Characterization of Magnetic Nanoparticles Using Energy-Selected Transmission Electron Microscopy

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Abstract: Fe, Co, and Ni magnetic nanoparticles have been characterized using energy-selected imaging in a high-resolution transmission electron microscope. The samples comprised Fe/FeO and Co/CoO nanoparticles synthesized by inert gas evaporation and a Ni/C nano-composite prepared by a sonochemical method. All of the particles examined were found to be between 5 and 30 nm in size, with the Fe and Co crystals coated in 5–10 nm of metal oxide layer and the Ni metallic crystallites embedded in an amorphous carbon spherical matrix.

Key words: analytical electron microscopy, energy-filtered transmission electron microscopy, magnetic nanoparticles

INTRODUCTION

Transmission electron microscopes (TEMs) equipped with in-column (Tsuno et al., 1997) or postcolumn (Krivanek et al., 1992) imaging spectrometers are now routinely used to obtain two-dimensional chemical maps of materials at spatial resolutions of better than 1 nm (Reimer et al., 1990; Berger et al., 1993, 1994; Krivanek et al., 1995; Körtje, 1996; Kurata, 1999). In this paper, we apply energy-selected imaging in the TEM, which is based on electron energy-loss spectroscopy (EELS), to characterize magnetic nanoparticles that are of interest for applications in the magnetic recording industry (Yoshizawa et al., 1988; Matijevic, 1989; Kneller and Hawig, 1991; Gleiter, 1992; Komarneni, 1992; Fendler, 1996). Results are presented for Fe and Co nanocrystalline powders synthesized by inert gas evaporation (Sánchez-López et al., 1997; Rojas et al., 1999) and Ni nano-composite synthesized by a sonication method (Rojas et al., 2000).

The chemical maps that are presented below were obtained using the “three-window background-subtracted elemental mapping” technique. For each element of interest, three energy-selected images are acquired using electrons that have suffered energy losses within the sample that lie close to the energy of an inner shell ionization edge for the chosen element (Hofer et al., 1997). Two (pre-edge) images are obtained at energy losses just below that of the edge and a third (post-edge) image is obtained at a slightly higher energy loss. The pre-edge images are required because the chemical signal of interest, which is contained in the post-edge image, is superimposed onto a power law background.
that decays with increasing energy loss. The pre-edge images are therefore used to calculate a spatially varying background, which is extrapolated to the energy of the post-edge image. This “background” image is subtracted from the original post-edge signal to provide a chemical map of the sample for each element of interest. Further details about the technique, as well as about EELS in general, are described in depth by Egerton (1986).

**Experimental Details**

Fe and Co nanoparticles were synthesized in a small high-vacuum chamber that had been evacuated with a turbo-molecular pump to a residual vacuum of better than $5 \times 10^{-7}$ torr (Fernández et al., 1999). Fe and Co foils (Goodfellow, 99.99%) were evaporated at a temperature of $\sim 1773$ K in a He atmosphere of 1 torr. The evaporated materials condensed in the form of ultrafine powders after losing their kinetic energy through collisions with the inert gas. The powders were oxidized using small doses of O$_2$ and then collected onto cold Cu substrates. Ni nanoparticles were provided by the laboratory of professor Gedanken at the Bar-Ilan University (Israel). The material was obtained using an ultrasonic method described by Koltypin et al. (1999), $0.02$ M Ni(COD)$_2$ in toluene was sonicated for 5 h under 1.5 atm Ar to produce a powder that contained Ni oxide dispersed in amorphous C. This powder was kept at $773$ K for $20$ h under a flow of Ar to reduce the Ni oxide to nanocrystalline metallic Ni embedded in an amorphous carbon matrix (Rojas et al., 2000).

The Fe, Co, and Ni powders were dispersed in ethanol and droplets of the suspensions were deposited onto holey C films for TEM examination. Samples were examined at 300 kV in a JEOL JEM-3000F field emission gun TEM (Kimoto et al., 1994, 1995; Crozier, 1995), which has a postcolumn Gatan GIF 2000 imaging spectrometer with a $(2k \times 2k)$ 794IF/20 charge-coupled device (CCD) camera and an additional Gatan 794 (1k $\times$ 1k) CCD camera at the level of the conventional plate camera (Hutchison et al., 1999). This microscope is in the ultra-high resolution configuration, with a low spherical aberration coefficient of 0.60 mm and a point resolution of between 0.16 and 0.17 nm, allowing high-resolution (HR) images to be obtained from the same areas of the samples that were chosen for chemical mapping. Energy-selected images were acquired at a nominal microscope magnification of 10k× or 4k× using a 20-eV wide energy-selecting slit and an objective aperture of semiangle 12.2 mrad. The typical acquisition time for each energy-selected image was $\sim 30$ s. The high brightness of the field emission source facilitated the acquisition of chemical maps from small areas of the samples. The application of energy-selected imaging to the characterization of low concentrations of B in an almost identical microscope has been described in detail by Zhu et al. (2001).

**Results**

**Fe Nanoparticles**

Figure 1a shows a representative TEM bright-field image obtained from the Fe/FeO$_x$ sample. The image has been defocused slightly in order to enhance the contrast of the agglomerated crystals, which are each between $\sim 5$ and $\sim 30$ nm in size. Some of the crystals exhibit strongly diffracting cores surrounded by lighter shells. The corresponding HRTEM image shown in Figure 1b confirms the presence of a shell around each crystal, with lattice fringes visible both in the cores (which are almost spherical) and in the surrounding 5–10-nm-thick shells. The lattice spacings in the cores correspond closely to those expected for pure Fe. The electron diffraction (ED) pattern in Figure 1c confirms the presence of both Fe and crystalline Fe oxide (either $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$) in the sample. This observation contrasts with X-ray diffraction results obtained after sample preparation, which suggested that the oxidized crystal surfaces were initially amorphous (Fernandez et al., 1999; Rojo et al., 1999).

Three-window chemical maps, which were obtained from two separate regions of the sample using the Fe-L$_{2,3}$, O-K, and C-K edges (corresponding to energy losses of 708, 532, and 284 eV, respectively), are shown in Figure 2. In each map, the black level corresponds to an intensity of zero, whereas the white level has been scaled arbitrarily to enhance features of interest. The clear signal in the O maps confirms that the Fe has oxidized strongly, while a comparison of the Fe and O maps shows that the ratio of Fe to O is highly variable across the sample. In the Fe maps, the cores of the agglomerated crystals are consistently brighter than the surrounding shells. They are correspondingly darker in the O maps, as expected for Fe-rich cores surrounded by Fe oxide shells. The intensity in the C maps originates primar-
Figure 1. Fe/FeO₃ sample: (a) Underfocused bright-field image; (b) HRTEM image exhibiting lattice spacings corresponding to pure Fe within crystallites; (c) ED pattern confirming presence of both Fe and Fe oxide within sample.

Corresponding results from the Co/CoOₓ sample are shown in Figures 3 and 4. (In this sample, the crystals chosen for examination were lying on the C support film.) The bright-field image in Figure 3a shows that, as in the Fe/FeO₃ sample, the Co nanocrystals are agglomerated and are between ~5 and ~30 nm in size. They are rarely elongated, and again exhibit darker cores that are surrounded by shells. HRTEM images and ED patterns (such as those shown in Figs. 3b and 3c, respectively) are also consistent with the presence of Co cores surrounded by crystalline shells of Co oxide. Three-window chemical maps obtained using the Co-L₂₃, O-K, and C-K edges (corresponding to energy losses of 779, 532, and 284 eV, respectively) are shown in
Figure 4. Variations in the ratio of Co to O along the chains of crystals provide further confirmation that the crystallites are Co-rich and are surrounded by Co oxide. In both of the areas examined, the intensity in the C maps originates partly from the support film and partly from C contamination that formed during imaging of the samples in the microscope. In the RGB images that are shown at the bottom of Figure 4, red, green, and blue now correspond to Co, C, and O, respectively. (Different colors have been chosen for C and O from those in Fig. 2.) The combination
of Co and O (red and blue) results in a clear definition of the shells around the crystallites in purple. As for the Fe/FeOₓ sample, Co is present in all of the regions of each sample that contain O. Similar results from less agglomerated Co particles have recently been obtained by Disko et al. (2001).

**Ni Nanoparticles**

The microstructure of the Ni/C sample is different from that of the Fe/FeOₓ and Co/CoOₓ samples examined above. The bright-field image shown in Figure 5a demonstrates that the crystallites are now embedded in well-defined regions of a more continuous matrix. Despite the fact that a different preparation method was used, the crystallites are again between ~5 and ~30 nm in size. Measurements made from HRTEM images and ED patterns (such as those shown in Fig. 5b,c) are now consistent with the presence of crystallites of pure Ni, and no evidence for the presence of either shells around the crystals or Ni oxide is seen. The three-window chemical maps shown in Figure 6 were obtained using the Ni-L₂,₃, O-K, and C-K edges (corresponding to energy losses of 855, 532, and 284 eV, respectively) and are with these conclusions. The maps show convincingly that the individual crystals are Ni rich and are embedded in a C matrix that contains some O (either within it or on its surface). The O concentration in the Ni particles is below the detection limit of the technique, which is estimated to be 5–10% for the Ni particles in this sample. In comparison with the C matrix that contains the crystallites, the large (~100 × 200 nm) object at the top left of the image contains both Ni and C and is much more strongly oxidized. This region is most likely to have retained a higher concentration of O as a result of a local deficiency of the C,

**Figure 3.** As for Figure 1, but for Co/CoOₓ sample.
that is required to reduce Ni oxide to Ni during the heat treatment stage of sample preparation, which is performed at 773 K. In the RGB image shown in Figure 6, red, green, and blue now correspond to C, Ni, and O, respectively. The differences in composition between the C-rich matrix, the Ni crystallites, and the O-rich region at the top left of the image are striking. Significantly, even the Ni crystallites at the very edge of the C matrix have not oxidized. Close examination of the C map suggests that even these crystals have a thin layer of C surrounding them. The presence of

**Figure 4.** As for Figure 2, but for Co/CoOx sample. RGB image formed with the red, green, and blue colors generated from the Co, C, and O maps.
yellow patches adjacent to some of the larger Ni-rich crystals in the color map indicates that small quantities of a Ni carbide may have formed at their edges. However, the fact that the regions are small and isolated suggests that the magnetic properties of the crystals are not affected substantially.

**Discussion and Conclusions**

Unique information has been obtained about the chemistry and the crystallography of these Fe, Co, and Ni nanocrystals, whose magnetic properties depend critically on the oxide or C layers that are protecting their outer surfaces.

All of the samples that were examined in this study were found to contain 5–30-nm-diameter crystalline nanoparticles of pure Fe, Co, or Ni. The Fe and Co nanocrystals were each coated with 5–10 nm of crystalline oxide and were agglomerated to form chains, whereas the Ni nanocrystals were unoxidized and were embedded in well-defined regions of an amorphous, C-rich matrix. The spatial resolutions of the chemical maps were estimated visually to be between 1 and 5 nm. Figure 7 shows graphs of the spatial resolutions of energy-selected images predicted for the microscope used for the present experiments. The graphs were calculated using equations given by Krivanek et al. (1995) and are plotted for a 20-eV-wide energy-selecting slit and several different energy losses as a function of objective aperture semiangle. Although a smaller objective aperture was available, a 12.2 mrad aperture was deliberately chosen in order to increase the signal that could be obtained from the thin samples being studied. The small sample thick-
nesses contributed to a low signal-to-noise ratio in the recorded energy-selected images, and, as a result, to an apparent decrease in spatial resolution. In some cases, small errors in alignment between the pre-edge and post-edge images may also have contributed to a decrease in resolution from that predicted in Figure 7, particularly for the lower intensities when images were recorded at higher energy losses. Low intensities and noise in such images may contribute to errors in background subtraction; in future experiments such errors may be reduced using techniques based on image spectroscopy (Thomas and Midgley, 2001a). Although the effects of multiple scattering can, in principle, be removed using Fourier deconvolution techniques (Thomas and Midgley, 2001b), these will not be significant for the low (typically below 50 nm) sample thickness examined here. It should also be noted that, if required, specimen thickness effects in such samples may be removed to first order by taking a ratio of the signals obtained from different elements.

It is worth mentioning that from the magnetic point of view, the Co/CoO₃ and Fe/FeO₃ samples present a interchange interaction between the antiferromagnetic MO₂ oxide layer and the ferromagnetic metallic nuclei. This kind of anisotropy gives place to a considerable increase in the sample coercitivity in relation with the bulk metallic sample. The Ni/C sample presents a super-paramagnetic behavior due to the small particle size.

Figure 6. As for Figure 2, but for Ni/C sample. RGB image formed with the red, green, and blue colors generated from the C, Ni, and O maps.

Figure 7. Predicted resolutions of chemical maps obtained at different energy losses, plotted as a function of objective aperture semiangle for an energy-selecting slit width of 20 eV, an accelerating voltage of 300 kV, a spherical aberration coefficient of 0.60 mm, and a chromatic aberration coefficient of 1.4 mm. Experimental energy-selected images were obtained using an objective aperture of semiangle 12.2 mrad.
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