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Description

This invention relates to high temperature strain-anneal processing of extremely rapidly solidified compositions comprising iron, one or more rare earth metals and boron to produce useful permanent magnets. More particularly, this invention relates to the hot consolidation and hot working of overquenched compositions comprising iron, neodymium and/or praseodymium, and boron to form useful, magnetically-aligned permanent magnets.

Background

High energy product, high coercivity permanent magnet compositions comprising, for example, iron, neodymium and/or praseodymium, and boron, and methods of making them are disclosed in European Patent Application 0 108 474 (General Motors Corporation). An illustrative composition, expressed in atomic proportions, is

$$Nd_{0.13}(Fe_{0.95}B_{0.05})_{0.87}.$$

It is substantially the composition of a specific stable intermetallic phase that possesses high coercivity when formed as fine crystallites about 20 to 400 nanometers in largest dimension.

Melts of the above family of compositions can be very rapidly quenched, such as by melt-spinning, to produce a solid material, e.g., a thin ribbon. When the rate of cooling has been controlled to produce a suitable fine crystalline microstructure (20 nm to 400 nm), the material has excellent permanent magnet properties. On the other hand, faster cooling (overquenching) produces a material with smaller crystallites and lower coercivity. However, as disclosed, such overquenched material can be annealed to form the suitable crystal size with the associated high coercivity and high energy product.

An interesting and useful property of this neodymium-iron-boron composition (for example) is that it is magnetically isotropic. A fine grain, melt spun ribbon can be broken up into flat particles. The particles can be pressed in a die at room temperature to form a unitary body of about 85% of the material's density. Bonding agents can be employed before or after the compaction. The making of such bonded magnets is disclosed in European Patent Application 84301453.1 (General Motors Corporation), filed 6 March 1984. It was surprising to find that such bonded magnets displayed no preferred magnetic direction. Values of intrinsic coercivity or maximum energy product were not dependent upon the direction of the applied magnetic field. There was no advantage in grinding the ribbon to very fine particles and magnetically aligning the particles before compaction.

Such magnetically isotropic materials are very useful because they can be easily pressed (without magnetic alignment) into bonded shapes. The shapes can be magnetized in the most convenient direction.

It is recognized that the iron-neodymium-boron type compositions might provide still higher energy products if at least a portion of the grains or crystallites in their microstructure could be physically aligned and if such alignment produced at least partial magnetic domain alignment. The material would then have a preferred direction of magnetization. The material would be magnetically anisotropic and would have higher residual magnetization and higher energy product in the preferred direction. This has now been accomplished using overquenched melt-spun material by hot working the material to consolidate it to full density and to effect plastic flow that yields magnetic alignment. The same improvement can be accomplished on finely crystalline, high coercivity material (e.g., $H_{ci}>1000$ Oe) if the hot work is performed rapidly before excessive grain growth occurs and coercivity decreases.

EP—A—101 552 describes a sintered anisotropic permanent magnet of the Fe-B-R type.

It is an object of the invention to provide a fully densified fine grain, anisotropic, permanent magnet formed by hot working a suitable material comprising iron, neodymium and/or praseodymium, and boron. This anisotropic magnet has higher residual magnetization and energy product than isotropic magnets of like composition.

It is an object of the invention to provide a method of treating overquenched compositions containing suitable proportions of iron, neodymium and/or praseodymium, and boron at suitable temperatures and pressures to fully densify the material into a solid mass, to effect the growth of fine, high coercivity crystallites and to cause a flow and orientation of the material sufficient to produce macroscopic magnetic anisotropy.

It is another object of the invention to treat suitable transition metal-rare earth metal-boron compositions that do not have permanent magnet properties because their microstructure is amorphous or too finely crystalline. The treatment is by a hot working process, such as hot pressing, hot die-upsetting, extrusion, forging, or rolling, to fully consolidate pieces of the material, to effect suitable grain growth and to produce a plastic flow therein that results in a body having magnetic anisotropy. It is found that the maximum magnetic properties in such a hot worked body are oriented parallel to the direction of pressing (perpendicular to the direction of flow). In the direction of preferred magnetic alignment, energy products are obtainable that are significantly greater than those in isotropic magnets of like composition.

Brief summary

The invention is defined in the appended claims.

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

A molten composition comprising iron, neodymium and/or praseodymium, and boron is prepared. Other constituents may be present, as will be disclosed below. An example of a preferred composition, expressed in terms of atomic proportions, is

$$Nd_{0.13}(Fe_{0.95}B_{0.05})_{0.87}.$$

The molten material is cooled extremely rapidly, as by melt spinning, to form a thin ribbon of solid material that does not have permanent magnet properties. Typically, the material is amorphous in microstructure. It will not produce an x-ray pattern containing many discrete diffraction maxima like that obtained from diffraction in crystalline substances. When highly magnified, as in a scanning electron microscrope micrograph, no discrete grains (or crystallites) will be apparent.

The ribbon or other thin, solid form may be broken, if necessary, into particles of convenient size for an intended hot working operation. The particles are heated under argon to a suitable elevated temperature, preferably 700°C or higher, and subjected to short term hot working under pressure, preferably at least 68,947.6 kPa (10,000 psi). Such processing may be accomplished by any of a number of known hot working practices. The material may be hot pressed in a die. It may be extruded, or rolled, or die-upset, or hammered, Whatever the particular form of hot working employed, the several individual particles are pressed and flowed together until the mass achieves full density for the composition. In addition, the hot mass is caused to undergo plastic flow. During the exposure at high temperature the nonpermanent magnet microstructure is converted to a suitable fine grain crystalline material. The flow of the hot, fine grain material produces a body, that upon cooling below its Curie temperature, has preferred direction of magnetization and provides excellent permanent magnet properties.

As suitably practiced, the high temperature working produces a finely crystalline or granular microstructure (for example, up to about 0.4 to 0.5 micrometers in greatest dimension). Care is taken to cool the material before excessive grain growth and loss of coercivity occurs. The preferred direction of magnetization of the hot worked product is typically parallel to the direction of pressing and transverse to the direction of plastic flow. A significantly higher energy product is obtained when the body is magnetized transverse to the direction of plastic flow.

As previously stated, material of like composition and similar microstructure has been made without hot working. Such materials have been magnetically isotropic and had lower maximum energy product.

In another embodiment of the invention the starting material may be a high coercivity (>1000 Oe) isotropic material. Suitable hot working of the material will fully densify it and effect plastic flow to orient the fine crystallites in a magnetically anisotropic structure. However the duration of the hot working must be short so that the crystallites do not grow so large that the desirable magnetic properties are lost.

These and other objects and advantages of the invention will become more apparent from a detailed description thereof, which follows. Reference will be made to the drawings, in which:

Figure 1 is a cross-sectional view of a hot pressing die for practicing one embodiment of the invention;

Figure 2 is a second quadrant, room temperature, 4πM versus H plot of a sample produced by hot pressing;

Figure 3a is a photomicrograph at 600× magnification of a sample compacted to 85% of theoretical density in accordance with earlier work;

Figure 3b is a photomicrograph at 600× magnification of a sample hot pressed in accordance with the method of the invention;

Figure 3c is a photomicrograph at 600× magnification of a sample extruded in accordance with the method of the invention;

Figure 4 is a second quadrant, room temperature, 4πM versus H plot of a sample produced by extrusion;

Figure 5 is a Scanning Electron Microscope micrograph at 43,600× magnification, illustrating the texture of the fracture surface of an extruded sample prepared in accordance with the method of the invention;

Figure 6 is a second quadrant, room temperature, 4πM versus H plot of a sample produced by die upsetting in accordance with the method of the invention; and

Figure 7 is a second quadrant, room temperature, 4πM versus H plot of a sample produced by a different die upsetting practice in accordance with the method of the invention.

Detailed description

The method of the present invention is applicable to compositions comprising a suitable transition metal component, a suitable rare earth component, and boron.

The transition metal component is iron or iron and (one or more of) cobalt, nickel, chromium or manganese. Cobalt is interchangeable with iron up to about 40 atomic percent. Chromium, manganese and nickel are interchangeable in lower amounts, preferably less than about 10 atomic percent. Zirconium and/or titanium in small amounts (up to about 2 atomic percent of the iron) can be substituted for iron. Very small amounts of carbon and silicon can be tolerated where low carbon steel is the source of iron for the composition. The composition preferably comprises about 50 atomic percent to about 90 atomic percent transition metal component—largely iron.

The composition also comprises from about 10 atomic percent to about 50 atomic percent rate earth component. Neodymium and/or praseodymium are the essential rare earth constituents. As indicated, they may be used interchangeably. Relatively small amounts of other rare earth elements, such as samarium, lanthanum, cerium, terbium and dysprosium, may be mixed with neodymium and praseodymium without substantial loss of the desirable magnetic properties. Preferably, they make up no more than about 40 atomic percent of the rare earth component. It is expected that there will be small amounts of impurity elements with the rare earth component.

The overquenched composition contains about 1 to 10 atomic percent boron.

The overall composition may be expressed by the formula

$$RE_{1-x}(TM_{1-y}B_y)_x.$$

The rare earth (RE) component makes up 10 to 50 atomic percent of the composition (x=0.5 to 0.9), with at least 60 atomic percent of the rare earth component being neodymium and/or praseodymium. The transition metal (TM) as used herein makes up about 50 to 90 atomic percent of the overall composition, with iron representing about 80 atomic percent of the transition metal content. The other constituents, such as cobalt, nickel, chromium or manganese, are called "transition metals" insofar as the above empirical formula is concerned.

Boron is present in an amount of about 1 to 10 atomic percent (y=about 0.01 to 0.11) of the total composition.

For convenience, the compositions have been expressed in terms of atomic proportions. Obviously these specifications can be readily converted to weight proportions for preparing the composition mixtures.

For purposes of illustration, the invention will be described using compositions of approximately the following atomic proportions:

$$Nd_{0.13}(Fe_{0.95}B_{0.05})_{0.87}.$$

However, it is to be understood that the method of the invention is applicable to a family of compositions as described above.

Depending on the rate of cooling, molten transition metal-rare earth-boron compositions can be solidified to have microstructures ranging from:

(a) amorphous (glassy) and extremely fine grained microstructures (e.g., less than 20 nanometers in largest dimension) through

(b) very fine (micro) grained microstructures (e.g., 20 nm to about 400 nm) to

(c) larger grained microstructures.

Thus far, large grained microstructure materials have not been produced with useful permanent magnet properties. Fine grain microstructures, where the grains have a maximum dimension of about 20 to 400 nanometers, have useful permanent magnet properties. Amorphous materials do not. However, some of the glassy microstructure materials can be annealed to convert them to fine grain permanent magnets having isotropic magnetic properties The present invention is applicable to such overquenched, glassy materials. It is also applicable to "as-quenched" high coercivity, fine grain materials provided the materials are exposed only for short times, e.g., less than five minutes, at high temperatures, over 700°C, during the hot working.

Suitable overquenched compositions can be made by melt-spinning. In melt-spinning experiments the material is contained in a suitable vessel, such as a quartz crucible. The composition is melted by induction or resistance heating in the crucible under argon. At the bottom of the crucible is provided a small, circular ejection orifice about 500 microns in diameter. Provision is made to close the top of the crucible so that the argon can be pressurized to eject the melt from the vessel in a very fine stream.

The molten stream is directed onto a moving chill surface located about 6.35 mm (one-quarter inch) below the ejection orifice. In examples described herein the chill surface is a 25 cm diameter, 1.3 cm thick copper wheel. The circumferential surface is chrome plated. The crucible and wheel are contained in a box that is evacuated of air and backfilled with argon. In the experiments the wheel is not cooled. Its mass is so much greater than the amount of melt impinging on it in any run that its temperature does not appreciably change. When the melt hits the turning wheel, it flattens, almost instantaneously solidifies and is thrown off as a ribbon. The thickness of the ribbon and the rate of cooling are largely determined by the circumferential speed of the wheel. In this work, the speed can be varied to produce an amorphous ribbon, a fine grained ribbon or a large grained ribbon.

In the practice of the method of the present invention, the cooling rate or speed of the chill wheel preferably is such that an amorphous or extremely fine crystal structure is produced. Such a structure will be amorphous or will have finer crystals than that which produces a permanent magnet as is, for example, less than about 20 nanometers in largest dimension. As a practical matter, the distinction between an amorphous microstructure and such an extremely fine crystalline microstructure is probably not discernible. What is desired is an overquenched material that has less than optimum permanent magnetic properties but that can be annealed to produce improved permanent magnet properties. However, in accordance with the method of the invention, the material is not separately annealed. It is, in effect, annealed while it is hot worked to produce a magnetic microstructure that has anisotropic magnetic properties.

A few examples will further illustrate the practice of the present invention.

Example 1

An overquenched, melt spun ribbon was prepared. A molten mixture was prepared in accordance with the following formula:

$Nd_{0.13}(Fe_{0.95}B_{0.05})_{0.87}$.

About 40 grams of the mixture was melted in a quartz tube that was about 10 cm long and 2.54 cm in diameter. The quartz tube had an ejection orifice in the bottom, which was round and about 600 μm in diameter. The top of the tube was sealed and adapted to supply pressurized argon gas to the tube above the molten alloy. The alloy was actually melted in the tube using induction heating. When the melt was at 1400°C, an argon ejection pressure of about 20.68 kPa (3 psig) was applied.

An extremely fine stream of the molten metal was ejected down onto the rim of the above described wheel. The wheel was made of copper and the perimeter surface was plated with chromium. The wheel was initially at room temperature and was neither heated nor cooled during the experiment, except from contact with the molten metal ejected into it. The wheel was rotated at a rim velocity of about 35 meters per second (m/s).

A solidified melt spun ribbon came off the wheel. It was about 30 μm thick and about one mm wide.

This material was cooled too rapidly to have useful permanent magnet properties. In other words, it was overquenched. Had the wheel been rotated slightly slower, the ribbon could have been produced to have a microstructure affording useful hard magnetic properties.

The ribbon was broken into short pieces and they were placed into a cylindrical cavity 12 of a round die 10 like that depicted in Figure 1. The cavity was 9.525 mm (3/8 inch) in diameter and the material was contained by upper and lower punches 14. The die was made of a high temperature nickel alloy with a tool steel liner, and the punches were tungsten carbide.

The die and the contents were rapidly heated under argon with an induction coil 16 to a maximum temperature of 750°C. The temperature was measured using a thermocouple (not shown) in the die adjacent the cavity. The upper punch was then actuated to exert a maximum pressure of 220632.32 kPa (32,000 psi) on the broken-up ribbon particles. Heating and pressure were stopped. The workpiece was cooled to room temperature on the die. However, the total time that the workpiece was at a temperature above 700°C was only about five minutes. The consolidated workpiece was removed from the die. The resulting cylinder was hard and strong. It had a density of about 7.5 grams per cubic centimeter, which is susbtantially its full density.

The magnetic properties of the material were determined by cutting a piece from the cylinder and grinding a small sphere, about 2 mm in diameter, from the cut off piece. The sphere was magnetized in a known direction by subjecting it to a pulsed magnetic field having a strength of about forty kilo gauss ($1 G=10^{-4}T$). The sphere was then placed in a vibrating sample magnetometer with the positive magnetic pole of the sphere aligned with the positive pole of the magnetometer. The sample was subjected to a gradually decreasing magnetic field from +10 kOe to −20 kOe (1 Oe=79.6 A/m) that produced corresponding decreasing sample magnetization (4πM). In this manner the second quadrant demagnetization plot (4πM versus H) was obtained for the particular direction of magnetization.

The sample was removed from the magnetometer and magnetized in a pulsed field as before in a different direction. It was returned to the magnetometer and a new demagnetization curve determined. This process was again repeated and the respective curves compared. The sample displayed magnetic anisotropy.

Figure 2 contains four different second quadrant plots of 4πM versus H. The second quadrant portion of a hysteresis loop provides useful information regarding permanent magnet properties. Three of these plots in Figure 2 represent good properties. The residual magnetization at zero field (H=0) is high and the intrinsic coercivity, i.e., the reverse field to demagnetize the sample (4πM=0) is high. The upper curve 18 represents a favorable direction of magnetization obtained in the spherical sample. The lowest curve 20 represents the data obtained from a direction relatively far removed from the aligned direction of the hot pressed compact. The middle line 22 is the demagnetization plot also generated in the vibrating sample magnetometer of an isotropic array of the same ribbon from which its hot compact was made. These ribbon samples were heated (annealed) at a rate of 160°C per minute to a temperature of 727°C, and then cooled at the same rate to room temperature. The data obtained was normalized to a sample density of 100%. Thus plot 22 is of an isotropic magnet of the same composition as the anisotropic magnet produced in this example.

A hysteresis curve was also prepared from a sample of the original overquenched ribbon. The second quadrant portion is produced as curve 24 in Figure 2. It has relatively low intrinsic coercivity and residual magnetization.

Thus, the hot pressing operation produced a fully densified body and also produced flow in the material that oriented the microstructure so that it became magnetically anisotropic. In the preferred direction of magnetization (represented by curve 18) the residual magnetization and energy product are greater than in the isotropic material.

In addition to having excellent permanent properties at room temperature the hot pressed body retains its properties during exposure at high temperatures in air. A hot pressed body of this example was exposed at 160°C in air to a reverse field of 4 kOe for 1507 hours. It suffered only minimal loss in permanent magnet properties.

Figure 3a is a photomicrograph of a cross-section of a bonded magnet that was compacted at room temperature to 85% of full density. The plate-like sections of the original ribbon are seen to line up and be preserved in the bonded magnet. Figure 3b is a photomicrograph at the same magnification of a hot pressed specimen fully densified in accordance with the invention. The flat ribbon fragments are still perceptible at about the same size as in the bonded magnet, but there are no voids in this fully densified specimen.

Example 2

Another overquenched, melt spun ribbon was prepared by the method described in Example 1. The nominal composition of the ribbon was in accordance with the empirical formula

$$Nd_{0.13}(Fe_{0.94}B_{0.06})_{0.87}.$$

The ribbons were produced by quenching the melt on a chill wheel rotating at a velocity of 32 m/s. The thickness of the ribbon was approximately 30 µm and the width approximately one millimeter. This cooling rate produced a microstructure that could not be magnetized to form a magnet having useful permanent magnet properties.

Ribbon pieces were compacted at room temperature in a die to form a precompacted body of about 85% full density. The precompact was then placed in the cavity of a high temperature alloy die similar to that described in Example 1. However, the die had a graphite liner. Carbide punches confined the precompact in the die cavity. The die and its contents were quickly heated under argon to 740°C and a ram pressure of 68,947.6 kPa (10 kpsi) was applied in an attempt to extrude the preform. An unexpected form of backward extrusion was obtained as the precompacted material flowed out from between the punches and displaced graphite die liner to form a cup-like piece. After cooling to room temperature this piece was removed from the die and it was found that the extruded portion of the sample was of sufficient dimensions to allow density measurement as well as magnetic measurement. The extruded portion was fully densified.

A 2 mm cube was ground from a portion of the extruded metal and it was tested in a vibrating sample magnetometer. By magnetizing and demagnetizing the sample transverse to the cube faces it was observed that the specimen displayed magnetic anisotropy. Three orthogonal directions are displayed in Figure 4 by curves 26, 28 and 30. The separations of these second quadrant plots from different directions of magnetization results from physical alignment of magnetic domains within the sample. The greater the separation of the plots, the greater the degree of magnetic alignment. It is seen that the alignment for the extruded sample was even more pronounced than for the sample of Figure 1. The demagnetization curves for the annealed ribbon 22 and the overquenched ribbon 24 are also included in this figure as in Figure 2. It is seen that the coercivity of the extruded sample is even higher than that of the annealed ribbons presumably because a more appropriate crystallite size was achieved during the extrusion. The magnetization of the extruded sample in its most preferred direction is higher and results in higher energy product than that obtainable in isotropic annealed ribbons.

Figure 3c is a photomicrograph at 600× magnification of a cross-section of the extruded sample. It is seen that greater plastic flow occurred in the extruded sample as evidenced by the reduction in thickness of the original ribbon particles. It is believed that this plastic flow is essential to alignment of the magnetic moments within the material and that this alignment is generally transverse to the plastic flow. In other words, with respect to this sample, the magnetic alignment is transverse to the long dimension of the extruded ribbons (i.e., up and down in Figure 3c).

Figure 5 is a scanning electron microscope micrograph at nearly 44,000× magnification of a fracture surface of the extruded sample. It shows the fine grain texture.

Additional hot press tests, like Example 1, and modified extrusion tests, like Example 2, were carried out at various die temperatures in the range of 700 to 770°C and pressures in the range of 68,947.6 to 206,842.8 kPa (10,000 to 30,000 psi). These tests showed that full densification could be realized even at the lower pressures and temperatures. However, the samples prepared at the lower temperatures and pressures appeared to be more brittle. Optical micrographs revealed the ribbon pieces to have cracks similar to those present in Figure 3a. Evidently, higher pressure is required at temperatures of 750°C and lower before such cracks disappear as in Figure 3b. The preferred magnetization direction for the hot pressed samples is parallel to the press direction and perpendicular to the direction of plastic flow. Greater directional anisotropy develops when more plastic flow is allowed, as in the extrusion tests.

Example 3

This example illustrates a die upsetting practice.

Overquenched ribbon fragments of Example 2 were hot pressed under argon in a heated die, like that in Figure 1, at a maximum die temperature of 770°C and pressure of 103,421.4 kPa (15 kpsi). A 9.525 mm (3/8″) cylindrical body, 100% density, was formed. This hot pressed cylinder was sanded to a smaller cylinder (diameter less than 1 cm) with its cylindrical axis transverse to the axis of the original cylinder. This cylinder was re-hot pressed in the original diameter cavity along its axis (perpendicular to the original press direction) so that it was free to deform to a shorter cylinder of 9.525 mm (3/8″) diameter (i.e., die upsetting). The die upsetting operation was conducted at a maximum temperature of 770°C and a pressure of 110,316.16 kPa (16 kpsi). As in previous examples the part was cooled in the die. A cubic specimen was machined from the die upset body and its magnetic properties measured parallel and transverse to the press direction in a vibrating sample magnetometer, as in the above Examples 1 and 2.

Second quadrant, room temperature 4πM versus H plots for these two directions are depicted in Figure 6. Curve 32 was obtained in the direction parallel to the die upset press direction and curve 34 in the direction transverse thereto and thus parallel to the direction of material flow. It is seen that this die upset practice produced greater anisotropy than the single hot pressing operation or the extrusion test. This translates to a B_r of 9.2 kG (1 G=10^{-4}T) and an energy produced of 18 MGOe (1 MGOe=7.86 KJ/m^3) compared with isotropic ribbon values of Br=8 kG (1 G=10^{-4}T) and energy product of about 12 MGOe (1 MGOe=7.86 KJ/m^3).

Example 4

This example illustrates a die upsetting practice similar to Example 3, except a fully dense, hot pressed sample was die-upset with pressure applied in the same direction as the original hot press pressure.

Overquenched ribbon fragments of Example 2 were hot pressed under argon in a heated die, like that depicted in Figure 1, at a maximum temperature of 760°C and pressure of 103,421.4 kPa (15 kpsi). A 9.525 mm (3/8inch) cylindrical body, 100% density, was formed. This hot pressed piece was sanded to a smaller diameter (less than about 1 cm) and die upset in the same diameter cavity in a direction parallel to the first press direction. The die upset operation was conducted at a maximum temperature of 750°C and a pressure of 82,737.1 kPa (12 kpsi). The sample was cooled in the die.

A cubic specimen was machined from the die upset body and its magnetic properties measured in a vibrating sample magnetometer parallel and transverse to the die upset press direction as in the above example. Second quadrant, room temperature, 4πM versus H plots for these two directions are depicted in Figure 7. Curve 36 was obtained in the direction parallel to the die upset press directions and curve 38 in the direction transverse thereto. It is seen that this practice of hot pressing followed by die upsetting in the same direction produced greater anisotropy than was obtained in any of the previous samples. It is seen in Figure 7 that in the preferred direction of magnetization (curve 36) the remnant magnetization was greater than 11 kG (1 G=10^{-4}T), while the intrinsic coercivity was still greater than 7 kOe. The maximum energy product of this sample was 27 MGOe (1 Oe=79.6 A/m) (1 MGOe=7.86 KJ/m^3).

It is believed that still grater alignment can be obtained by a practice that provides greater plastic flow at elevated temperature. One may define an alignment factor by

$$(B_r)_{parallel}/(B_r)_{perpendicular},$$

where B_r is residual induction (at H=0) measured parallel to and perpendicular to, respectively, the press direction. An alignment factor of 2.46 was obtained in Example 4. An alignment factor of 1.32 has been achieved by die upsetting (like in Example 3). An alignment factor of 1.18 has been achieved for extrusion (like in Example 2).

This practice of high temperature consolidation and plastic flow can be viewed as a strain anneal process. This process produces magnetic alignment of the grains of the workpiece and grain growth. However, if the grain growth is excessive, coercivity is decreased. Therefore consideration (and probably trial and error testing) must be given to the grain size of the starting material in conjunction with the time that the material is at a temperature at which grain growth can occur. If, as is preferred, the starting material is overquenched, the workpiece can be held at a relatively high temperature for a longer time because some grain growth is desired. If one starts with near optimal grain size material, the hot working must be rapid and subsequent cooling prompt to retard excessive grain growth. For example, hot pressing experiments have been carried out on neodymium-iron-boron melt-spun compositions that have been optimally quenched to produce optimal grain size for achieving the highest magnetic product. During such hot pressing the material was over 700°C for more than five minutes. The material was held too long at such temperature because the coercivity was always reduced although not completely eliminated. Therefore, optimal benefits were not obtained.

Hot pressure eperiments were also conducted on annealed ingot that had a homogenized, large grain microstructure. When magnetized, such ingots contained very low coercivity, less than 500 oersted. The present hot pressing strain-anneal practice produced a significant directional dependence of B_r in the ingot samples, but no coercivity increase. It had been hoped that the strain-anneal practice would induce recrystallization in the ingot which would allow for development of the optimal grain size. The failure to obtain a coercivity increase in these experiments indicates that the strain-anneal practice is not beneficially applicable to large grained materials.

Thus, this high temperature-high pressure consolidation and hot working of suitable, transition metal, rare earth metal, boron compositions yields magnetically anisotropic product of excellent permanent magnet properties. For purposes of illustration, the practice of the present invention has been described, using specific composition of neodymium, iron and boron. However, other materials may be substituted or present in suitably small amounts. Praseodymium may be substituted for neodymium or used in combination with it. Other rare earth metals may be used with neodymium and/or praseodymium. Likewise, other metals, such as cobalt, nickel, manganese and chromium, in suitably small amounts, may be used in combination with iron. The preferred compositional ranges are described above.

While the invention has been described in terms of preferred embodiments thereof, it will be appreciated that other embodiments could readily be adapted by those skilled in the art. Accordingly, the scope of the invention is to be considered limited only by the following claims.

Claims

1. A method of making a magnetically-anisotropic permanent magnet through plastically deforming by hot-working an amorphous or finely crystalline alloy material, which alloy material is produced by rapid quenching and comprises iron, neodymium and/or praseodymium, and boron, to result in a body having a fine grain structure of crystal grain size up to 500 nanometres and cooling the body.

2. A method of making a permanent magnet according to claim 1, in which the hot-working is a hot-pressing operation by which the alloy material is consolidated into a fully-densified body.

3. A method of making a permanent magnet according to claim 1, in which the hot-working is carried out at an elevated temperature and pressure and for a time sufficient to consolidate the alloy material into a fully-densified body and to cause subsequent additional plastic flow of at least a portion of that body.

4. A method of making a permanent magnet according to claim 1, in which the alloy material is heated above 700°C, and is subjected to such a pressure as to hot-work it into a substantially non-porous body and to cause plastic flow of that body, followed by immediate cooling of that body to form said body having said fine grain structure.

5. A method of making a permanent magnet according to claim 1, in which the alloy material is subjected to a hot die-upsetting process at an elevated temperature and pressure to cause plastic flow in the body, a preferred magnetic direction in the resultant body being parallel to the die-upset press direction.

6. A method of making a permanent magnet according to claim 1, in which a melt-spun molten mixture consisting essentially of iron, neodymium and/or praseodymium and boron is quenched at such a rate as to form an over-quenched, thin, solid ribbon material, and pieces of the ribbon material are hot-worked at an elevated temperature and pressure and for a time sufficient to consolidate the pieces into a fully-densified body and to cause plastic flow of at least a portion of that body.

7. A hot-worked anisotropic permanent magnet comprising iron, neodymium and/or praseodymium, and boron, in which the magnet has a plastically-deformed, fine-grained microstructure of crystal grain size up to 500 nanometres.

8. A hot-worked anisotropic permanent magnet according to claim 7, obtainable by plastic deformation of an amorphous or finely crystalline material by a hot die-upsetting process, which magnet has a preferred magnetization direction parallel to the pressing direction used in the hot die-upsetting process.

Patentansprüche

1. Verfahren zur Herstellung eines magnetisch anisotropen Permanentmagneten durch plastische Verformung durch Warmbearbeitung eines amorphen oder feinkristallinen Legierungsmaterials, das durch rasches Abschrecken hergestellt ist und Eisen, Neodym und/oder Praseodym und Bor enthält, so daß sich ein Körper mit feinkörniger Struktur mit einer Kristallkorngröße bis zu 500 nm ergibt, und Abkühlen des Körpers.

2. Verfahren zur Herstellung eines Permanentmagneten nach Anspruch 1, bei dem die Warmbearbeitung ein Warmpreßvorgang ist, durch den das Legierungsmaterial zu einem vollständig verdichteten Körper verfestigt wird.

3. Verfahren zur Herstellung eines Permanentmagneten nach Anspruch 1, bei dem die Warmbearbeitung bei erhöhter Temperatur und Druck ausgeführt wird während einer Zeit, die ausreicht zur Verfestigung des Legierungsmaterials zu einem vollständig verdichteten Körper, und um nachfolgend zusätzliches plastisches Fließen mindestens eines Teiles des Körpers zu verursachen.

4. Verfahren zur Herstellung eines Permanentmagneten nach Anspruch 1, bei dem das Legierungsmaterial auf über 700°C erhitzt und einem solchen Druck unterworfen wird, daß es zu einem im wesentlichen nichtporösen Körper warmbearbeitet wird und plastisches Flißen des Körpers verursacht wird, gefolgt von unmittelbarem Abkühlen des Körpers, um den Körper mit der Feinkornstruktur auszubilden.

5. Verfahren zur Herstellung eines Permanentmagneten nach Anspruch 1, bei dem das Legierungsmaterial einer Warmmatrizen-Stauchverformung bei erhöhter Temperatur und erhöhtem Druck unterworfen wird, um plastisches Fließen in dem Körper zu verursachen, wobei eine bevorzugte Magnetrichtung in dem sich ergebenden Körper parallel zu der Matrizen-Stauchdruckrichtung liegt.

6. Verfahren zur Herstellung eines Permanentmagneten nach Anspruch 1, bei dem eine Schmelzspinn-Gemischschmelze, die im wesentlichen aus Eisen, Neodym und/oder Praseodym und Bor besteht, mit solcher Geschwindigkeit abgeschreckt wird, daß ein über-abgeschrecktes dünnes massives Bandmaterial gebildet wird, und Stücke des Bandmaterials bei einer erhöhten Temperatur und erhöhtem Druck während einer Zeit warmbearbeitet werden, die ausreicht, die Stücke zu vollständig verdichteten Körpern zu verfestigen und plastisches Fließen mindestens eines Teils des Körpers zu verursachen.

7. Warmbearbeiteter anisotroper Permanentmagnet, der Eisen, Neodym und/oder Praseodym und Bor umfaßt, wobei der Magnet eine plastisch verformte feinkörnige Mikrostruktur mit Kristallkorngröße von bis zu 500 nm besitzt.

8. Warmbearbeiteter anisotroper Permanentmagnet nach Anspruch 7, erzielbar durch plastische Verformung eines amorphen oder feinkristallinen Materials mit einem Warmmatrizen-

Stauchverfahren, wobei der Magnet eine bevorzugte Magnetisierungsrichtung parallel zu der bei dem Warmmatrizen-Stauchverfahren benutzten Druckrichtung besitzt.

Revendications

1. Procédé de fabrication d'un aimant permanent magnétiquement anisotrope per déformation plastique par façonnage à chaud d'un matériau constitué d'un alliage amorphe ou finement cristallin, ce matériau d'alliage étant produit par trempe rapide et contenant du fer, du néodyme et/ou du praséodyme, et du bore afin qu'il forme un corps ayant une structure à grain fin dont la dimension des grains cristallins est inférieure ou égale à 500 nm, et par refroidissement du corps.

2. Procédé de fabrication d'un aimant permanent selon la revendication 1, dans lequel le façonnage à chaud est une opération d'estampage à chaud au cours de laquelle le matériau d'alliage est consolidé sous forme d'un corps pleinement densifié.

3. Procédé de fabrication d'un aimant permanent selon la revendication 1, dans lequel le façonnage à chaud est réalisé à des pression et température élevées et pendant un temps qui suffit pour que le matériau d'alliage soit consolidé sous forme d'un corps pleinement densifié et pour qu'une partie au moins de ce corps subisse ensuite un fluage plastique supplémentaire.

4. Procédé de fabrication d'un aimant permanent selon la revendication 1, dans lequel le matériau d'alliage est chauffé à plus de 700°C et est traité à une pression telle qu'il subit un façonnage à chaud qui en fait un corps pratiquement non poreux et qu'un fluage plastique de ce corps est provoqué, l'opération étant suivie par un refroidissement immédiat de ce corps afin que celui-ci forme ledit corps ayant une structure à grain fin.

5. Procédé de fabrication d'un aimant permanent selon la revendication 1, dans lequel le matériau d'alliage est soumis à une opération de refoulement à chaud dans une matrice, à des pression et température élevées afin qu'un fluage plastique soit provoqué dans le corps, une direction magnétique préférentielle du corps résultant étant parallèle à la direction de compression lors du refoulement dan la matrice.

6. Procédé de fabrication d'un aimant permanent selon la revendication 1, dans lequel un mélange filé à l'état fondu et consistant essentiellement en fer, en néodyme et/ou en praséodyme et en bore est trempé à une vitesse telle qu'il forme un matériau constituant un mince ruban solide hypertrempé, et des morceaux du matériau constituant le ruban sont façonnés à chaud, à pression et température élevées et pendant un temps suffisant pour que les morceaux soient consolidés sous forme d'un corps pleinement densifié et pour qu'un partie au moins de ce corps subisse un fluage plastique.

7. Aimant permanent anisotrope façonne à chaud, contenant du fer, du néodyme et/ou du praséodyme et du bore, l'aimant ayant une microstructure à grain fin déformée plastiquement, la dimension des grains cristallins étant inférieure ou égale à 500 nm.

8. Aimant permanent anisotrope façonné à chaud selon la revendication 7, qui peut être obtenu par déformation plastique d'un matériau amorphe ou finement cristallin par une opération de refoulement à chaud dans une matrice, l'aimant ayant une direction d'aimantation préférentielle parallèle à la direction de compression utilisée dans l'opération de refoulement à chaud dans une matrice.

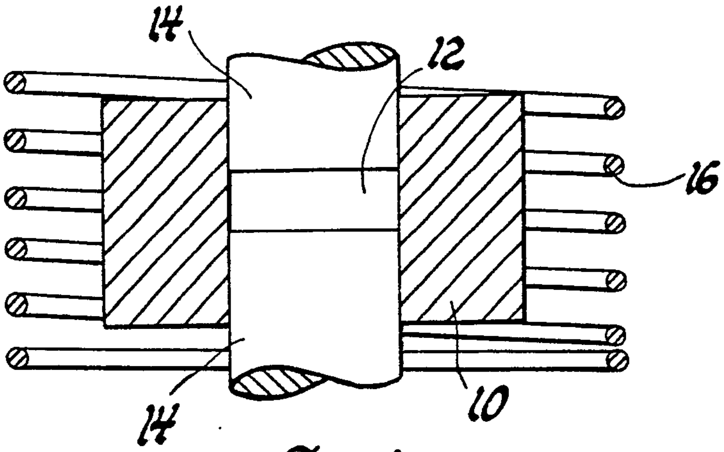
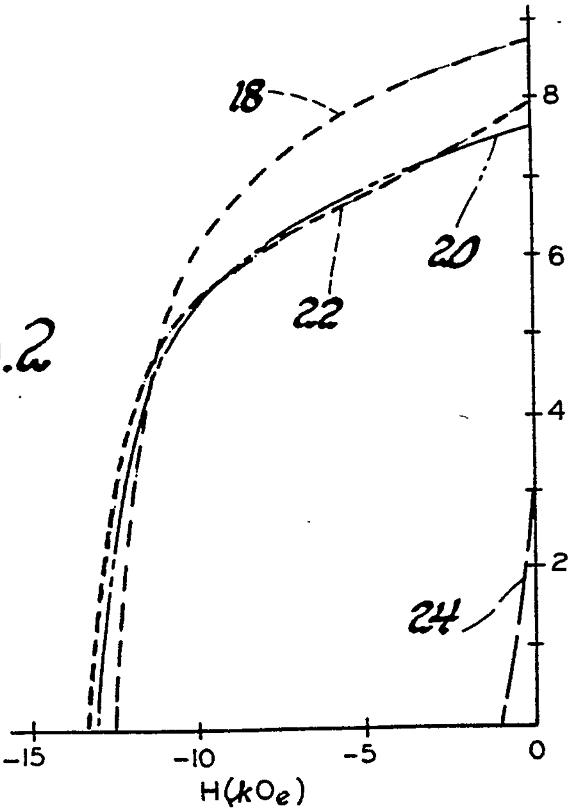


Fig.1

Fig.2



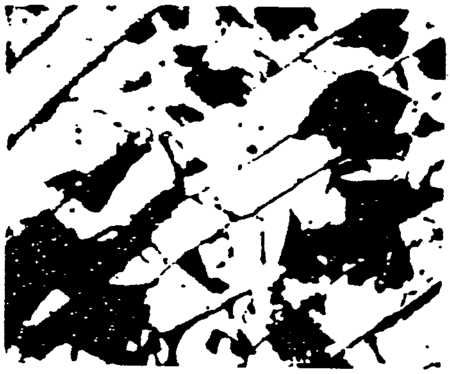


Fig.3a

Fig.3b

Fig.3c

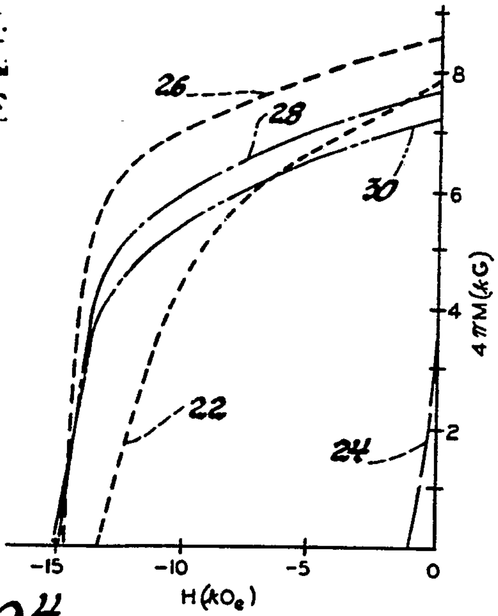


Fig.4

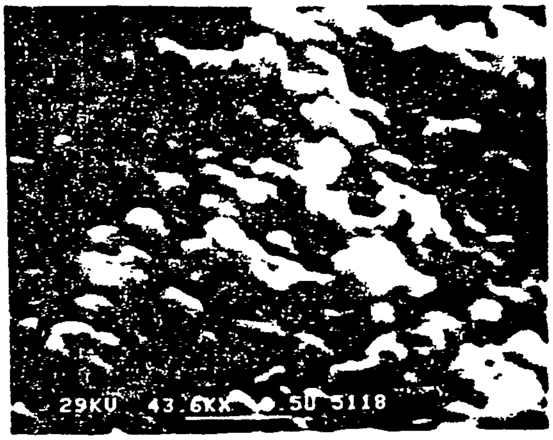


Fig.5

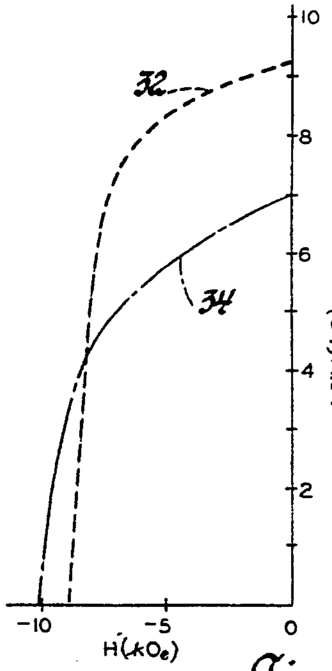


Fig.6

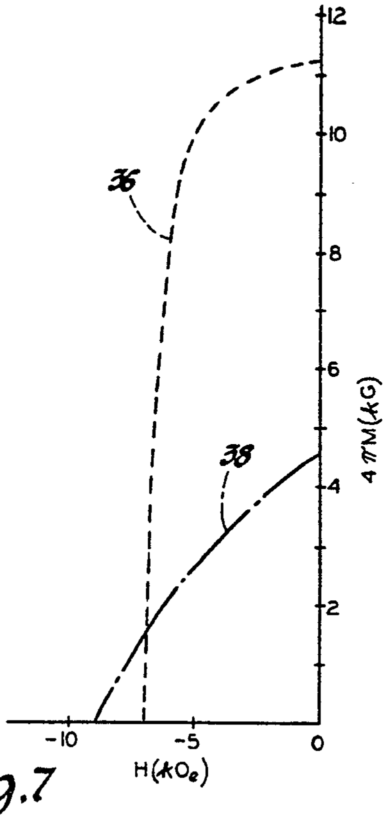


Fig.7