Magnetic Hysteresis and Rotational Energy Barriers in C-Coated Co and RE/TM Fine Particle Ferromagnets

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***Abstract*— We use a Kratschmer-Huffman C-arc method to synthesize C-coated transition metal (TM) and rare earth (RE)-TM nanocrystals. The theme of this research is C-arc synthesis of magnetic materials and assessment of potential use in xerography, ferrofluids, data storage, MRI image enhancement, etc. Here we focus on materials with potential for data storage. TM particles include Co[C]. $Sm_{1-x-y}Co_xC_y$ nanocrystals have been produced using a Sm_2Co_7 precursor, as have nanocrystalline $Fe_{1-x-y-z}Nd_xB_yC_z$ using $Fe_{14}Nd_2B$. Characterization by XRD and HRTEM identify phases and particle sizes. SQUID magnetometry is used to determine magnetic hysteretis, temperature, and time dependent response.**

I. INTRODUCTION

An exciting adjunct of fullerene production is formation of C-coated metal or metal carbide nanocrystals. Our group has described the preparation of carbon coated ferromagnetic nanocrystals [1,2] and suggested applications for fine particle magnets where adherent, protective carbon coatings are important. Here we review the synthesis C-coated Co[C], Sm-Co-C and Fe-Nd-B-C nanocrystals of interest for potential applications. The magnetic particles produced by this process are predominantly monodomain. C-coatings provides an effective oxidation barrier. Our data offers a link between fullerene-related nanocrystals and fine particle magnetism. Her we discuss initial efforts to produce carbon-coated $Sm_{1-x-y}Co_xC_y$ and $Fe_{1-x-y-z}Nd_xB_yC_z$ with the aim of engendering larger magnetocrystalline anisotopy important for thermal stability at room temperature.

II. EXPERIMENTAL PROCEDURE

Carbon-coated nanocrystals (typically 10-100 nm. and averaging ~20 nm in diameter) have been produced by the Krätschmer-Huffman carbon arc process. In this process composite rods have been drilled and packed with a mixture of C-graphite and metallic powders (Co, Sm_2Co_7, or $Fe_{14}Nd_2B$) and either graphite cement or dextrin powder as a binder. Rods were baked to drive off H_2O and to sinter the powders. For Co[C] we have successfully consumed rods with up to 66 wt.% Co. 1/4" diameter rods are placed in an upper electrode (anode) position in a DC carbon arc with a C-counterelectrode employed. Rods were consumed under arc conditions of 100 A, with a fixed voltage of ~ 20 V and 125-500 Torr He gas pressure. Soots containing mixtures of graphite, amorphous C, C-coated nanocrystals, and fullerenes were removed from the reactor walls and from a cathode deposit (pancake). These were characterized by XRD, TEM and HRTEM. Elemental analysis was performed on selected samples. Magnetic propeties were determined by SQUID magnetometry.

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III. RESULTS AND DISCUSSION

A. Structure and Morphology

Results of magnetic studies of Co[C] and other elemental transition metal nanocrystals are described in references [1-3]. Among the more significant results has been the observation of ~20 (±8-10) nm nanoparticles with adherent graphitic C coatings as illustrated in Figure 1(a). In this size range the

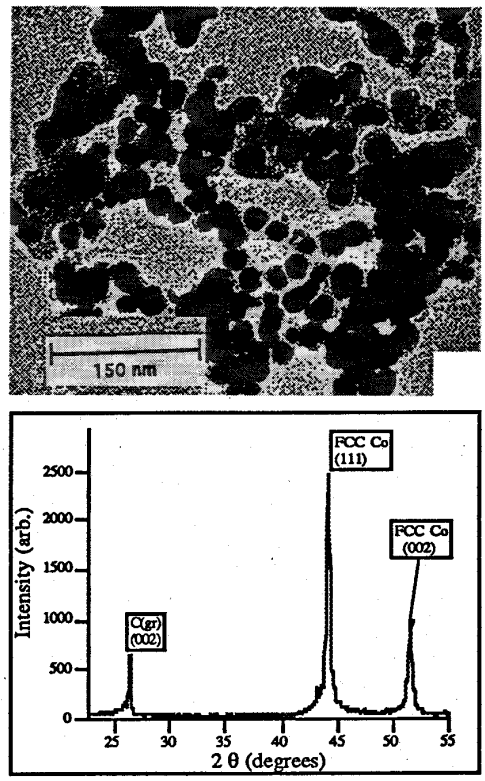

Fig. 1. (a) TEM image of C-coated Co nanoparticles produced by a carbon arc starting with Co-packed anodes of nominal composition 50 wt% Co. (b) XRD Intensity vs. 2θ for the same with FCC Co peaks labeled.

metastable FCC configuration of Co is observed as shown in the XRD pattern for a sample containing 66 wt% Co. The observation of FCC Co has been confirmed by electron diffraction on individual particles, by XRD on dilute samples and most recently by XRD on concentrated samples. The XRD on concentrated samples offers the most convincing data to date on the predominance of FCC Co nanocrystals. Using the FWHM of the XRD peaks of Figure 1(b) in the Debte Scherrer formula predicts a particle sie of 20-28 nm., in excellent agreement with the TEM observtions.The experimental details as to the synthesis of soots containing large concentrations of Co nanocrystals is described in [3].

$Sm_{1-x-y}Co_xC_y$ nanocrystals have been produced from precursors with nominal compositions of up to 35 wt. % Sm_2Co_7 with the rest carbon (from dextrin and graphite) Preliminary TEM results show these to be ~ 20 nm. particles of nearly spherical shape. XRD reveals FCC Co and $SmCo_5$ as predominant among the several phases observed, with some evidence for Sm-oxides indicating incomplete encapsulation. Work is in progress to determine nanoparticle chemistry variation and to investigate post synthesis annealing and their influence on magnetic properties.

$Fe_{1-x-y-z}Nd_xB_yC_z$ nanocrystals have been produced from precursors with nominal compositions of up to 35 wt. % $Fe_{14}Nd_2B$ supplied by Crucible Research. Structural and microstructural characterization is underway. Initial magnetic properties measurements are reported here.

B. Magnetic Properties

Interest in fine particle magnets stems from the strong variation of their technical magnetic properties, notably the coercivity, H_C, with particle size. H_C for many elemental alloy and oxide ferromagnets have been observed to have maxima, H_C^{max}, as a function of particle size (several 100 nm.) corresponding to the limiting size for monodomain ferromagnets. For these fine particle magnets the possibility of thermally activated switching and consequent reduction of the coercivity as a function of temperature must be considered as a consequence of a superparamangetic response. This switching can be described by an Arrhenius law for which the activation energy barrier is K<V> where K is the magnetic anisotropy energy density and <V> is the particle volume. The switching frequency becomes larger for smaller particle size, smaller anisotropy energy density and at higher temperatures. Above a blocking temperature, T_B, hysteresis loops are observed to collapse, i.e $H_C = 0$.

B.1. Co[C] Nanoparticles

Initial results of the magnetic studies of Co[C] nanocrystals are described in references [1] and [2]. Recently, we have demonstrated that we can encapsulate up to 66 wt. % Co in nanoparticles [3]. Figure 1 illustrates the variation of the specific magnetization of Co[C] nanocrystals with composition. The lower 4 compositions represent nominal concentrations based on a mass balance in the precursor rods. In that C is lost in hydrocarbons and to our vacuum system these naminal compostions are typically low. The 66 wt. % point represents the results of chemical analysis ~~of the~~ resulting soot. The line drawn is that expected for soots of a given composition assuming the nanoparticles to have the same specific magnetization as bulk Co. It is seen that this is relatively good model for our nanoparticles.

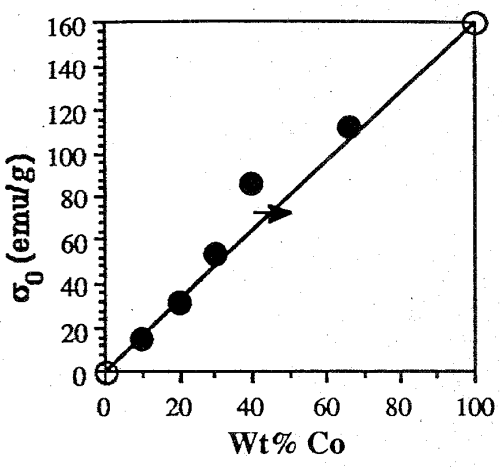

Fig. 2. Specific magnetization of Co[C] nanocrystals .

Superparamagnetic response is observed [1] for these particles above a blocking temperature, T_B ~ 160 K, and therefore these materials are not particularly exciting for room temperature applications in which a thermally stable hysteretic response is desired (e.g magnetic recording). On the other hand ferrofluidic applications, applications in MRI enhancement agents may all be viable. These results suggest that to achieve the goal of stable hysteresis at room temperature, either the particle volumes and/or the magnetic anisotropy must be increased so as to increase rotational energy barriers.

B.1. $Sm_{1-x-y}Co_xC_y$ Nanoparticles

The Sm-Co system has several notable permanent magnet phases including $SmCo_5$, Sm_2Co_7 and Sm_2Co_{17}. These phases are interesting due to their large moments and large anisotropy constants which give rise to large coercivities in bulk magnets. Here we describe magnetic properties of $Sm_{1-x-y}Co_xC_y$ nanocrystals (with Co and $SmCo_5$ the predominant magnetic species). Fig. 3(a) illustrates a typical 5 K hysteresis curve for $Sm_{1-x-y}Co_xC_y$ nanocrystals (< 5 wt. %) immobilized in epoxy. Rounded hysteretic response is consistent with a collection of particles with randomly aligned easy axes, as is the ratio M_r/M_S ~ 0.5. Fig. 3(b) shows the switching field distribution (SFD) for the same material. For these particles switching field distributions (SFD) range from ~2.5 - 4. A bimodal distribution is observed and attributed to both Co and $SmCo_x$ nanocrystals. A large SFD has been reduced by aligning Co nanoparticles. Similar efforts are underway for Sm-Co-C nanocrystals. Observations of H_C > 100 Oe for the wall soot and > 450 Oe for the pancake material, at 300 K suggest that these materials may be potentially interesting RT magnets. The difference between the Hc(T) for the two samples is attributed to different thermal histories.

Fig. 4 shows a typical temperature dependence of the coercivity, H_C, showing T_B to greatly exceed RT.

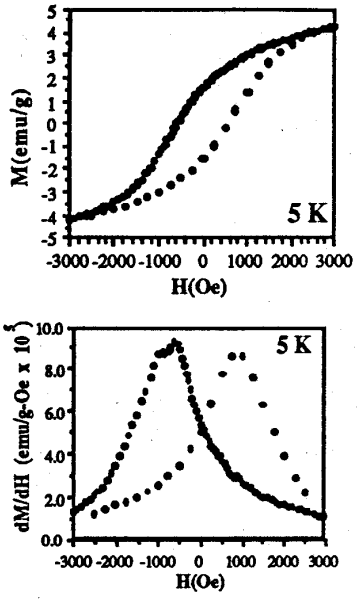

Fig. 3. (a) M(H) (per g soot) at 5 K for $Sm_{1-x-y}Co_xC_y$ nanocrystals (pancake) and (b) SFD at 5 K for the same).

A $\sqrt{T}$ dependence of H_C is again seen to be approximately obeyed in two temperature regimes. A contribution at low temperature is similar to that observed previously for Co[C] nanocrystals. Fig. 4(b) shows the field dependence of the

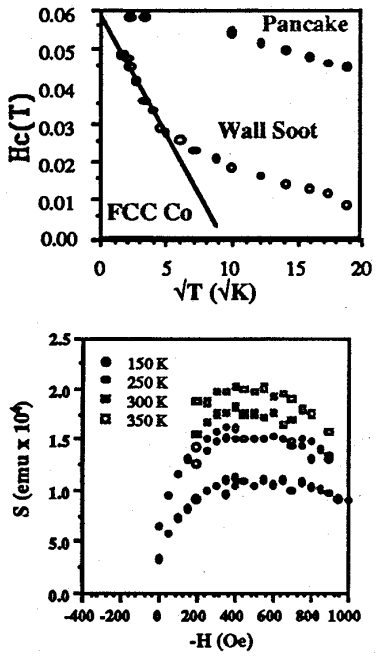

Fig. 4: Coercivity as a function of $T^{1/2}$ for $Sm_{1-x-y}Co_xC_y$ nanocrystals. Low T behavior is believed due to an FCC Co phase. The high T behavior is due to $SmCo_5$. For wall soot $T_B > 700$ K. T_B for particles collected in the pancake is much larger. (b) S(T,H) for Sthe same.

magnetic relaxation rate, S = dM/dln(t), at various temperatures. The response is thermally activated, roughly proportional to the SFD at the given temperature, and peaked at a field equal to the coercive field. These results are consistent with a model for thermally activated switching over rotational energy barriers.

B.1. $Fe_{1-x-y-z}Nd_xB_yC_z$ *Nanoparticles*

Here we report initial results in $Fe_{1-x-y-z}Nd_xB_yC_z$ ferromagnet synthesis and magnetic properties. Powders of nominal composition $Fe_{14}Nd_2B$ were mixed with 65 wt % C (graphite and dextran] and consumed under standard arc conditions. The large magnetization Fig. 6 indicates initial succes in producing magnetically concentrated materials in this system. The 5 K Hc (900 Oe) is the largest observed in our naonocrystals to date.

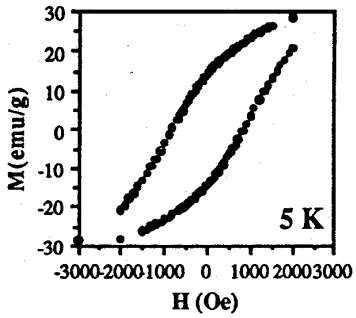

Fig. 6. M(H) (per g soot) at 5 K for $Fe_{1-x-y-z}Nd_xB_yC_z$ nanocrystals.

IV. CONCLUSION

The Kratschmer-Huffman carbon arc method has been used to produce carbon-coated TM and RE-TM(carbide) nanocrystals. Monodomain particles of Co magnets exhibit superparamagnetic response with hysteresis below T_B. Protective carbon coatings and novel magnetic properties make these potentially interesting for applications. To be viable for recording or other applications requiring stable moments at RT larger particles and/or magnetic anisotropy is needed. $Sm_{1-x}Co_xC_y$ fine particle magnets have large blocking temperatures making them attractive as thermally stable magnets at RT. Initial studies of $Fe_{1-x-y-z}Nd_xB_yC_z$ fine particle magnets also show promise.

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