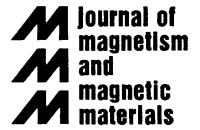




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Synthesis of ethylene–glycol-based magnetic fluid using silica-coated iron particle

T. Atarashi^a, Y.S. Kim^b, T. Fujita^c, K. Nakatsuka^{d,*}

^a*Nittetsu Mining Co. Ltd, 2-1, Kakeshita Hirai, Hinode town, Nishitama, Tokyo, 190-0182, Japan*

^b*Dong-A University, 840, Hadan-Dong, Saha-ku, Pusan, 604-714, South Korea*

^c*Akita University, 1-1, Tegata Gakuencho, Akita 010, Japan*

^d*Graduate School of Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan*

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Abstract

Ultra fine iron particles stable up to 150°C in the air is prepared by thermally reducing coprecipitated magnetite, the surface of which has been coated with amorphous silica in aqueous sodium silicate solution. The particle magnetization curve exhibited a saturation value of 1.57×10^{-4} Wbm/kg including silicate as a coating material, corresponding to the doubling of magnetization of magnetite which can be dispersed as magnetic fluid, and a coercive force of about 1.6×10^4 A/m. A magnetic fluid stable against the atmosphere of the air for long periods is obtained by dispersing this silica-coated iron particles into ethylene glycol. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Silica coating; Iron-dispersed magnetic fluids

1. Introduction

The studies for synthesizing magnetic fluids with strong magnetization have been carried out to obtain ultra-fine metal particles, such as by spark erosion [1], vacuum evaporation [2], electrolytic precipitation [3], thermal decomposition of carbonyl iron [4] and so on. Some of them succeeded in obtaining a strongly magnetizable magnetic fluid, mainly by dispersing them into non-polar

solvents. But in all cases the problem remained in time dependent decrease of magnetization due to the lack of oxidation resistance against a natural atmosphere. In order to stabilize iron particles from oxidation, a stable protective layer should be introduced on the surface. Considering that the size of the iron particle for magnetic fluid should be of an order of 10 nm, the formation of silica layer, which is generally known as protective layer of iron, with precisely controlled thickness may not necessarily be easy. In this paper the introduction of amorphous silica layer on the surface of magnetite which is precipitated from aqueous solution, and the succeeding thermal reduction of magnetite to iron in hydrogen gas atmosphere is investigated.

* Corresponding author. Fax: + 81-22-217-7375.

E-mail address: nakatuka@igt.earth.tohoku.ac.jp (K. Nakatsuka)

2. Experimental studies and results

2.1. Preparation of iron particles

Magnetite was prepared by the usual co-precipitation procedure, by adding NaOH solution into

the mixed solution of ferric and ferrous chlorides (molar ratio 2 : 1) until the pH reaches 12 at room temperature, and the suspension was kept at 70°C for 30 min. After the suspension was cooled down to room temperature, sodium silicate aqueous solution was added into the suspension, controlling its

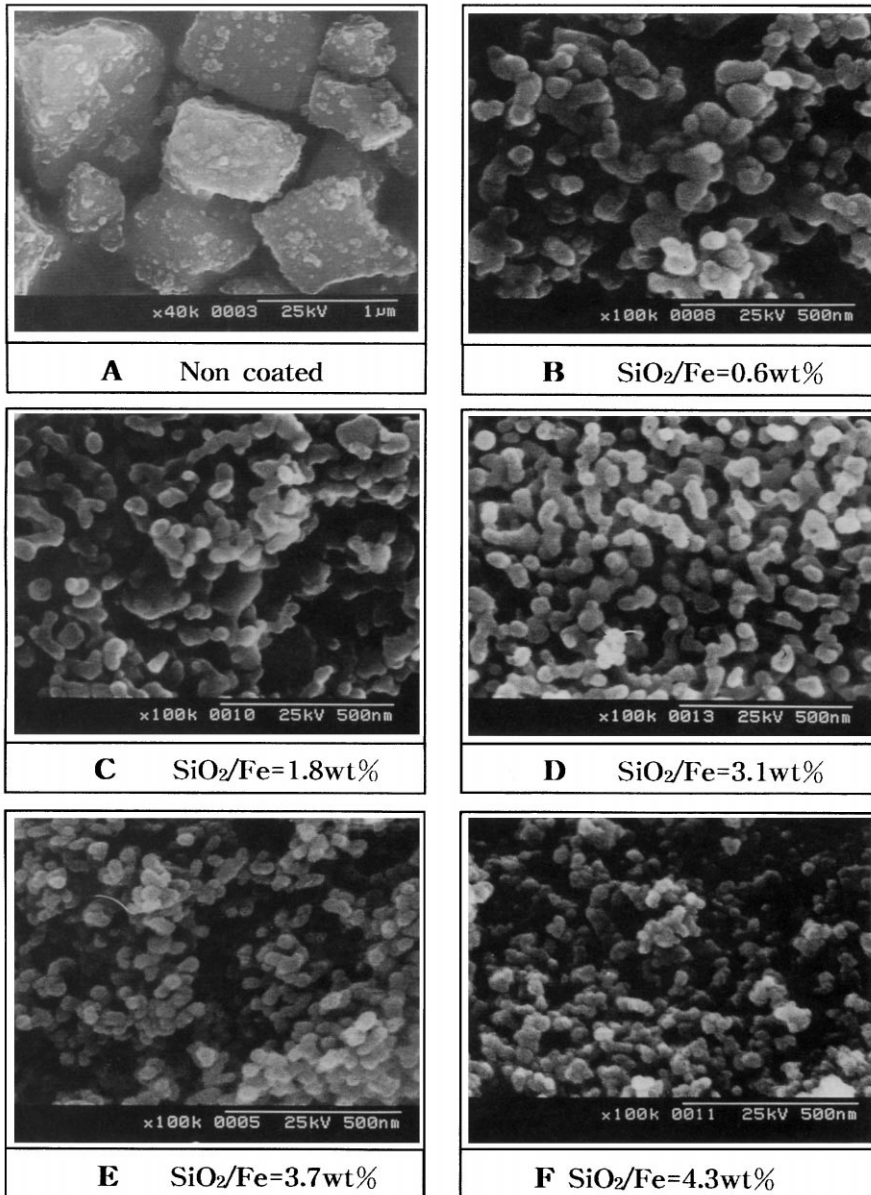


Fig. 1. SEM micrograph of reduced iron particles coated with silica.

pH between 8 and 11. Then the suspension was warmed up to 80°C for completing the precipitation of silica. The suspension was washed, filtered and dried at 100°C in the air. The dried powder was reduced by heating it in H₂ gas at 500–650°C in the electric furnace.

Fig. 1 shows the SEM photographs of particles reduced at 500°C, for different amount of water glass addition. Mean size and magnetization of reduced particles are dependent on several factors: SiO₂/Fe ratio in the solution, pH at silica precipitation stage, temperature and time duration of reduction, and so on. Particle size is obtained by reducing Au evaporation from Fig. 1.

Fig. 2 shows the magnetization and mean diameter of thermally reduced particles in the same conditions, as a function of the amount of used sodium silicate expressed as SiO₂/Fe ratio at the silica coating stage. Mean particle size and magnetization decreases with increasing amount of silica, suggesting that the reduction of magnetite is accompanied with the grain growth of iron particles when the added amount of silica is insufficient. In this case it is not confirmed whether a thin silica layer is formed on a magnetite particle or whether

ultra fine silica particles are aggregated on a magnetite particle in the solution, because the resolution of TEM observation is insufficient to detect the surface structure of the magnetite particle. But when the same coating experiment is conducted on iron particles of 1 μm size, the presence of clear thin amorphous silica layer is confirmed on the sliced section of particles by focussed ion beam (FIB) processor of several 10 nm-thickness. From this result we assume that the reduced iron particle in this case is covered with a silica layer.

Fig. 3 shows the influence of heating temperature in H₂ gas on magnetization and mean size of iron particles obtained from magnetite with a fixed SiO₂/Fe ratio at the silica-coating stage. The magnetization and the mean particle diameter increase with heating temperature, suggesting the existence of diffusion of iron through surface silicate layer in the thermal stage.

The highest particle magnetization in the vicinity of 10 nm particle size was 1.76×10^{-4} Wb·m/kg (140 emu/g) in the sample prepared under the condition of SiO₂/Fe = 0.037 in starting material and succeeding heating conditions of 550°C and 5 h. Fig. 4 shows the weight change of powders when

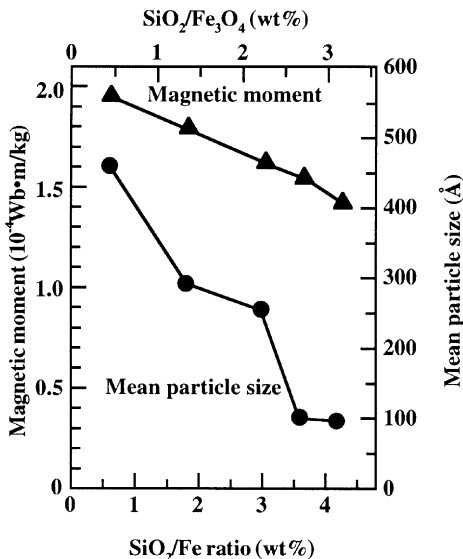


Fig. 2. Magnetization and mean size of silica-coated iron particles reduced at 500°C, as a function of the amount of silica used for coating. H₂: 0.51/min, reduction time: 5 h.

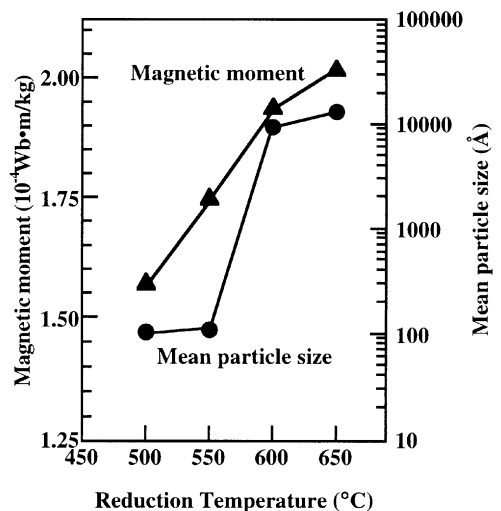


Fig. 3. Magnetization and mean size of silica-coated iron particles with SiO₂/Fe ratio of 0.037, as a function of heating temperature for reduction. H₂: 0.51/min, reduction time: 5 h.

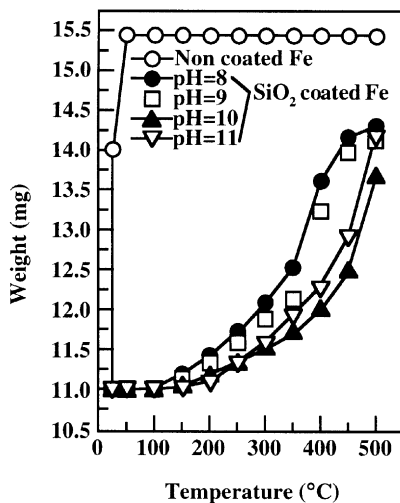


Fig. 4. Effect of pH of aqueous solution in the stage of silica coating on the oxidation resistance of reduced iron particles. H_2 : 0.5/min, reduction time: 5 h.

they are heated in the air. The degree of oxidation resistance depends on the amount of sodium silicate and pH in the stage of SiO_2 precipitation. Silica-coated iron powders are stable below $150^\circ C$. Above $150^\circ C$ powders are oxidized with a rise in temperature, presumably depending on the diffusibility of oxygen through thin silicate layer. The difference of oxidation resistance due to pH in silica precipitation stage probably reflects on the inhomogeneity and density of silicate layer on the surface.

2.2. Dispersion of powder into ethylene glycol

Surface of the silica-coated iron particle will have relatively high negative surface charge in neutral or alkaline aqueous solution. Thus, the method of ionic magnetic fluid preparation by Massart [5] will be applicable to hydrophilic solvent without the assistance of the specific adsorptive ion species. The silicate-coated iron powder of about 10 nm size, with a magnetic moment of 1.57×10^{-4} Wb-m/kg in 8×10^5 A/m and coercive force of about

1.6×10^4 A/m, was washed with sodium oleate solution and then dispersed into ethylene glycol by adding dodecyl benzene sulfonate (DBS) and tetramethyl ammonium hydroxide (TMA). The purpose of using oleate and DBS is to make iron part which may be partially exposed on the surface hydrophilic. The role of TMA is the same as that in the ionic magnetic fluid developed by R. Massart [5]. When the surface-coated iron powder of 8.0 vol% was suspended in ethylene glycol, more than 96% of iron powder remained dispersed in the solvent. Its viscosity was 1.8 P and the magnetic induction of the fluid was 8×10^{-4} Wb-m/kg in 8×10^5 A/m.

3. Conclusion

Iron particulate of about 10 nm size, which is stable against oxidation in the air below $150^\circ C$, is synthesized from magnetite, preliminarily coated with silica polymerized from sodium silicate aqueous solution, by thermally reducing magnetite in H_2 gas at the appropriate temperature. It is confirmed that the obtained particulate can be dispersed into ethylene glycol by making its surface hydrophilic and adding tetramethyl ammonium hydroxide, to obtain magnetic fluid. The key point to improve its characteristics will be in the condition of surface modification, for obtaining dense and smooth silicate film with minimum thickness enough to protect iron from oxidation in the air.

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