Co, 17 at% Pr-3 at% Ce-80 at% Co alloys as secondary components were arc melted, charged into a ball mill with argon gas, thereafter finely ground for 10 hours to form fine powder of 1-20 μm, and compacted under a pressure of 5 t/cm² in a magnetic field of 800 kA/m, heated at 800-900 °C for 1 hour, applied to a pulse magnetic field of 4000 kA/m, then the demagnetization curves thus measured was compared with the result of binary 19.5 at% Pr-80.5 at% Co alloy and shown in Fig. 4. As understood therefrom, the Ce series alloy is not changed in coercive force iH_c, but increased in residual flux density Br. In case of adding Ti and Cu, coercive force iH_c is increased, but Br is decreased. Moreover, Fig. 5 shows the relationship between atomic % of secondary components as (20-x) at% Pr-x at% X-80 at% Co (X is a secondary component) and coercive force and residual flux density, respectively.

Example 4

As an example of a manufacturing method, the case of a 18.5 at% Pr-Co alloy is explained.

(1) In the present invention, the above alloy was arc melted, homogenized at 1050 °C, roughly ground, and the thus obtained powder was further finely ground to 1-20 μm in a ball mill sealed with argon gas therein for 10 hours, and the fine powder was compacted under a pressure of 5 t/cm² in a magnetic field of 800 kA/m to have already obtain high coercive force iH_c of 455 kA/m.

(2) The above alloy was further heated at 850 °C among 750-900 °C for 1 hour, and a superhigh coercive force iH_c of 1270 kA/m and a residual flux density Br of 0.82 T were obtained.

(3) However, when the above alloy was ball milled for 4 hours, which has hitherto been carried out, there was obtained the highest value 500 kA/m substantially equal to the value of Schweizer et al (IEEE Trans. Mag. Sept. (1971) 429) shown in Fig. 3, but at a temperature of 1100 °C, a coercive force has already been at a lowering stage in the present invention. Moreover, since the particle size of an alloy powder was fine, a result almost close to sintering was obtained by heating at 850 °C, and specific gravity in this case reached above 95% of alloy and Vickers hardness was about 500.

Example 5

A Pr-Co alloy was formed into a film by rf-magnetron sputtering method. A target is a composite type arranged Pr chip on a Co plate. Here, the number of the Pr chips were changed to make composition 19.5 at% Pr-80.5 at% Co alloy. Before sputtering, the chamber was evacuated to high vacuum condition at first, then filled with sputtering gas in atmosphere having a pressure of 5 mTorr. Thereafter, the sputtering was carried out for forming thin films at an applied power of 50 W. As a substrate, quartz (SiO₂) was used, and substrate temperature was 650-700 °C. When it is measured by a micromagnetometer, there was obtained a superhigh coercive force of more than 1200 kA/m in substantially the same manner as in the alloy powder magnet.

In the present invention, the reason of limiting the alloy powder, the thin film permanent magnet material and the manufacturing condition is described as follows.

(1) In the Pr-Co alloy, the reason why Pr is 15-30 at% as a main component and a coercive force is 80 kA/m is because not more than 15 at% of Pr can not obtain permanent magnet materials having high coercive force more than 80 kA/m, and more than 19.5 at% of Pr is rather desiring to obtain coercive force more than 80 kA/m steadily, and more than 30 at% of Pr cannot be observed magnetization at room temperature so as to be useless as a magnet material.

(2) If Mg and Ca mixed as a refining agent and inevitable impurities in a process for manufacturing alloy are remained by exceeding 0.5 at%, the permanent magnet properties are deteriorated, so that these impurities should preferably be less than 0.5%.

(3) The reason why total amount of 0.2-13 at% of at least one element selected from the group consisting of B, C, Ti, Fe, Cu, W, Ce and Sm was added as a secondary component is because if the each addition amount is less than 0.1 at%, there is no adding effect, and if the each addition amount exceeds 8 at%, the permanent magnet properties are deteriorated, so that the total addition amount was limited to 0.2-13 at%.

(4) The reason why Pr of a main component of permanent magnet material of the other element added into an alloy or a thin film as a secondary component is limited to 15-30 at% and a coercive force to more than 80 kA/m is because thin films of Pr-Co alloy are invented as an entirely novel material, and any scope of composition of alloy other than this composition cannot obtain permanent magnet properties.

(5) The reason why sputtering atmosphere is limited to first vacuum and then argon gas atmosphere because the formation of a thin film is extremely difficult in the atmosphere of air or in vacuo, but a thin film of good quality having less impurities can be obtained by sputtering in atmosphere of at least one sort of gas selected from nitrogen, oxygen, argon, krypton and xenon.

The present invention provides a permanent magnet of Pr-Co alloy having extremely high coercive force, which has never been observed as permanent magnet, obtained by compacting a fine powder of 1-20 μm of Pr-Co alloy, or by mechanical alloying a fine powder, heat-treating and sintering, or by forming into a thin film having the same component, thereby exhibiting industrially large effects such as extremely high coercive force and improving high efficiency of permanent magnetic properties.

Claims

1. A permanent magnet material of a high coercive force Pr-Co alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and having more than 80 kA/m of coercive force.
2. A permanent magnet material of a high coercive force Pr-Co alloy consisting essentially of 19.5-30 at% of Pr and the remainder Co and inevitable impurities, and having more than 80 kA/m of coercive force.
3. A permanent magnet material of a high coercive force Pr-Co alloy consisting essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities as essential component, and at least one element selected from the group consisting of 0.1-8 at% of B, C, Si, Mn, Fe, Ni, Cu, Mo, W and Pt and 0.1-5 at% of O, Al, Ti, Y, Rh, Pd, La, Ce, Sm, Tb, Dy and Au as a secondary component, and having more than 80 kA/m of coercive force.
4. A permanent magnet material of a high coercive force Pr-Co alloy consisting essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities as essential component, and at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and having more than 80 kA/m of coercive force.
5. A permanent magnet material of a high coercive force Pr-Co alloy consisting essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities as essential component, and at least one element selected from the group consisting of 0.1-8 at% of Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and having more than 80 kA/m of coercive force.
6. A permanent magnet material of a high coercive force Pr-Co alloy which is a thin film of an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and having more than 80 kA/m of coercive force.
7. A permanent magnet material of a high coercive force Pr-Co alloy which is a thin film of an alloy consisting essentially of 15-30 at% of Pr, the remainder Co and inevitable impurities as essential

component, and at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component, and having more than 80 kA/m of coercive force.

- 5 **8.** A method of manufacturing a permanent magnet material of an ultrahigh coercive force Pr-Co alloy comprising finely grinding an alloy powder consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities into 1-20 μm in a ball mill for 5-30 hours, and further finely-grounding alloy powder made from each metallic coarse grain of the same components by mechanical alloying, compacting or injection molding in a magnetic field, and further heat-treating or sintering at 300-10
1180 °C.
- 15 **9.** A method of manufacturing a permanent magnet material of a high coercive force Pr-Co alloy comprising finely grinding an alloy powder consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities, and as a secondary component at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm into 1-20 μm in a ball mill for 5-30 hours, and further finely-grounding alloy powder made from each metallic coarse grain of the equal components by mechanical alloying, compacting or injection molding in a magnetic field, and further heat-treating or sintering at 300-1180 °C.
- 20 **10.** A method of manufacturing a permanent magnet material of a high coercive force Pr-Co alloy comprising forming a thin film of an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities on a substrate at room temperature in an atmosphere of at least one sort of sputtering gas selected from the group consisting of nitrogen, oxygen, argon, krypton and xenon, and heating the films thus obtained to 300-800 °C, or forming the films onto the substrate heated to 300-800 °C, and obtaining a permanent magnet material having more than 80 kA/m of coercive force.
- 25 **11.** A method of manufacturing a permanent magnet material of a high coercive force Pr-Co alloy comprising forming a thin film of an alloy consisting essentially of 15-30 at% of Pr and the remainder Co and inevitable impurities and at least one element selected from the group consisting of 0.1-8 at% of B, C, Fe, Cu and W and 0.1-5 at% of Ti, Ce and Sm as a secondary component on a substrate at room temperature in an atmosphere of at least one sort of sputtering gas selected from the group consisting of nitrogen, oxygen, argon, krypton and xenon, and heating the films thus obtained to 300-800 °C, or forming the thin films onto the substrate heated at 300-800 °C, and obtaining a permanent magnet material having more than 80 kA/m of coercive force.
- 30 **12.** The use of the permanent magnet material as defined in any one of claims 1 to 7 in magnetic recording media, electromagnetic activators, magneto-resistant heads and bias magnetic field supplying elements.
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- 40
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FIG. 1

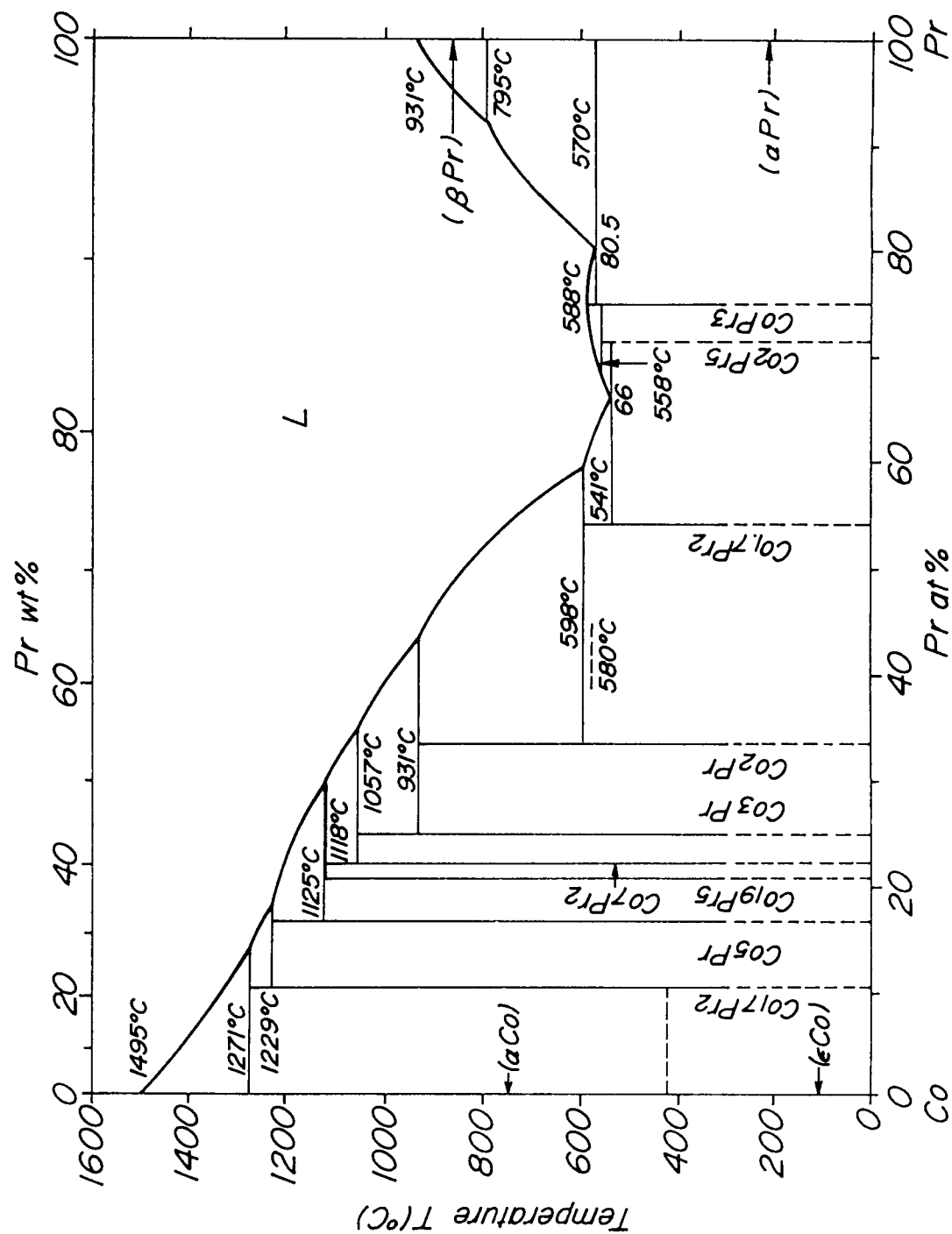


FIG. 2

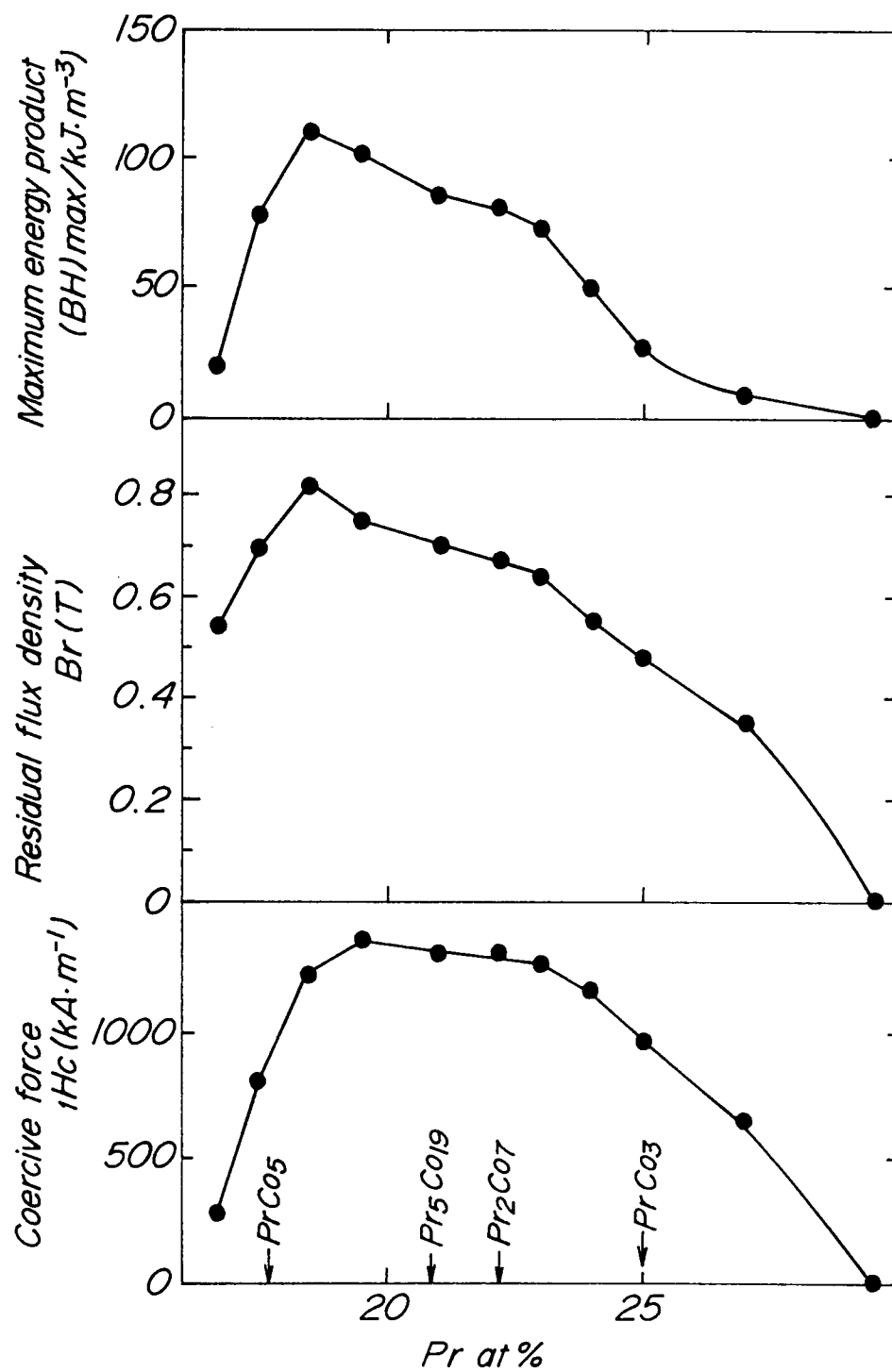


FIG. 3

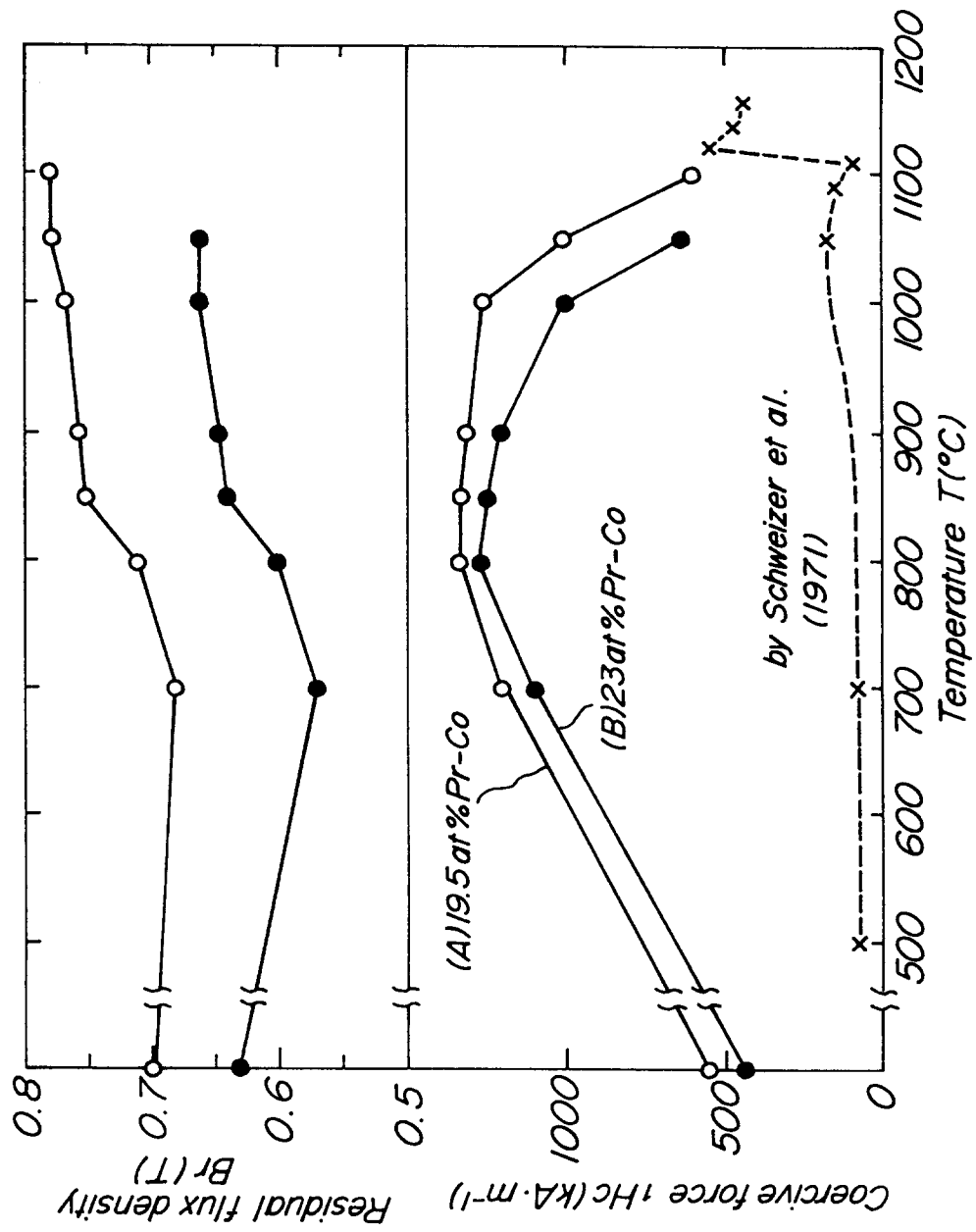


FIG. 4

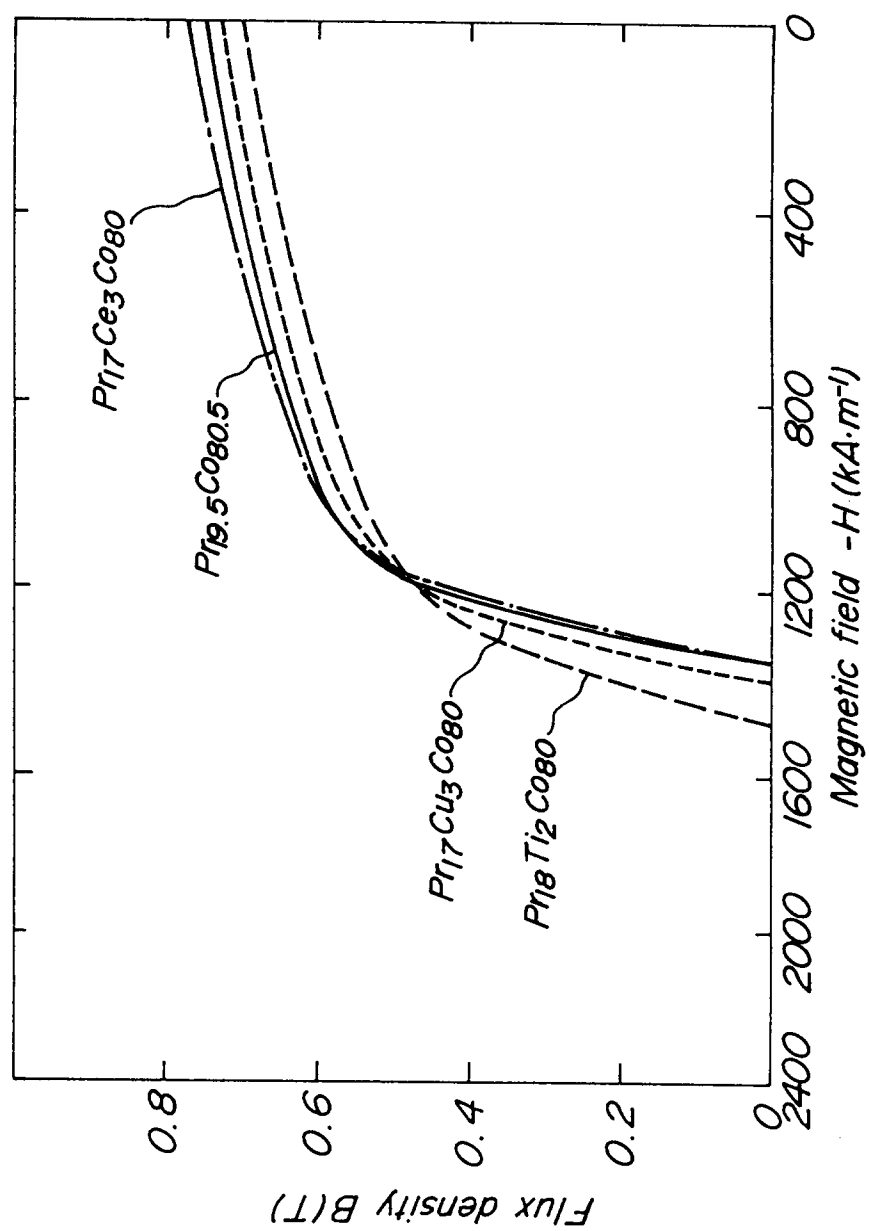
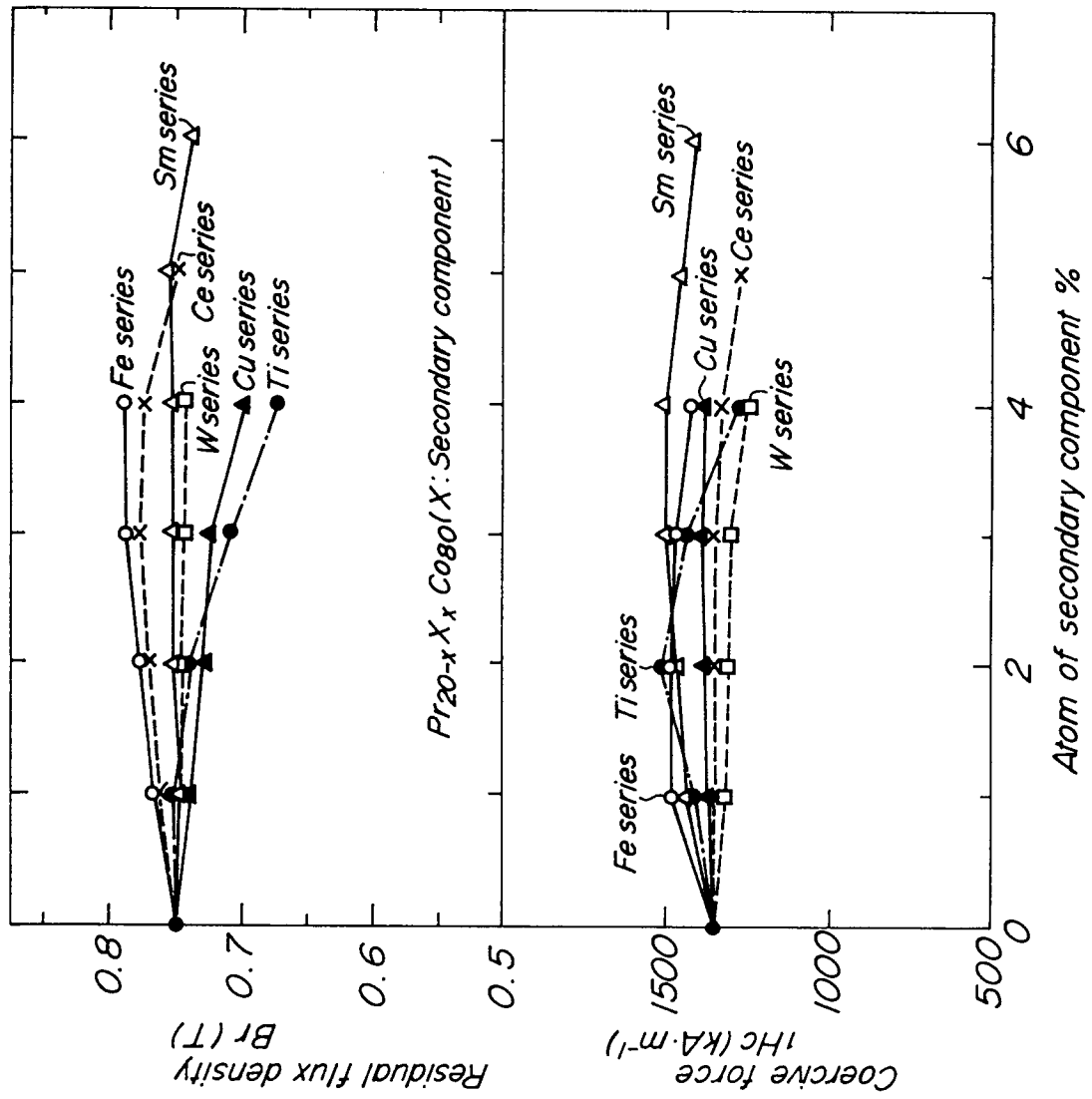


FIG. 5





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 12 0423

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	CHEMICAL ABSTRACTS, vol. 101, no. 12, 17 September 1984, Columbus, Ohio, US; abstract no. 102690w, W.WALLACE ET AL 'praseodymium-cobalt (PrCo5)permanent magnets' page 747 ;column 2 ; * abstract * & PROC.INT.WORKSHOP RARE EARTH-COBALT PERM.MAGNETS THEIR APPL.1983,7TH 239-45(GB)	1,2	H01F1/055 H01F10/12
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 March 1995	Examiner Decanniere, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			