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(54) **Rapid compaction of rare earth-transition metal alloys in a fluid-filled die.**

(57) A novel method is provided for making large, fully densified rare earth-transition metal magnets. The method involves rapid compaction of very finely crystalline rare earth-transition metal alloy particles (2) retained in a die (12), using pressure applied to a substantially incompressible fluid medium (6) surrounding said particles (2).

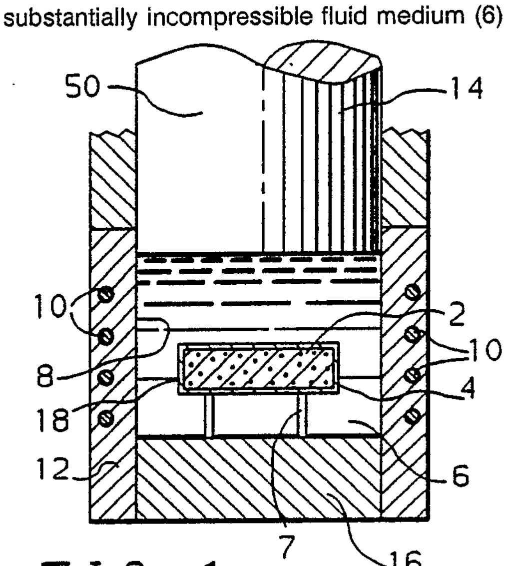

FIG. 1

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RAPID COMPACTION OF RARE EARTH-TRANSITION METAL ALLOYS IN A FLUID-FILLED DIE

This invention relates to the hot-forming of rare earth-transition metal alloys to form densified compacts as specified in the preamble of claim 1, for example as disclosed in EP-A-0 133 758.

Background

Permanent magnets based on compositions containing iron, neodymium and/or praseodymium, and boron are now in commercial usage. These magnets contain grains of tetragonal crystals in which the proportions of transition metal (TM), rare earth (RE), and boron are exemplified by the empirical formula $RE_2TM_{14}B_1$ and where at least part of the transition metal is iron. These magnet compositions and methods for making them are described in EP-A-0 108 474 and EP-A-0 144 112 incorporated herein by reference. The grains of the tetragonal crystal phase are surrounded by a small amount of a second phase that is typically rare earth-rich and lower-melting compared to the principal phase.

A preferred method of making magnets based on these compositions is the rapid solidification of an alloy from a melt to produce very fine grained, magnetically-isotropic particles. Melt-spinning or jet-casting is an efficient method of producing rapidly ribbon flakes which may be directly quenched to near optimum single magnetic domain size or overquenched and heated to promote suitable grain growth. The flakes can be comminuted, as desired, to relatively large, air-stable particles which are convenient for further processing.

It is also known that fine grained RE-TM-B particles can be hot-pressed and/or hot-worked and plastically deformed to make isotropic and anisotropic permanent magnets with exceptionally high energy products. This practice is described in EP-A-0 133 758, which is also incorporated herein by reference.

A typical hot-processing practice entails overquenching an alloy of a preferred RE-TM-B composition such as $Nd_{0.13}(Fe_{0.95}B_{0.05})_{0.87}$. The thin, friable ribbon is then crushed or ground into particles of a convenient size for an intended hot-pressing operation (50-325 mesh, e.g.). The particles are heated in a non-oxidizing atmosphere to a suitable elevated temperature, preferably about 650°C or higher, and subjected to pressures high enough to achieve a magnetically-isotropic, nearly full-density compact or a magnetically-anisotropic plastically-deformed compact. EP-A-0 133 758 discloses that processing may be accomplished by hot-pressing in a die, extrusion, rolling, die-upsetting, hammering or forging, for example. Hot isostatic pressing is useful to make fully-dense isotropic magnets, but has a slow cycle time.

These processes are all useful to form moderately sized magnets having simple shapes. The present invention relates particularly to an improved method of hot-forming and/or hot-working rare earth-transition metal powders or compacts to make relatively large permanent magnets with consistent densities and magnetic properties.

A method of hot-forming rare earth-transition metal alloys in accordance with the present invention is characterised by the features specified in the characterising portion of claim 1.

As used herein, the term "hot-working" shall mean the application of heat and pressure to a workpiece to cause material flow therein. Such flow induces magnetic anisotropy in substantially amorphous to very finely crystalline RE-TM-B alloys. The term "hot-forming" shall mean the application of heat and pressure to a workpiece to cause consolidation thereof and may or may not include hot-working.

Summary of the Invention

In general, preferred RE-TM-B compositions of magnetic interest comprise, on an atomic percentage basis, 50-90% of iron or mixtures of cobalt and iron, 10-40% rare-earth metal that necessarily includes neodymium and/or praseodymium and at least about one-half percent boron. Preferably, iron makes up at least 40 atomic percent of the total composition, and neodymium and/or praseodymium make up at least 6 atomic percent of the total composition. The preferred boron content is in the range of from about 0.5 to about 10 atomic percent for the total composition, but the total boron content may be higher than this without unacceptable loss of permanent magnetic properties. It is preferred that iron makes up at least 60% of the non-rare earth metal content, and it is also preferred that neodymium and/or praseodymium make up at least 60% of the rare-earth content.

Permanently magnetic alloys of particular interest are those which contain a predominant $RE_2TM_{14}B_1$ phase. This phase tolerates the presence of substantial amounts of elements other than those mentioned above such as aluminium, silicon, phosphorus, gallium, and transition metals other than iron or iron and cobalt, without destruction of permanent magnetic properties. The presence of other elements may be used to tailor magnetic properties. For example, the addition of the heavy rare-earth elements improves magnetic coercivity, and the addition of cobalt has been found to increase Curie temperatures.

In accordance with a preferred practice of the present invention, alloy particles with a substantially amorphous to very finely crystalline microstructure (e.g. an average grain size less than 50 nm) are disposed in a thin-walled container which is flexible at hot-forming temperatures. The particles and container together comprise a workpiece for rapid omni-directional compaction. A container may be made out of a material such as mild steel, stainless steel, copper, tin, aluminium, nickel, glass, or any other material which is plastic at hot-forming temperatures and is not severely degraded by the fluid or semi-fluid present in the die cavity. Similarly, the material of the container should not degrade the RE-TM-B alloy contained therein. The workpiece is then positioned in a die cavity which is larger than the workpiece and is surrounded by a medium which is a substantially incompressible fluid at hot-forming temperatures. This may be accomplished by surrounding the container with a low-melting alloy such as Cu-10Ni or a glass which is molten at hot-forming temperatures, for example. A pre-compact of suitable green strength can be used as the workpiece without a container.

The workpiece and compression medium are heated to the desired hot-forming temperature for the RE-TM-B powder. Compaction is preferably accomplished by ramming the medium in a forge or other hot-forming apparatus at a pressure of about 20-80 tons per square inch (276-1,100 MPa). It is preferred that the forming dwell time be limited to reduce the chilling effect of the ram on the compression medium in the die cavity. The preferred temperature range for compaction is above about 700°C but low enough to prevent grain growth beyond about 800 nanometres, and preferably below about 400 nm, during the time needed for rapid compaction in the medium.

In another preferred practice, a suitable RE-TM-B powder is similarly dispersed in a container which is sized to seal with the die walls near the bottom of the die. A compression medium is disposed above the container. An empty cavity portion is provided for the material in the container to flow into when pressure is applied to the medium fluid by a ram. When the container is subjected to forming-pressure, the RE-TM-B powder deforms and moves into the empty cavity. This causes substantial orientation of the grains in the RE-TM-B alloy resulting in magnetic anisotropy.

Detailed Description

The invention will be better understood in view of the accompanying drawings and the detailed description. In the drawings:

Figure 1 shows RE-TM-B powder in a container preparatory to rapid omni-directional compaction in a fluid-filled die in a hot press.

Figure 2 shows a fully densified RE-TM-B compact after rapid omni-directional compaction in the fluid-filled die of Figure 1.

Figure 3 shows RE-TM-B powder in a thin-walled container at the bottom of a fluid-filled die in a hot press preparatory to hot-working to cause the container to flow into an empty portion of the die cavity.

Figure 4 shows a hot-worked RE-TM-B compact after rapid compaction in the fluid-filled die of Figure 3.

In accordance with a preferred embodiment of the invention and with reference to Figure 1, particles 2 of a suitable RE-TM-B alloy with a substantially amorphous to finely crystalline microstructure are placed in a thin-walled, malleable container 4. Container 4 is preferably sealed with respect to the compression medium by welding, brazing or some other suitable method. A compression medium 6 may be cast around the container and allowed to solidify or medium 6 may be contained in another container (not shown). The RE-TM-B container 4 is supported by suitable props such as stilts 7. The combination of the RE-TM-B alloy particles 2, container 4 and the medium 6 (workpiece 18) are then heated to forming-temperature. This may be done partially or completely outside the forming-die, if desired, to increase cycle time in the press. Die cavity 8 shown in the drawings is heated by electrical resistance coils 10 located in die 12. The medium is located between upper ram 14 and lower ram 16. Both rams are free to reciprocate in die 8.

To form a densified permanent magnet compact, medium 6 and workpiece 18 are heated to the desired forming-temperature. For $RE_2TM_{14}B_1$ alloys of the Nd/Pr-Fe-B family, a temperature of about 650°C to 800°C is particularly suited. Extended periods at high temperatures are preferably avoided to prevent excessive grain growth and deterioration of magnetic properties. Deterioration generally begins at grain growth larger than about 400 to 800 nanometres.

Compression medium 6 is chosen to be plastic but substantially incompressible at such forming-temperatures. A suitable material would be lead, a glass-ceramic blend with a softening temperature of about 650°C or any other composition or alloy with an appropriate melting or softening temperature. Once the temperature is reached, either top ram 14 or bottom ram 16 or both are moved to compress the workpiece 18 in the die cavity. Since medium 6 is substantially incompressible, the force of the movement is transferred isostatically to the powder 2 in container 4.

Container 4 shown in Figures 1 and 2 initially has a right-circular cylindrical shape. For such a container, rapid isostatic pressing causes the top, bottom and sides of the workpiece to indent as shown at detail 20. Alloy particles 2 inside container 4 are consolidated to substantially 100% of the theoretical alloy density. The consolidated alloy has substantially isotropic magnetic properties: i.e., it can be magnetized to equal magnetic strength in any direction. Workpiece 18 can be very large depending on the tonnage of the hot press or forge. Therefore, this invention is particularly useful for making big blocks of material suitable for cutting into smaller magnets of a desired shape.

The workpiece could also be shaped to deform non-uniformly when compacted in the medium. Such deformation would result in magnetic anisotropy in the workpiece with the crystallographic c-axes of the RE-TM-B particles being perpendicular to the direction of material flow.

Another means of providing magnetic anisotropy is shown in Figures 3 and 4. Container 30 is sized to form a substantially fluid-tight seal 32 between first chamber 34 and second chamber 36 of die cavity 38. Second chamber 36 is initially empty except for the presence of the container 30. First chamber 34 is filled with an incompressible medium 40 as described above. Die 42 is heated by means of electrical resistance coils 44. Once container 30 and alloy particles 46 (workpiece 48) and medium 40 are heated to a suitable temperature, a top ram 50 is actuated causing a downward force on the top 52 of workpiece 48 causing it to deform into and fill the second chamber 36. The crystallographic c-axis (the preferred axis of magnetic orientation) of the RE-TM-B particles would be parallel to the direction of applied pressure and normal to the direction of workpiece flow.

Example

Each sample was made by filling a mild steel can of the dimensions indicated in the Table with melt-spun, overquenched, roughly crushed, magnetically isotropic $Nd_{.13}(Fe_{.95}B_{.05})_{.87}$ ribbon particles. The particles were densified by tapping to about 45% of the theoretical alloy density of about 7.55 g/cc. The cans were welded shut without evacuation since negligible oxygen contamination would occur from air left in the container. The cans had average wall thicknesses of about 3 mm. Samples 1 to 4 had right-circular cylindrical shapes while samples 5 and 6 were square.

The cans were cast in a blend of glass and ceramic that was viscous at temperatures between about 650°C and 800°C. They were heated for the times indicated to elevate the temperature of the can and its contents prior to hot-forming. They were heated outside the die until near the softening temperature and heating was completed in the die cavity. A knuckle press with a double-acting ram was used to very rapidly compact the heated samples at about 750 MPa. The samples were removed from the press and rapidly quenched in an oil-bath. The compression medium was melted away from the samples with a blow-torch. A small segment was cut away from the outside edge and centre of each hot-formed sample. A 3 x 3 mm cube was machined from the segment and its magnetic properties were measured in a PAR vibrating sample magnetometer. The densities of the two samples were measured and averaged. The results are reported in the Table.

TABLE

No.	Workpiece Dimension (mm)	Maximum Temperature (°C)	Heating Time (min)	HC_i* (kOe)	B_r* (kG)	Energy* Product (MGOe)	Average Density (g/cc)
1	31 diam 50 long	690	70	- -	7.8 7.8	13.7 13.6	7.54
2	31 diam 50 long	732	70	11.8 11.8	7.1 7.1	10.6 10.3	7.55
3	83 diam 50 long	690	70	13.7 13.9	7.1 7.3	12.4 13.1	7.48
4	83 diam 50 long	690	40	14.6 14.3	8.0 8.3	13.75 15.0	6.86
5	50 square 50 long	660	70	14.1 14.1	8.0 7.8	14.2 13.7	7.43
6	50 square 50 long	690	70	13.7 13.8	7.7 7.6	13.0 12.95	7.53

* Top No. for each sample is for segment taken from outer edge after hot-forming. Bottom number is for segment taken from centre.

The overquenched starting alloy was magnetically-soft having very little coercivity. All of the rapidly-compacted samples showed good coercivities and energy products. The highest energy product was measured in the sample heated to about 690 °C for the shortest time, 40 minutes. It would probably be advantageous to achieve uniform heating in shorter times by using induction, microwave, or some other heating means.

Some of the samples exhibited cracks throughout. This was probably due to cooling stresses between the different materials. It is believed that this could be eliminated by a more carefully controlled cooling cycle. For example, the temperature could be rapidly dropped a few degrees below the temperature at which grain growth in the alloys takes place (about 650 °C) and cooled very slowly thereafter. The compacting medium could also be removed before the workpiece was cooled.

An important advantage of the subject method over conventional hot, isostatic compaction in a gaseous medium is the faster cycle time in the compacting press. In accordance with this invention, the sample need be retained in the press only long enough to cycle the rams. The workpieces can be heated outside the press if desired. In fact, a fast cycle time in the press is desirable to prevent chilling of the compacting medium by the rams. In gas-isostatic pressing, the cycle time is directly related to the rather slow, controlled pressure build-up time which may be several hours for a large sample.

Claims

1. A method of hot-forming rare earth-transition metal alloys to form densified compacts, characterised in that the method comprises disposing particles (2;46) of said alloy having a substantially amorphous to finely crystalline microstructure in a protective container (4;30); disposing said container (4;30) in a die (12;42) filled with a medium (6;40) which is fluid and substantially incompressible at hot-forming temperatures such that said medium (6;40) substantially surrounds said container (4;30); heating said alloy particles (2;46) to a hot-forming temperature above about 650 °C; rapidly applying a pressure on said medium (6;40) to consolidate the alloy particles (2;46) in said container (4;30) to near full theoretical density; and cooling said consolidated alloy to prevent excessive grain growth therein.

2. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to claim 1, characterised in that said medium (6) envelopes said container (4), and the pressure rapidly applied to said medium (6) isostatically consolidates said alloy particles (2).

3. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to claim 1, characterised in that the die (42) has a first chamber (38) for retaining said medium (40) therein and a second, interconnected chamber (36) in the shape of a desired magnet shape; said container (30) is

disposed in said die (42) so that it forms a seal between said first and second chambers (38,36); and the pressure exerted on the medium (40) is such that the container (30) is deformed and moves into the second chamber (36) to take up said magnet shape.

4. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to claim 1, characterised in that the alloy comprises about 10-50 atomic percent rare-earth metal including at least 6 atomic percent neodymium and/or praseodymium, about 50 to 90 atomic percent transition metal including at least 40 atomic percent iron, and at least 0.5 atomic percent boron, the average size of the grains in said alloy being less than 50 nanometres; the container (4) is a malleable container; the consolidated alloy is cooled at such a rate that grain growth beyond an average size of about 800 nanometres is prevented; and the method includes magnetizing said consolidated alloy in a suitable magnetic field.

5. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to any one of claims 1, 2 or 3, characterised in that the rare earth-transition metal alloy comprises at least 6 atomic percent neodymium and/or praseodymium and at least 40 atomic percent iron.

6. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to any one of claims 1, 2 or 3, characterised in that the rare earth-transition metal alloy comprises at least 6 atomic percent neodymium and/or praseodymium, at least 40 atomic percent iron and at least 0.5 atomic percent boron.

7. A method of hot-forming rare earth-transition metal alloys to form densified compacts according to any one of claims 1, 2 or 3, characterised in that the container (4;30) is made of mild steel, stainless steel, copper, tin, aluminium, nickel, glass or a combination thereof.

8. A method of hot-forming rare earth-transition metal alloys to form densified compacts, characterised in that a green compact of particles of said alloy having a substantially amorphous to finely crystalline microstructure is disposed in a die (12) filled with a medium (6) which is fluid and substantially incompressible at hot-forming temperatures such that said medium (6) surrounds said compact; said compact is heated to a hot-working temperature above 650 °C; a pressure above 250 megaPascals is rapidly applied on said medium (6) to isostatically consolidate the compact substantially to full theoretical density; and said consolidated compact is cooled to prevent grain growth in the alloy to greater than 800 nanometres average diameter.

9. A method of hot-forming rare earth-transition metal alloys to form densified compacts, characterised in that the method includes pressing particles of said alloy into a coherent green compact; providing a die (42) which has a first chamber (34) for retaining a fluid and a second interconnected chamber (36) in the shape of a desired magnet; disposing said green compact in said die (42) so that it forms a seal between to said first and second chambers; filling said first chamber (34) with a material (40) which is a substantially incompressible fluid at forming-temperatures; heating said fluid (40) and compact to the forming-temperature; ramming the fluid (40) in the first chamber (34) to exert pressure on the compact so that it is deformed, consolidated and displaced into the second chamber (36); and cooling said consolidated compact to prevent grain growth in the alloy to greater than 800 nanometres average diameter.

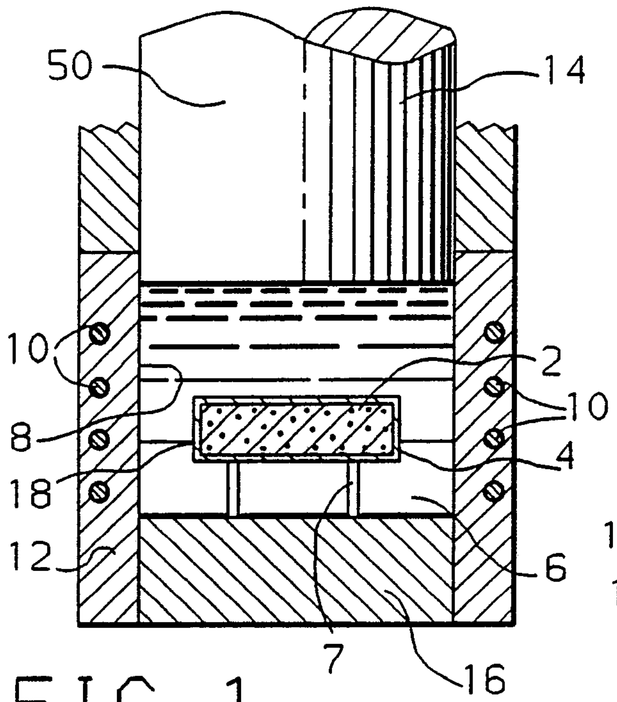

FIG.1

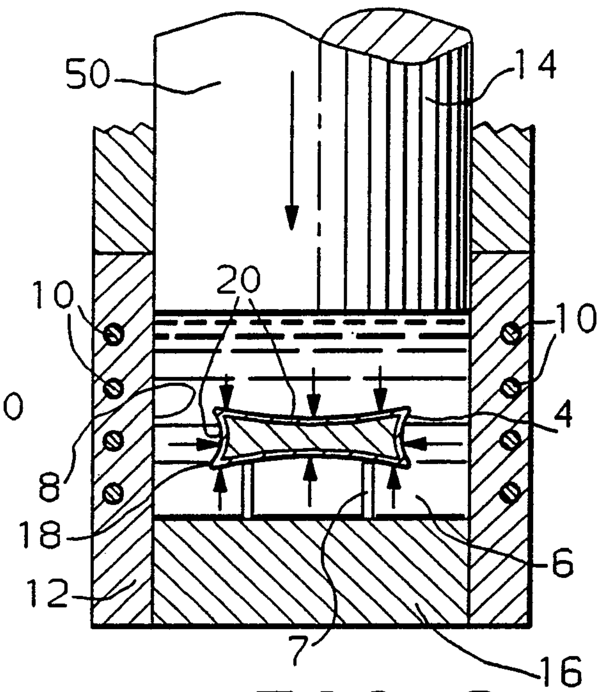

FIG.2

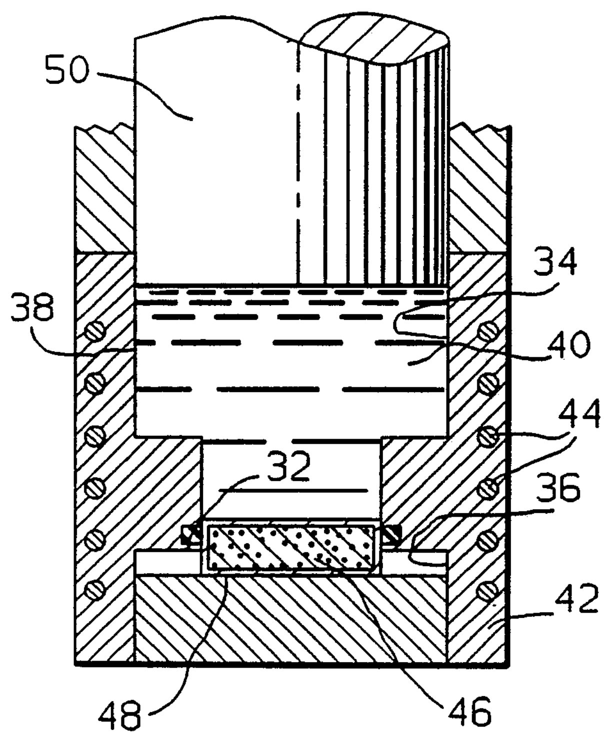

FIG.3

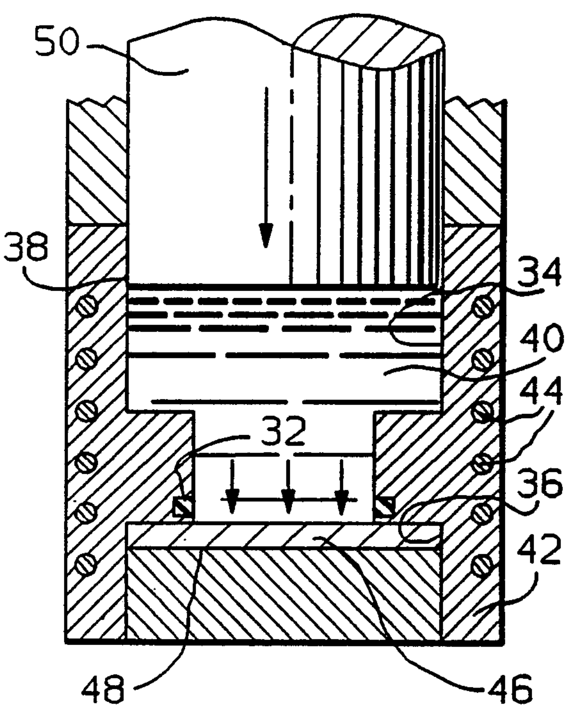

FIG.4