

[54] SPUTTERED MAGNETIC MATERIALS
COMPRISING RARE-EARTH METALS AND
METHOD OF PREPARATION

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148/103, 105, 108, 121, 102

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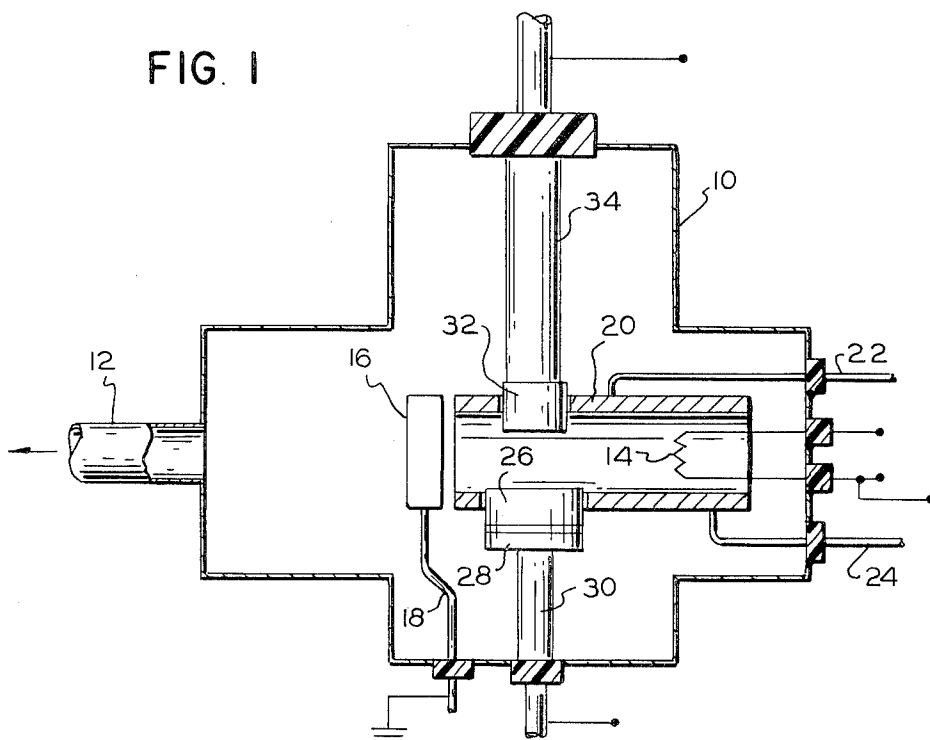
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[57] ABSTRACT

Magnetic materials of the transition metal-rare-earth
metal type are formed by high-rate sputter-deposition
techniques which permit formation of thick bodies of
magnetic materials having new and unique properties.

24 Claims, 2 Drawing Figures

FIG. 1



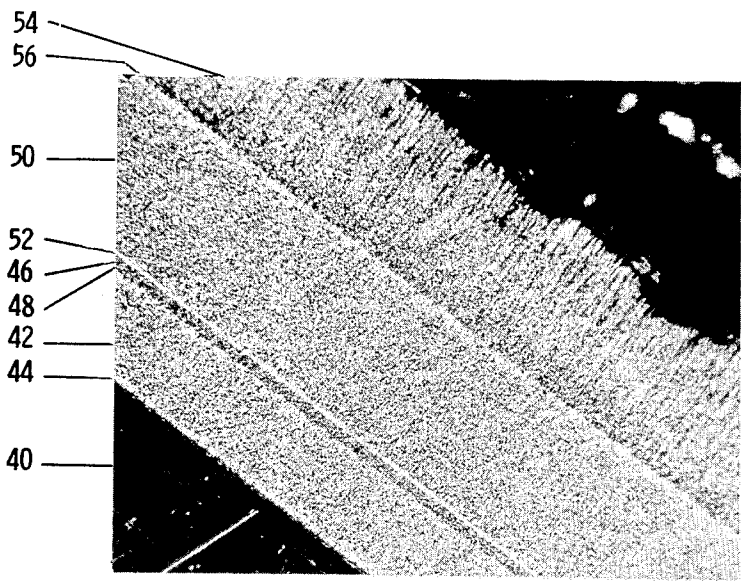


FIG. 2

SPUTTERED MAGNETIC MATERIALS COMPRISING RARE-EARTH METALS AND METHOD OF PREPARATION

BACKGROUND OF THE INVENTION

The invention herein described was made in the course of or under a contract or subcontract thereunder with Advanced Research Projects Agency.

Various transition metal-rare-earth metal compounds or alloys have been utilized recently in the construction of high performance permanent magnets. Commercial magnets have generally been produced by using traditional powder metallurgy techniques or by various casting techniques. However, magnets prepared by these techniques, while having high intrinsic coercive force values, are inherently limited by particle deformation, oxidation, low density, lack of chemical homogeneity and microstructural uniformity, or difficulties in preparing magnets having the desired geometry, size and direction of magnetization.

Recently it was discovered that thin films of sputter deposited cobalt-rare-earth compositions had desirably high magnetic properties. The technique of formation and the resulting compositions are described in U.S. Pat. No. 3,615,911. However, films formed by the technique disclosed in such patent displayed a thickness dependency and the coercivity of the film decreased when the film thickness went over 10,000 Angstroms. Also, while films produced in accordance with U.S. Pat. No. 3,615,911 have high coercivity, the limited amount of magnet material available in a magnet prepared in accordance with such patent limits the usefulness of the films produced.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new and improved method for preparing thick bodies of magnetic materials of the transition, metal-rare-earth metal type, which bodies have superior magnetic properties.

It is a further object of the invention to provide new and improved permanent magnetic materials of the transition metal-rare-earth metal type having exceptionally high coercivity values.

These and other objects of the invention are obtained by high-rate sputtering of a transition metal and a rare-earth metal from a target to a suitable supporting member. The magnetic materials prepared by this technique are characterized by their high density, fine grain size and texture, and uniformity of composition and physical properties. Permanent magnet materials of the invention possess one or more desirable properties, such as exceptionally high intrinsic coercive force values, uniform magnetic properties as measured in the plane of the deposit, anisotropic magnetic properties as measured normal to the plane of the deposit, and remanence and maximum energy product values that are consistent with the high coercivity values and magnetic anisotropy of the deposition material. The maximum intrinsic coercive force of the material is attained by heat-treating the sputter-deposited material, values as high as 35,000 oersteds having been obtained.

The high rate deposition at room temperature results in an exceptionally fine, equiaxed grain structure that is best described as microcrystalline, that is, the X-ray diffraction patterns of deposited material are characteristic of an amorphous rather than a crystalline struc-

ture. While annealing of the deposited material at higher temperatures results in development of a discernible grain structure and the appearance of distinctive X-ray diffraction lines, at annealing temperatures less than 1,000°C., the ultimate grain size is still substantially less than 10 microns.

DRAWINGS

FIG. 1 is a schematic illustration of sputtering apparatus that may be utilized in the practice of the invention; and

FIG. 2 is a photomicrograph of a sputter deposited material illustrating certain features of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The magnetic materials of the invention are preferably prepared by a high-rate sputter deposition technique. By high-rate is meant a deposition rate so as to deposit materials on a substrate at a rate greater than 0.5 mils per hour. It has been found that the high deposition rate is significant in producing magnet materials having physical and magnetic properties and thicknesses and shapes useful for bulk magnet applications. Other related vapor deposition methods that might be used for some materials include RF sputtering, diode sputtering, electron beam evaporation and ion plating.

FIG. 1 illustrates a DC triode sputtering apparatus which was utilized in the preparation of the magnetic materials of the invention. Such apparatus includes a stainless steel chamber 10 connected to a suitable oil diffusion pump (not shown) through an exhaust manifold 12. Mounted within the chamber 10 is a tungsten filament cathode 14 and an opposing anode 16. The anode is water-cooled, being supported upon tubes 18 which conduct cooling water to and from the anode through the walls of chamber 10. Anode 16 is grounded.

Extending between the cathode 14 and the anode 16 is a hollow-walled, tubular discharge containment shield 20 supported upon tubes 22, 24 which serve as conduits for conducting cooling water to and from the shield.

The target of the material to be sputtered is indicated at 26 and is mounted upon a backing plate 28, which in turn is welded to a hollow stainless steel stem 30 through which cooling water is circulated to cool the target to a proper temperature. The target material is deposited upon a substrate 32 which may be of suitable material and which is likewise mounted upon a hollow stem 34 through which cooling water may be circulated to maintain the substrate at the desired temperature. The target 26 and substrate 32 are positioned within apertures formed in the shield 20.

For a deposition run, sputtering chamber 10 is evacuated and baked at 100°C. for 12 hours. After bakeout and cooling the system pressure is preferably less than 5×10^{-8} Torr. During sputtering a krypton gas atmosphere of from 1 to 3×10^{-3} Torr is maintained within the chamber. Krypton gas of 99.99 percent purity is admitted into the chamber while continuously pumping at a rate of approximately 1 liter per second.

Targets typically consist of 1.5 inch diameter \times 0.35 inch thick disc of the target material mounted to a 0.25 inch thick OFHC copper backing plate. Targets may be prepared by mixing powders of the desired magnet constituents and suitably bonding them together. For example, samarium-cobalt and praseodymium-cobalt tar-

gets have been prepared by mixing 325 mesh cobalt powder with minus 100 mesh rare-earth-rich samarium-cobalt and praseodymium-cobalt alloy powder. Yttrium-cobalt targets were prepared by mixing a cobalt powder directly with unalloyed yttrium powder. The mixed powders were consolidated and simultaneously bonded to the copper backing plate using a high energy rate forming process. Other types of targets which were successfully used included a hexagonal array of praseodymium rods in a cobalt matrix, a lamellar array of praseodymium strips in a cobalt matrix, and a target composed directly of intermetallic PrCo_5 or SmCo_5 compound. Alloys could also be used as target materials.

The substrates 32 were one inch diameter metal discs electron beam welded to the stem 34. In place of water cooling it would be possible to use chilled nitrogen gas or other material as a cooling medium for sub-zero temperature deposits. Elevated temperature deposits may be made by permitting the substrate to heat intrinsically due to the normal heat input from the plasma or by positioning an auxiliary Nichrome heater behind the substrate. Virtually any material can be used for the substrate 32, it being only governed by the dual requirement that it be capable of maintaining the desired deposition temperature and that it be compatible with the deposited material at that temperature. The substrates were metallographically polished and ultrasonically cleansed before installation in the sputtering chamber. After mounting, the substrate surface was ion etched for 5 to 10 minutes at a potential of minus 100 volts DC and a current of 30 milliamps prior to the start of each deposition run to clean the surface and promote adherence of the deposited material. A target substrate spacing of 0.625 inch was normally used.

The target was maintained at a negative potential of 1,500 volts DC, with the resistance-heated tungsten cathode maintained at a negative potential of 30-40 volts DC attaining a plasma current of 3 to 18 amperes. A high-speed current limiter was used in the target circuit to minimize the effects of arcing. The target current was normally 100 to 200 milliamps. A negative substrate bias of 20 to 50 volts DC may be applied during the deposition runs to enhance the surface mobility of the deposited atoms and purify the deposited material.

Preferably the deposition is maintained at the maximum rate consistent with smooth operation of the deposition system and the type of material being deposited. The preferred rate is in excess of 1.5 mils per hour, but may be as low as 0.5 mil per hour. Deposits of up to 0.25 inches thick have been produced, although there is no limit to the thickness of deposits that can be produced other than the ability of the apparatus to accommodate large bodies of material. The deposits should have a thickness of at least about 0.001 inch. The desirability of such thickness can be seen from FIG. 2, which is a photomicrograph (250X) of sputter deposited PrCo_5 . The stainless steel substrate upon which the deposit was made is indicated at 40. Upon such substrate a layer 42 of PrCo_5 of 2.6 mil thickness was laid down at a rate of 1.8 mil per hour. It will be observed that the central portion of the layer 42 is a fine, equiaxed structure of uniform appearance. However, the boundary area 44 between the substrate 40 and layer 42 is non-uniform and exhibits evidence of some interaction between the substrate and the overlying deposit. Upon the layer 42 further PrCo_5 was de-

posited at a rate of 0.3 mil per hour to form a layer 46 of 0.4 mil thickness. Again the boundary area 48 between the layers 42, 46 exhibits interaction of the layers, while the layer 46 has a distinctly different appearance than the layer 42. Next a layer 50 of 4.5 mil thickness was laid down at 1.8 mil per hour and again interaction is apparent in the boundary area 52. Finally, a 4.6 mil layer 54 was laid down at 0.3 mil per hour. Interaction at the boundary area 56 is apparent, but it is also possible to observe a distinct columnar structure in the layer 54 evidencing the value of the high rate deposition in attaining a deposit of desired properties. Composition analysis indicated that the 0.3 mil per hour deposits contained only 28 percent Pr rather than the expected 38 percent which is attributed to the volatilization of the Pr which occurs at the lower rate. The selection of the rare-earth metal and transition metal to be used in forming a magnetic material by the method of the invention is determined by the type of magnet desired. All of the rare-earth metals and yttrium form compositions in combination with a transition metal, that is, cobalt, iron or nickel, that exhibit magnetic properties. However, only the lighter rare-earth metals, that is, yttrium and elements of atomic number 57 through 63, will form high-performance permanent magnet materials. Similarly all of the transition metals form magnetic materials in combination with rare-earth metals, but only cobalt or a cobalt-iron mixture will provide a high performance, permanent magnet material. To form permanent magnet materials the composition should be substantially within the range R_aM_b , where R is a rare-earth metal of the class indicated above, M is cobalt or iron-cobalt, and a and b are in a mol ratio between 1:4 and 1:10. In an iron-cobalt type material the cobalt should have a minimum mol ratio of one mol cobalt per 3 mol iron.

Other magnetic compositions such as for magnetostrictive applications may also be prepared in accordance with the invention. Such compositions comprise the heavier rare-earth metals, primarily those of atomic number 64 to 71, inclusive, and mixtures thereof in combination with iron or nickel, or mixtures thereof. While the mol ratio may be varied a ratio of about one mol rare-earth metal to two mols transition metal is preferred and iron is the preferred transition metal.

The invention is further illustrated by the following specific examples:

EXAMPLE I

A SmCo_5 sputtering target was fabricated by mixing 52 grams of high-purity, 325 mesh cobalt powder with 68 grams of Co-60 weight percent Sm powder prepared by hand-grinding the cast alloy (Molybdenum Corporation of America, Low-Melting Alloy No. 392) to -100 mesh size in an iron mortar. The mixed powders were placed on a 1.625-inch diameter by 0.25-inch thick OFHC copper backing disc positioned inside a 2.5-inch OD and 2.375-inch ID stainless steel can with a 1.625-inch ID mild steel liner. The can was welded shut, evacuated to approximately 1×10^{-6} Torr, heated to 400°C. and compacted using a Model 1220F Dynapak. This operation served both to consolidate the powders and to bond them to the copper backing plate. The resultant target was removed from the can, machined to a 1.5-inch diameter and electron beam welded to a stainless steel stem. The completed assembly was installed in the sputtering chamber as illustrated in FIG. 1.

The substrate was a 1.0-inch diameter by 0.1875-inch thick AISI 304 stainless steel disc electron beam welded to a stainless steel stem. A rectangular slot 0.875-inch long, 0.25-inch wide and 0.125-inch deep was machined in the back of the substrate to accommodate the poles of a standard horseshoe-type Alnico 5 permanent magnet. The magnet provided an in-plane magnetic field of approximately 1,000 Oe at the center of the substrate. The substrate was metallographically polished, ultrasonically cleaned and installed in the sputtering chamber with the substrate surface parallel to and 0.625-inch from the surface of the target.

The sputtering chamber was helium leak tested and baked at 100°C. for 12 hours. The system pressure after cooling was 3×10^{-8} Torr with a pressure rate of rise for the sputtering chamber of 5×10^{-9} Torr/sec. High-purity krypton sputtering gas was then admitted to the chamber and maintained at an indicated system pressure of 1 to 2×10^{-3} Torr during the deposition run. The critical surfaces in the sputtering chamber were ion etched to promote adherence of the deposited material and prevent peeling. The discharge containment shield was etched for 5 minutes at -100 VDC and 2A, the anode was etched for 5 minutes at -300 VDC and 30 mA, and the substrate was etched for 10 minutes at -100 VDC and 30 mA.

Both the target and the substrate were water-cooled during the deposition run, the substrate being maintained at 20°C. The target voltage was -1,500 VDC and the target current was held at 100 mA for the first 5 minutes of operation to condition the target surface and then increased to the normal operating value of 200 mA. The plasma was generated using a filament current of 28 to 32 A, a plasma potential of -40 VDC, and a plasma current of 3.3 to 3.8 A. A -35 VDC bias was applied to the substrate to give a bias current of 70 to 90 mA. A 30-mil thick deposit was produced in 19.3 hours at an average deposition rate of 1.55 mil/hr. A total of 18.93 grams of alloy was removed from the target and 3.37 grams of this was deposited on the substrate for a deposition efficiency of 17.8 percent.

The as-deposited magnet material was microcrystalline with a hardness of 560 DPH. Several 0.1-inch diameter discs were ultrasonically machined from the deposit, surrounded by RCO_5 getter-material to inhibit oxidation and heat-treated in an all-metal vacuum system for 2 hours at temperatures ranging from 200° to 1,100°C. The magnetic properties of these specimens were measured using a Princeton Applied Research vibrating sample magnetometer coupled to a 75-kilogauss superconducting magnet. Selected intrinsic coercive force values as a function of annealing temperature are given in Table I. The maximum intrinsic coercive force value obtained was 35 kOe for a specimen annealed for 2 hours at 600°C. Moreover, the variation in this value as a function of measurement direction in the plane of the deposit was less than 1 percent. The heat-treated material was further characterized by a fine, equiaxed grain structure with an average grain size that was still less than 1 micron after 2 hours at 1,000°C.

EXAMPLE II

A PrCo_5 deposit was prepared using the exact procedure of Example I. The target was composed of 66.5 grams of cobalt powder and 54.5 grams of Co-72 weight percent Pr alloy (Molybdenum Corporation of

America, Low-Melting Alloy No. 382). A 37-mil thick deposit was produced in 24 hours at an average deposition rate of 1.54 mil/hr. The best magnetic properties for this material were obtained after a 4 hour anneal at 600°C. The intrinsic coercive force was 11.5 kOe, the remanence was 7 kG and the maximum energy product was 10 MGOe.

The magnet materials prepared in accordance with the invention are characterized by a fiber texture with the fiber axis perpendicular to the plane of the deposit. Both the specific crystallographic direction that serves as the fiber axis and the strength of the texture are a function of composition and of the deposition and annealing conditions. The occurrence of a fiber texture in a sputter-deposited magnet material is responsible for the unique in-plane isotropy and out-of-plane anisotropy of the magnetic properties of this material and can be exploited to provide magnets with otherwise unattainable direction-of-magnetization characteristics; for example, discs or annuli magnetized in a radial direction.

Magnet material of the invention is essentially 100 percent dense thus maximizing the possible energy product and eliminating the oxidation-induced degradation of magnetic properties which results from surface oxidation of particles in insufficiently dense powder compacts. In the instance of sputtered deposits such oxygen as may be present is uniformly dispersed throughout the deposited material and has no deleterious effect upon the magnetic properties of the deposited material. The oxygen is believed to form a fine dispersion of oxide and there is reason to believe such finely dispersed oxides may, in fact, be beneficial in providing "pinning sites" to impede domain wall motion. The sputtering technique utilized herein makes possible, of course, control of the oxygen content or that of any other alloying element within the deposit. The sputter-deposited magnet material is further characterized by high hardness values that range from 500-600 DPH for room temperature deposits to more than 800 DPH for heat-treated material. The sputter-deposited material in common with material prepared by powder metallurgy or the direct casting technique is relatively brittle. However, the high quality of the deposited material should provide the best mechanical properties possible subject to the inherently brittle nature of the base compound. In addition, the sputter-deposited material can be bonded to the substrate as an integral part of the deposition process whenever additional strength is required.

A magnetic field may be applied at the substrate surface, if desired, to influence the orientation of the crystallographic structure. Such a field could be established by use of electromagnets or by permanent magnets including using a permanent magnet as the substrate.

The microcrystalline magnet material prepared in accordance with the invention at room temperature by high-rate sputter-deposition exhibits a characteristic response to elevated temperature heat treatment. As noted previously, both intrinsic coercive force and hardness values can be increased significantly by appropriate annealing treatment. Table I illustrates a change in hardness and intrinsic coercive force as a function of annealing temperature for SmCo_5 deposited at room temperature and annealed for two hours at the indicated temperatures. It should be noted that the material prepared in accordance with the invention is sim-

ilar to that prepared by powder metallurgy techniques in that the coercive force curve has high and low temperature peaks. This distinguishes the material of the invention from the thin film prepared by the process described in U.S. Pat. No. 3,615,911, which material has a single, low temperature peak in the coercivity curve as plotted against substrate temperature. Moreover, the patent reports low temperature deposition, followed by annealing results in a decrease in coercivity whereas deposition at low temperature and annealing of the materials of the invention greatly increases the coercivity value. Also the present material shows no decrease in magnetic property upon increase in thickness. Just why the product of the invention should exhibit magnetic characteristics different from those obtained by the process described in U.S. Pat. No. 3,615,911 is not known, although there is a difference in appearance and structure of bulk materials deposited at a high rate as compared to thin film materials of the type described in the patent.

TABLE I

Annealing Temperature	Intrinsic Coercive Force	Hardness
As-Deposited at 20°C	0 kOe	560 DPH
600°C	35 kOe	—
750°C	15 kOe	—
1000°C	—	1100 DPH
1100°C	25 kOe	—

Having illustrated and described certain preferred embodiments of the invention, it will be apparent the invention permits of modification in arrangement and detail.

We claim:

1. A sputtered-deposit of a magnetic material consisting essentially of a rare-earth metal (R) selected from the class consisting of yttrium and elements of atomic number of 57 to 71, inclusive, and mixtures thereof, and a transition metal (M) selected from the class consisting of cobalt, iron and nickel, and mixtures thereof, said deposit having a thickness greater than 0.001 inch and having been formed at a deposition rate in excess of 0.5 mil per hour, said material having a grain size less than 10 microns.

2. A magnetic material as set forth in claim 1 having permanent magnetic properties, R being selected from the class consisting of yttrium and elements of atomic number of 57 through 63, inclusive, and mixtures thereof, and M is a metal selected from the class of cobalt and iron and mixtures thereof.

3. A magnetic material as set forth in claim 2 wherein R and M are in a ratio of between about 4 to 10 parts M per part R on a mol basis.

4. A magnetic material as set forth in claim 2 wherein M is a mixture of cobalt and iron containing at least about 25 mol percent cobalt.

5. A magnetic material as set forth in claim 2 wherein M is cobalt.

6. A magnetic material as set forth in claim 2 having the composition RM_5 .

7. A magnetic material as set forth in claim 6 wherein R is selected from the class consisting of samarium, praseodymium, and yttrium.

8. A magnetic material as set forth in claim 2 having the composition R_2M_{17} .

9. A magnetic material as set forth in claim 6 having the composition $SmCo_5$.

10. A magnetic material as set forth in claim 6 having the composition $PrCo_5$.

11. A magnetic material as set forth in claim 1 consisting essentially of a sputtered deposit including a rare-earth metal selected from the class consisting of elements of atomic number 64 to 71, inclusive, and mixtures thereof, and a transition metal selected from the class consisting of iron and nickel and mixtures thereof.

12. A magnetic material as set forth in claim 11 wherein the transition metal is iron.

13. A magnetic material as set forth in claim 11 wherein the transition metal is nickel.

14. The method of forming magnetic materials which comprises forming a target consisting essentially of a rare-earth metal selected from the class comprising yttrium and elements of atomic number 57 to 71, inclusive or mixtures thereof, and, a transition metal selected from the class consisting of iron, cobalt and nickel, and mixtures thereof, sputtering said target upon a substrate in an inert atmosphere under conditions to deposit the sputtered mixture at a rate in excess of 0.5 mil per hour, until a deposit is obtained of at least about 0.001 inch in thickness.

15. The method of claim 14 wherein the material deposited upon said substrate is heated to anneal the same.

16. The method of claim 14 wherein said substrate and depositing material are maintained at a temperature not in excess of room temperature during deposition and the mixture deposited is subsequently annealed.

17. The method of claim 16 wherein the deposited material is $SmCo_5$, and said annealing is performed at 600°C.

18. The method of claim 16 wherein the deposited material is $PrCo_5$ and the deposit is annealed at 600°C.

19. The method of claim 14 wherein said target is formed of a mixture of finely divided rare-earth and transition metals.

20. The method of claim 14 wherein said target is formed as an array of discrete bodies of the rare-earth metal and transition metal.

21. The method of claim 14 wherein said target comprises an intermetallic compound of the rare-earth metal and transition metal.

22. The method of claim 14 wherein said target comprises an alloy of the rare-earth metal and transition metal.

23. The method of claim 14 wherein a magnetic field is applied to the area of deposition on said substrate.

24. The method of claim 14 wherein the rate of deposit is at least about 1.5 mils per hour.

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