HYDROTHERMAL SYNTHESIS AND MICROSTRUCTURAL CONTROL OF HEMATITE PARTICLES

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ABSTRACT

Hematite particles of various shapes and sizes have been prepared hydrothermally at different pHs and temperatures from ferric chloride solution. Particle size decreases with increase in pH and decrease in residual iron concentration during precipitation as observed from Transmission Electron Microscope (TEM). A comparison of particle size from TEM and mean crystalline diameter (MCD) from XRD data reveals that the particles prepared are polycrystalline in nature with different degree of polycrystallinity. The degree of polycrystallinity decreases with increase in the pH of precipitation. Monodispersed pseudocubic polycrystalline particles obtained at lower pH exhibit very high coercivity. Various sizes of pseudocubic particles have also been prepared by varying the synthesis temperature, the coercivity of which is linearly increasing with increase in the size of the particles. By the developed process iron oxide of required size, shape and magnetic properties can be engineered. Formation of polycrystalline nature of particles is explained in terms of aggregation of very fine particles formed as an intermediate during conversion to hematite.

Key Words : Hematite, Hydrothermal synthesis, Polycrystalline, Nano-material.

INTRODUCTION

Continual efforts with a higher priority have been devoted to produce monodispersed iron oxide particles of uniform in shape, size and composition as ideal constituents for varieties of advanced materials. The demand has increased dramatically because of enormous development in the electronic industries (1). Iron oxide is the major constituents of such materials, the quality of which controls the final products are the grain size, shape, hardness, permeability, magnetic losses etc. Various preparation techniques such as gel-sol (2-4), ceramic (5), spray roasting (6), and hydrothermal precipitation (7-13) have been adopted to prepare these particles. Among them hydrothermal precipitation technique has several advantages such as (i) low reaction temperature (ii) effective control of size and shape of the particles (iii) incorporation of less impurities (iv) regeneration of lixiviant. Hydrothermal precipitation of iron oxide from carboxylate and nitrate precursor has been reported (7, 13). Hematite powders of different morphology were prepared (9) hydrothermally by controlling various parameters from ferric chloride solution. The coercivity value of 0.534 kOe for amorphous iron oxide nanocrystals with modified layers prepared hydrothermally was reported by Li et al. (12). By hydrothermal route the present author has reported the formation of monodispersed pseudocubic, trapezoidal and hexagonal particles of various sizes with different degree of polycrystallinity (8). The

present author (10, 11) has also studied the intra-/inter particle as well as subparticle growth mechanism of the hydrothermally prepared hematite particle. There is a wide variation in magnetic properties depending on the size and shape of the hematite particle. Unusually high coercivity, H_c of the order of 4 kOe for pseudocubic particles of size 650 nm prepared at pH 3 (8). In order to understand the various factors responsible for such unusual behaviour and establish the mechanism of formation, different sizes of pseudocubic shape iron oxide have been prepared at pH 3 and compared with that of the iron oxide prepared at pH 7.

EXPERIMENTAL

Hydroxide slurry prepared from ferric chloride and ammonia solution at pH 3 & 7 was subjected to hydrothermal conversion to hematite at different temperature in a stainless-steel titanium lined autoclave (PARR, Model 4542). Stirring rate was fixed at 400 rpm. After cooling the solid samples were filtered and washed several times with double distilled water to make the filtrate free from chloride. Finally the precipitates were washed three time with acetone and dried at 60°C for 20 h. The hematite phase formation was established by differential thermal analysis (DTA) and X-ray powder diffraction (XRD) using CuKα radiation. Particle size and morphology were determined by transmission electron microscopy (TEM). Magnetic hysteresis measurements were carried out using a vibrating sample magnetometer (VSM, PARR model 4500) by applying a magnetic field of 15 kOe at room temperature (298 K). The initial ac susceptibility (χ_{ac}) measured by a low field ac susceptibility-hysteresis apparatus.

RESULTS AND DISCUSSION

The X-ray diffraction peak position of the prepared samples matched well with the reported value of American Society for Testing and Materials (ASTM) card file. TG-DTA traces showing no exo/endo-peaks in the temperature range of 25-1000°C indicating the absence of other less stable phases of iron oxide.

Transmission Electron Micrographs for the sample prepared at pH-3 and pH-7 were represented in figure 1. At higher pH of precipitation the TEM showed very fine trapezoidal shape of particles of average size 150 nm with little agglomeration. However, at pH-3 very uniform size pseudocubic monodispersed particles were obtained with average size 0.67 nm. The size of the particle is measured from the micrograph by average linear concept method. By varying the temperature at a fixed iron concentration different sizes of hematite particles have been prepared and represented in figure 2. The particle size increases with increase in temperature. The average particle size of hematite decreases with the increase in pH of precipitation. The mean crystalline diameter (MCD) value evaluated from XRD line width for {104} peak using Debye-Scherrer formula (14) at different pH is given in Table-1. For the sample prepared at pH-3, particle size obtained from TEM was much higher than that evaluated from mean crystalline diameter. Therefore the crystallite diameters obtained from the XRD are in direct contrast with the particle size obtained from TEM which suggests that the particles are polycrystalline in nature and the degree of polycrystallinity decreases for the particle prepared at higher pH (Table-1). The number of subparticle estimated for the hematite particle prepared at pH 3 is of the order of 6.7×10^4 as compared to 2×10^2 for the particle prepared at pH 7 at 180°C. The polycrystalline nature of these particles can be best understood from the formation mechanism suggested below.
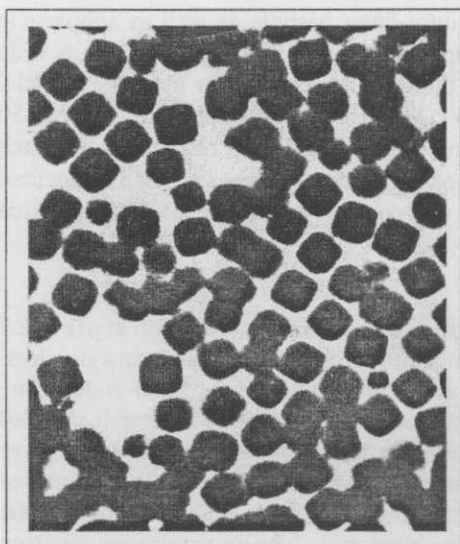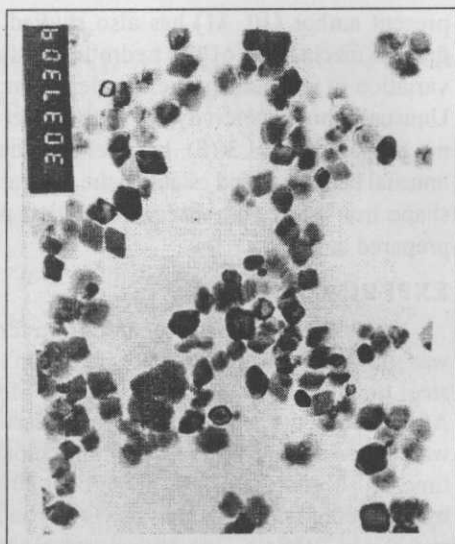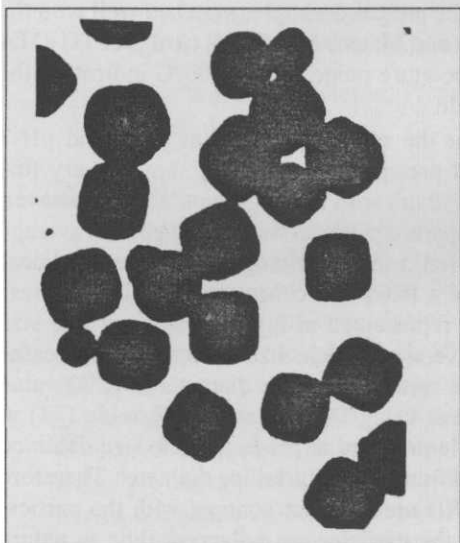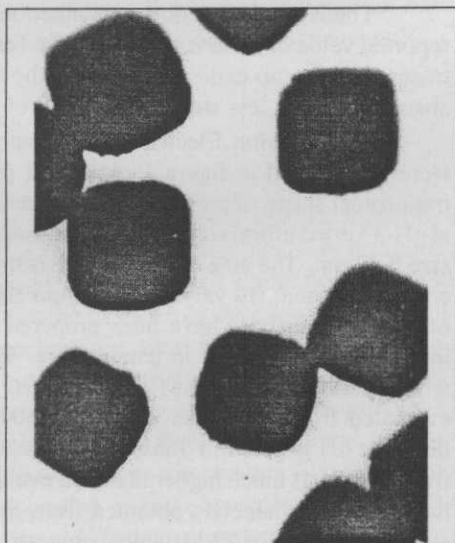
Fig. 1 : *Transmission Electron Micrographs of hematite particles prepared at different pH : (a) pH 3, average particle size - 670 nm and (b) pH 7, average particle size - 150 nm.*

Fig. 2 : *Transmission Electron Micrographs of hematite particles prepared at different temperature : (a) 160°C, average particle size - 350 nm and (b) 200°C, average particle size - 800 nm.*

Table 1 : Microstructure and magnetic measurement of hematite particle prepared at different pH.

pH	Particle size, nm	MCD, nm	Subparticle number	Coercivity Hc, kOe	Ac magn susceptibi-lity, χ_{ac} emu/g.Oe	Remanent Magnetis-ation, Mr emu/g
pH 3	670	16.5	~ 6.7 x 10^4	2.3	4.12	0.24
pH 7	150	25.0	~ 2.0 x 10^2	15.5	0.51	0.14

MECHANISM OF FORMATION

The formation mechanism of various shapes of hematite particles is not clear. The polycrystalline nature of particle can be explained in terms of aggregation of very fine particles formed as an intermediate during conversion to hematite. Matijevic (15) reported the formation of hydroxo/chloro complex are accelerated by heating and the complex grow to very fine hematite by internal dehydration. Formation of such very fine hydrous iron(III) oxide has also been reported earlier in the hydrolysis reaction iron(III) chloride and nitrate solution investigated by gel filtration, centrifusion and light scattering techniques (16-18). It is certain that irrespective of the nature of the complex formation, certain Fe^{3+} concentration is necessary for the formation of polycrystalline particles of definite shape and size. The preferential adsorption of Fe^{3+} hydroxo complex to a specific plane resulted in growth of primary particles which than aggregate in an orderly manner and start growing as individual polycrystals of different shapes and sizes. The adsorption process needs to stop after a certain size of the particle is attained, which depends on the availability of the ferric hydroxo complex in the system. The degree of polycrystallinity is higher at low pH of 3 (Table-1) due to the fact that the availability of Fe^{3+} is more than that at pH 7. The polycrystalline nature of the particle is also supported by the magnetic data.

MAGNETIC EVIDENCE

Magnetic hysteresis measurements has been carried out using a vibrating sample magnetometer at a maximum field of 15 kOe. The magnetization measured at this field remained same (0.6 emu/g) for both the sample. The initial susceptibility measured by low field ac susceptibility-hysteresis apparatus with a maximum field of 0.005 kOe also showed a strong dependence on the size and internal structure of the particles. The susceptibility value for the iron oxide particle prepared at pH 7 is about 10 times higher than that of the cubic particle prepared at pH 3. The magnetic data for both the oxides were represented in Table-1. The pseudocubic shape particles exhibit unusually very high coercivity (4.1 kOe) as compared to the trapezoidal particles (0.51 kOe) prepared at pH 7. The internal structure of the particles seems to be important in deciding their Hc. The small size of the subparticles with large surface to volume ratio and their aggregation lead to pinning of spins at the grain boundary. Due to small size the trapezoidal particles consisting of smaller number of subparticles and exhibit lower coercivity value as compared to the cubic particles consisting of large number of subparticles.

At a fixed pH (3) and iron concentration the synthesis temperature was varied to obtained different size of the pseudocubic iron oxide particles. A correlation between the size of the pseudocube with that of the magnetic properties is represented in Table-2. The coercivity value for the cubic particles are directly proportional to the particle size. As the

subparticle size remains almost constant for all the cubic particles, the degree of polycrystallinity increases with increase in the size of the pseudocube. Therefore, higher the size of the polycrystalline particle, higher the degree of aggregation, which is responsible for higher coercivity value.

Table 2 : Particle size and magnetic properties of pseudocubic hematite particle prepared at different temperature.

Temp. °C	Fe Conc., g/L	Particle size, nm	MCD, nm	Subparticle number	Coercivity Hc, kOe
160	30	350	16.0	~ 1.0 x 10^4	3.0
180	30	670	16.5	~ 6.7 x 10^4	4.1
200	30	800	15.5	~ 13.7 x 10^4	4.8

CONCLUSIONS

The hematite particles prepared through hydrothermal route under different synthesis conditions were found to be polycrystalline in nature. The degree of polycrystallinity increases with increase in the size of the particle. Monodispersed pseudocubic particles prepared at lower pH of 3 exhibited very high coercivity and is directly proportional to the size of the particle. The large number of small oriented subparticles inside the pseudocube may be the origin of the large coercivity.

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