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(54) RARE EARTH METAL ALLOY MAGNETS

(71) We, MAGNETIC POLYMERS LIMITED, a British Company of Kennedy Tower, St. Chad's Queensway, Birmingham B4 6EG, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to rare earth metal alloy magnets and to a method of producing them.

Finely divided particles of magnetic alloys are used, for example, to make magnets wherein the magnetic alloy particles are sintered or polymer or metal bonded together in known manner with magnetic orientation of the individual particles to produce magnets of outstanding properties, for example field strength. The fine magnetic alloy particles, for example of the order of 1—10 μ particle size, are usually produced by attritor or ball milling. Such methods have several disadvantages: for example, water and oxygen contamination are known to be particularly troublesome in reducing the performance of the magnets produced therefrom; the mechanical equipment involved tends to be cumbersome to operate and maintain; and mechanical milling also creates plastic deformation of the magnetic alloy particles which can undesirably alter the magnetic characteristics.

British Patent Specification No. 1,313,272 (Philips) describes and claims a method of manufacturing a magnetic material for the manufacture of a permanent-magnetisable body, the magnetic material consisting of a pulverulent alloy having a composition in the system M-R which is within the region of homogeneity which includes the compound M_5R , in which region of homogeneity all alloys have the same hexagonal crystal structure as M_5R , wherein M is Co or a combination of Co with one or more of the elements Fe, Ni and Cu and R is one or more of the elements yttrium, thorium and the rare earth metals, the method comprising the step of pulverising a

casting of the alloy in a hydrogen-comprising atmosphere. The only methods described in that specification for pulverising the alloy casting are mechanical milling methods, which have the disadvantages mentioned above.

It has been known for some time that rare earth metal intermetallic compounds (alloys) such as $LaNi_5$ and $SmCo_5$ can be used as hydrogen storage compounds owing to their ability at room temperature to take up large quantities of gaseous hydrogen at high pressures and to release the hydrogen at approximately normal atmospheric pressures. Various practical applications for these materials have been suggested, including use in rechargeable battery electrodes, hydrogen pressure buffers, refrigerators (hydrogen cryogenerators) and as hydrogen purifiers. In their major potential use for hydrogen fuel storage, it has been a disadvantage that most of the rare earth metal alloys in question crumble spontaneously to powder on hydride formation, and even expensive fine pore filters, or magnetic filters if the alloy hydride happens to be magnetic, may not prevent very fine dusts of these powders from contaminating equipment receiving the hydrogen.

The present invention is based upon our research discovery that crumbling to form a powder of the alloy on hydride formation and decomposition (hereinafter referred to as "hydride decrepitation") can be advantageously applied to magnet manufacture so as elegantly to avoid the disadvantages of alloy particle size reduction by mechanical milling and to provide desirable magnetic properties, with considerable potential for industrial application and automation.

The present invention accordingly provides a magnet body comprising magnetically oriented particles of magnetic alloy powder the magnetic alloy having at least one component which is a rare earth metal, cerium or yttrium, and having been subjected to a hydrogen-containing atmosphere at such temperature and

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pressure that it is at least partly converted to a hydride and thereafter having been subjected to conditions of temperature and pressure such that the hydride decomposes.

5 The invention also provides a method of producing a magnet body as defined above comprising the steps of subjecting a solid magnetic alloy having at least one component which is a rare earth metal, 10 cerium or yttrium to a hydrogen-containing atmosphere at such temperature and pressure that the alloy is at least partly converted to a hydride, subjecting the hydride to conditions of temperature that the alloy is at least partly converted to a 15 hydride to conditions of temperature and pressure such that it decomposes, thereby recovering a powder of the alloy, and bonding or sintering the alloy powder to 20 form the magnet body while the powder particles are oriented in a magnetic field.

We have found that the hydride decrepitation reduces the magnetic alloy to powder apparently without destruction or 25 deformation of its magnetic microstructure, and this has the advantage that the properties of the magnet bodies according to this invention may be adjusted as desired, for example by variation of the alloy 30 composition or by subsequent deliberate deformation of the powdered alloy particles, without having to make allowance for the alterations in properties which may occur incidentally while the alloy is being 35 reduced to a given particle size by mechanical milling.

It has also been found that a significant improvement in magnetic properties, as represented by the BH loop shape can be 40 obtained when the alloy powder is prepared according to the present invention from mechanically milled alloy powder even when this mechanical milling has reduced the alloy particles to a size such that 45 substantially no hydride decrepitation takes place upon hydride formation and decomposition.

The finely divided magnetic alloy particles produced by the hydride 50 decrepitation have very clean surfaces which are highly reactive and must therefore be protected from oxidation and other contamination for optimum performance in the magnets made 55 therefrom. This can be achieved to some extent by sintering the powdered alloy directly to form a magnet, but at least for polymer or metal bonded magnets the particles are preferably coated with a 50 protective material such as a metal, for example, copper, zinc, cadmium, aluminium, tin, cobalt, nickel or alloys thereof or an organic polymeric material.

It is an advantage of the present invention 55 that such coating of the powdered magnetic

alloy can be conducted *in situ* without removing the magnetic alloy from the protective atmosphere of a chamber used for the hydrogen decrepitation. For 70 example, a metal such as zinc, which may be present in the decrepitation chamber (but separated from the magnetic alloy therein) or in a separate chamber communicating therewith, can be heated under low pressure 75 to vapour coat the suitably agitated magnetic alloy particles. Any other convenient coating procedure can also be used, the extremely clean surfaces of the magnetic alloy particles being well suited, for example, for electroless coating by 80 dispersion in solutions of appropriate metal salts or for the use of hydrogen absorbed in the magnetic alloy particles for *in situ* reduction of such metal salts. The coated 85 magnetic alloy particles may be made into magnets by known techniques of sintering (preferably using known sintering additives for metal-coated alloy particles) or polymer or metal bonding with magnetic orientation of the particles during molding into the 90 desired magnet shape.

Suitably, the magnetic alloy comprises at least one further component which is a transition metal. Preferably, the magnetic alloy comprises a phase of the formula A_xB_y , 95 wherein one element of A represents at least one transition metal, B represents at least one rare earth metal, cerium or yttrium and x and y approximate to at least one of the following pairs of integers: 2:1, 5:1, 7:2, 17:2. 100 Most preferably, for permanent magnets (having a high Curie Temperature), A comprises cobalt and/or iron; B comprises samarium or praseodymium or cerium-enriched mischmetal and x:y approximates 105 5:1, 7:2 or 17:2, but this invention can also be practised on other magnetic alloys, e.g. magnetostrictive alloys of the type Fe_2B , wherein B is as defined above, especially 110 terbium, dysprosium, holmium or mixtures thereof.

A stainless steel reaction chamber is found to be suitable for containing the magnetic alloy while it is subjected 115 to the pressurised hydrogen atmosphere. Stainless steel is impervious and unreactive to pressurised hydrogen under the conditions employed and is not sufficiently magnetised in use to affect 120 removal of the powdered magnetic alloy from the chamber.

The hydrogen is readily removable from the hydride simply by reducing the pressure. At ambient temperatures, hydride 125 formation with $SmCo_5$ magnetic alloy, for example, occurs initially at about 50 atm. H_2 pressure, and removal of the hydrogen to regenerate the alloy can be effected by 130 reducing the pressure to e.g. 50 μ Hg.

It is a further advantage of the method 130

according to this invention that it can be practised on virtually any convenient sample of the magnetic alloy in question, since the hydride formation can be begun on a large body or bodies of the magnetic alloy e.g. 5 mm in diameter, and may be repeated to reduce progressively the particle size of the magnetic alloy. The disintegration of the magnetic alloy particles is preferably assisted by external stimuli such as agitation, ultrasonic vibration, or alternating magnetic fields, which help to propagate cracks produced in the magnetic alloy particles by the hydride formation. With SmCo_5 , it has been found that particles about 40μ in size quickly produced by the hydride formation tend to exhibit cracks which lend themselves to propagation by external stimuli as aforesaid to reduce the 40μ particles toward the range of $1-10 \mu$ preferred for magnet formation. Such external stimuli are preferably applied while the magnetic alloy is in the hydride form, which tends to be more brittle than the magnetic alloy *per se*.

For effective ultrasonic, mechanical or magnetic vibration of the magnetic alloy particles it is desirable to use a liquid which conveys the vibrations to the particles, and this has an added advantage in another modification of the invention wherein cyclic temperature changes are used to enhance the disintegration of the magnetic alloy. Cyclic variations from ambient temperature to that of liquid N_2 are preferred, in which case the freezing of the liquid (if present) within the cracks in the particles may help to widen the cracks. Cyclic variations, above ambient temperature may enhance the disintegration generally, but do not have the above added advantage in the presence of solvent. The magnetic alloy can be hydrogenated at sub zero temperatures (e.g. that of solid carbon dioxide) with the advantage of increasing hydrogen absorption by the magnetic alloy. The low temperatures will also ensure a more brittle type of material. It is preferred to use temperature increases only for annealing the magnetic alloys before hydride formation, to drive off unwanted gases and to adjust the grain size of the magnetic alloy in a manner which may enhance its disintegration upon hydride formation, but it may sometimes be necessary to heat the alloy to approximately 100°C in order to activate it, usually when it has been exposed to the atmosphere for long periods. The magnetic alloy grain size may be a factor also in determining the minimum particle size achievable by the method of this invention. Pressure cycling of the hydrogen (e.g. once every 10 minutes, preferably every 3 to 4 minutes) can also be used to stimulate cracking and in general the higher

the pressure the better, e.g. $180-220$ atmospheres. Magnetic vibration may also help propagate crack growth by magnetostriction.

The hydrogen should be as pure as possible, depending on the level of impurities which can be tolerated in the magnets to be produced from the magnetic alloy particles. The hydrogen gas may be passed through filtering means such as a palladium membrane to remove impurities.

Another potentially valuable modification of the method according to this invention is the use of a storage cell comprising a solid hydrogen storage compound, for example magnesium hydride comprising 5 weight percent of nickel, from which hydrogen can be generated by heating and in which the hydrogen can be reabsorbed and recovered for further use after decomposition of the magnetic alloy hydride. Each such cycle of hydrogen generation and reabsorption tends to purify the hydrogen, thus minimising any build-up of impurities therein. It is thought that the cyclic heating and cooling of such a hydrogen store to generate and reabsorb the hydrogen can be harnessed to "pump" the hydrogen to and from the magnetic alloy reaction chamber in suitably designed apparatus, thus eliminating or reducing the need for mechanical pumping. The heating and cooling involved in the aforementioned annealing of the alloys can possibly be harnessed in a similar way, and the possibility of recycling the hydrogen, by whatever method, is economically attractive for commercial practice of the method of this invention. The hydrogen storage cell has the additional advantage of facilitating attainment of high gas pressures without the progressive decline in pressure which occurs as an ordinary gas cylinder becomes depleted (in the absence of expensive pressure-boosting recirculation equipment).

The formation and the decomposition of the alloy hydride appear to occur very rapidly, and can readily be followed by measuring the temperature in the reaction chamber, the hydride formation being exothermic and the decomposition endothermic. A rapid rise in temperature can be observed as soon as sufficient pressure of hydrogen is applied to the magnetic alloy, the hydride formation apparently being almost instantaneous, especially after repeated cycles have broken up large particles of the magnetic alloy to expose a greater surface area to the gas. The specific hydride-forming pressure for any given sample of magnetic alloy is readily found by routine experiment, and may vary depending on such factors as the nature of the magnetic alloy used, its surface

condition, the presence of impurities, and the temperature.

5 A rapid fall in temperature is similarly observed when the pressure is reduced to a level at which the decomposition of the hydride takes place. These clear temperature changes lend themselves admirably to automatic control of the operating cycles for commercial production.

10 An embodiment of the invention will now be described by way of Example with reference to the accompanying drawing which shows schematically suitable apparatus for practising the method according to the invention, the symbol X indicating a tap.

15 In the drawing, A is a source of suitably pure hydrogen, which on a laboratory scale is a hydrogen cylinder feeding the hydrogen either directly or through a purifying palladium membrane. Line L feeds the pure hydrogen under pressure to the stainless steel pressure vessel B provided with suitable means (not shown) for inserting the sample carrier C, preferably of stainless steel, containing the magnetic alloy sample D. The pressure vessel B can be vented through valve R and evacuated by the pump G, expelling the hydrogen to atmosphere, but the preferred alternative is to recycle the hydrogen, preferably without mechanical pumping, using the aforementioned hydrogen store compound as the source A.

20 When hydride formation occurs in the magnetic alloy sample D the resulting temperature rise is detected by the thermocouple E and the corresponding pressure drop by a suitable pressure transducer P, and this data is recorded or otherwise processed by suitable recording and/or control equipment F. Q is a direct reading pressure gauge. Ultrasonic or mechanical vibration may be applied to the alloy hydride to assist its disintegration by mechanical or ultrasonic means indicated at V which may be in any convenient form and may be replaced or augmented by any other suitable means of agitation. The aforementioned liquid or additions or solvents may be added through a suitable inlet port S, if not already present in the sample carrier C when the latter is placed in the vessel B.

25 When the required number of hydride formation cycles has been completed, with suitable external stimuli if required, to reduce the magnetic alloy sample D to the desired particle size, the coating metal M may be vaporised (in the absence of solvent) by heating means T with the vessel B under vacuum to coat the particles with the aid of further ultrasonic or other agitation. Alternatively the coating material may be

added to the reactive powder through inlet port S and coating carried out by appropriate techniques.

The following Example illustrates the invention.

EXAMPLE

70 A 15 gm sample of SmCo_5 was crushed to a particle size of ca. 1—2 mm inside a sample chamber (of copper so that the temperature will equilibrate quickly). The system was then pumped out to a pressure of ca. 20 μ Hg initially; flushed out with hydrogen twice; and then hydrogen was admitted at a pressure of 50 atm. The temperature and pressure were monitored to determine when hydride formation occurred and then cycling was carried out by quickly pumping out the system to a pressure of ca. 50 μ Hg (a temperature drop of 25°C was detected) and then quickly readmitting hydrogen (a temperature rise of 40°C was detected). In this experiment the temperature was allowed to stabilise between each cycle, though under normal operating conditions this would not be necessary. The pressure cycling was necessary here because SmCo_5 will accept greater lattice strain before fragmenting than some other magnetic alloys and hence is more difficult to break up. The alloy powder was polymer bonded to form a permanent magnet body in the usual way, and a further sample of the powder was similarly bonded after mild mechanical milling which introduced a desired degree of plastic deformation.

WHAT WE CLAIM IS:—

1. A magnet body comprising magnetically oriented particles of magnetic alloy powder, the magnetic alloy having at least one component which is a rare earth metal, cerium or yttrium, and having been subjected to a hydrogen-containing atmosphere at such temperature and pressure that it is at least partly converted to a hydride and thereafter having been subjected to conditions of temperature and pressure such that the hydride decomposes.
2. A magnet body according to Claim 1, wherein the alloy powder particles have individual protective coatings.
3. A magnet body according to Claim 2, wherein the protective coating material is a metal or metal alloy.
4. A magnet body according to Claim 3, wherein the coating metal is copper, cadmium, aluminium, tin, or an alloy thereof.
5. A magnet body according to Claim 3, wherein the coating metal is cobalt or nickel or an alloy thereof.
6. A magnet body according to Claim 3,

- wherein the coating metal is zinc or an alloy thereof.
- 5 7. A magnet body according to any one of the preceding claims, wherein the magnetic alloy has the composition A_xB_y in which A is at least one transition metal, B is at least one rare earth metal, cerium or yttrium, and x:y approximates any of the ratios 2:1, 5:1, 7:2 and 17:2.
- 10 8. A magnet body according to Claim 7, wherein A is cobalt, B is samarium or praseodymium or cerium-enriched mischmetal, and x:y approximates 5:1, 7:2 or 17:2.
- 15 9. A magnet body according to any one of the preceding claims, wherein the powder is polymer bonded, metal bonded, or sintered to form said body.
- 20 10. A magnet body according to Claim 1 substantially as described in the foregoing Example.
- 25 11. A method of producing a magnet body according to any one of the preceding claims, comprising the steps of subjecting a solid magnetic alloy having at least one component which is a rare earth metal, cerium or yttrium to a hydrogen-containing atmosphere at such temperature and pressure that the alloy is at least partly converted to a hydride, subjecting the hydride to conditions of temperature and pressure such that it decomposes, thereby recovering a powder of the alloy, and bonding or sintering the alloy powder to form the magnet body while the powder particles are oriented in a magnetic field.
- 30 12. A method according to Claim 11, wherein the hydrogen recovered from the decomposed hydride is recycled for further hydride formation.
- 35 13. A method according to Claim 12, wherein a storage cell comprising a solid hydrogen storage compound is used to store the hydrogen between cycles of the hydride formation.
- 40 14. A method according to Claim 12, wherein the storage compound is heated to release the stored hydrogen and is cooled to reabsorb the hydrogen.
- 50 15. A method according to Claim 14, wherein the heating and cooling of the storage compound is used to pump the hydrogen to and from the alloy.
- 55 16. A method according to any one of Claims 11 to 15, wherein vibration or agitation is applied to the hydride and/or to the alloy to assist the powder formation occurring by hydride decrepitation.
- 60 17. A method according to Claim 16, wherein a liquid is in contact with the hydride and/or alloy to help in transmitting the vibration or agitation to the hydride and/or alloy.
18. A method according to any one of Claims 11 to 17, wherein temperature changes are applied to the hydride and/or alloy to assist the powder formation occurring by hydride decrepitation. 65
19. A method according to Claim 18, wherein a liquid is in contact with the hydride and/or alloy and the temperature changes include reduction of the temperature to cause freezing of said liquids. 70
20. A method according to Claim 18 or 19, wherein the temperature is reduced by means of liquid nitrogen. 75
21. A method according to any one of Claims 11 to 15, wherein the alloy is mechanically milled prior to the hydride formation to a particle size at which it undergoes substantially no hydride decrepitation upon hydride formation and decomposition. 80
22. A method according to any one of Claims 11 to 21, wherein the alloy is heat treated before it is subjected to any hydride formation. 85
23. A method according to any one of Claims 11 to 22, wherein the hydride formation and decomposition are monitored by detection of a temperature rise due to hydride formation and a temperature drop due to hydride decomposition. 90
24. A method according to any one of Claims 11 to 23, wherein the alloy powder particles are subsequently provided with individual protective coatings. 95
25. A method according to Claim 24, wherein the protective coating material is a metal or metal alloy, and is applied as a vapour evaporated from a heated source of said coating metal under reduced pressure with agitation of the powder particles to ensure complete coating thereof. 100
26. A method according to Claim 24, wherein the protective coating material is a metal or metal alloy, and is applied by electroless coating from a solution of an appropriate metal salt. 110
27. A method according to any one of Claims 24 to 26, wherein the protective coatings are applied to the powder particles before the powder is removed from the apparatus in which the hydride formation and decomposition is carried out. 115
28. A method according to any one of Claims 11 to 27, wherein the hydride formation and decomposition are carried out in a stainless steel reaction vessel. 120
29. A method according to Claim 11, substantially as described with reference to

the accompanying drawing or in the foregoing Example.

- 5 30. A polymer bonded magnet body produced by a method according to any one of the preceding Claims 11 to 29.

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