

ADH/3809

FINE-GRAINED ANISOTROPIC POWDER FROM MELT-SPUN RIBBONS

This invention pertains to permanent magnet materials based on iron-neodymium-boron type compositions. More particularly, this invention relates to a method for treating such materials as specified in the preamble of claim 1, so that the
5 powders are magnetically anisotropic.

Permanent magnets and magnetic materials based on iron, neodymium (and/or praseodymium) and boron are used worldwide in commercial applications.
10 U.S. Patents 5,056,585, 4,851,058 and 4,802,931 to Croat, for example, disclose a broad range of compositions that characterize the iron-neodymium-boron permanent magnet family. As indicated in these patents and in other publications, the
15 magnets contain a transition metal (TM) component, usually iron or iron mixed with cobalt; a rare earth element (RE) component, usually neodymium including mixtures of neodymium with praseodymium and small amounts of the other rare earth group elements; and
20 boron. As normally employed in commercial use, these compositions usually consist essentially, on an atomic percentage basis, of about 10 to 18 percent of the rare earth constituent, at least 60 percent of which is neodymium and/or praseodymium, a small amount up to
25 about 10 percent boron, and the balance mainly iron or iron and cobalt. Preferably, these magnet compositions contain 70 percent or more of iron or iron and cobalt. The compositions may also contain small amounts of additives for processing or for the
30 improvement of magnetic properties. They contain the tetragonal crystal phase $RE_{1-x}TM_xB$ where RE and TM are as indicated above and below.

Sintered versions of these magnetic materials have received wide commercial acceptance. Sintered

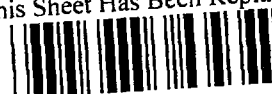
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magnets are made by preparing a crystalline powder or particles containing a grain of the tetragonal crystal phase RE_2TM_4B where RE is principally neodymium and/or praseodymium and TM is generally iron or iron and cobalt. The grains are typically one micrometre or larger such that the powder can be magnetically aligned, compacted into a green compact and sintered in vacuum or a non-oxidizing atmosphere. Sintering produces a fully-dense body having magnetic coercivity. Such a sintered permanent magnet is characterized by relatively large grains (i.e., greater than a few μm in diameter) of the 2-14-1 phase with an intergranular phase having a rare earth element content greater than the 2-14-1 phase.

U.S. Patents 4,981,532 and 5,110,374 (Takeshita et al) disclose a practice of treating an ingot or a powder of large-grained, polycrystalline material that includes the RE_2Fe_4B phase. In the treatment, hydrogen is introduced into the polycrystalline material to form a hydride(s). Subsequently, the hydride is decomposed and the hydrogen removed (desorbed) in order to recrystallize the 2-14-1 grain structure. In accordance with this practice, it is possible to form a powder that is either magnetically isotropic or magnetically anisotropic. Thus, one starts with a material that is crystalline, contains grains of appreciable size ($> 1 \mu m$) of the essential 2-14-1 phase and recrystallizes the grains so as to form usually smaller grains which may be aligned so as to constitute a magnetically anisotropic material. There is also a substantial market for permanent magnet compositions of fine grain structure ($< 500 \text{ nm}$ in average largest dimension) prepared by starting with a melt-spinning or other suitable rapid solidification process. The resultant

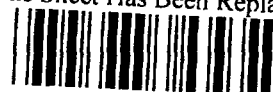


powder can be used to make magnetically-isotropic, resin-bonded magnets, as well as hot-pressed and hot-worked magnets.

The manufacture of rapidly solidified versions of the RE-TM-B family of permanent magnets starts with a molten alloy of suitable composition and produces melt-spun ribbon particle fragments. The rapid solidification practice is usually carried out by containing the molten alloy in a heated vessel under a suitable non-oxidizing atmosphere. The molten alloy is ejected in a very fine stream from the bottom of the vessel through a small orifice onto the peripheral surface of a spinning, cooled quench wheel. The quench wheel is usually made of a suitable high-conductivity copper alloy and may have a wear-resistant coating on the circumferential quench surface of the wheel. The wheel is typically water cooled so that prolonged melt spinning production runs may be carried out without any unwanted decrease in the rate of heat extraction from the molten alloy that impinges upon the wheel. It is necessary to maintain a suitably high heat extraction rate in order to consistently obtain the desired very fine grain microstructure.

The rate of cooling of the molten alloy is dependent upon a number of factors such as the amount of superheat in the molten alloy, the temperature of the quench wheel, the rate of flow of the molten alloy through the orifice onto the spinning wheel, and the velocity of the peripheral surface of the spinning wheel. All other factors being considered, the most readily controlled parameter of the cooling of the molten alloy is the velocity of the peripheral surface of the quench wheel.

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In the melt-spinning of a specific composition, it is possible to obtain a range of permanent magnet properties in the melt-spun material by varying quench wheel speed. The phenomenon is well disclosed and described in U.S. Patents 4,802,931, 4,851,058 and 5,056,585. As disclosed in these patents, by employing a given RE-TM-B composition and employing successively increasing quench wheel speeds starting with a relatively slow speed, it is possible to obtain a series of fine-grained crystalline products that respectively display values of magnetic coercivity that continually increase toward a maximum value and then decrease from that value. At the same time the values of magnetic coercivity are increasing, the values of magnetic remanence also increase over at least a part of the increasing wheel speed range as the cooling rate is increased. In the manufacture of many members of the family of rapidly solidified RE-TM-B magnets, it is preferred to operate the quench wheel rate slightly faster than the wheel speed at which maximum coercivity is obtained in the melt-spun ribbon. These materials are then extremely fine-grained or even apparently amorphous, and they can be annealed or hot-worked to a condition of desired high coercivity and magnetic remanence.

Such melt-spun materials are magnetically isotropic. It would be advantageous to have a practice for the treatment of such extremely fine-grained or amorphous materials which would produce magnetic anisotropy in such melt-spun ribbon particles. It has been possible in the prior art to produce magnetically-anisotropic powder from a melt-spun ribbon material by producing overquenched, melt-spun ribbon, hot-pressing the ribbon particles into a fully-densified body, hot-working the body to

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form elongated grains of magnetically-anisotropic material, and pulverizing or comminuting the hot-worked body to form the magnetically-anisotropic powder. Such a magnetically-anisotropic powder has
5 very good permanent magnet properties. However, it would be desirable to be able to produce a magnetically-anisotropic material directly from (or in) the melt-spun ribbon particles.

A method of making a fine-grained,
10 magnetically-anisotropic permanent magnet powder according to the present invention is characterised by the features specified in the characterising portion of claim 1.

Accordingly, it is an object of the present
15 invention to provide a method of producing magnetically-anisotropic powder material from a melt-spun powder that is initially very fine grained (typically less than 50 nanometres in grain size) or even apparently amorphous in its microstructure. It
20 is a more specific object of the present invention to introduce such magnetically-anisotropic properties into a melt-spun material by a practice of absorbing hydrogen into the fine-grained material and then removing the hydrogen under conditions which produce a
25 fine-grain material having anisotropic magnetic properties.

In accordance with a preferred embodiment of the present invention, these and other advantages are accomplished as follows.

30 The practice of the present invention is preferably applicable to a melt-spun material of the RE-TM-B type described that has been melt-spun to an optimally-quenched or to an overquenched condition. This is to say that the quench rate, typically through
35 control of the wheel speed, is such that the



coercivity of the as-quenched powder is optimal as is, or is less than could have been obtained using a somewhat lower wheel speed or lower cooling rate. The resulting material has a very fine-grained
5 microstructure of average grain size less than about 50 to 100 nanometres. It may even be substantially amorphous (i.e., have no readily perceptible crystallinity as indicated by x-ray diffraction pattern or by suitable microscopic technique such as
10 transmission electron microscopy, TEM).

The practice of the present invention is particularly applicable to those RE-TM-B compositions that contain, on an atomic percentage basis, about 10 to 16 percent of rare earth element where at least 60
15 percent of the rare earth composition is neodymium and/or praseodymium. The compositions also preferably contain a small amount of boron up to about 10 atomic percent. The balance of the composition is substantially transition metal, preferably iron or
20 iron with small amounts of cobalt (where cobalt is no more than 40 percent of iron plus cobalt). Preferably, the iron or iron plus cobalt content is at least 70 percent of the total composition. However, as will be disclosed hereinafter, small amounts of
25 additional alloying constituents may be employed to enhance the magnetically-anisotropic characteristics of the final powder. Examples of such additives, usually employed in amounts of less than one percent by weight of the overall composition, include (alone
30 or in combination) gallium, zirconium, carbon, tin, vanadium or tantalum.

Whilst the practice disclosed in U.S. Patents 4,981,532 and 5,110,374 was successfully carried out by recrystallization of a polycrystalline
35 large-grained ingot material, the inventors have

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discovered surprisingly that it is possible to employ an analogous practice on essentially a non-granular material that will produce 2-14-1 grains (with an intergranular phase) that have sufficient alignment so as to display magnetic anisotropic properties.

Starting with an optimally-quenched or overquenched melt-spun material, pulverized ribbon fragments of said material are subjected to hydrogen at a suitable elevated temperature under atmospheric pressure or slightly sub-atmospheric pressure for a brief period of time so as to form hydrides of the iron and rare earth constituents present in the material. Hydrogen is then evacuated from the environment around the powder to totally withdraw (or desorb) it from the powder. The hydrogenation and dehydrogenation is preferably carried out at a temperature in the range of about 700°C to 850°C. The period of hydrogenation and the period for hydrogen removal are both of the order of one hour or less. Upon removal of the hydrogen from the solid material and cooling to room temperature, it is found that a fine-grained material has been produced having grains less than about 500 nanometres, preferably less than 300 nanometres, in average dimension. The microstructure consists essentially of said fine grains of the $RE_2Fe(Co)_{14}B$ tetragonal crystal phase with a rare earth element-rich grain boundary phase about each of the tetragonal grains. Surprisingly, the resultant material, when pulverized to a powder, can be aligned in a magnetic field and hot-pressed or consolidated with a resinous bonding agent or other suitable binding material to produce a magnet which has preferred magnetic boundaries in the properties of magnetic alignment.

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Whilst the present invention has been described in terms of preferred embodiments thereof, other objects and advantages of the invention will become more clearly apparent from a detailed description thereof which follows.

Example 1

An alloy was prepared having the following composition on a weight percent basis: total rare earth content, 31.2 percent (of which 95 percent was neodymium, about 4 percent was praseodymium, and the balance incidental impurity amounts of other rare earths); cobalt, 2.5 percent; boron, 0.94 percent; gallium, 0.5 percent; and zirconium, 0.08 percent, with the balance iron and incidental impurities such as aluminium, silicon, and carbon. Expressed in terms of atomic proportions, the RE content was about 14.5 percent, the cobalt content about 2.5 percent, boron about 6 percent, gallium about 0.5 percent, zirconium about 0.08 percent and the balance iron. This molten alloy material was inductively heated in a quartz crucible to a temperature of 1420°C in a dry, substantially oxygen-free atmosphere. The material was ejected under a slight pressure of 20.7 kPa (3 psig) of argon atmosphere through a 0.635 mm (0.025 inch) diameter orifice in the bottom of the crucible onto the circumferential edge of a 254 mm (10 inch) diameter copper quench wheel. The material was melt-spun in portions at a variety of wheel speeds ranging from 13 metres per second to 24 metres per second. In the Table 1 below, the demagnetization properties of the as-melt-spun material at the respective wheel speed are summarized.

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Table 1

Wheel Speed (m/sec)	B_r (kG)	H_{ci} (kOe)	BH_{max} (MGOe)
13	7.22	17.70	10.81
15	7.26	17.80	11.0
17	7.53	17.96	12.0
20	5.19	11.92	3.91
22	3.18	2.38	0.99
24	1.39	0.53	0

5 It is seen that by varying the wheel speed whilst keeping the other parameters of the apparatus that affect rate of cooling substantially constant, a range of magnetic properties is obtained in the material produced. This range is characterized by an increasing magnetic coercivity with increasing wheel speed to a maximum magnetic coercivity and substantially maximum magnetic remanence values at a wheel speed of about 17 metres per second. Thereafter, the permanent magnet properties decrease as the cooling rate increases. This is due to the fact that, as the cooling rate increases, the rapidly-solidified material becomes a finer and finer grain size and reaches a near amorphous condition at the higher wheel speeds. It is preferable to practice the process of this invention on the optimally-quenched or overquenched materials. In other words, it is preferable to apply the practice of the present invention in the case of this example to material that has been melt-spun at a wheel speed of 17 metres per second or greater (up to about 24 m/sec).

The melt-spun samples produced at the various wheel speeds were then subjected to a hydrogen

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absorption-desorption practice as follows. A sample was placed in a furnace initially at ambient temperature. The furnace was evacuated of air and back-filled with hydrogen to a pressure of about 86,659.3 Pa (650 torr). The contents of the furnace were heated to 800°C over a period of 35 minutes. The melt-spun sample in the hydrogen atmosphere was maintained at 800°C for three minutes. The hydrogen was then pumped out of the furnace utilizing a vacuum pump with the pumping continuing so as to reach a pressure of 133.322×10^{-2} Pa (10^{-2} torr). The desorption step at a temperature of about 800°C was continued for 10 minutes, and then the treated melt-spun ribbon particles were removed from the furnace and were cooled to room temperature within 10 minutes under vacuo. The ribbon particles had retained their shape. They had not been comminuted by the hydrogen treatment process.

This described process of hydrogen absorption-desorption was chosen as a result of some experimentation on a variety of melt-spun samples. In general, it is preferable to carry out the hydrogen absorption on the melt-spun material at a sub-atmospheric hydrogen pressure above about 79,993.2 Pa (600 torr). A pressure range of 79,993.2 to 101324.7 Pa (600 to 760 torr) is suitable. A pressure of about 86,659.3 Pa (650 torr) is preferred. Hydrogenation temperatures in the range of about 700°C to 850°C are preferred, with hydrogenation times up to one hour being suitable. Thereafter, the sample was maintained for an additional period of up to one hour during hydrogen desorption. It is preferable to continually pump the hydrogen from the furnace by evacuating the furnace to a pressure of 133.322×10^{-2} Pa (10^{-2} torr) or less. The ribbon particles are then



comminuted to a powder of suitable size for further processing into resin-bonded or hot-pressed magnets. Very fine particle sizes, e.g., - 0.025 mm (-500 mesh), show greater magnetic anisotropy but tend to show reduced values of magnetic coercivity.

The results of the above specific hydrogen absorption-hydrogen desorption practice are summarized in the following Table 2. The data summarized is a result of aligning the treated hydrogen and desorbed powder of 0.043 mm (325 mesh) (obtained by crushing the ribbon particles) in a magnetic field of 18 kiloOersted strength. The magnetization-demagnetization properties of the aligned powder were then measured in a direction parallel to the direction of alignment and in a direction transverse, i.e., perpendicular, to the direction of alignment. The demagnetization properties are summarized in the following Table 2 for the respective melt-spun samples.

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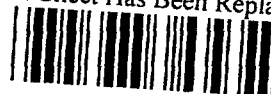


Table 2

Wheel Speed <u>(m/sec)</u>	B_r (kG)		H_{ci} (KOe)		BH_{max} (MGOe)	
	<u>Parallel</u>	<u>Perpendicular</u>	<u>Parallel</u>	<u>Perpendicular</u>	<u>Parallel</u>	<u>Perpendicular</u>
17	7.86	6.85	13.25	13.62	13.3	9.80
20	7.78	6.84	12.86	13.25	12.59	9.63
22	7.70	6.93	13.64	13.92	12.51	10.02
24	7.78	6.76	12.73	13.06	12.89	9.44

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It is seen by examination of the magnetic properties summarized in the above table that each of the rapidly-solidified materials that were subjected to hydrogen absorption-hydrogen desorption yielded a permanent magnet material that displayed preferred or stronger magnetic properties in the direction parallel to the direction of original particle alignment. In other words, the material displayed magnetic anisotropy. The average grain size of the material was about 250 to 300 nanometres as detected by transmission electron microscopy (TEM). Preferably, the average grain size of the product should be no greater than about 500 nanometres. As a result, the rapidly-solidified, magnetically-anisotropic material is suitable for many applications that require slightly higher magnetic properties than the magnetically-isotropic form of the rapidly-solidified, permanent magnet material.

Example 2

Alloys of the following compositions were prepared for melt-spinning into an overquench condition and for subsequent processing by the hydrogen absorption-hydrogen desorption process. The several alloys were composed as follows, where TRE stands for total rare earth content consisting of about 95 percent by weight neodymium, 5 percent praseodymium and the balance trace amounts of other rare earth elements. The following compositions are given on a weight percent basis.

E alloy contained 30.5 percent TRE, 2.5 percent cobalt, 0.95 percent boron and the balance iron.

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Alloy 223 contained 31.3 percent TRE, 2.5 percent cobalt, 0.91 percent boron, 0.17 percent tin and the balance iron.

Alloy 364 contained 31.3 percent TRE, 2.5 percent cobalt, 0.84 percent boron, 0.08 percent niobium and the balance iron.

Alloy 320 contained 30.0 percent TRE, 2.5 percent cobalt, 0.95 percent boron, 0.84 percent vanadium and the balance iron.

Alloy 374 contained 30.1 percent TRE, 2.5 percent cobalt, 1.0 percent boron, 0.49 percent gallium, 0.10 percent tantalum and the balance iron.

Each of these materials was melt-spun as described in Example 1 above. Each was melt-spun at a wheel speed of 20 metres per second so as to produce an overquenched material. The overquenched samples were successively subjected to a hydrogen absorption-hydrogen desorption process exactly like the specific practice described in Example 1. Following cooling from the hydrogen desorption step, powdered materials were aligned in a magnetic field and their magnetic properties measured. The properties are summarized in the following Table 3.

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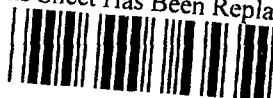


Table 3

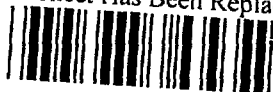
<u>Alloy</u>	<u>B_r (kG)</u>		<u>H_{ci} (KOe)</u>		<u>BH_{max} (MGOe)</u>	
	<u>Parallel</u>	<u>Perpendicular</u>	<u>Parallel</u>	<u>Perpendicular</u>	<u>Parallel</u>	<u>Perpendicular</u>
E	7.33	6.63	11.74	11.92	10.87	9.26
223	7.84	6.89	11.91	12.29	11.85	9.56
364	7.18	6.64	12.88	13.03	10.29	8.83
320	7.44	6.64	12.94	13.04	11.73	9.91
374	7.58	6.94	12.40	12.67	11.52	9.68



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It is seen that each of the above compositions displayed magnetic anisotropy after being processed by the hydrogen absorption-hydrogen desorption process. It is seen that alloy 223
5 containing a small amount of tin, alloy 320 containing a small amount of vanadium and alloy 374 containing small amounts of gallium and tantalum displayed stronger magnetic properties than alloy E with no additives other than the basic iron-cobalt-rare
10 earth-boron composition or alloy 364 containing a small amount of niobium.

Thus, in general, the practice of the present invention is applicable to optimally-quenched or overquenched materials based on the RE-TM-B system.
15 It is possible to obtain a fine-grained (preferably less than about 300 nanometres in average largest dimension, suitably no greater than about 500 nanometres) magnetically-anisotropic material. This has been accomplished by absorbing hydrogen into metal
20 particles that do not contain large grains of the 2-14-1 phase. Indeed, the starting material consists of material that is extremely fine-grained or material in which identifiable grains are not readily observable. The rapidly-quenched material is usually
25 characterized by an x-ray diffraction pattern with diffuse or no peaks; in other words, a pattern that is characteristic of an extremely fine-grained or amorphous material. Upon hydrogenation, if the material is quenched to freeze the microstructure and
30 an x-ray diffraction pattern produced, diffraction peaks characteristic of neodymium hydride, iron boride and alpha iron are observed. There is no semblance of the essential 2-14-1 phase for permanent magnet properties in the hydrogenated structure. Following
35 hydrogen desorption and the heat treatment that is



concomitant with the hydrogen absorption and desorption steps, very small grains of the 2-14-1 phase, preferably less than about 300 nanometres in average greatest dimension, are detected by TEM. Also
5 detectable by TEM is a rare earth element-rich grain boundary phase around the 2-14-1 grains which contributes to the magnetic coercivity of the material.

Thus, in summary, a practice is employed of
10 rapidly absorbing hydrogen into a rapidly-solidified, fine-grained material at a suitable temperature, preferably of the order of 700°C to 850°C without inducing rapid grain growth of the material. After a brief period of hydrogen absorption, typically less
15 than one hour, the hydrogen is removed from the material as rapidly as practical. This process is also preferably carried out at a temperature of the order of 700°C to 850°C. The hydrogen is removed in a matter of minutes, preferably less than 60 minutes.
20 The dehydrogenated material is then rapidly cooled to room temperature, such as by back-filling the furnace with argon, so as to retain the necessary fine-grain character of the material.

The magnetically-anisotropic powder thus
25 formed will usually be magnetically aligned and bonded or formed into a permanent magnet body of desired shape. There are known practices to form such permanent magnets. The hydrogen treated-hydrogen desorbed particles may be reduced to a suitable
30 particle size for the shaping of the desired magnet configuration. Typically, the particles will be mixed with or coated (encapsulated) with a suitable bonding resin(s), stabilizers and the like. The particles may also be aligned and hot-pressed to a fully-dense,
35 anisotropic permanent magnet.



Whilst the present invention has been described in terms of a specific embodiment thereof, it will be appreciated that other forms which fall within the scope of the present invention could
5 readily be adapted by those skilled in the art. Accordingly, the scope of the present invention is to be considered limited only by the scope of the following claims.

The disclosures in United States patent
10 application No. 903,067, from which this application claims priority, and in the abstract accompanying this application are incorporated herein by reference.

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Claims:

1. A method of making a fine-grained, magnetically-anisotropic permanent magnet powder from alloy particles consisting essentially of grains of the tetragonal crystal phase $RE_2(Fe_xCo_{1-x})_{1.4}B_1$ with an intergranular phase surrounding the grains, where RE represents one or more rare earth elements including at least 60 percent neodymium and/or praseodymium, the value of x is in the range of 0.6 to 1, and the composition of the intergranular phase is richer in rare earth element content than the tetragonal crystal phase, which method includes the steps of heating the particles in a hydrogen atmosphere at a temperature for forming metal hydrides in the particles, and thereafter removing hydrogen from the particles and cooling the particles to form said magnetically anisotropic powder, characterised in that the composition of said alloy particles is such that, in molten precursor form, the alloy is susceptible to being rapidly cooled to solidification over a determinable and controllable range of cooling rates within which range a series of fine-grained crystalline products is formed that respectively display (a) values of magnetic coercivity that continually increase toward a maximum value and decrease from said maximum value as the cooling rate is increased and (b) values of magnetic remanence that increase over at least a part of such range as the cooling rate is increased, and said method includes the steps of rapidly solidifying said molten precursor composition at a maximum magnetic coercivity value cooling rate or greater to form alloy particles in which the average grain size is no greater than about 100 nanometres; heating the particles in a hydrogen atmosphere at a pressure no greater than atmospheric

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pressure at said temperature for forming metal hydrides in the particles, and thereafter removing hydrogen from the particles and cooling the particles to form said magnetically anisotropic powder, the time and temperature of hydrogen treatment and removal being such that the average grain size of the 2-14-1 phase in the powder is no greater than 500 nanometres.

2. A method of making a fine-grained, magnetically-anisotropic permanent magnet powder according to claim 1, in which the alloy comprises, on an atomic percentage basis, 10 to 18 percent of a rare earth element including at least 60 percent neodymium and/or praseodymium, 0.5 to 10 percent boron, and at least 70 percent iron or mixtures of iron with cobalt.

3. A method of making a fine-grained, magnetically-anisotropic permanent magnet powder according to claim 1, in which said molten precursor composition is cooled at a maximum coercivity value cooling rate or greater so as to form particles in which the average grain size is no greater than about 50 nanometres, the particles are heated in a hydrogen atmosphere at a pressure in the range of about 79,993.2 to 101324.7 Pa (600 to 760 torr) at a temperature in the range of 700°C to 850°C for forming said metal hydrides in the particles, and thereafter removing hydrogen from the particles and cooling the particles to form said magnetically anisotropic powder, the time and temperature of hydrogen treatment and removal being such that the average grain size of the 2-14-1 phase is no greater than 300 nanometres.

4. A method of making a fine-grained, magnetically-anisotropic permanent magnet powder according to any one of claims 1 to 3, in which the rapidly-solidified precursor composition comprises at least one additive selected from the group consisting

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of carbon, gallium, tantalum, tin, vanadium and
zirconium.

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