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13. ABSTRACT (Maximum 200 Words) A combined experimental and theoretical investigation of advanced nanostructured magnetic materials has been carried out. Novel physical systems have been synthesized and studied including: hard/soft nanocomposites, magnetic nanowires, thermally processed multilayer films, and nanoparticle-assembled composites. Emphasis has been focused on exchange coupling at grain boundaries, incoherent magnetization reversal, and magnetization dynamics. The design of nanomagnets with controlled properties has been emphasized, and unprecedented advances have been made in high-temperature permanent magnets, high-coercivity nanocluster magnets, and hard and soft magnetic nanotubes prepared with chemical methods.				
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2. Objectives

The goal of this research has been to further the understanding and application of advanced magnetic materials for applications of the U.S. Air Force. Particular emphasis was placed on improved high-temperature properties and higher energy permanent magnets. The research was focused into three areas: (1) cluster-assembled advanced magnets; (2) high-temperature Sm-Co based magnets; and (3) novel materials and processing methods. All three areas utilized our extensive experience with techniques for controlling material structure on the nanometer scale, and a broad set of experiments will be performed over a wide temperature range. X-ray and electron-diffraction, magnetization, Mössbauer effect and novel processing methods have been pursued. The results are correlated with theoretical work on interfacial-exchange-interaction, random-anisotropy, and micromagnetic calculations on realistic models for experimental systems. Beneficial properties obtained from nanoscale two-phase systems are a particular emphasis of this research. Collaborative work with external university, industrial and international laboratories broadened and extended the program, and resulted in 38 publications and numerous invited and contributed conference presentations.

3. Status of Effort

A significant advance has been made in preparing a hybrid Sm-Co-Cu-Ti with record hard properties at high temperature ($H_c = 12.3$ kOe at 500°C). The significance of the work is that a simple, four-element alloy without Zr substitution can achieve significant properties including a positive change of coercivity with increasing temperature. Additional experimental and theoretical research has given an understanding of exchange-coupled hard magnet materials and their dependence on nanostructure. Excellent results on NdFeB/ \bullet Fe exchange-coupled multilayer magnets have been achieved.

Significant advances have been made in fabrication of nanostructures with characteristic dimensions that span the important magnetic exchange lengths involved. These include the domain wall thickness giving the length over which the magnetization changes direction in the presence of magnetic anisotropy, the exchange length which controls the scale over which exchange dominates magnetostatic forces, and the coherence length which measures the scale below which magnetization reversal can be coherent. This understanding allows the prediction and control of properties in nanomagnets that are important for various applications. Several examples of new findings and highlights are outlined below.

4. Accomplishments/New Findings/Highlights

4.1 Hybrid High-Temperature Permanent Magnets

The effects of transition-metals such as Fe, Cu, Zr, and Ti substitutions in Sm-Co permanent magnets have been the subject of thorough investigation for many years. Recently, they have found renewed attention in the context of high-temperature permanent magnets. For example, Ti-

substituted $\text{Sm}_2\text{Co}_{17}$ -type permanent magnets have excellent high temperature magnetic properties with $H_c = 12.3$ kOe at 500°C . We investigated how Fe and Ti affect the magnetic properties of sintered Sm-Co magnets by varying the Fe content of $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Ti})_z$ samples. A coercivity of 10.8 kOe at 500°C has been achieved for a transition-metal ratio of 7.3. In combination with the positive effect of the Fe on the magnetization, this coercivity makes the material a promising candidate for high-temperature applications. Higher transition-metal ratios cause the coercivity to drop, as expected, from the phase structure of Sm-Co magnets. The temperature dependence of the coercivity is explained in terms of the temperature dependence of the magnetic properties of the grain-boundary phase. TEM is used to investigate the difference between Ti-containing and Zr-containing magnets. Both compositions exhibit the cellular microstructure characteristic of sintered Sm-Co magnets, with cell sizes of about 100 nm. The main difference is the absence of the lamellar phase in the Ti-containing samples.

4.2 Magnetism of Sputtered Sm-Co-Based Thin Films

Granular Sm-Co and Sm-Co-Cu-Ti thin films were produced by thermal processing of sputtered Sm-Co single layers and $\text{SmCo}_5/(\text{CuTi})$ multilayers. Single layer SmCo_z films with nominal compositions ranging from SmCo_3 to $\text{SmCo}_{7.5}$ were prepared by co-sputtering. In-plane anisotropy was found in the composition range of $z < 5.5$, whereas for $z > 5.5$ the films exhibit three-dimensional random anisotropy. A coercivity of 49.6 kOe at 300 K was obtained in a film with the nominal composition SmCo_4 . Sm-Co-Cu-Ti films were sputtered on Si substrates with a Cr underlayer of 90 nm and coverlayer of 18 nm. The structure of the multilayer is $(\text{SmCo}_5 45\text{\AA}/\text{CuTi} X\text{\AA}) \times n$, ($X = 2-10$, $n = 38 - 44$), corresponding to a total thickness of the Sm-Co-Cu-Ti layers of about 200 nm. X-ray diffraction patterns show that after annealing between 500°C and 550°C for 30 minutes, the hexagonal 1:5 phase forms with average grain size of 8 nm. Electron micrographs of the processed films show that grains with diameters of 5 to 10 nm are embedded in a matrix. Both the grains and the matrix phase exhibit the CaCu_5 structure, but the matrix is probably Cu-rich. The hysteresis loops show that these films have large coercivities of up to 50.4 kOe. Ti plays an important role in realizing the coercivity, in spite of the quite small fraction of Ti in the films. A SmCo_5 single layer and SmCo_5/Cu and SmCo_5/Ti multilayers do not exhibit the granular structure observed in the Sm-Co-Cu-Ti thin films, and the coercivities of the annealed SmCo_5/Ti and SmCo_5/Cu films did not exceed 20 kOe and 10 kOe, respectively. This behavior is reminiscent of the coercivity mechanism in Cu- and Ti- substituted bulk Sm-Co magnets, where Ti helps to form Cu-rich grain boundaries necessary to realize domain-wall pinning. The magnetization reversal in the films is analyzed using \bullet m plots.

4.3 Exchange Coupling and Remanence Enhancement in Nanocomposite Multilayer Magnets

After experimental evidence of intergrain exchange coupling was reported, the nanocomposite magnets with high remanence and large energy products were predicted. However, the experimental values of the maximum magnetic energy product of nanocomposite bulk magnets have been much less than the theoretically predicted ones. We report the exchange coupling and the remanence enhancement in nanocomposite $(\text{Nd,Dy})(\text{Fe,Co,Nb,B})_{5.5}/\alpha\text{-Fe}$ thin films prepared by sputtering and heat treatments. The coercivity of an individually Ti-buffered $(\text{Nd,Dy})(\text{Fe,Co,Nb,B})_{5.5}$ layer is as large as 1.85 T, while a high remanence of $J_r = 1.31$ T and a high maximum energy

product of $(BH)_{\max} = 203 \text{ kJ/m}^3$ are achieved in the nanocomposite multilayer films. The well-designed multilayer films consist of magnetically hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase with the grain size of 40 nm and magnetically soft $\alpha\text{-Fe}$ phase existing in the form of the continuous layers. Our results suggest that the nanocomposite multilayer films with well-distributed fine grains of the hard and soft magnetic phases could constitute a new generation of permanent-magnet materials.

4.4 CoPt Hard Magnetic Nanoparticle Films Synthesized by High-Temperature Chemical Reduction

Synthesis of hard magnetic CoPt nanoparticle films by hydrogen reduction of a Co nitride and Pt chloride mixture has been achieved. Thin porous alumina film is adopted as carrier of the initial aqueous solution and the final reducing products of CoPt nanoparticles. It is found that chemical ordering of CoPt $L1_0$ starts at 400°C . Partial phase transformation occurs in the alumina substrate when the treating temperature is higher than 600°C , but it does not affect the ordering and the magnetic properties of CoPt nanoparticles. The film coercivity increases with increasing treating temperature, and reaches a maximum value of 24.2 kOe when the reduction is carried out at 700°C for 2 hours.

4.5 Magnetic Nanotubes Produced by Hydrogen Reduction

FePt and Fe_3O_4 nanotubes are produced by hydrogen reduction in nanochannels of porous alumina templates and investigated by electron microscopy, x-ray diffraction, and superconducting quantum interference device magnetometry. Loading the templates with an Fe chloride and Pt chloride mixture, followed by hydrogen reduction at 560°C , leads to the formation of ferromagnetic FePt nanotubes in the alumina pores. An Fe nitrate solution, thermally decomposed at 250°C and reduced in hydrogen for 2.5 h at the same temperature, yields Fe_3O_4 tubes. The versatility of the method indicates that materials with a wide range of parameters can be produced.

5. Personnel Supported and Associated with Project

Faculty: Professors David J. Sellmyer, Yi Liu, Ralph Skomski; Visiting Professors: I. Al-Omari, W. Liu; Postdoctoral Research Associate: Y. Sui; Graduate Research Assistant: Jian Zhou.

6. AFOSR Publications

Thirty-eight publications listed below have resulted from this grant from April, 2001 to the present, and several others are accepted for publication or submitted.

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13. R. Skomski, J. Zhou, and D.J. Sellmyer, FINITE-TEMPERATURE MICROMAGNETISM OF Sm-Co PERMANENT MAGNETS, *Rare Earth Magnets and Their Applications*, Ed. G.C. Hadjipanayis and M.J. Bonder, (Rinton Press, 2002), p. 814.
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