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K. Bridger

Martin Marietta Laboratories, Martin Marietta Corporation, Baltimore, Maryland

J. Watts

Martin Marietta Laboratories, Martin Marietta Corporation, Baltimore, Maryland

M. Tadros

Martin Marietta Laboratories, Martin Marietta Corporation, Baltimore, Maryland

Gang Xiao

The Johns Hopkins University, Baltimore, Maryland

Sy_Hwang Liou

University of Nebraska-Lincoln, sliou@unl.edu

See next page for additional authors

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Authors

K. Bridger, J. Watts, M. Tadros, Gang Xiao, Sy_Hwang Liou, and C.L. Chien

Magnetic characteristics of ultrafine Fe particles reduced from uniform iron oxide particles

K. Bridger, J. Watts, and M. Tadros

Martin Marietta Laboratories, Martin Marietta Corporation, Baltimore, Maryland 21227

Gang Xiao, S. H. Liou, and C. L. Chien

The Johns Hopkins University, Baltimore, Maryland 21218

Uniform, cubic 0.05- μm iron oxide particles were formed by forced hydrolysis of ferric perchlorate. These particles were reduced to $\alpha\text{-Fe}$ by heating in hydrogen at temperatures between 300 and 500 °C. The effect of reduction temperature and various prerelation treatments on the microstructure of the iron particles will be discussed. Complete reduction to $\alpha\text{-Fe}$ was established by ^{57}Fe Mössbauer spectroscopy and x-ray diffraction. Magnetic measurements on epoxy and polyurethane films containing these particles with various mass fractions gave coercivities as high as 1000 Oe. The relationship between the magnetic measurements and the microstructure will be discussed. Na_2SiO_3 is found to be the best coating material for the process of reducing iron oxide particles to iron.

I. INTRODUCTION

For high-density recording media, the development of material with high magnetization and coercive force is required. One of the best candidates is small iron particles. The pseudomorphic reduction of iron oxide particles to iron is an important process in the production of these materials. Many workers have studied this process, with the objective of producing nonporous, single-domain iron particles. One of the major challenges has been the prevention of particle sintering. It is known that sintering tends to occur at reduction temperatures above 350 °C.¹ Additions of various dopants (e.g., silver, tin, and cobalt) have been proposed to minimize sintering.^{1,2} Other methods have included coating the oxide particles with barium dodecyl sulfonate³ and silicic acid.⁴ The variation of porosity in the particles with dehydration temperature was also studied.⁴ It was found that on dehydration of FeOOH , the starting oxide, porous hematite particles were formed and that this porosity was carried over to the iron.

As part of an overall program studying the variation in magnetic properties of submicron iron particles with size and packing fraction we have prepared uniform, nonporous, cubic iron particles $\approx 0.05 \mu\text{m}$ in size. In this paper we report the effects of reduction temperature and various coating materials on the particle morphology and magnetic properties. The study of nonporous cubic iron particles and the detailed preparation procedures will be presented elsewhere.⁵

II. EXPERIMENT

The preparation of small iron particles was done as follows. First, uniform iron oxide particles were prepared by the forced-hydrolysis method.⁶ In the forced-hydrolysis method, acidic solutions of ferric salts are aged at elevated temperatures to promote hydrolysis of the ferric ion. This leads to nucleation and growth of oxide particles. Particle size and shape are controlled by the nature and concentration of the anion, reaction temperature, and the aging time. The iron oxide particles prepared by the method above were

either freeze dried immediately or premixed with a coating material and then freeze dried. The coatings used include sodium silicate (Na_2SiO_3), polyvinylalcohol (PVA), silicic acid, barium dodecyl sulfonate, and silica. The coating materials were added either as an aqueous solution (e.g., 0.1 M or 0.001 M Na_2SiO_3 , 0.1% PVA, or 0.001 M silicic acid) or as a dispersion (e.g., silica).

The freeze-dried powders were reduced under hydrogen in a tube furnace. Samples for magnetic characterization were carefully weighed in a glove box and then mixed with a known weight of a polyurethane or epoxy resin. The slurries thus formed were milled for 20 min in a small shaker (Wigg-L-bug) and were cast on microscope slides. The iron particles on the slides were characterized by x-ray diffraction, Mössbauer spectroscopy, and magnetization measurements. Samples for electron microscopy were prepared by first milling a quantity of powder in toluene and then dispersing the particles using an ultrasonic bath.

III. RESULTS AND DISCUSSIONS

The effects of heat treatment on particle morphology are exceptionally important, especially in as far as the morphology changes affect magnetic properties.^{1,2,4,7} In general, sintering of the particles leads to lower coercivities and is thus undesirable. A number of pretreatments have been suggested to minimize this sintering. In the following, we discuss the effect of various coating materials as well as no coating and reduction temperature on the particle morphology and magnetic properties.

The particles before and after hydrogen reduction are routinely checked by x-ray, TEM, and Mössbauer spectroscopy. Mössbauer spectra on particles before hydrogen reduction show that $\alpha\text{-Fe}_2\text{O}_3$ is the only phase. The spectra show that the particles after hydrogen reduction are exclusively $\alpha\text{-iron}$ with a phase purity $> 95\%$. This indicates that the hydrogen reduction process efficiently converts all oxide particles into $\alpha\text{-iron}$. Furthermore, the procedures for handling the iron particles, and the methods for dispersing the

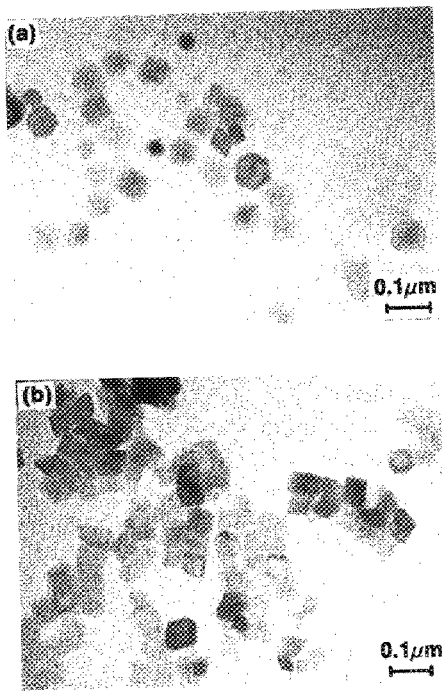


FIG. 1. TEM of uncoated (a) iron metal and (b) oxide particles.

iron particles are effective in preventing oxidation. This is significant because these particles are pyrophoric, i.e., they spontaneously ignite in air. No evidence of superparamagnetism was seen from the Mössbauer spectra and from the magnetic measurements.

Electron micrographs of a typical sample before and after reduction at 400 °C are shown in Fig. 1. The cubic shape of the particles is maintained during the reduction process, and the sizes appear to be similar—at least to a first approximation. Electron diffraction patterns confirmed the x-ray diffraction analysis that the particles are indeed α -iron.

Magnetic properties of specimens containing ultrafine iron particles depend on the size, shape, volume fraction, and dispersion of the particles. In this work great care has been taken to ensure a good dispersion of the iron particles in

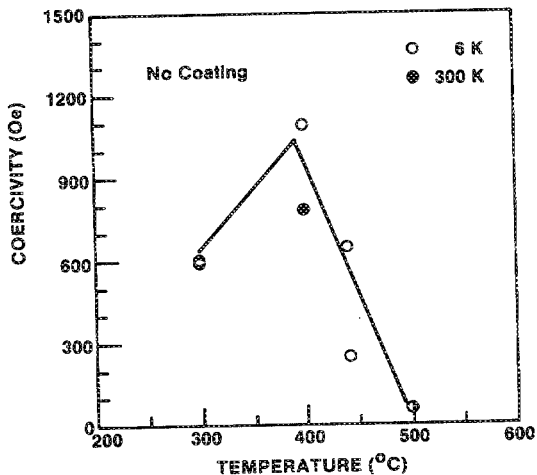


FIG. 2. Variation of coercivity of iron particles (uncoated) with reduction temperature.

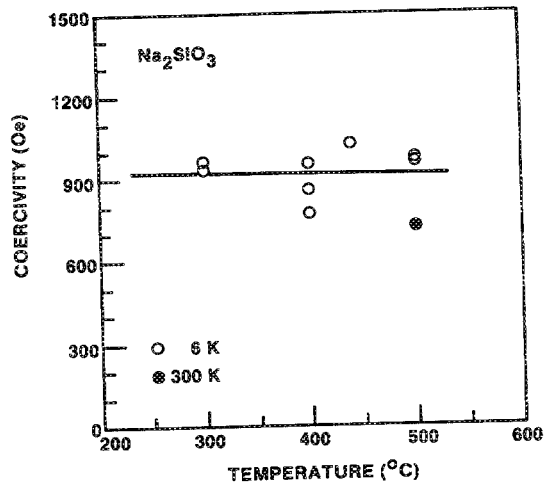


FIG. 3. Variation of coercivity of iron particles (Na_2SiO_3) with reduction temperature.

a polymer film at a known mass fraction. Films with volume fraction less than 1% are used in the magnetic measurement. The coercivity of the uncoated particles versus reduction temperature is shown in Fig. 2. Initially H_c increased with increasing reduction temperature to about 1100 Oe at 400 °C. High values of H_c around 1000 Oe are in keeping with the ultrafine ($< 0.1 \mu\text{m}$) nature of these particles.⁸ However, above 400 °C, the value of H_c drastically decreased, and at 500 °C, H_c is only 60 Oe, similar to the value for bulk iron. This drop-off in H_c is indicative of substantial sintering between the particles occurring at the higher reduction temperatures. Indeed, we have observed sintering

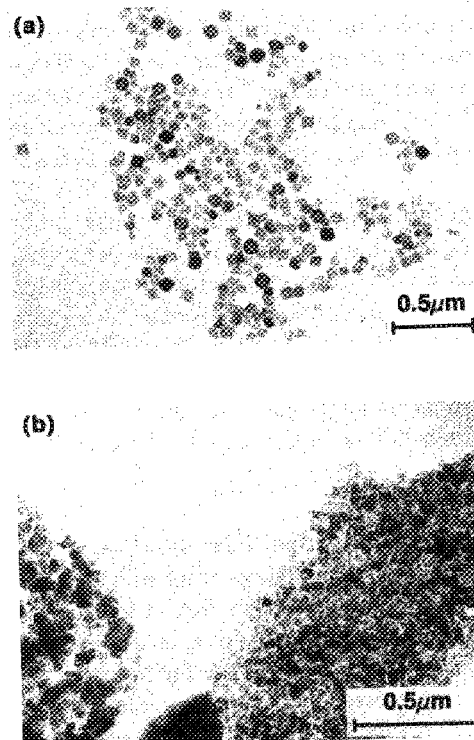


FIG. 4. TEM of Na_2SiO_3 -coated (a) iron oxide and (b) metal particles.

behavior in TEM micrographs. Several materials, including Na_2SiO_3 , PVA, silicic acid, and barium dodecyl sulfonate have been tried as coating materials to prevent iron particles from sintering during hydrogen reduction. Of these, Na_2SiO_3 appears to be the most suitable. As shown in Fig. 3, the values of H_c for particles with Na_2SiO_3 coating remain very high (about 1000 Oe) for a wide range of reduction temperatures. Even with hydrogen reduction at 500 °C, H_c shows no sign of decreasing. Indeed, detailed electron micrographs of iron particles coated with Na_2SiO_3 , as shown in Fig. 4, indicate little or no sintering between the particles.

For particles coated with PVA and reduced at 500 °C, H_c values are all below 200 Oe. In the case of silicic-acid-coated particles reduced at 500 °C, H_c is even lower, at about 50 Oe. The TEM micrographs indicate that these particles have sintered into rodlike structures.

Two samples reduced at 400 °C with barium dodecyl sulfonate coating produced rather high H_c values: 530 and 970 Oe. Barium dodecyl sulfonate appears to be also promising as a coating material.

In summary, we have succeeded in preparing pure sub-micron iron particles with uniform size and high coercivity. Na_2SiO_3 is found to be the best material for the process of reducing iron oxide particles to iron.

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