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Encapsulated Nanoparticles of Iron Metal

K. J. Klabunde,* D. Zhang, G. N. Glavee, and C. M. Sorensen

Departments of Chemistry and Physics, Kansas State University, Manhattan, Kansas 66506

G. C. Hadjipanayis

Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716

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Metastable iron–magnesium particles as intimate mixtures were prepd. by co-depositing Fe and Mg vapors with a hydrocarbon diluent at 77 K, followed by warming to room temperature. Upon heat treatment phase segregation was accomplished with reasonable control. Core-shell particles (Fe as core) were formed, where Fe particles were encapsulated, and with appropriate heat treatment could be completely protected from surface oxidation. Crystallite sizes of the Fe core ranged from 3 to 26 nm depending on the heat treatment procedure. The magnetic properties of these encapsulated particles indicated extremely soft ferromagnetism with very low coercivities and with little size dependency. These results coupled with earlier findings suggest that coercivity can be controlled (dominated) by surface coating in such small particles.

Introduction

Although numerous studies of the magnetic properties of nanoparticles of iron metal have been reported, the question as to whether surface contamination by thin oxide (Fe_2O_3/Fe_3O_4) coatings was present has not been satisfactorily resolved.[1–9] From the point of view of a chemist, the synthesis of gram quantities of pure, oxide-free nanoparticles of any oxophilic metal is a genuine nightmare. Even working under the best anaerobic conditions (parts per million oxygen in argon), surface oxidation cannot be avoided with such high surface area, reactive materials. And since it is becoming increasingly clear that even the smallest contamination by magnetic oxides (e.g., Fe_3O_4) can have dramatic effects on coercivity and saturation magnetization values of nanoparticles,[10,11] there is a need to develop a means of encapsulating the Fe particles in a protective coating while still retaining the morphology of a free flowing powder.

Results and Discussion

The approach we have used is to create metastable alloy particles of the thermodynamically immiscible pairs Fe–Li and Fe–Mg by codepositing the vapors of Fe and Mg (or Li) into a freezing hydrocarbon matrix at 77 K (the procedure has been described in detail earlier).[12] Initially a frozen matrix containing Fe and Mg atoms/clusters is formed which upon slight warming allows accretion into larger Fe–Mg alloy-like particles.[13a] In this way the growth of Fe–Mg particles at low temperature is controlled by *kinetic* parameters, such as metal concentration, rate of temperature increase, and mobility of metal atoms and the smaller clusters. As the growth continues the clusters/particles become less mobile and growth eventually stops. In this way individual particles (not films) are produced by this matrix method.[13b] Although this process is somewhat analogous to earlier reports of the production of granular film composites of Fe–Ag,[14] Fe–Mg,[15] and Fe–Hg,[16] product morphology is completely different due to the hydrocarbon matrix diluent, and free-flowing powders are obtained.

Since Fe–Mg and Fe–Li metals are immiscible under thermodynamic control,[17] we reasoned that by careful heat processing of these metastable alloy particles, phase separation could be achieved to yield a core-shell structure where Mg(Li) would form a coating around the nanoparticles of Fe (Figure 1). Indeed, this approach works very well, and Fe atoms/clusters migrate to the center of the particles. Although it could not be predicted *a priori* that this type of core-shell structure would be formed, we considered that under heating thermodynamic factors would be controlling, in that Fe–Fe bonds are stronger than Mg–Mg or Fe–Mg bonds and that this should

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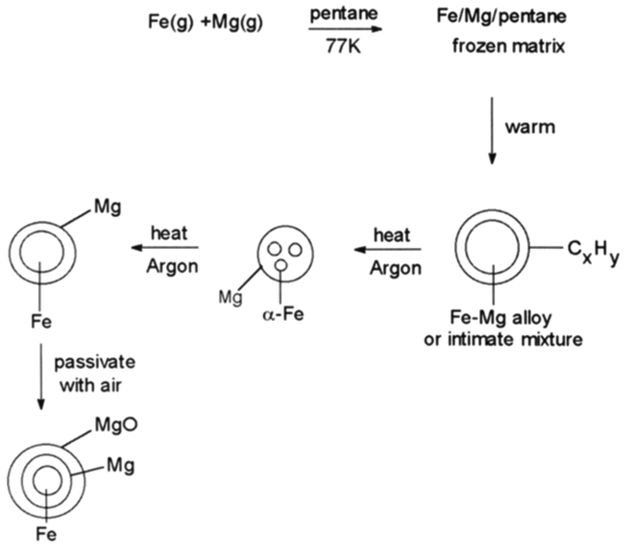

Figure 1. Schematic of the formation of Fe–Mg alloy nanoparticles followed by phase segregation.

encourage the formation of a coating of Mg on an Fe core.[18] This has been found to be the case with both Fe–Mg and Fe–Li.[12] However, with Fe–Ag alloy particles, the situation is not so simple, and a mixture of Fe_n, Ag_n, and unprotected Fe–Ag particles was formed.[19]

One of the advantages of this approach where Mg (or Li) is the second component is that it behaves as a sacrificial metal. That is, if traces of oxygen enter any apparatus where the nanoparticles are being manipulated, MgO is formed (itself a good protective coating).

Heat treatment of the as-prepared samples leads to increasing α-Fe particle sizes as seen in Figure 2. Mössbauer spectroscopy after heat treatment and subsequent exposure to air showed the presence of iron oxide for heat treatments at temperatures $T \leq 200$ °C.[20,21] On the other hand, for $T > 250$ °C no oxide was detected. This implies the magnesium formed an encapsulation effective for protecting the iron only when heat treatment was greater than 250 °C, which corresponds to α-Fe sizes greater than 7 nm.[22] The Fe-core/Mg-shell structure, which we designate as [Mg]Fe, is illustrated by TEM photos of heat-treated, passivated samples (Figure 3 and 4). The darker areas are due to α-Fe particle cores, while the lighter outer shells are [MgO]Mg (MgO oxide coated Mg metal). *We believe the α-Fe cores are single crystals since TEM measurements and XRD crystallite sizes calculated by line broadening (Scherrer equation) are in good agreement.*

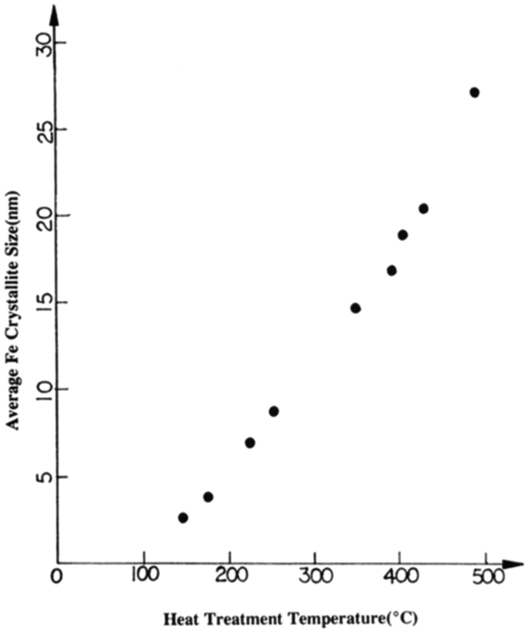

Figure 2. α-Fe crystallite sizes of Fe–Mg powders (formed in cold pentane). Heat-treated at different temperatures for 60 min.

Figure 3. TEM micrograph of passivated Fe–Mg powders heat processed at 180 °C.

Magnetization data were collected for a series of samples. For fresh, unheat-treated, unpassified Fe–Mg (4:7 atomic ratio) alloy particles, a plot of magnetization (σ, emu/g iron) vs applied field is shown in Figure 5. The saturation magnetization σ_s, inferred from the high-field limit of these

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[18] (a) A popular expression for the spontaneous ordering of surface adsorbates is "molecular self-assembly". In our Fe–Li and Fe–Mg metastable alloy particles, there is "atomic self-assembly" into core-shell structures when experimental heating parameters are correct. (b) A reviewer has suggested that the temperature variation of the surface energy of iron vs magnesium may be important here.

[19] Easom, K.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanaysis, G. C. *Polyhedron*, in press.

[20] Samples were placed in glass vials under Ar, the screw cap was loosened, and air was allowed to slowly leak in overnight.

[21] Samples were placed in sealed glass vials under Ar and heated at the desired temperature for 1 h.

[22] We believe that our individual particles phase segregate independent of each other. Upon prolonged heating at 430 °C or above, the particles begin to neck together and to amalgamate, and particles along with α-Fe crystallite sizes grow further. This is undesirable since we want to preserve small particle size. With such a system, we cannot be sure if individual particles completely phase segregate before the onset of interparticle amalgamation. Nonetheless, there are similarities to earlier studies of precipitation of crystallites in bulk alloys such as Co–Cu (see: Becker, J. J.; *Trans. A.I.M.E.* **1957**, *209*, 59–63 and discussion in Cullity (ref 23 pp 418–421). Thus, it is difficult to be sure if the volume fraction of α-Fe is affecting our results as was the case in the Becker work.

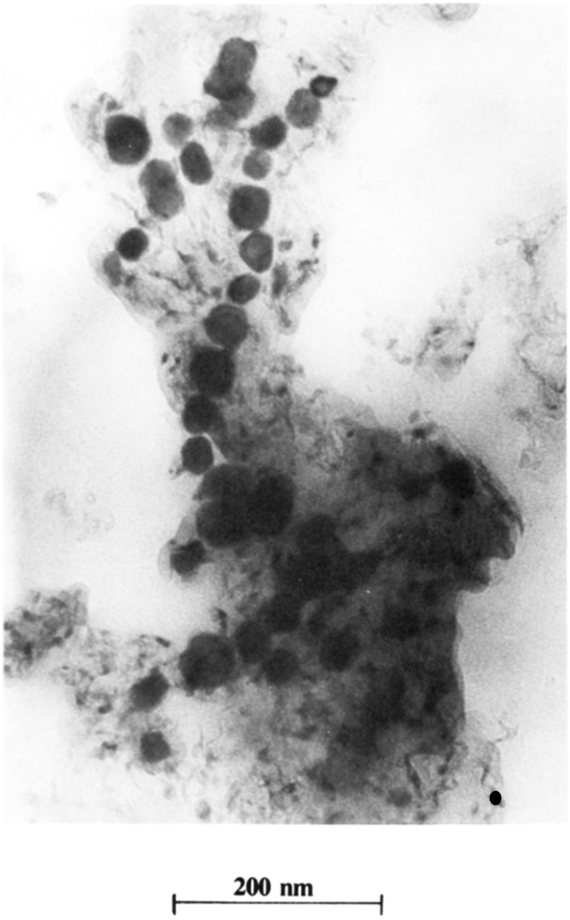

Figure 4. TEM micrograph of passivated Fe–Mg powders heat processed at 430 °C.

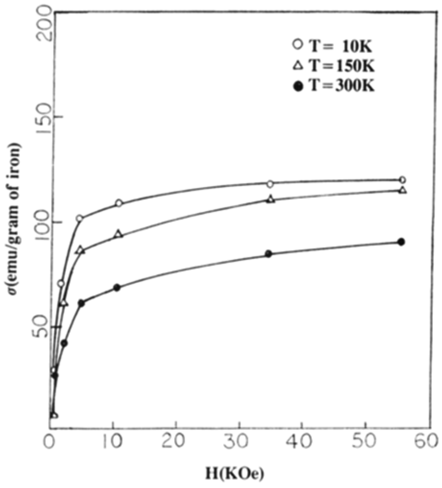

Figure 5. Magnetization curves of a fresh Fe–Mg sample with a Fe:Mg atomic ratio of 4:7.

plots is much lower than for bulk α-Fe (220 emu/g at 300 K). However, upon heat treatment and α-Fe crystallite growth, σ_s changed dramatically (Figure 6) and approaches the bulk value as the α-Fe particle diameter increases.

Further magnetic studies for the well encapsulated, $d > 7$ nm samples showed superparamagnetic behavior as identified by σ vs H/T curves after a small ferromagnetic fraction was subtracted. This ferromagnetic fraction increased with heat treatment, hence average size, until at $d = 20$ nm, the whole sample was ferromagnetic. Coercivity measurements as a function of size are shown in Figure 7, where we see small values independent of size.

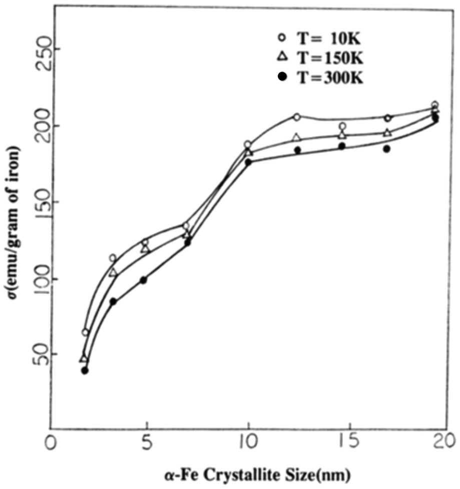

Figure 6. Saturation magnetization values (σ, emu/gram of iron) of Fe–Mg particles (Fe:Mg = 4:7; field strength 55 000 Oe). Smaller particles contained some iron oxide. Note that in the 10–20-nm range near "bulklike" σ_s values were observed.

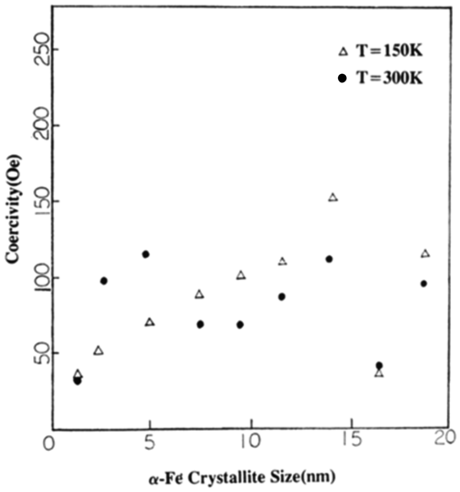

Figure 7. Coercivities of Fe–Mg particles (Fe:Mg = 4:7) with different α-Fe crystallite sizes. Error estimates are ±10%.

These nonzero H_c values must be due to the small ferromagnetic fraction, but the behavior of the H_c is contrary to an increase of H_c with increasing size expected for particles smaller than the single domain size. To explain this, we speculate that the average size increases as a result of increasing ferromagnetic fraction, but the average size of this fraction alone does not change significantly with heat treatment. We remark that the calculated superparamagnetic size for spherical iron particles with bulk crystalline anisotropy is $d = 13$ nm in accord with the size range of our α-Fe crystallities.[23,24]

We believe these [Mg]Fe particles represent the first examples of free-flowing powder samples of nanoscale α-Fe that do not have surface contamination by magnetic iron oxide but instead are coated by a nonmagnetic protective shell. And since we have shown that iron oxide coatings can have dramatic effects on H_c in such small particles,[10] it is obvious that these [Mg]Fe particles are undergoing magnetic domain spin flips that are controlled by a completely different process. Thus, there are no magnetic spins in the shell material that can pin the spins of the

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(23) Cullity, B. D. Introduction to Magnetic Materials; Addision-Wesley: Reading, MA, 1972; p 386.

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α-Fe core. It appears that the Mg coating has little effect on inhibiting a flip of the α-Fe magnetic moment; there is no induced exchange anisotropy.

An important conclusion is that surface coatings in such small particles can *dominate* the magnetic memory property H_c. Thus, in the absence of surface contaminants of magnetic iron oxides and instead coated with metallic Mg, nanoscale α-Fe particles exhibit a very, soft magnetic behavior. Our results suggest that it is the surface coating on α-Fe that dictates size dependent behavior in this property H_c of fine particles.

One final point is that these heat processed particles are completely air stable, even for months at a time. The outer Mg coating is itself protected by a MgO thin coating.

Controlling coercivities and magnetization values in nanoparticles now seems more likely, and more will be learned about surface chemical effects as more core-shell particles are prepared and studied.

We are currently carrying out further investigations, for example with [Mg]Fe, [Li]Fe, [Fe_3O_4]Fe, [Ag]Fe, [In]Fe, [Bi]Fe, and [FeS]Fe systems.

Experimental Section

General procedures for the preparation and characterization of bimetallic, metastable fine particles have been described before.[12,24]

For the Fe–Mg combination, the metals used, and synthetic isolation procedures were as follows:

Metals: Iron metal chips, 99.99+ % (Fischer Scientific); pieces from a magnesium metal rod 99.9+ % purity (Aldrich Chem. Co.); pentane, HPLC grade (Fischer Scientific).

The pentane was dried by refluxing over CaH_2 under a flow of N_2 for at least 6 h. About 200 mL was freshly distilled and freeze–thaw degassed.

The metal vapor reactor[25,26] was set up with two W-Al_2O_3 crucibles, one for Fe and the other for Mg vaporization. After pumpdown and cooling the reactor to 77 K, 40–50 mL of pentane was deposited on the inner walls. The vaporization of iron was initiated *after* a steady vaporization of Mg was achieved (pentane codeposition continued at a rate of 2–3 mL/min). Typical vaporization rates were about 30 mg/min (6×10^{-4} mol/min) and 19 mg/min (8×10^{-4} mol/min) for Fe and Mg, respectively. After about 50 min the metal evaporators were shut off and an additional 30–40 mL of pentane was deposited. The reactor was isolated from the pumping system, the liquid N_2 dewar removed, and the reactor allowed to warm to room temperature. The liquid pentane was removed by reapplying vacuum. Then the reactor was back filled with Ar, and the chamber removed under a flow of Ar and quickly covered and transferred to the inert-atmosphere box.

A series of Fe–Mg composites were prepared with atomic ratios of Fe/Mg of 1/2, 4/7, 1/1, and 1/3. Preparation of pure Fe and pure Mg powders was carried out similarly. In all cases about 80% of the metals vaporized were recovered as black, free flowing powders.

For further treatments, samples of 70–100 mg were transferred into Pyrex glass tubes in an inert (Ar filled) atmosphere box. The tubes were temporarily sealed, removed, and then flame sealed. Heat treatments were carried out by wrapping each sample in heating tape and heating to the desired temperature for specified times. For temperatures below 400 °C, 1 h of heating was sufficient to achieve a stable structure, and longer times had little effect. After heat treatment the samples were opened in the inert-atmosphere box, and samples prepared for XRD, Mössbauer, SQUID, and other analyses.[12,24]

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