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FINAL REPORT
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FUNDAMENTAL MAGNETIC STUDIES OF IRON-RARE-EARTH-METALLOID ALLOYS

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FINAL TECHNICAL REPORT

The aim of this research was to deepen our understanding of strongly magnetic rare earth - transition metal compounds and alloys. Such materials have high potential as hard or semi-hard permanent magnet materials with energy related and other applications.

Our efforts were focused in the following three areas:

(i) The search of Fe-rich new phases and compounds with high magnetization, anisotropy and Curie temperature that can be used for permanent magnet development.

(ii) the use of rapid solidification techniques (melt-spinning) to prepare these phases into fine grain microstructures that can lead to high coercivities.

(iii) The relationship of hard magnetic properties to microstructure and magnetic domain structure determined by transmission electron microscopy.

The grant provided support for a female graduate, Antonia Tsoukatos, who plans to finish her Ph.D. in approximately three years. We have been working closely with our collaborator, Professor Dave Sellmyer at the University of Nebraska along with his group. In addition we are collaborating with Dr. Y. Wang who is visiting from the Academy of Science in Beijing, China. Our program so far has been very successful leading to eight publications and numerous presentations at scientific meetings (see publications and presentations section). In the following section we give a brief description of our recent work.

A. $RFe_{10}(TiV)_2$-Type Alloys

R-Fe-Ti alloys with the $ThMn_{12}$ structure have some interesting magnetic and physical properties that make them suitable for permanent magnet development. The Sm-containing alloys have a large anisotropy field $\sim$ 90 kOe, a magnetization $4\pi M_S = 12$ kG, a relatively high Curie temperature of about 300°C and they are more corrosion resistant than Nd-Fe-B. However, despite the large anisotropy field we found that it was much more difficult to obtain a high coercivity in these systems with the 1:12 structure. After considerable effort we managed to increase the coercivity of melt-spun ribbons to about 11 kOe from the initial value of 2.5 kOe. This was done through a variation of composition and heat treatment. Below we describe our efforts that led to the high coercivity.

Effect of Annealing Temperature

Several samples with composition $Sm_xFe_yT_z$ (T = Si, Ti, V, Al, Cu, Mo or a mixture of these) and $8 < x < 20$, $76 < y < 89$, and $6 < z < 12$ were prepared by arc-melting starting materials of at least 99.9% purity under purified argon gas. In some samples, a small amount of B or C was added. Pieces of ingots were made into ribbons by using the melt-spinning technique.

For optimum magnetic hardening the ribbons were heat-treated at temperatures ranging from 750° to 1050°C for times ranging from 5 to 15 minutes. The crystallization temperature was determined by differential scanning calorimetry (DuPont 900 differential scanning calorimeter). The crystal structure was determined with x-ray diffraction using Cu-K_α radiation. Microstructure studies were made using transmission electron microscopy (JEOL 100C electron microscope). The magnetic measurements were made with a vibrating sample magnetometer with a maximum applied field of 17.7 kOe. The results of x-ray diffraction, electron microscopy, and thermomagnetic measurements showed that the crystallized alloys have the $ThMn_{12}$-type structure when annealed above 800°C. For lower annealing temperatures some alloys have the $TbCu_7$-type structure. The maximum coercivity was 7.7 kOe and several samples with composition Sm-Fe-Ti-B and Sm-Fe-Ti-(Si,Al) had $H_c > 6.5$ kOe.

Effect of Vandium Substitutions

The effects of vanadium substitution on the magnetic properties of Sm-Fe-Ti-V melt-spun ribbons and the magnetic properties and microstructure of sintered Sm-Fe-Ti based magnets were studied. The highest coercivity, $H_c = 10.65$ kOe, was obtained in heat- treated melt-spun samples containing Ga and Zr, $Sm_8Fe_{76}Ti_6Zr_2V_8$, $Sm_8Fe_{75.5}Ga_{0.5}Ti_8V_8$. This is the highest value of the coercivity reported in alloys with the $ThMn_{12}$- type structure. Bulk magnets were prepared into nearly single 1:12 phase by the usual powder metallurgy technique. However, their highest coercivity ($\sim$ 2 kOe) was much less than that of the corresponding ribbons. The low coercivity of sintered magnets has been attributed to their nonuniform microstructure.

Also the intrinsic magnetic properties of as cast $SmFe_{10}(TiV)$ alloys have been studied. The anisotropy constants K_1 and K_2 of the $SmFe_{10}TiV$ compound were found to be positive. At room temperature, K_1 is large, but K_2 increases with decreasing temperature and becomes predominant at cryogenic temperatures. The coercivity and anisotropy field data suggest that the microstructure is very important in achieving the high coercivity. The change of coercivity with temperature may be attributed to the temperature dependence of the magnetocrystalline anisotropy of the material.

B. R-Fe(Co)-C Alloys

As-cast Dy-Fe-C

As cast $Dy_{15}Fe_{77}C_8$ alloys develop high coercivities with values exceeding 15 kOe after a heat treatment of 900°C. Thermomagnetic data show the presence of two phases: the anisotropic $Dy_2Fe_{14}C$ phase with a Curie temperature (T_c) around 300°C and DyFeC with T_c around 40 K.

Scanning electron microscope data showed a microstructure consisting of a continuous matrix phase with two other phases randomly distributed in the matrix phase. The majority phase has an Fe/Dy ratio corresponding to $Dy_2Fe_{14}C$. The first minority phase is richer in Dy showing a ratio of Fe/Dy $\sim$ 1. This is probably the phase with T_c around 40 K. A similar B-rich phase has been reported in R-Fe-B magnets but with different composition RFe_4B_4. The other phase which is sparsely found in the sample is believed to be Dy_2Fe_{17}. Transmission electron microscope studies verified the existence of these phases. The C-rich phase was found to have lattice parameters a = 8Å and c = 24 Å.

This type of microstructure can explain the magnetic hysteresis behavior of the Dy-Fe-C magnets. The domain walls move easily inside the matrix phase resulting in the steep increase of magnetization at low fields. Localized domain wall pinning possibly takes place at the boundary region between the $Dy_2Fe_{14}C$ and DyFeC phase resulting in the higher coercivities. Lorentz microscope studies are required to verify this hypothesis.

Cobalt Substituted R-Fe(Co)-C Alloys.

The formation of tetragonal $R_2(FeCo)_{14}C$ phase has been examined in as-cast and melt-spun $R_{14}Fe_{78-x}Co_xC_8$ alloys with cobalt substitutions (R = Y, Dy, Nd). The magnetic properties over a temperature range and the microstructure have been studied as a function of cobalt content. The Curie temperature is increased with Co content but the anisotropy K is decreased. High cobalt content leads to the formation of 1:5 phase. High coercivities up to 40 kOe have been developed in as-cast and melt-spun $Dy_{14}Fe_{78-x}Co_xC_8$ alloys with Co content at zero and 32 at %, respectively. As-cast $Nd_{16}Fe_{78-x}Co_xC_8$ alloys did not show any permanent magnetic properties although they had the 2:14:1 phase. However, melt-spun and powdered Nd-Fe-Co-C samples showed a coercivity with the highest value (8 kOe) corresponding to a melt-spun $Nd_{14}Fe_{78}C_8$ samples. Microstructure studies showed that the high H_C in ribbons is due to the fine grain size which is in the range of 500 - 1000 Å.

C. Publications and Presentations

Publications

1. G. C. Hadjipanayis, N. Venkateswaran and J. Strzeszewski, *Origin of High Coercivities in As-cast Dy-Fe-C Magnets*, J. de Physique C8, 639 (1988).

2. E. W. Singleton, T. Strzeszewski and G. C. Hadjipanayis, *High Coercivities in Rapidly Quenched Sm(Fe,T)$_{12}$-Type Magnets*, Appl. Phys. Lett. 54, 1934 (1989).

3. G. C. Hadjipanayis, *A Search for New Phases and Processing Techniques for Permanent Magnet Development*, Mat. Sci. Engn. B3, 431 (1989).

4. J. Strzeszewski, Y. Z. Wang, E. W. Singleton and G. C. Hadjipanayis, *High Coercivity in Sm(FeT)$_{12}$-Type Magnets*, IEEE Trans. Magn. MAG-25, 3309 (1989).

5. K. D. Aylesworth, Z. R. Zhao, D. J. Sellmyer and G. C. Hadjipanayis, *Growth and Control of the Microstructure and Magnetic Properties of Sputtered $Nd_2Fe_{14}B$ Films and Multilayers*, Journal of Magnetism and Mag. Matl. 82, 48 (1989).

6. Y. Wang, G. C. Hadjipanayis, A. Kim and D. J. Sellmyer, *Magnetic and Structural Properties in Sintered Sm-Fe-Ti Magnets*, J. Appl. Phys. (in press).

7. K. D. Aylesworth, D. J. Sellmyer and G. C. Hadjipanayis, *Magnetic and Structural Properties of High Coercivity $Pr_2Fe_{14}B$: Pr Cosputtered Films*, J. Appl. Phys. (in press).

8. Y. Z. Wang and G. C. Hadjipanayis, *Magnetic Properties of Sm-Fe-Ti-V Alloys*, Appl. Phys. Lett. (in press).

Presentations

1. G. C. Hadjipanaysis, A. Tsoukatos, J. Strzeszewski, O. A. Pringle and G. J. Long, *New Magnetically Hard R-Fe-Oxide Phases*, Bull. Am. Phys. Soc. 34, 566 (1989), March APS Meeting, St. Louis.

2. E. W. Singleton, J. Strzeszewski and G. C. Hadjipanayis, *Magnetic Properties and Microstructure of Melt-spun $Sm(Fe,T)_{12}$ Type Magnets with High Coercivities*, Bull. Am. Phys. Soc. 34, 976 (1989), March APS Meeting, St. Louis.

3. K. D. Aylesworth, D. J. Sellmyer, and G. C. Hadjipanayis, *Growth, Microstructure and Magnetic Properties of Nanostructured NdFeCoB/Ta Multilayers*, Bull. Am. Phys. Soc. 34, 624 (1989), March APS Meeting, St. Louis.

4. K. D. Aylesworth, Z. R. Zhao, D. J. Sellmyer and G. C. Hadjipanayis, *Growth, Microstructure and Magnetic Properties of Cosputtered $R_2Fe_{14}B$ Films with Ag, Fe, Ta or Pr*, Midwest Solid State Conf., Rolla, MO 1989).

5. K. D. Aylesworth, Z. R. Zhao, A. Nazareth and G. C. Hadjipanayis, *Growth, Microstructure and Magnetic Properties of Cosputtered Rare Earth-Iron-Boron*, Bull. Am. Phys. Soc. 35, 401 (1990), March APS Meeting, Anaheim, CA.

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