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FERROMAGNETIC INTERMETALLIC COMPOUNDS AND METHOD OF PREPARATION

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This application is a continuation-in-part of U.S. patent application Ser. No. 302,708, filed Aug. 16, 1963, now abandoned, entitled "Ferromagnetic Intermetallic Compounds and Method of Preparation," by F. Holtzberg et al.

This invention relates to new rare earth intermetallic compounds and, more particularly, to compounds having the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy, and Ho; and M is a transition metal selected from the group consisting of Pd and Pt and their preparation.

When A is Gd, the compounds Gd_5Pd_2 and Gd_5Pt_2 are ferromagnetic below a temperature of $T_c=61°$ C. which is a higher ferromagnetic Curie temperature than for the pure Gd metal ($T_c=16°$ C.). When A is Tb, Dy, or Ho, the compounds Tb_5Pd_2, Dy_5Pd_2, Ho_5Pd_2, Tb_5Pt_2, Dy_5Pt_2 or Ho_5Pt_2 first become metamagnetic and then ferromagnetic at temperatures between liquid nitrogen and liquid helium temperatures.

The rare earth metals and their compounds are important magnetic materials because they generally exhibit higher magnetic moments than the iron group metals (e.g., Fe, Co, and Ni) and their compounds.

The magnetic moment of the rare earth elements is either the sum or the difference of the spin and orbital moments of the unpaired electrons in the 4*f* shell, the difference resulting for the lighter and the sum for the heavier elements. The outer bonding orbitals effectively shield the 4*f* shell so that chemical bond formation has little effect on the total magnetic moment. In contrast, the unpaired 3*d* electrons of the iron group metals are directly involved in bond formation and magnetic coupling so that the compounds and alloys of these elements generally have different moments.

The Curie temperatures for the rare earth elements, however, are relatively low, e.g., Dy, $T_c=80°$ K. and Gd, $T_c=290°$ K. As a consequence, the practical application of these elements as magnetic materials is limited to low temperature systems such as cryogenic systems. The possibility of increasing the Curie temperature of rare earth metals by alloying with other elements increases the range of their practical applicability in magnetic and electronic devices such as transformers and relays for which a high permeability is desired.

Heretofore, most investigations of the rare earth-palladium and rare earth-platinum systems have been confined to rare earth concentrations less than 50% and to compounds of the type AM_3 (where A is a rare earth element and M is a Pd or Pt) which have been described structurally (A. E. Dwight, J. W. Downey, and R. A. Conner, Jr., "Some AB_3 Compounds of the Transition Metals," acta Cryst, 14, 75, 1961). In the previous investigations, there has been no discussion of the magnetic properties of these compounds.

It is an object of the invention to prepare rare earth intermetallic compounds.

It is another object of the invention to prepare new rare earth intermetallic compounds which are ferromagnetic.

It is a further object of the invention to prepare rare earth intermetallic compounds having the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy, and Ho and M is a transition metal selected from the group consisting of Pd and Pt.

Another object of the invention is to prepare a rare earth intermetallic compound having the formula

Gd_5Pd_2[71.4 at.(78.7 wt.)percent Gd]

A still further object of the invention is to prepare a rare earth intermetallic compound having the formula

Tb_5Pd_2[71.4 at.(78.9 wt.)percent Tb]

Yet another object of the invention is to prepare a rare earth intermetallic compound having the formula

Dy_5Pd_2[71.4 at.(79.2 wt.)percent Dy]

Still another object of the invention is to prepare a rare earth intermetallic compound having the formula

Ho_5Pd_2[71.4 at.(79.6 wt.)percent Ho]

A further object of the invention is to prepare a rare earth intermetallic compound having the formula

Gd_5Pt_2[71.4 at.(66.8 wt.)percent Gd]

Further another object of the invention is to prepare a rare earth intermetallic compound having the formula

Tb_5Pt_2[71.4 at.(67.2 wt.)percent Tb]

Further still another object of the invention is to prepare a rare earth intermetallic compound having the formula

Dy_5Pt_2[71.4 at.(67.6 wt.)percent Dy]

Another further object of the invention is to prepare a rare earth intermetallic compound having the formula

Ho_5Pt_2[71.4 at.(67.9 wt.)percent Ho]

The foregoing and other objects, features, and advantages of the invention will become apparent from the more particular description of a preferred embodiment of the invention.

The new rare earth intermetallic compounds disclosed herein have the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy, and Ho and M is a transition metal selected from the group consisting of Pd and Pt. The following rare earth intermetallic compounds are examples of the invention:

Gd_5Pd_2[71.4 at.(78.7 wt.)percent Gd]
Tb_5Pd_2[71.4 at.(78.9 wt.)percent Tb]
Dy_5Pd_2[71.4 at.(79.2 wt.)percent Dy]
Ho_5Pd_2[71.4 at.(79.6 wt.)percent Ho]
Gd_5Pt_2[71.4 at.(66.8 wt.)percent Gd]
Tb_5Pt_2[71.4 at.(67.2 wt.)percent Tb]
Dy_5Pt_2[71.4 at.(67.6 wt.)percent Dy]
Ho_5Pt_2[71.4 at.(67.9 wt.)percent Ho]

These rare earth intermetallic compounds having the formula A_5M_2 are prepared by mixing appropriate amounts (5 moles) of the rare earth element selected from the group consisting of Gd, Tb, Dy, and Ho and 2 moles of the transition metal selected from the group consisting of Pd and Pt of the component elements in finely divided form and then heating to melt and react the component elements. The heating is accomplished by using one or the other following metallurgical procedures.

One procedure involves placing the sample mixture in an inert refractory metal crucible (e.g., tantalum, molybdenum, etc.) which in turn is evacuated and sealed (e.g., by cold welding). The crucible is now placed in a quartz vacuum system centered in a radio frequency induction heating coil. An ambient atmosphere of helium or argon is often used in place of the vacuum. Power is delivered to the coil at a rate such that the crucible temperature is raised to a temperature between 1400° C. to 1600° C.

This temperature is maintained until the reaction is completed. The power is now turned off and the crucible rapidly cools to room temperature. Since there is a finite solubility of tantalum in the melt, the following arc melting process of preparing these compounds is preferred.

The other and preferred procedures used in preparing the rare earth intermetallic compound disclosed in the invention is an arc melting procedure. Appropriate quantities of the rare earth and palladium in finely divided form are mixed in amounts corresponding to those desired in the final compounds and pressed into a pellet for convenient handling. This pellet is then placed in an arc furnace of a commercially available type (e.g., Model AF–92 MRC Manufacturing Corp. or one similar to that described in FIGURE 3 of U.S. Patent No. 2,989,480). The furnace chamber is evacuated and flushed with an inert gas, such as argon, neon, krypton, xenon, or helium, three times to purge the chamber. In such a furnace, a movable cathode is used to strike an arc to the water-cooled copper hearth (anode) which contains several wells or shallow depressions to hold the metals being melted and reacted. The arc is struck to the anode in the vicinity of the reactants, which are fused (melted) by the heat of the arc. Since the cathode is mounted through a ball and swivel joint, the molten material can be stirred by precessing the cathode tip around the periphery of the melt.

After the sample has been fused, the arc is interrupted and the solidified melt is turned over in the well then remelted in the arc. By repeated turnings and melting, homogeneity in the sample can be achieved. Temperatures in excess of 3500° C. can readily be generated. Such a temperature is more than sufficient to fuse the metals Gd, Tb, Dy, Ho, and Pd; however, the cooled anode keeps a thin layer of the materials being fused in a solid condition, on the cold anode surface, so that the melt itself does not ever contact the metal of the anode. Alloying of the anode and the melt is thus avoided.

These rare earth intermetallic compounds are brittle metallic materials which form a protective oxide coating in ambient atmospheres.

The compounds have the following magnetic properties; Gd_5Pd_2 is ferromagnetic below 61° C. with a saturation moment of 197 emu per gram in agreement with the moment calculated for an atomic moment of 7 Bohr magnetons per Gd atom. The saturation magnetization decreases with increasing temperature, T, according to the $(T)^{3/2}$ law up to $T=0.8T_c$. The Curie temperature T_c, where the magnetic moment disappears is at 334° K. Gd_5Pd_2 is a soft magnetic material with a coercive force less than 100 oersteds and the magnetization $\sigma_{H,T}$ saturates at constant temperature T with a field H to the saturation value $\sigma_{\infty,T}$ following the law

$$\sigma_{H,T=\infty,T}\left(1-\frac{a}{H}\right)$$

with a magnetic hardness

$$a=\left(\frac{\sigma_{\infty,T}-\sigma_{H,T}}{\sigma_{\infty,T}}\right)H=110 \text{ oersteds}$$

which value is lower than a Gd=359 oe. for pure gadolinium metal.

Since the Gd_5Pd_2 has a coercive force and hardness lower than Gd metal and a saturation magnetization higher than most iron group metals and their alloys (approximately 25,000 gauss at 0° K. compared with the approximate value for iron of 21,000 gauss) thus the Gd_5Pd_2 is useful in electronic and magnetic devices such as transformers or relays in computer circuitry. At room temperature (20° C.) Gd_5Pd_2 has a magnetic moment of 45% of the saturation value available. (Gd is paramagnetic at this temperature.) Since the Curie temperature is at 61° C., and the variation of the magnetization with temperature is high around room temperature, Gd_5Pd_2 is used as core material in thermal switching, control, and safety devices.

In contrast to the Gd_5Pd_2, the compounds Tb_5Pd_2, Dy_5Pd_2, and Ho_5Pd_2 have paramagnetic-metalmagnetic transitions (Neel points T_N) below liquid nitrogen temperature (e.g., the T_N for Dy_5Pd_2 is 41° K.; Tb_5Pd_2 is 62° K. and Ho_5Pd_2 is 33° K.), and become ferromagnetic at still lower Curie temperatures (e.g., Dy_5Pd_2, $T_c=25°$ K.; Tb_5Pd_2, $T_c=30°$ K.; and Ho_5Pd_2, $T_c=10°$ K.) with a high coercive force (e.g., the H_c for Tb_5Pd_2 is 12,800 oe.; Dy_5Pd_2 is 9700 oe. and Ho_5Pd_2 is 1300 oe.) The extreme magnetic hardness makes these compounds useful as permanent magnets in cryogenic circuits and devices operating around liquid helium temperature (4.2° K.) which is the normal operating temperature for cryogenic circuitry.

The similarity in chemical properties of Pd and Pt reflects in the similarity in magnetic properties of A_5Pd_2 and A_5Pt_2, for example, Gd_5Pd_2 and Gd_5Pt_2 are isostructural and have the same ferromagnetic Curie temperature.

Example I.—Gd_5Pd_2 [*71.4 at.* (*78.7 wt.*) *percent* Gd]

7.87 grams of Gd metal filings and 2.13 grams of Pd powder are thoroughly mixed and pressed into pellets which are placed in a tantalum crucible which is evacuated and sealed by cold welding. The crucible is placed on a pedestal in an evacuated quartz cylinder and heated to 1600° C. for 2 minutes with a radio frequency induction heating coil and rapidly cooled to room temperature. The resulting product is Gd_5Pd_2.

Example II.—Gd_5Pd_2 [*71.4 at.* (*78.7 wt.*) *percent* Gd]

7.87 grams of Gd metal filings and 2.13 grams of Pd powder are mixed and pressed into a pellet. The pellet is placed in a well of the water-cooled copper hearth of an arce melting furnace. The furnace chamber is evacuated and flushed with argon gas three times to purge the chamber of reactive gases. An arc is struck between the tungsten cathode and the water-cooled hearth of the arc furnace. A current of 150 amps at 40 volts liquified the sample in about 10 seconds. The melt is stirred by precessing the cathode around the periphery of the melt for about 30 seconds, and then the power is turned off and the melted sample allowed to solidify and cool. The sample is then inverted and the above arc melting, cooling and turning procedure is repeated until a homogeneous product is obtained. Since the sample is in direct contact with the cold copper hearth, the cooling is essentially a quench from the molten state. Micrometallurgical examination revealed the completeness of the reaction by showing a single phase compound. This compound is Gd_5Pd_2.

Example III.—Tb_5Pd_2 [*71.4 at.* (*78.9 wt.*) *percent* Tb]

The process of Example II is repeated except that 7.89 grams of Tb and 2.11 grams of Pd are used instead of the amounts of the Gd and Pd of Example II. The resulting compound is Tb_5Pd_2.

Example IV.—Dy_5Pd_2 [*71.4 at.* (*79.2 wt.*) *percent* Dy]

The process of Example II is repeated except that 7.92 grams of Dy and 2.08 grams of Pd are substituted for the amounts of Gd and Pd of Example II. The resulting compound is Dy_5Pd_2.

Example V.—Ho_5Pd_2 [*71.4 at.* (*79.6 wt.*) *percent* Ho]

The procedure of Example II is repeated except that 7.96 grams of Ho and 2.04 grams of Pd are substituted for the amounts of Gd and Pd used in Example II. The resulting product is Ho_5Pd_2.

Example VI.—Gd_5Pt_2 [*71.4 at.* (*66.8 wt.*) *percent* Gd]

6.68 grams of Gd metal filings and 3.32 grams of platinum powder are mixed and pressed into a pellet. This pellet is now placed in the well of a water-cooled copper hearth of an arc melting furnace. The furnace chamber is evacuated and flushed with argon gas three times to purge the chamber of reactive gases. An arc is struck between the tungsten cathode and the water-cooled hearth

of the arc furnace. A current of 150 amperes at 40 volts liquified the sample in about 10 minutes. The melt is stirred by precessing the cathode around the periphery of the melt for about 30 seconds, and then the power is turned off and the melted sample allowed to solidify and cool. The sample is then inverted and the above arc-melting, cooling, and turning procedure is repeated until a homogeneous product is obtained. Since the sample is in direct contact with the cold copper hearth, the cooling is essentially a quench from the molten state. Micrometallurgical examination revealed the completeness of the reaction by showing a single phase compound. This compound is Gd_5Pt_2.

Example VII.—Tb_5Pt_2 [*71.4 at.* (*67.2 wt.*) *percent* Tb]

The process of Example VI is repeated except that 6.72 grams of Tb and 3.28 grams of Pt are used instead of the amounts of the Gd and Pt of Example VI. The resulting compound is Tb_5Pt_2.

Example VIII.—Dy_5Pt_2 [*71.4 at.* (*67.6 wt.*) *percent* Dy]

The process of Example VI is repeated except that 6.75 grams of Dy and 3.24 grams of Pt are substituted for the amounts of Gd and Pt of Example VI. The resulting compound is Dy_5Pt_2.

Example IX.—Ho_5Pt_2 [*71.4 at.* (*67.9 wt.*) *percent* Ho]

The procedure of Example VI is repeated except that 6.79 grams of Ho and 3.21 grams of Pt are substituted for the amounts of Gd and Pt used in Example VI. The resulting product is Ho_5Pt_2.

Rare earth intermetallic compounds having the formula A_5M_2 (wherein A is selected from the group consisting of the Gd, Tb, Dy, and Ho; and M is a transition metal selected from the group consisting of Pd and Pt) have been prepared and found to be ferromagnetic.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A rare earth intermetallic compound having the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy, and Ho, and M is a transition metal selected from the group consisting of Pd and Pt.

2. The rare earth intermetallic compound

Gd_5Pd_2 [71.4 at. (78.7 wt.) percent Gd]

3. The rare earth intermetallic compound

Tb_5Pd_2 [71.4 at. (78.9 wt.) percent Tb]

4. The rare earth intermetallic compound

Dy_5Pd_2 [71.4 at. (79.2 wt.) percent Dy]

5. The rare earth intermetallic compound

Ho_5Pd_2 [71.4 at. (79.6 wt.) percent Ho]

6. The rare earth intermetallic compound

Gd_5Pt_2 [71.4 at. (66.8 wt.) percent Gd]

7. The rare earth intermetallic compound

Tb_5Pt_2 [71.4 at. (67.2 wt.) percent Tb]

8. The rare earth intermetallic compound

Dy_5Pt_2 [71.4 at. (67.6 wt.) percent Dy]

9. The rare earth intermetallic compound

Ho_5Pt_2 [71.4 at. (67.9 wt.) percent Ho]

10. The process of preparing a rare earth intermetallic compound having the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy and Ho, and M is a transition metal selected from the group consisting of Pd and Pt which comprises:

(1) mixing together in finely divided form A and M in proportions such that a rare earth compound produced by heating has the above formula;

(2) arc melting the thus formed mixture in an inert atmosphere on a cold copper hearth;

(3) turning the thus formed melt and again arc melting in an inert ambient atmosphere and then cooling to room temperature;

(4) repeating steps 2 and 3 a plurality of times; and

(5) cooling rapidly to room temperature.

11. The process of preparing a rare earth intermetallic compound having the formula A_5M_2 wherein A is a rare earth selected from the group consisting of Gd, Tb, Dy and Ho, and M is a transition element selected from the group consisting of Pd and Pt which comprises:

(1) mixing together in finely divided form A and M in a 5:2 molar ratio;

(2) arc melting four times the thus formed sample mixture in an argon atmosphere on a copper hearth and turning the sample mixture between each melting; and

(3) cooling rapidly to room temperature.

References Cited

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