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(71) Applicant: **FORD MOTOR COMPANY LIMITED**
Eagle Way
Brentwood Essex CM13 3BW(GB)

㊹ GB

(71) Applicant: **FORD FRANCE SOCIETE ANONYME**
344 Avenue Napoléon Bonaparte B.P. 307
F-92506 Rueil Malmaison Cedex(FR)

㊹ FR

(71) Applicant: **FORD-WERKE AKTIENGESELLSCHAFT**
Werk Köln-Niehl Henry-Ford-Strasse
Postfach 60 40 02
D-5000 Köln 60(DE)

㊹ DE

(72) Inventor: **Patel, Suresh G.**
4651 Barlett Drive
Canton Michigan 48187(US)
Inventor: **Hadjipanayis, George C.**
3012 Gary Avenue
Manhattan, KS 66502(US)
Inventor: **Christoduoulou, Christodoulos**
5600 Penn Avenue
Pittsburgh PA 15206(US)
Inventor: **Abbott, Edward H.**
3204 Farmbrook
Ann Arbor Michigan 48104(US)
Inventor: **Erickson, Robert H.**
5216 Whispering Oak
West Bloomfield Michigan 48003(US)

(74) Representative: **Messulam, Alec Moses et al**
A. Messulam & Co. 24 Broadway
Leigh on Sea Essex SS9 1BN(GB)

(54) Multiphase permanent magnet of the Fe-B-MM type.

(57) A method is disclosed for producing a permanent magnet of the Fe-B-MM type, comprising: (a) preparing a metallic powder having a mean particle size of 2-5 microns and having a composition comprising, by atomic weight percent: 60-80% Fe, 1-8% Al, 6-10% B, .1-.43% oxygen, 0-5% Dy and/or 0-10% Ni, and 12-22% MM,

where MM is a misch metal (preferably having at least four naturally occurring insoluble cerium earth metals with a least 20% of the misch metal consisting of cerium and lanthanum), the powder having essentially a multiphase crystalline structure dominated by at least two $R_2Fe_{14}B$ phases; (b) aligning such powder in a magnetic field; (c) compacting the aligned powder into shapes; (d) sintering such shapes at a temperature and for a period of time (i.e., in the range of 1000-1100°C for .5-9 hours) to fuse the powder and increase the proportion of said $R_2Fe_{14}B$ phases to at least 70% by volume of the shapes; and preferably (e) anealing the sintered shapes at a temperature (i.e., in the range of 550-650°C for 1-4 hours) to cause the shapes to consist essentially of at least two $R_2Fe_{14}B$ phases comprising the matrix and the phase RFe_4B_4 and the R-rich phase residing essentially in the grain boundaries.

MULTIPHASE PERMANENT MAGNET OF THE Fe-B-MM TYPE

This invention relates to iron based permanent magnets and a method of making such magnets.

Major permanent magnet materials currently in use today are AlNiCo, hard ferrite, rare earth-cobalt stabilized with iron, and rare earth-iron magnets which have been stabilized with boron.

The AlNiCo and ferrite materials (such as strontium or barium ferrite) have proved to be inexpensive with costs typically about $1.50 per pound of material, but their magnetic properties do not provide a sufficiently high energy product or coercivity that would be suitable for applications such as an automotive starter motor or a magnetic imagining device (cat scan). Such magnets have exhibited energy products at the level of about 4 MGOe, and a coercivity at the level of less than 4 KOe.

At the opposite end of the cost spectrum is the rare earth-cobalt-iron and rare earth -iron-boron magnets, each of which have proven to be highly expensive with a cost factor of at least about $80.00 per pound of material. Technology for making iron stabilized rare earth-cobalt magnets is taught in U.S. patents 4,081,297; 4,369,075; and 4,131,495. This type of magnet usually contains rare earths and cobalt in amounts of up to 50-60% by weight. Cobalt is strategic material and the main source of cobalt for the United States is from Southern Africa, particularly Zaire. Thus, political considerations frequently affect the availability and price of cobalt. This type of magnet also contains intermetallic compounds of rare earth and cobalt which exhibit extremely large magnetocrystalline anisotropy. An energy product of at least about 24 MGOe (several times over the conventional AlNiCo or ferrite permanent magnets) is obtainable with a samarium-cobalt permanent magnet. Even higher saturation magnetization, a higher energy product, and a higher operating temperature can be obtained with the presence of the intermetallic compound Sm_2Co_{17}. To improve the coercive force by partial substitution of iron or copper, even higher energy products have been obtained. But two characteristics still stand in the way of applying such rare earth-cobalt permanent magnets to automotive applications, namely, the high cost of the materials and a high energy product and/or coercive field which is in excess of flux density desired.

Researchers turned to the use of rare earth-iron magnets stabilized with boron in an effort to overcome the need for cobalt. By selecting certain of the rare earths to be of the light, more abundant type, the cost factor has been reduced only slightly (see U.S. patents 4,541,877; 4,597,938; 4,585,473). The rare earth selected for these disclosures was Nd in amounts of 15-20% with boron in the range of 8-12%; in some cases, Dy and/or Tb was added to the Nd. These materials generally had high coercivity levels but also a high cost due to selection and purity of rare earths. The materials were anistropic, and if modified to isotropic, the energy product was reduced to below 13 MGOe.

To further reduce the cost of acquiring the special purified rare earth materials for such permanent magnets, it has been suggested that misch metal (MM) be employed. Misch metal is a more concentrated form of rare earth metals obtained in the early stages of the chemical treatment of the ores containing naturally occurring rare earths. The specific composition of the misch metal will depend on the ore employed (the ore content will vary somewhat between different geographical locations but will exhibit essentially the same primary rare earths in essentially similar amounts). The most common misch metal composition consists of 52% cerium, 20% La, 15.7% Nd, 4.8% Pr, and about 6% other rare earths. Misch metal will have a content that reflects to a large extent the combination of rare earths found in the ore from which it is refined. Didymium is sometimes referred to as misch metal, but it is more expensive because it is extracted from the original misch metal through additional chemical processes. Cerium and lanthanum are the easiest rare earths to remove from misch metal and thus Didymium reflects this ease of elimination in varying degrees. The most common compositions of Didymium consist essentially of: (i) 90% Nd-10% Pr, (ii) 80% Nd-5% Pr, (iii) 50% Nd-40% Ce-10% Pr, and (iv) 60% Pr-20%Nd-20% La.

In most cases where misch metal is mentioned as an alternative for introducing the rare earth materials, it is done so without discussing as to cost or desired chemistry and without any samples or data demonstrating how to make MM work (see U.S. patents 4,152,178 and 4,090,892). Where chemistry was of some importance, the teaching was limited to quenching of ribbons of such material which is not practical for making permanent magnets (see U.S. patent 4,496,395).

In almost all of the research to date in rare earth-iron-boron magnets, the direction has been to create predominantly single-phase magnetic matrix material, reducing any nonmagnetic secondary phases to minimum. It has been frequently thought by prior art researchers that the appearance of secondary nonmagnetic phases in the rare earth-boron type permanent magnets prevented such magnets from having highly reproducible magnetic parameters. Accordingly, a continuous attempt has been made to reduce the appearance of nonmagnetic secondary phases.

There is an increasing need for lighter weight permanent magnets which are at the same time economical and have magnetic properties tailored to specific applications with increased performance.

The invention is a method for producing a permanent magnet of the Fe-B-MM type, comprising: (a) preparing a metallic powder having an average particle size of about, but above, 2 microns and having a composition consisting essentially of, by atomic weight percent: 12-22% misch metal, 1-8% Al, 6-10% B, less than .43% oxygen, substitutional agents of up to 5% Dy as a substitute or adjunct of misch metal and/or up to 10% Ni as a partial substitute or adjunct of Al, up to 3-10% of a modifying agent for modifying physical properties other than magnetic properties, and the remainder Fe, said substitutional and/or modifying agents only being present in an amount that would not prevent Fe from being present in an amount of substantially at least 60%, the powder having essentially a crystalline structure dominated by at least two $R_2Fe_{14}B$ phases (the misch metal preferably comprising at least four naturally occurring insoluble cerium earth metals and at least 20% of such earth metals consisting of cerium and/or lanthanum); (b) aligning such powder in a magnetic field; (c) compacting the aligned powder into shapes preferably of blocks, arcs, cubes or cylinders; (d) sintering such shapes at a temperature (preferably in the range of 1000-1100°C) and for a time period to fuse said powder, redistribute phases, and increase the proportion of said $R_2Fe_{14}B$ phases to at least 70% by volume of said shapes; and preferably (e) annealing the sintered shapes at a temperature in the range of 550-650°C to cause the microstructure to consist essentially of iron and the magnetic phases $R_2Fe_{14}B$ in the matrix, and a high proportion of the nonmagnetic phases RFe_4B_4 and a rare earth-rich phase (i.e., R-FE-O) in the grain boundaries.

The resultant permanent magnet cylinders will be characterized by magnetic properties intermediate that of commercial ferrite magnets and commercial R-FE-B type magnets (where R consists essentially of Nd in high amounts). This invention replaces Nd by a combination of aluminum, misch metal, and/or small amounts of Dy and/or Ni. It has been found that by this substitution and by the process control parameters herein, a permanent magnet of intermediate range magnetic properties can be produced at low cost. When the rare earth Dy is added as an oxide (Dy_2O_3), it is done so in an amount of 2-5% with the total content of Dy in the mixture being in the restricted range of 1-1.5%.

This invention provides a more economical permanent magnet of the Fe-B-MM type which has controlled magnetic coercivities much more effectively tailored to the needs of automotive applications; the permanent magnet is advantageously made from an alloyed powder designed to have a controlled coercive field in the range of 4-8 KOe, an energy produce in the range of 10-17 MGOe, and M_s of at least 65 Emu/gram, and desirably a T_c of at least 250°C.

The permanent magnet embodying the invention employs dual magnetic phases in a new, advantageous manner, redistributes the nonmagnetic phases in a novel manner, is much less costly than the known iron-boron-rare earth (Fe-B-R) or rare earth-cobalt type magnets, and yet exhibits, desirably, an energy product in the range of 14-17 MGOe and a coercivity in the range of 5-8 KOe.

The magnet includes a phase redistributing the agent that increases the coercivity and energy product of such material and promotes impediment phases for greater domain wall pinning.

Preparation of Metal Alloy Powder.

The magnets of this invention are made by powder metallurgy techniques and are iron-misch metal based (more than 70% by weight). Iron is one of the most abundant elements on earth and is very inexpensive. Misch metal is also very abundant and because it does not need the purification process of purer rare earth elements (like neodymium) it is much less expensive. Boron acts as a fluxing agent for sintering.

The coercive fields are significantly increased with the addition of controlled amounts of Al which promotes impediment phases or locking of dual iron-rich intermetallic phases and redistributes the nonmagnetic phases. Al can be added as an element or as ferro aluminum to the melt for the ingot.

The substitution or addition of Dy for MM can be made either to the melt for the as-cast samples, i.e., through the addition of elemental Dy, or by blending the as-cast powder with Dy_2O_3 (which is much less expensive) and then proceeding with the aligning, compacting and sintering procedure. Ni and other modifying agents, such as up to 3% Cr for corrosion resistance or up to 10% cobalt, can be added as elements to the melt for the as-cast ingot.

The combination of chemical composition, control of such composition during processing, and heat treatment leads to a special microstructure having a multiphase (magnetic) system. This is quite different from the Fe-Nd-B microstructure where only one predominant magnetic phase ($Fe_{14}Nd_2B$) is observed.

For purposes of the preferred mode, an arc melted ingot (under an argon atmosphere) is formed from a starting melt consisting essentially of, by atomic weight percent: 12-22% MM, 1-8% Al, 6-10% B, up to 5%

Dy and/or 10% Ni as a substitute or adjunct of MM or Fe, respectively, up to 3-10% of an agent for modifying physical properties other than magnetic properties, .1-.43% oxygen, and the remainder Fe, with iron being present in an amount of at least 60%. Misch metal, as used herein, means a material having at least four naturally occurring insoluble cerium earth metals with at least 20% of such earth materials consisting of cerium and/or lanthanum. Cerium earth metals is a group consisting of La, Ce, Pr, Nd, Sm, and Sc; such metals are often referred to as light rare earth metals. The misch metal will contain typically 3-4% heavy rare earth metals. Such misch metal may be derived from Indian sources which have been analyzed to contain 52% Ce, 20% La, 15.7% Nd, 4.8% Pr, 3-4% heavy rare earth metals. Synthetic misch metals (labeled Didymium) have been devised to contain 60% Pr, 0% Ce, 20% La, and 20% Nd; 40% Ce, 0% La, 50% Nd, and 10% Pr; 90% Nd, 0% Ce, 0%, La, and 10% Pr; 5% Ce, 0% La, 80% Nd, and 15% Pr. Such synthetic misch metals result from the elimination of Ce and/or La. For purposes of this invention, only those Didymiums which have Ce and/or La in an amount of 20% will suffice for use in the process described herein.

This invention advantageously and preferably uses misch metal that results from an early stage of beneficiating rare earth ores, prior to the removal of Ce or La. However, certain of the Didymiums can be used as indicated (resulting from a later stage of rare earth processing) as long as Ce and/or La constitute at least 20% of the Didymium.

Misch metal is often produced by beneficiating monazite ore to a concentrated combination of rare earth salts; these commercial salts are then converted to chlorides and subjected to electrolysis of such fused anhydrous rare earth chlorides in NaCl or KCl (see the cited references in U.S. patent 4,597,938, or "The Metallurgy of Non-Ferrous Metals", The Rare Earth Metals, by W.H. Dennis, Chapter 21 (1954), or Rare Metals Handbook, by Clifford Hampel, Chapter 16 (1954)).

The introduction of aluminum is important to this invention because it promotes redistribution of nonmagnetic phases (such as a rare earth-rich phase designated R-Fe-O which forms at the temperature level of about 600°C), primarily to the grain boundaries, and promotes impediment between dual magnetic phases as a result of such redistribution. If aluminum is present in an amount less than 1%, the coercivity will fail to increase after sintering. If aluminum is added in an amount greater than 8%, the remanence and T_c will be adversely affected. Boron, if used in an amount less than about 6%, will fail to produce $R_2Fe_{14}B$ phases, and if added in an amount greater than 10%, will adversely affect the magnetic properties of the shape.

The introduction of a small amount of Dy, either as an oxide or as a rare earth metal, is desirable to increase the coercive field above that obtained with misch metal or to offset the loss in coercivity as a result of using aluminum or misch metal at the low end of the prescribed ranges. Ni is added as a substitute or adjunct for Fe and functions to increase coercivity when using Al or misch metal at the low end of the prescribed ranges. However, the chemical system can function with or without the presence of Dy or Ni. It has been found that if Dy is added in an amount less than 1%, the desired benefits of an increase in anisotropy and an increase in coercive field will not be obtained. If added in an amount greater than 5%, there may be a reduction in remanence. Ni can be used in a similar fashion but with less effectiveness.

Modifying agents, such as 0-3% chromium, can be added to the melt to enhance corrosion resistance of the magnet material, or 0-10% cobalt my be added to enhance the Curie temperature. Such modifying agents are added to influence the physical properties of the material that are not magnetic properties.

The ingots resulting from arc melting have a purity of at least 99.8% and the ingredients thereof are first crushed under argon using a micro-mill. The powder resulting is then ball milled under moisture-free toluene using an attritor to achieve uniform particle size and homogeneous composition. The milling time is controlled to produce an average particle size that is preferably in the range of 2-5 microns, but may not be smaller than about 2 μ's, and specifically a critical particle size of 1.72 micrometers for certain types of chemistry.

Sintering, particle size, and oxygen concentration are interrelated factors for the development of the better hard magnetic properties. Improper processing of the ingot can result in the oxidation of the measured rare earths leading to a decrease of magnetic properties. Preferably, no vacuum is used during milling to dry; the powder should not be dried. It appears that the decrease in remanence and coercivity after sintering corresponds to a critical particle size at which the Fe-MM-B crystallites are affected significantly by the formation of bulk oxides, which size is 1.7 microns. For powder particles larger than the critical powder size, all the oxygen is chemisorbed and does not tend to reduce the rare earth content. For powder particles smaller than the critical powder size, the oxygen is partially chemisorbed and partially in the form of bulk oxides. It has been found that the corresponding critical maximum oxygen concentration for the type of alloys under consideration for this invention, to promote excellent properties, is 0.43 weight percent. By controlling oxidation of the powder through particle size control, liquid toluene cover, and lower sintering temperatures, the magnetic properties are increased.

Preparation of Shapes for Subsequent Sintering

The alloyed powder mixture must be protected against oxidation; it is preferably protected by a liquid cover or toluene, of other inorganic solvent protector, that is added in amounts that thoroughly wet the powder without much excess liquid. The wet powder is measured in predetermined quantities and aligned in magnetic fields in the range of 5-10 KOe. These measured quantities are then subsequently and slowly pressed with about 5000 pounds in a compaction die in a direction perpendicular to the applied field, allowing the toluene to escape. Preferably, the shapes are pressed as blocks, cubes, cylinders or arcs. The pressure under which the powder mixture is compacted is about 50,000 psi (40,000-60-000 psi) to render a presintering density of 70-80%. The shapes are green bodies characterized by dominant magnetic phases designated $R_2Fe_{14}B$ which is present in an amount of about 65-75%. The remainder of the green body is comprised of nonmagnetic phases RFe_4B_4 and Rx-Fe-O (rare earth-rich) where x is at least 30-40. The magnetic properties of such green bodies comprise an energy product of 10-15 MGOe, a remanence of 65-80 Emu/gram, and a coercivity of 4-8 KOe. The intrinsic coercivity of such green bodies is about 7.0 KOe.

Sintering and Subsequent Heat Treatment

The pressed shapes are heated in a high vacuum (i.e., 10^{-4} Torr or more), preferably in stages, first to about 400°C for 8-15 minutes to de-gas all of the toluene, and then to the temperature range of 1000-1100°C for .5-9 hours (preferably one hour). The shapes are then quenched to room temperature with a quenching rate of 100-200°C/minute, using flashing of argon (high purity). Sintering is carried out in a high vacuum of about 10^{-4} Torr or more. Cooling is carried out until the shapes are below at least 50°C and preferably 25°C.

The hard magnetic properties can be obtained with or without a post-sintering heat treatment. Without the heat treatment, the process is easier and therefore less expensive, but H_c is slightly lower. The heat treatment consists of heating to a temperature level of 550-650°C for about 1-4 hours (preferably 190 minutes) in a high vacuum, then cooled by flashing argon.

The resulting permanent magnets will have a crystalline microstructure characterized by a matrix dominated by at least two $R_2Fe_{14}B$ phases; for example, one being with a light rare earth and the other with a heavy rare earth, resulting in distinctly different magnetic properties. Since each of the $R_2Fe_{14}B$ phases have different magnetic properties, their coexistence tends to create domain wall pinning that leads to an increase in coercivity. This is clearly reflected on the "effective initial curves" of A.C. demagnetized samples where there is a critical field below which the domain walls are unpinned leading to an increase in magnetization. The nonmagnetic phases will constitute 15-20% by volume of the final material with the rare earth-rich phase predominating in the grain boundaries. The increased redistribution of the nonmagnetic phases to the grain boundaries is a unique aspect of this invention. One of the interesting aspects of such resulting permanent magnet is the thermal demagnetization characteristic. A generally square or rectangular hysteresis loop tends to suggest that uniformity in coercivity is related to the presence of two $R_2Fe_{14}B$ phases causing a locking in domain walls leading to such hysteresis squareness. This microstructure tends to lock the domain walls against sliding and thus maintains a high level of coercivity and remanence.

Crystal size of the resulting permanent magnet will be in the range of 5-10 microns. Essentially, by volume, 70-75% of the magnet material will be the iron-rich intermetallic ferromagnetic phases, 1-5% boron-rich phase, and about 15-19% rare earth-rich phase. The latter two nonmagnetic phases will reside essentially in the grain boundary.

Examples

Considerable experimentation was carried out to develop the unique processing parameters that functions best with the lean chemistry of this invention. Such processing controls have been optimized to be as described in the best mode, using oxidation protection by toluene and high vacuum, mean particle size control of about 2 microns, degassing, sintering temperature of 1040°C for one hour, cooling by argon flashing, and annealing at 650°C for two hours followed also by argon flashing to cool. The data for such process parameter optimization is not presented in the tables. The data presented in Tables I and II demonstrates the lean chemistry necessary to function with such processing. For each of the samples, an arc melted ingot of approximately 100 grams was first crushed under argon using a micro mill and then ball milled for varying periods of time to give an average particle size of about 2 microns and an oxygen content of about .4%. Ball milling was carried out under moisture-free toluene using an attritor to achieve uniform particle size and homogeneous composition. The particle size and oxygen concentration was measured using micrographs obtained with Jeol 100 C scanning electron microscope. In all cases, iron was present in the range of 60-80% atomic weight as the remainder for the chemistry. In Table I, the rare earth constituency was modified and varied throughout the samples utilizing misch metal in various combinations along with varying aluminum amounts and the presence or absence of Dy or Ni. The use of a post-heat treatment (annealing) was generally used but sometimes eliminated as indicated. The effectiveness of these variables are reflected in the level of H_c (KOe), M_s (Emu/gram), and T_c (°C).

All of the samples listed in Table I fall within the broad operational chemistry ranges of this invention, whereas the samples of Table II fall outside the invention herein. In Table I, samples 1-8 illustrate the effect of varying Al while maintaining B at 8-10% and MM at the high end of the inventive range (18-22%). Sample 5 demonstrates the effect of not using a post heat-treatment (annealing). Samples 9-21 illustrate the addition by Dy (added as an oxide after milling of the alloy powder) along with variations in the amount of MM and/or Al. Samples 22-27 depict the use of Ni as an adjunct to Al, MM and/or Dy.

In Table II, sample 1 shows the properties of a standard Fe-Nd-B magnet material. Sample 2 shows the effect of using Nd and MM. Samples 3 and 5-10 illustrate the elimination of aluminum. Samples 5-8 and 11 show the effect of exceeding or underusing the limits for MM or B.

While particular examples of the invention have been illustrated and described, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention, and it is intended to cover in the appended claims all such changes and equivalents as fall within the true spirit and scope of the invention.

TABLE I

Sample	Chemistry					Annealing	Physical Properties		
	MM	B	Al	Dy	Ni		H_c (KOe)	M_s (Emu/Gram)	T_c (°C)
1	20	8	5	--	--	Yes	4.0	68	260
2	20	8	8	--	--	Yes	5.5	70	250
3	22	10	5	--	--	Yes	9.0	65	260
4	22	8	5	--	--	Yes	7.0	65	250
5	22	8	5	--	--	No	4.0	65	250
6	20	10	3	--	--	Yes	4.0	75	265
7	18	8	8	--	--	Yes	3.9	70	250
8	18	10	4	--	--	Yes	8.1	65	245
9	18	8	1	1	--	Yes	4.5	83	265
10	14	8	1	2	--	Yes	4.0	84	265
11	14	8	3	1	--	Yes	4.3	82	260
12	20	8	5	1	--	Yes	6.0	65	270
13	14	8	1	2	--	Yes	6.8	70	250
14	14	8	2	2	--	Yes	7.0	68	250
15	16	8	5	2	--	Yes	5.5	80	260

TABLE I - Continued

Sample	Chemistry					Annealing	Physical Properties		
	MM	B	Al	Dy	Ni		H_c (KOe)	M_s (Emu/Gram)	T_c (°C)
16	22	8	5	1	---	Yes	9.0	63	260
17	12	8	1	4	---	Yes	6.0	80	260
18	14	8	1	3	---	Yes	9.5	88	260
19	18	8	1	5	---	Yes	10.5	82	260
20	13	10	1	5	---	No	5.0	73	258
21	13	10	1	5	---	Yes	8.9	82	260
22	16	8	1	0	3	Yes	5.5	90	245
23	14	8	2	0	3	Yes	8.4	82	240
24	14	8	1	2	6	Yes	9.1	72	255
25	16	8	1	0	6	Yes	4.5	89	245
26	18	8	1	0	5	No	4.0	80	260
27	16	8	1	0	8	Yes	4.0	70	250

TABLE II

Sample	Chemistry MM	 B	 Al	 Dy	 Other	Annealing	Physical Properties H_c(KOe)	 M_s(Emu/Gram)	 T_c(°C)
1	0	10	0	--	Nd-20		12	150	310
2	10	8	0	--	Nd-8		8	120	300
3	16	8	0	--	Ni-8		3.5	60	250
4	20	8	10	--	--		3.5	55	250
5	10	10	0	--	--		0.5	--	--
6	24	8	0	--	--		6.0	55	--
7	20	4	0	--	--		1.0	50	--
8	20	14	0	--	--		6.0	50	--
9	20	8	0	3	--		2.5	75	265
10	20	8	0	--	--		1.0	60	260
11	20	8	9	--	--		5.5	60	250
12	18	8	8	--	--		4.0	55	250
13	16	8	1	--	--		2.0	87	245
14	17	8	3	--	--		1.0	65	250
15	18	10	3	--	--		2.5	75	250
16	18	8	5	--	--		2.5	80	250
17	16	8	3	--	--		1.5	80	255

Claims

1. A method of making an iron based permanent magnet, comprising:

(a) preparing a metallic powder having an average particle size about, but above, 2 microns and a composition consisting essentially, by atomic weight percent, of: 12-22% misch metal, 1-8% Al, 6-10% B, less than .43% oxygen, substitutional agents of up to 5% Dy as a substitute or adjunct of misch metal and/or up to 10% Ni as a partial substitute or adjunct of Al, up to 3-10% of a modifying agent for modifying physical properties other than magnetic properties, and the remainder Fe, said substitutional and/or modifying agents only being present in an amount that would not prevent Fe from being present in an amount of substantially at least 60%, said powder having essentially a multiphase crystalline structure dominated by at least two $R_2Fe_{14}B$ phases;

(b) aligning said powder in a magnetic field;

(c) compacting said aligned powder into a shape; and

(d) sintering said shape at a temperature and for a period of time to fuse said powder, redistribute intermetallic phases, and increase the proportion of said $R_2Fe_{14}B$ phases to at least 70% by volume of said shape, said sintered shape being cooled to a temperature of 50°C or less, said powder being protected against oxidation during, prior to and between at least steps (b) through (d).

2. The method as in claim 1, in which said misch metal of step (a) consists of at least four naturally occurring insoluble cerium earth metals and at least 20% of such misch metal consists of cerium and lanthanum.

3. The method as in claim 1, in which said powder is formed of an alloy of Fe-Al-MM-B and said Dy, if present, is added to said powdered alloy as an oxide.

4. The method as in claim 1, in which in step (d) said cooling is carried out at a rate of 100-200°C per minute.

5. The method as in claim 1, which additionally comprises a step (e) of annealing said sintered shape to a temperature in the range of 550-650°C for a period of 1-4 hours, and thereafter quenching to room temperature.

6. The method as in claim 5, in which said sintering and annealing is carried out in a vacuum of at least 10^{-4} Torr.

7. The method as in claim 6, in which said cooling of step (d) and quenching of step (e) is carried out by flashing high purity argon.

8. The method as in claim 1, in which the sintered shape has a crystalline structure additionally comprising nonmagnetic phases of RFe_4B_4 and a rare earth-rich phase residing essentially in the grain boundaries of said alloy.

9. The method as in claim 1, in which said at least two $R_2Fe_{14}B$ phases have different magnetic properties causing domain wall pinning and a resultant increase in coercivity.

10. The method as in claim 1, in which step (b) is carried out by use of a magnetic field of 5000-8000 Oersteds.

11. The method as in claim 1, in which step (c) is carried out by use of a pressure of 40,000-60,000 psi.

12. The method as in claim 1, in which said shape is a block, arc, cylinder or cube.

13. The method as in claim 1, in which sintering of step (d) is carried out at a temperature of 1000-1100°C for a period of .5-9 hours.

14. The method as in claim 1, in which the heat-up for sintering is carried out in two stages, whereby said shape is heated to about 400°C for 8-15 minutes and then heated to the sintering temperature.

15. The method as in claim 1, in which protection is carried out by use of a covering of an anti-oxidation agent during step (a) and by use of a vacuum during steps (b) through (d).

16. The method as in claim 15, in which said agent is toluene.

17. The method as in claim 1, in which step (d) is carried out to provide a sintered density of greater than 99% of theoretical density.

18. The method as in claim 1, in which the crystal size of the sintered shape is in the range of 5-10 angstroms

19. The product resulting from the practice of claim 1, characterized by a coercivity of at least 4-8 Oe, a remanence of at least 65 Emu/gram, an energy product of 10-17 MGOe, and a Curie temperature of at least 250°C.

20. The method as in claim 1, in which said misch metal is the result of electrolysis of fused anhydrous rare earth chlorides in Na, Cl or KCl.

21. The method as in claim 1, in which said misch metal is the result of beneficiating monzite ore to a concentrated combination of rare earth salts and then subjecting the latter to electrolysis.

22. A method for producing permanent magnet materials of the Fe-B-MM type, comprising:

(a) preparing a metallic powder having a mean particle size of 2-5 microns and an alloyed composition comprising, by atomic weight percent, of: 60-80% Fe, 1-8% Al, 6-10% B, and 12-22% MM, where MM is a misch metal having at least four elements comprised of naturally occurring insoluble cerium earth metals and at least 20% of MM consists of cerium and/or lanthanum, said powder having essentially a multiphase crystalline structure dominated by the $R_2Fe_{14}B$ phases;

(b) aligning said powder in a magnetic field;

(c) compacting said aligned powder into cylinders; and

(d) sintering said cylinders at a temperature in the range or 1000-1100°C to increase the proportion of said $R_2Fe_{14}B$ phase to at least 75% by volume.

23. A permanent magnet formed of a sintered alloy comprising misch metal, boron, Al and Fe, the sintered alloy having a crystalline microstructure with, by volume, 70-75% or iron-rich intermetallic ferromagnetic phases, 1-5% of a boron-rich phase, and about 15-19% of a rare earth-rich phase, the latter two nonmagnetic phases residing essentially in the grain boundaries of the microstructure.

24. The magnet of claim 23, in which there are at least two iron-rich phases, one formed with heavy rare earth metals and the other with light rare earth metals, said two phases resulting in domain wall pinning to increase coercivity.

25. The magnet as in claim 23, in which said magnet exhibits physical properties of: H_c of 4-8, KOe, M_s of at least 65 Emu/gram, and an energy product of 10-17 MGOe.