

Magnetic coating on Hematite in α -Fe₂O₃-BaCl₂ mixed system

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Abstract : Hydrothermally prepared hematite showed polycrystalline, pseudocubic shape particles having 6500Å size for pH 3 sample. This behaviour changed for higher pH and approached almost single crystalline, hexagonal shape of 600Å size for pH 10 samples through intermediate size almost trapezoidal shape at pH 4.5 and 7. Such variation in size and shape was shown to influence the magnetic properties of the hematite. Addition of BaCl₂ to α -Fe₂O₃ in 2:1 ratio and annealing at 900 C results in coating of magnetic material (barium hexaferrite) on the surface of the particles due to surface reaction of Fe³⁺ and Ba²⁺ in the system. Large size particles (6500Å) of pH 3 sample with low surface to volume ratio yielded low volume fraction of magnetic phase which could not be detected by XRD, but confirmed from the 20 fold rise in a.c magnetic susceptibility (χ). In pH 10 sample however, the volume fraction of magnetic phase was high which could be detected by both XRD and a.c χ .

Keywords : Hematite, Magnetic Coating, Susceptibility.

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1. Introduction

A large number of studies have been devoted to understand the influence of preparation conditions and process parameters on the microstructure of hematite particles. For example, Fisher and Shrewtman [1] produced ellipsoidal hematite particles from ferric hydroxide dispersion in the presence and in the absence of oxalic acid, but

the solids so prepared were imperfect having fissures and holes. Similar shape particles have also been obtained by homogeneous precipitation from ferric salt solution [2]. Elongated spheroidal particles were precipitated by refluxing solutions of ferric salts and ammonium acetate [3]. Spindle type particles of narrow size distribution were prepared by forced hydrolysis of ferric chloride solutions in the presence of phosphate and hypophosphite ions [4]. Monodispersed pseudocubic shape particles were prepared by gel-sol method by many workers [5-6]. The shape of particle have been found to depend on the process parameters like ion concentration, pH of precipitation, solvent and anions. Thus, pseudocubic and platelet type particles have been obtained by gel-sol method while spindle type particles were obtained by the similar method in presence of phosphate ions [5]. Similarly control of preparation methods and process parameters have been found to yield particles with size in the range 100A to 20,000A [4,7].

The varying microstructure of hematite particles thus obtained by controlling preparation conditions have been shown to have considerable influence on their magnetic properties. For example magnetic susceptibility, magneto-crystalline anisotropy, coercivity etc. are affected by microstructure. In addition, these properties are also influenced by introducing additives like Al[8], Mn[9], Ti[10], Co[11] etc. in the lattice of oxides[12] or in the surface grains [13-14]. Amongst all the additives used, only Co^{2+} ion has been shown to form surface coating affecting Morin transition temperature (T_m), a.c. susceptibility and local magnetic parameters obtained by Mossbauer studies [11]. However much less attention has been given towards the effect of microstructure on magnetic properties.

The present paper describes the influence of microstructure on magnetic properties as well as on the magnetic coating of the surface of hematite grains in $\alpha\text{-Fe}_2\text{O}_3\text{-BaCl}_2$ mixed system sintered at 900C.

2. Experimental

To prepare hematite ($\alpha\text{-Fe}_2\text{O}_3$) phase, a hydroxide slurry was made using Ammonia from above Iron(III) solution at pH 3, 4.5, 7 and 10. The slurry was heated at 180C for 3 hours inside stainless steel autoclave lined with titanium. The solid sample

obtained were filtered, washed with deionised water and acetone and dried at 60C for 24 hours. The raw samples thus prepared were thoroughly mixed with BaCl₂ (99% purity) in the ratio of 1:2 in an agate mortar for 2 hours. The mixed powders were annealed at 900C for 12h. All powder handling, grinding and subsequent heat treatments were performed in air. After the heat treatment, the samples were cooled to room temperature and then washed thoroughly with distilled water to remove unreacted BaCl₂ in the mixture and then dried at 100C.

The structure was identified using X-ray diffraction with Cu-K α radiation. Thermogravimetry (TG) and differential thermal analysis (DTA) were used for identifying the presence of other less stable phase of iron oxide in the precipitates. Particle size and morphology were determined using transmission electron microscope (TEM). Magnetic properties were measured using a.c magnetic susceptibility setup with a maximum applied field upto 10 Oe.

3. Results and Discussion

XRD spectrum of raw samples prepared at pH 3, 4.5, 7 and 10 were identical and the characteristic peaks matched well with the hematite phase reported in ASTM card file (Fig.1). The other phases of hematite like goethite, maghemite, akaganeite etc. were absent as confirmed from temperature dependence of TG and absence of exo/endo-thermic peaks in the DTA curve (Fig. 2). Transmission electron micrographs (TEM) of the samples are shown in Fig-3. The particle size measured from these micrographs by average linear intercept method [15] were shown as a function of pH of precipitation (Table-1). With increasing pH of precipitation, the particle size was found to drastically reduce from 6500A at pH 3 to 600A at pH 10 sample. The morphology as shown in the micrographs were found to be monodispersed pseudocubic shape in pH 3, an intermediate shape between pseudocubic and trapezoidal in pH 4.5, trapezoidal shape in pH 7 and almost hexagonal in pH 10 sample (Fig.-3). Though the broad features of XRD spectra like peak positions and the intensities for the samples prepared at different pH were identical, the line width of corresponding peaks particularly the maximum intensity peak (104) differed from one pH to another. The mean crystallite diameter

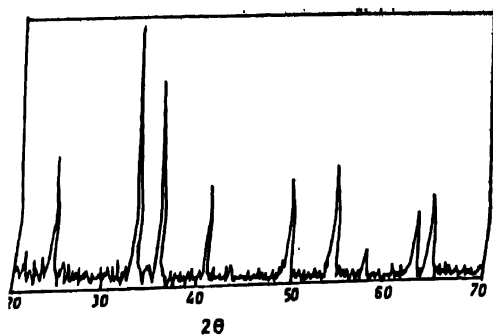


Fig. 1. Powder XRD pattern of hydrothermally prepared hematite

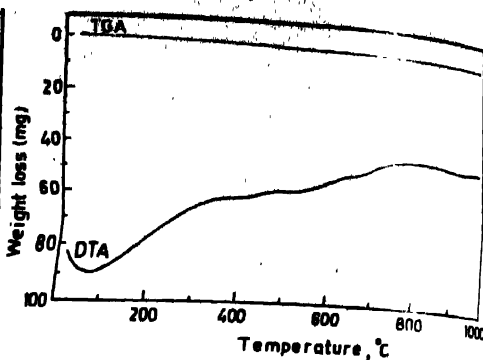
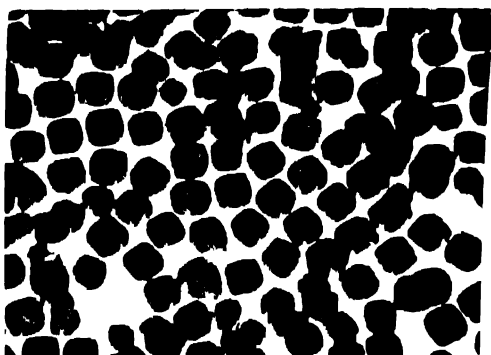
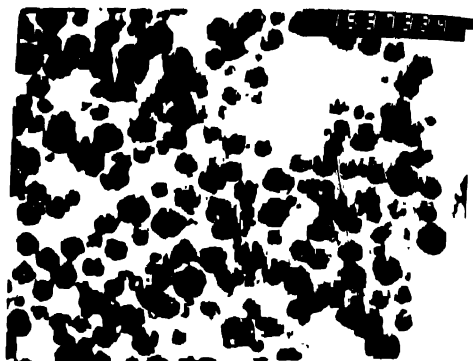


Fig. 2. TG and DTA of hydrothermally prepared hematite



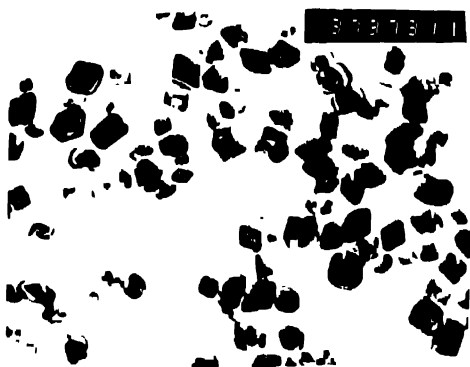
(a)

1 μm



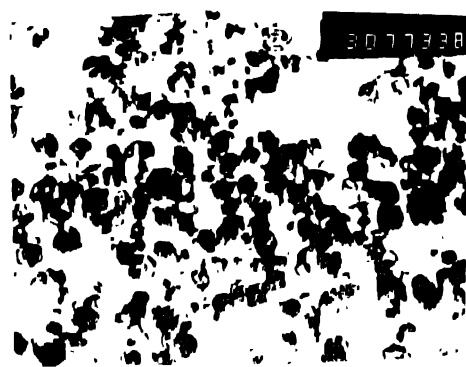
(b)

1 μm



(c)

0.5 μm



(d)

0.5 μm

Fig. 3. Transmission Electron Micrographs of hematite at different pH, (a) pH 3 (b) pH 4.5 (c) pH 7 and (d) pH 10.

MCD) evaluated from the XRD line width using Debye-Scherrer formula [16] at different pH is given in Table-1. For samples prepared at pH 3, particle size obtained from EM was found to be fifteen times higher than that evaluated from mean crystallite diameter (Table-1). With increasing pH of precipitation, this ratio decreased to almost one at pH 10. The inconsistency arising from both TEM and MCD values for particle size indicated that the particles are polycrystalline in nature i.e the grains as seen in TEM micrographs actually contain smaller subparticles inside them. The polycrystalline nature of particles decreases with increase in pH of precipitation and attains almost single crystalline nature for pH 10 sample. The detailed mechanism for occurrence of microstructural variation in different pH of precipitation is discussed in our earlier paper [17]

TABLE-1. pH dependence of particle size and mean crystallite diameter of $\alpha\text{-Fe}_2\text{O}_3$.

pH of precipitation	3	4.5	7	10
Particle Size(A)	6500	2500	1200	600
MCD ₁₀₄ (A)	430	530	540	525

The effect of microstructure on magnetic properties of hematite are shown in Table-2. Low value of a.c. magnetic susceptibility (χ) in pH 3 sample as compared to the reported values [18] is attributed to the presence of large number (3400) of subparticles inside the pseudocube. The small size of the subparticles with large surface to volume ratio and their aggregation lead to pinning of spins at the grain boundary. With increase in pH of precipitation the χ attained the reported bulk value of 4×10^{-5} emu/gmOe [18]. This behavior is compatible with MCD values which was in the range 525A to 540A for

pH 4.5 to 10 but 430A for pH 3. Thus, with increasing size of subparticle the χ increases due to reduced S/V ratio, pinning of spins and aggregation of subparticles. In addition, morphology, low angle grain boundaries, defects and dislocations take part in deciding such behaviour. Effect of annealing the raw samples mixed with BaCl_2 on χ is shown in Table-2. For pH 3 sample annealed with BaCl_2 , the χ was found to increase by 20 times. For pH 10 sample this factor went upto 50 with intermediate values for pH 4.5 and 7. The large rise in χ for these BaCl_2 mixed sample cannot be due to the weak ferromagnetic phase of hematite.

TABLE-2. pH dependance of a. c. magnetic susceptibility of raw and BaCl_2 mixed and annealed $\alpha\text{-Fe}_2\text{O}_3$.

pH of precipitation	a. c magnetic susceptibility (χ) $\times 10^{-5}$ emu/gmOe	
	Raw	BaCl_2 mixed
3	2.61	56.3
4.5	5.96	142.9
7	11.7	252.6
10	7.9	388.2

This can only arise if a magnetic phase forms due to reaction of BaCl_2 with hematite. In addition, the amount of rise in χ depending on pH imply that the microstructure particularly size and shape of the particles influence the final magnetic properties. Smaller rise in χ for pH 3 samples with large size pseudocubic particles of 6500A as compared to the much larger rise in pH 10 sample of 600A hexagonal particles indicates that the magnetic phase forms a coating on the surface of grains. This is because of the fact that large size of pseudocubic particles in pH 3 sample leaves a less number of Fe ions on the surface of grains as compared to the number of ions

inside them, providing a smaller volume fraction of the magnetic phase as compared to pH 10 sample. In pH 10 sample XRD clearly showed extra lines corresponding to the magnetic phase, barium hexaferrite formation (Fig. 4). In pH 3 sample such lines could not be seen in the XRD due to reduced volume fraction of this phase.

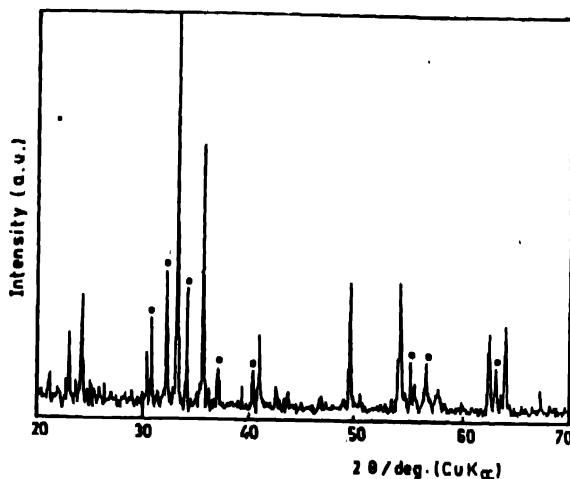


Fig. 4. Powder X-Ray diffraction pattern of BaCl_2 mixed and annealed $\alpha\text{-Fe}_2\text{O}_3$ sample prepared at pH 10.

It is expected that coating of barium hexa-ferrite on weak ferromagnetic material (hematite) having different microstructure will induce a high coercivity similar to hard ferrite. These materials are therefore of particular interest for applications in magnetic fluids, magnetic ink, permanent magnets, catalysts etc.

4. Conclusion

Control of pH of precipitation in the preparation of hematite by hydrothermal method has been shown to yield particles of varying microstructure. Such particles mixed with BaCl_2 at high volume fractions and annealed at 900°C produces a magnetic phase (Ba-hexaferrite) which coats the surface of the particles as evidenced from a.c magnetic susceptibility and XRD studies.

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