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Journal of Magnetism and Magnetic Materials 252 (2002) 1–3

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Synthesis and properties of iron ferrofluids

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Abstract

We study the preparation and properties of metallic iron particles, synthesized by thermal decomposition of $Fe(CO)_5$ in the presence of a stabilizer. By varying the iron carbonyl/polymer ratio, the particle size can be varied from 2 to 10 nm. Particles are characterized by magnetization measurements, transmission electron microscopy (TEM), small angle X-ray scattering and cryo-TEM. Cryo-TEM pictures show linear structures of particles. From susceptibility measurements, it is seen that particles oxidize fast on exposure to air.

Keywords: Iron colloids; Synthesis; Transmission electron microscopy; Small angle X-ray scattering; Oxidation

1. Introduction

In scientific research on ferrofluids, magnetite particles are used frequently, probably because the synthesis is easy and known for long [1]. However, the polydispersity of these particles is always large (around 25%) and control of their size in the synthesis is limited. In contrast, metallic magnetic particles can be made quite monodisperse and in different sizes. Another advantage of metallic particles is their large magnetization compared to metal oxides. A convenient and controlled method for the synthesis of metallic iron particles is the thermal decomposition of iron carbonyl compounds [2–4]. To investigate the properties of these particles, we study dispersions of iron colloids, synthesized by thermal decomposition, in which we systematically vary the radius of particles over a broad range. The particles are characterized by magnetization measurements, transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) to study the effect of size on suspension properties. Preliminary studies of the particles were done with cryo transmission electron microscopy (cryo-TEM). This technique images a liquid film of a dispersion cooled sufficiently rapidly such that the solvent does not crystallize, but forms a glass. Because of this preparation method it is possible to look at the structure and arrangements of particles *in the solvent*.

2. Experimental

The synthesis was carried out by heating different amounts of $Fe(CO)_5$ and modified polyisobutene (PIB) in decalin under nitrogen atmosphere (at approximately 170°C). The size of the particles was tuned by varying the $Fe(CO)_5$/polymer ratio. Dispersions were always kept under nitrogen atmosphere, unless stated otherwise.

Magnetization measurements were performed using a MicroMag 2900 alternating gradient magnetometer (Princeton Measurements Corporation). TEM micrographs were made from formvar coated copper grids on a Philips CM10H electron microscope. SAXS measurements were performed at the DUBBLE beamline at the ESRF in Grenoble at a wavelength of 0.124 nm. Cryo-TEM samples were prepared on 200 mesh quantifoil R2/2 copper grids. After placing a droplet of the dispersion onto the grid, the liquid was blotted with filter paper. In this way a liquid film was obtained in the grid holes ($d = 2\,\mu m$) which was thin in the middle (approximately one particle diameter) and thicker on the edges of the

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0304-8853/02/$ - see front matter
PII: S0304-8853(02)00620-0

hole. Then the specimen was plunged into liquid nitrogen, which caused the solvent decalin to glassify. The sample was placed into a cryo-holder which was mounted and examined in a Philips CM12H electron microscope at –170°C and 120 kV.

3. Results and discussion

Particles with different average radii in the size range 2–10 nm, with a polydispersity of approximately only 10% can be synthesized. Sizes measured with different techniques correspond reasonably well with each other (Table 1). In addition, SAXS measurements yielded straight Guinier plots, which indicate the absence of aggregates in the liquid. From the interparticle spacing derived from the structure factor peak in more concentrated samples, a polymer layer thickness of 7.0 ± 0.4 nm, equal for every system, was determined. Susceptibility measurements show that particles oxidize fast (timescale of minutes) to a non-magnetic oxide on exposure of dispersions to air. This oxidation causes an increase of particle radius by a factor of approximately 1.3, determined from Guinier plots (Table 1).

On TEM-pictures (Fig. 1) it can be seen that, at least in the dry state, the larger particles (dispersion E) form linear structures as a consequence of magnetic interaction, whereas the smaller ones, which have smaller magnetic moments (dispersion C), do not.

Preliminary cryo-TEM pictures were made and an example of a concentrated sample of dispersion C in

Table 1
Particle radii from different techniques

	a_{TEM} (nm)	a_{AGM} (nm)	a_{SAXS} (nm)	$a_{SAXSoxidized}$ (nm)
A	2.1 ± 0.3	2.3	2.2	2.8
B	6.0 ± 0.7	4.2	4.9	5.9
C	6.6 ± 1.4	5.2	6.0	9.0
D	6.9 ± 1.0	5.4	8.8	10.6
E	8.2 ± 1.5	—	9.5	—

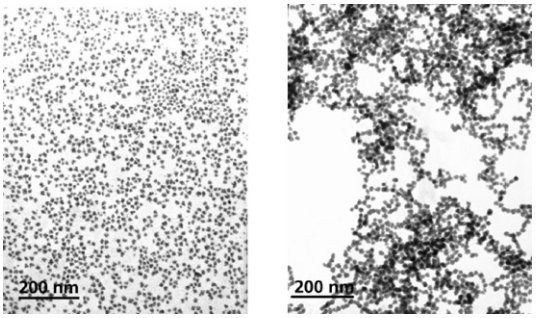

Fig. 1. TEM pictures of iron particles of system C (left) and system E (right).

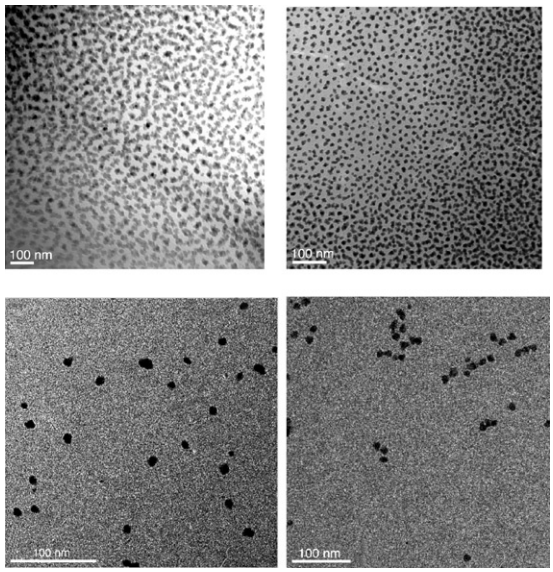

Fig. 2. Cryo-TEM pictures of (a) (top left) dispersion C (concentrated). The picture shows linear structures of magnetic particles arranged at the largest possible distance from each other, (b) (top right) dispersion C (dilute). The increase in film thickness from left to right across the sample can be seen: (c) (bottom left) dispersion B (dilute), (d) (bottom right) dispersion D (dilute).

Fig. 2a remarkably shows that these magnetic particles *in a liquid film* do form linear clusters with mutual distances that are almost equal for all clusters. This probably can be understood by the magnetic interactions between these particles, which favor a head to tail alignment. The mutual interaction between two parallel chains however, seems to be repulsive and apparently causes the chains to arrange at the largest possible distance from each other. The origin of this phenomenon is still unclear, but will be further investigated. In Fig. 2b, a picture of a more dilute sample C, the increase in film thickness across the sample can be seen quite clearly. On the left side of the picture one sees a single layer of separate particles, whereas at the right side particles within different layers can be seen. Furthermore, the particle concentration is larger in this thicker area, because bigger particles are excluded from the thinner film regions. When comparing pictures of dilute samples of smaller particles (dispersion B, Fig. 2c) and bigger particles (dispersion D, Fig. 2d), one clearly sees only separate particles B, while particles D are mostly grouped together in linear small chains because of their larger magnetic moments.

4. Conclusions

Metallic iron particles can be synthesized in a broad size range (2–10 nm) and sizes determined with different

techniques correspond well with each other. Cryo-TEM is a promising technique to study the structure of ferrofluids. In a liquid film of a concentrated dispersion, particles are arranged into linear structures, presumably because of their magnetic interaction. In dilute samples, only large particles do form small clusters. When exposing dispersions to air, particles oxidize fast and grow considerably on oxidation.

Acknowledgements

We thank I. Dolbnya, R. van Tol, E. Homan and K. Kassapidou for their assistance with the SAXS measurements. We also thank P. Frederik en P. Bomans for helping us with performing cryo-TEM. Finally, we thank Stichting Technische Wetenschappen for financial support.

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