MAGNETIC SEPARATION OF GdC, ENCAPSULATED IN CARBON NANOPARTICLES

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Abstract—Single crystal particles of α-GdC2 have been encapsulated into carbon polyhedral shells by the carbon arc-discharge technique. These particles range in size from 20 to 50 nm and are paramagnetic in nature. The phase and stoichiometry of these crystals have been determined using a combination of techniques, such as X-ray diffraction and high-resolution electron microscopy. As reported for α-LaC2 earlier, the crystal structure of bulk α-GdC2 is also tetragonal, and it is metallic and undergoes hydrolysis. However, the encapsulation of the monoscale crystals in carbon shells prevents their hydrolysis indefinitely. These nanometer-sized particles, which can be preferentially extracted using powerful magnetic fields, may have useful applications in several fields of science.

Key Words—Gadolinium carbide, nanotubes, carbon shells, encapsulation.

The discovery in 1991 by Iijima[1,2] of nested carbon nanotubes and nanopolyhedra as a by-product of fullerene production has sparked a significant amount of interest into the research of these novel forms of carbon. Theoretical calculations[3–8] have shown that these materials would possess unique electrical, thermal, and mechanical properties that could be of value to several diverse fields of science. The successful production of endohedral fullerenes by several researchers[9–12] prompted our first attempt at filling the cavities of the tubes and polyhedra with highly electropositive elements. Our results, reported previously, showed successful encapsulation of single-crystal, nanometer-sized particles of α-LaC2 into about 50% of the carbon polyhedral shells using arc-discharge conditions that favored the growth of carbon nanotubes and polyhedra[13].

In order to effectively utilize the benefits of such high-density nanoparticles (density of α-LaC2 is 5.32 g cm−3), it would be desirable to extract them preferentially from the rest of the products of the arc-discharge experiments. Encapsulated materials of a variety of sizes and morphologies are difficult to separate in bulk using either physical or chemical means. Magnetic means of extracting α-LaC2 particles would not be successful, as they are only weakly diamagnetic. Our initial attempts at encapsulating a ferromagnetic element (Fe) were not successful, and this may be due to several factors, among them the higher ionization potential of Fe compared to that of La, or the lower melting temperature and higher vapor pressures of the carbides of Fe compared to those of α-LaC2. In this paper we report the successful encapsulation of Gd, one of the four ferromagnetic elements. The paramagnetic properties of the carbon-shell encapsulated, single crystals of α-GdC2 are also reported.

Analogous to our production of α-LaC2 encapsulated in carbon nanoparticles[13], the arc-discharge experiments were run using 7.9-mm-diameter, 30.5-cm-long graphite anodes, which were drilled to a depth of 23 cm with a 3.2-mm drill and packed with either Gd2O3, which has negligible magnetic susceptibility, or pure Gd metal. The carbon arc conditions were a DC current of 75 A, and gap distances of 2–5 mm and 2–8 mm from the 12.7-mm-diameter cathode for the Gd2O3 and Gd runs, respectively.

The corresponding He pressures were 1,000 Torr (Gd2O3) and 500 Torr (Gd), and the Gd: C molar ratios were 2.5:100 (Gd2O3) and 8.2:100 (Gd). Under these conditions a cylindrical boule grows outward from the end of the graphite cathode. The central core section obtained from this cylindrical growth on the end of the cathode was powdered. A sample of the Gd-containing powder (ca. 50 mg)
obtained from the GdO₃-packed anode case was heated in air in a TGA, and the weight of the residual ash was 31.2%. XRD analysis of the ash showed it to be pure GdO₃. From these results we calculate the Gd content to be 2.8 at%, which is slightly higher than the original 2.3 at% Gd (present as Gd₂O₃) in the anode.

The powders were dispersed in ethanol by sonication, and then deposited on holey carbon-coated Cu grids, and air-dried for characterization by transmission electron microscopy (TEM). Most of the electron microscopy used to study these materials was carried out on a JEOL 2000-FX TEM operated at 200 kV. The Atomic Resolution Microscope at the National Center for Electron Microscopy, Lawrence Berkeley Laboratories, as well as a Philips CM-30 TEM equipped with a Link windowless detector, were also used for high-resolution microscopy and elemental analysis, respectively.

Arc-discharge experiments, run with either a metal or an oxide in the anode, produced significant quantities of carbon nanopolyhedra, with roughly bides.

Arc-discharge experiments using pure Gd metal in the anode showed that it consisted of GdC₆, GdC₃, and graphite. The products from the experiments involving GdO₃ are the same, but the relative peak heights were significantly lower in the latter due to the presence of substantial amounts of amorphous material (mostly carbon). The presence of the GdC₃, GdC₂, GdC, and graphite species in the product from the arc-discharge experiments using GdO₃ or Gd metal distinguishes it from our previous work on La₂Cu₃O₇, where only La₂Cu₃O₇ was observed.

One potentially interesting aspect is the modification of the density of the nanopolyhedra when they are filled with a high-density material such as graphite. Filled nanoparticles GdCₓ (6.94 g/cm³) will have densities that range from 3-5 g/cm³ vs. approximately 1.7 to 2 g/cm³ for GdC. Immersion of higher-index lattice planes was limited by the line resolution of the 2000-FX. Further verification of the phase of the encapsulated particles was obtained by measurement of the angles of different sets of fringes, which matched very well with those from theoretical calculations for tetragonal crystals

Accurate measurement of the lattice fringe spacings from several high-resolution images of the magnetically extracted nanoparticles showed that the spacings matched well with the interplanar spacings of the (101), (002), and (110) planes of α-GdC. Imaging of higher-index lattice planes was limited by the line resolution of the 2000-FX. Further verification of the phase of the encapsulated particles was obtained by measurement of the angles of different sets of fringes, which matched very well with those from theoretical calculations for tetragonal crystals.

Specific magnetic properties of these materials were investigated using a magnetometer (PAR model 4500 VSM) capable of stabilized sample temperatures from 4 to 325 K and magnetic field strengths up to 10,000 Oersted. To accommodate as much material as possible in the VSM probe chamber, the samples were pressed and formed into discs 3 mm diameter by 2 to 3 mm long, consisting typically of 5 to 50 milligrams of material. Random samplings of Gd-carbon materials were collected from core and soot material, and magnetically extracted samples were pulled at room temperature using a 5 kG samarium cobalt magnet.

Temperature-dependent magnetic moment data for the Gd-carbide encapsulates over the range 4 to 300 K are shown in Fig. 3. Based upon the XRD analyses, the paramagnetic response of the Gd-carbide sample appears to be the result of gadolinium dicarbide, which in bulk form has an antiferromagnetic transition temperature of 42 K[16]. Since the GdC₂ crystal sizes observed by TEM are on the order of 100 nm or less, and their moments are essentially isolated and uncoupled, a clear antiferromagnetic transition for GdC₂ at 42 K is not observed. For GdC, particles of this size, the thermal energy required to overwhelm the energy barrier of stationary moments and flip them in an external field is expected to be relatively small; therefore, the net magnetic moment should follow the Curie law 1/T dependence down through the transition temperature. These encapsulated GdC₂ crystals fulfill this requirement, and are thus consid-
Fig. 3. Moment vs. temperature for Gd-carbon encapsulate sample generated from Gd$_2$O$_3$ packing. The fitted curve is a least-squares fit to $1/T$ Curie law.

Based on the study of high-resolution images obtained from the predominantly amorphous regions of carbon containing a fine dispersion of Gd, as verified by elemental analysis using energy dispersive spectroscopy (EDS), we can speculate on a possible encapsulation mechanism for the GdC$_2$ nanocrystals in the carbon polyhedral shells. We speculate that the Gd/C amorphous material (with only a few atomic percent Gd in carbon) phase segregates into ultrathin aggregates of Gd carbides in a matrix of amorphous carbon. The high-resolution image in Fig. 4 suggests that the carbide may crystallize prior to the carbon shell. Specific planes of the crystallized carbide particles appear to promote the graphitization of the carbon layer planes from the inside out; the high resolution image in Fig. 5 illustrates GdC$_2$ crystals surrounded by carbon shells that are incompletely graphitized. The encapsulation of the GdC$_2$ crystal within the graphitic carbon shell may occur via one or a combination of two modes. The completion of the crystallization of the carbon polyhedral shell may occur from the outside in, causing a reduction in the volume of the carbon surrounding the GdC$_2$ crystal. Such a phenomenon would account for the presence of a void adjacent to the carbide crystal inside the graphitic shell. More likely, the placement of the 12 pentagons to close the polyhedral shell and the polyhedron structure is simply incompatible with the shape of the encaged GdC$_2$ crystal, causing the formation of a void. Figure 6 illustrates a high-resolution image of a completely crystallized carbon polyhedron containing a single crystal of $\alpha$-GdC$_2$ and a void region.

Although the concentration of Gd-filled nanoparticles was high, filled nanotubes themselves were observed only on extremely rare occasions. An example of such a metal-filled nanotube is shown in Fig. 7.

As is evident from Fig. 7, the end of the
multilayer nanotube is capped by many carbon layers. It is therefore unlikely that the Gd material in the interior was drawn into the tube by capillary action. Furthermore, the meniscus indicates a contact angle greater than 90° (measured value is about 135°), which is indicative of non-wetting behavior. Thus, if the Gd material were drawn in by capillary action, one would have to involve the unlikely scenario that this material expands upon solidification to cause an inversion of the meniscus. Since we were unable to observe lattice fringes in the Gd material inside the tube, we could not assign its stoichiometry or phase.

In summary, we have been able to encapsulate single crystals of α-GdC₂ in carbon polyhedral shells by DC arc-discharge techniques. However, unlike encapsulated polyhedra of α-LaC₂, encapsulated GdC₂ is paramagnetic, and can be easily extracted at room temperature. Useful applications of such nanometer sized particles can be expected in several fields of technology.

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Note added in proof: Another study of encapsulates of gadolinium carbide has recently appeared, Majetich et al., Phys Rev B 48, 16845 (1993); these authors have studied encapsulated GdC₃, in contrast to the work reported here by us, which is of the more strongly paramagnetic GdC₂ encapsulates.

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