CARBON COATED NANOPARTICLE COMPOSITES SYNTHESIZED IN AN RF PLASMA TORCH

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ABSTRACT

FeCo alloy nanoparticles are synthesized in an RF plasma torch reactor and characterized using X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). Bare, uncoated particles exhibit a chain-like agglomeration morphology marked by large ring- and bridge-like structures surrounding open voids. Acetylene was used to generate large numbers of carbon-coated nanoparticles similar to those produced in carbon arc reactors. Conventional TEM of this powder revealed numerous particles below 50 nm in diameter embedded in a carbonaceous matrix. These results establish RF plasma torch processing as a well-characterized, scalable alternative to carbon arc synthesis of encapsulated nanoparticles.

INTRODUCTION

Carbon-coated nanoparticles [1-4] represent one of the most promising classes of magnetic nanocomposites. Composed of nanophase ferromagnetic material encapsulated by graphitic or amorphous carbon, these systems often display interesting physical or magnetic properties because of their small size and reduced dimensionality [5]. In addition to providing an effective barrier to oxidation and corrosion [6], the encapsulating carbon overcoat can act as a form of "nanolamination". This versatile nanostructure can perform several important functions simultaneously: preventing coarsening and particle coalescence, attenuating interparticle magnetic interactions, and reducing eddy current losses in high frequency environments. Numerous technological applications have been suggested for magnetic nanoparticles, including use as data storage media [7], magnetic inks and ferrofluids, xerographic toners [2], and biomedical imaging contrast agents. Here we discuss FeCo nanoparticles, whose very low magnetocrystalline anisotropy and large saturation magnetization make them valuable for applications requiring magnetically soft materials.

If commercial applications for nanoparticles are to be realized, synthesis routes capable of producing large quantities of product (kilograms/day) must be developed. Early research relied on modified Huffman-Kratschmer carbon arc reactors to produce gram quantities of soot, but scaling this technology to kilogram yields has proven difficult. Recently, second-generation synthesis routes have begun to appear, including tungsten-arc and blown-arc techniques [8]. These new reactors permit large amounts of soot to be produced quickly, but more importantly they afford a greater degree of control over the processing parameters. In this work, radio frequency (RF) plasma torch synthesis is presented as an efficient, highly scalable, electrode-less synthesis route using pure metal starting materials and a gaseous carbon source. The flow conditions in the reactor are uniform and well-characterized [9], a key ingredient in understanding the resulting particle morphology and coating mechanisms.

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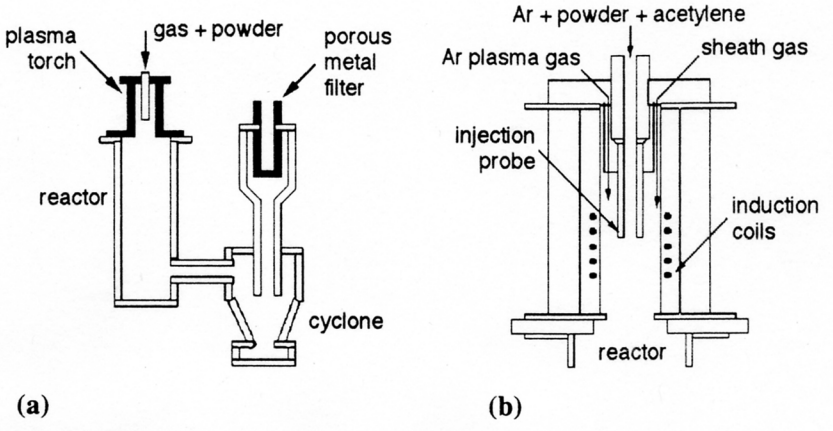

Fig. 1a. Overview of RF plasma torch reactor showing plasma torch head, expansion and reaction vessel, cyclone separator, and porous metal filters. **1b.** Detailed schematic of plasma torch head used to produce nanoparticles.

Here we report the successful synthesis of FeCo nanoparticles in an RF plasma torch using metal powder starting materials and acetylene as the carbon source. After a brief description of the experimental apparatus and production parameters, X-ray powder diffraction and transmission electron micrographs are presented for coated and uncoated nanoparticles. The performance of the RF plasma is compared to existing nanoparticle generation methods and future extensions of this fruitful technique are discussed.

EXPERIMENTAL PROCEDURE

Nanoparticles were synthesized in a radio frequency (RF) plasma reactor (Fig. 1a) consisting of a plasma torch head (Tekna Model PL-50), a gas expansion and reaction vessel, a cyclone separator, and two 5 μm porous metal filters. A 60 kW RF power supply (Lepel) was used to energize the torch head with 6.6 A delivered at 8.8 kV and 3 MHz. The torch head (Fig. 1b) consists of a inner quartz tube surrounded coaxially by a ceramic heat shield. Water-cooled copper coils outside the larger ceramic tube inductively couple the RF energy to the plasma gas in the inner quartz tube. A high flow-rate gas sheath between the inner and outer tube minimizes heat transfer to the torch body. Argon flowing at 40 standard liters per minute (slpm) was used as the plasma gas while the sheath gas consisted of 80 slpm of Ar mixed with 9 slpm of hydrogen. Metal feedstock powders were entrained in a 3 slpm Ar flow and injected axially into the gas stream just above the plasma via a tubular injection probe. A screw-driven vibratory powder feeder dispatched a mixture of 6-10 micron Fe powder and 1.6 micron Co powder to the carrier gas at a rate of 2 g/min. This ability to continuously feed starting material to the plasma has clear advantages over carbon arc reactors where synthesis must be stopped periodically to install a new consumable electrode. Acetylene could also be mixed with the powder feed gas between the vibratory feeder and the injection probe. The torch was operated nominally for 30 minutes before powder collection, producing approximately 50 g of product in this time. This compares favorably with the yields achieved using carbon arc reactors, typically only a few grams per hour in optimized systems. During each 30 minute session the pressure in the reactor vessel climbed steadily from 300 torr to 600 torr as the powder collected on the filters and the effective speed of the vacuum system decreased.

Two synthesis protocols were used to produce the nanoparticles reported here. The first used a mixture of 50 wt. % Fe and 50 wt. % Co. The goal of this run was to produce uncoated FeCo alloy in the absence of carbon. The second protocol used a mixture of 70 wt. % Fe and 30 wt. % Co with a 1.5 slpm acetylene flow as the carbon source. In both cases a black, powdery reactor product was separately collected from the reactor vessel walls and the porous metal filter traps by gently cleaning the surfaces with a brush.

X-ray powder diffraction was performed on the nanoparticle-containing soots using a Rigaku diffractometer fitted with a fixed tube Cu target and a bent graphite monochromator. TEM was used to characterize the soot structurally and examine the coating morphology. Micrographs were recorded on a Philips EM-420T operated at 120 kV using Cu grids with amorphous carbon substrates.

RESULTS AND DISCUSSION

Fig.2 is a conventional TEM micrograph of bare FeCo nanoparticles produced in the plasma torch reactor using the first processing protocol. With only argon and hydrogen gases present in the plasma during particle production (no carbon source), the particles nucleate and agglomerate without carbon coatings. Surface tensions acting during the liquid phase of particle growth have spheroidized many of the particles in this micrograph. Examples of chain-of-spheres agglomerates are also seen in this field of view (upper left), possibly caused by magnetic interactions between the particles during flocculation. Chain-like morphology has also been seen in FeCo samples produced in carbon arc reactors [10], but here the chains were often arranged in large rings or bridges not seen in carbon arc soot. These rings were approximately circular, surrounded empty space, and manifested at several length scales (diameters from 40 to at least 300 nm). In the absence of an external magnetic field, the minimum energy configuration of a chain of magnetic spheres is a closed ring. The reactor product shown in Fig. 2 was pyrophoric and oxidized readily on first contact with air; this is typical of ultrafine powders that lack a passivating or protective layer. Higher magnification microscopy (not shown) revealed thin coatings on some particles, most likely due to the post-synthesis oxidation observed during powder collection.

Fig. 3 is a conventional TEM micrograph of carbon coated FeCo nanoparticles produced in the plasma torch reactor using the second synthesis protocol. Numerous particles with diameters < 20 nm can be seen embedded in a matrix of carbonaceous material. The unusual "stringy" contrast exhibited by the carbon matrix has appeared before in carbon arc soot produced using high-abundance Co and CoBSi starting materials [10]. Although further investigation into this morphology is clearly needed, Co is a well-known catalyst of single-walled carbon nanotubes [11]. In other fields of view traces of free graphitic carbon were seen as well as occasional nanoparticles encapsulated within graphitic cages. Although quantitative statistics were not compiled, the average particle size appears to be smaller in the coated sample compared to the bare FeCo sample, suggesting the carbon coating may have intervened in particle coalescence and coarsening pathways. No chains-of-spheres were seen in the coated sample.

X-ray powder diffraction (XRD) of the two samples revealed only FeCo alloy, fcc Co, Fe oxide, and carbon, although the possibility of Fe carbide could not be ruled out. The carbon-containing sample (Fig. 4, upper trace) contains predominantly FeCo alloy with small amounts of fcc Co and graphite. The sample produced using the carbon-less synthesis protocol shows only FeCo and Fe oxide. The peaks at 30.2°, 35.6°, 43.3°, 53.7°, 57.2°, and 62.9° match exactly the six most intense reflections of γ-Fe_2O_3. The small shoulder at 36.8° is consistent with the most intense peak of Fe_3O_4. The presence of oxide peaks in XRD is expected in the uncoated sample given the large, unprotected surface area and the visible evidence of vigorous oxidation observed during powder collection. Presumably, the high cobalt abundance (nominally 50 wt. %) prevents the remainder of the alloy powder from oxidizing readily.

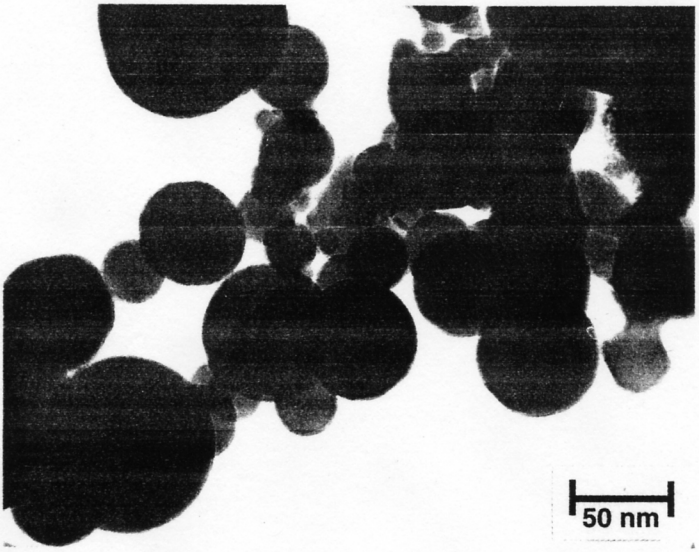

Fig. 2. Conventional TEM of bare (uncoated) FeCo nanoparticles collected from the RF plasma torch reactor wall. No carbon source was used during this synthesis.

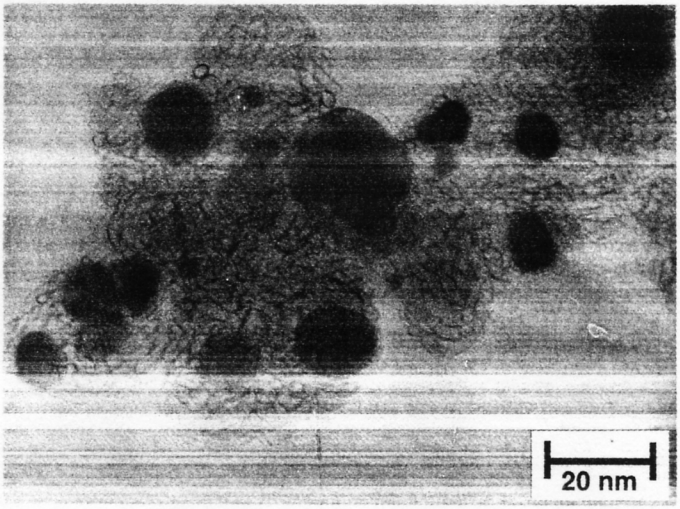

Fig. 3. Carbon coated FeCo nanoparticles produced in an RF plasma torch using metal powder feedstocks and acetylene as the carbon source. The processing conditions used to generate this product are described in the text.

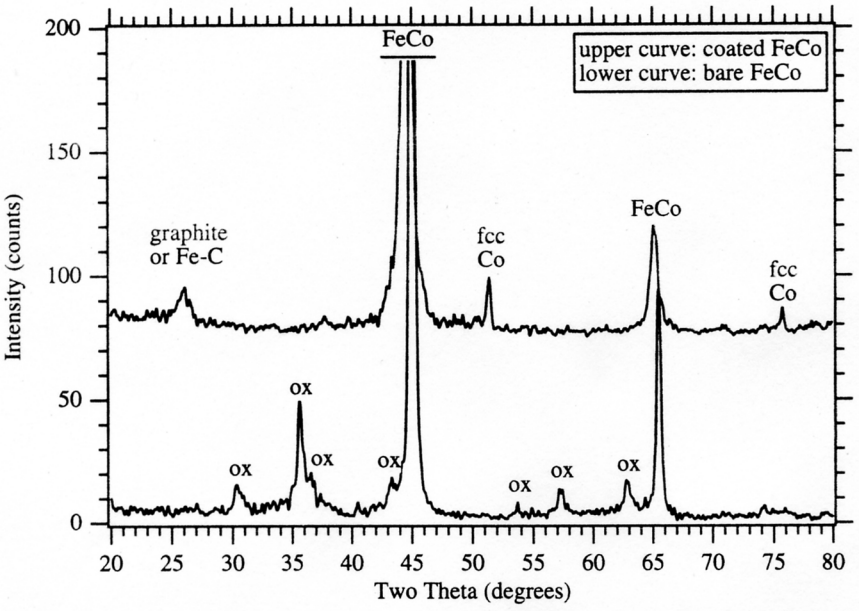

Fig. 4. X-ray powder diffraction of bare and carbon coated FeCo nanoparticles collected from the reactor wall. The lower trace (bare FeCo, no carbon) shows signs of the oxidation ("ox" indicates oxide peaks) expected from ultrafine particles lacking a protective carbon coating.

CONCLUSIONS

FeCo alloy nanoparticles were synthesized in an RF plasma torch reactor utilizing Ar as the plasma gas. Bare, uncoated particles were produced from a 50 wt. % Fe, 50 wt. % Co metal powder mixture. The resulting ultrafine powder oxidized upon contact with air, producing a mixture of FeCo alloy and γ-Fe_2O_3 as revealed by XRD. Conventional TEM of the particles showed chain-like agglomerates that were frequently arranged in a bridging, ring-like morphology. When a mixture of 70 wt. % Fe and 30 wt. % Co powders were processed in the plasma torch in the presence of acetylene as a gaseous source of carbon, coated nanoparticles (similar to those produced in carbon arc reactors) were generated in abundance. XRD of the carbon-containing powder detected predominantly FeCo alloy and small amounts of fcc Co and graphite. Conventional TEM of the soot revealed numerous particles below 50 nm in diameter embedded in a matrix of carbon.

These results establish RF plasma torch processing as a viable alternative to tungsten-arc, blown-arc, and other second generation techniques for producing carbon-encapsulated nanoparticles. The plasma torch process has been very well characterized, the synthesis parameters are well-behaved from a process control perspective, and the technique is easily scalable to industrial levels.

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