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Monodispersed spindle-type goethite nanoparticles from Fe^{III} solutions

L. C. Varanda,*[a] M. P. Morales,[b] M. Jafelicci, Jr[a] and C. J. Serna[b]

[a]*Instituto de Química de Araraquara, UNESP, CP 355–14801-970 Araraquara–SP, Brazil. E-mail: lvaranda@posgrad.iq.unesp.br*
[b]*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco–28049, Madrid, Spain*

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A new synthetic route for producing monodispersed and single crystal acicular goethite particles with small particle size and a high axial ratio adequate for use as a high density magnetic recording media precursor is reported. It essentially consists of the hydrolysis of alkaline Fe^{III} suspensions in the presence of carbonate by a three-step procedure, the formation of ferrihydrite primary particles, the ferrihydrite dissolution and nucleation of goethite, and the growth of the goethite nuclei. Changing the temperature of heating during ageing achieved a separation of the two last stages. X-Ray diffraction, transmission electron microscopy, infrared spectroscopy and surface area data have been used to determine the mechanism responsible for the formation of goethite particles with controlled size and shape. The best conditions to prepare monodispersed goethite particles have been established. The results show that uniform goethite particles of (a) 60 nm length with an axial ratio of 6 and (b) 230 nm length with a high axial ratio of 10, can be obtained by using an [OH]/[Fe] molar ratio of 0.35 in the initial suspensions with carbonate or sodium hydroxide, respectively. The [OH]/[Fe] molar ratio determines the particle size and elongation by controlling the hydrolysis reaction rate, while the carbonate ions promote a constant [OH] in the solution, keeping the pH around 10 during the entire synthesis process. This procedure, associated with the appropriate temperature control, leads, under certain conditions, to highly homogeneous goethite particles with sizes smaller than those obtained using sodium hydroxide with the same [OH]/[Fe] ratio.

Introduction

Magnetic recording systems are one of the most rapidly developing areas of high technology in the world today.[1] The introduction of high recording densities on recording media has, of course, meant a dramatic reduction in the size of an actual bit and a dramatic increase in the track density on the surface of the media.[2] One of the limits is based on the signal to noise ratio and also the question of the stability of increasingly small written bits.[1,3–5]

The recording media characteristics have been improved significantly over the years and in particular by the introduction of metal particle (MP) pigments.[5–11] The most common precursor for MP pigments is acicular goethite particles, α-FeOOH. Nowadays, goethite particles used as a precursor in the magnetic recording media manufacture are smaller than 100 nm in length.[10,12] It has been previously shown that the characteristics of the precursor in terms of defects or impurities coming from the preparation method are responsible for the magnetic behavior of the final magnetic pigments.[1,7,10]

Different methods have been reported for the synthesis of acicular goethite particles.[13–20] In general, the crystal size obtained from particles formed by oxidation of Fe^{II} solutions are smaller than those obtained in alkaline Fe^{III} solutions.[15] However, goethite particles as small as 100 nm in length have been obtained by hydrolyzing iron(III) solutions in two steps; initial precipitation of ferrihydrite and subsequent nucleation and growth of the goethite particles by heating at a constant temperature.[16] In the previous work it was concluded that iron(III) solutions aged at low pH ([OH]/[Fe] molar ratios lower than 2) and low temperature give rise to small acicular crystals of goethite, although the particles always showed a broad size distribution.

Following the method of Atkinson *et al.*,[16] in this work we have developed a new synthetic route for producing monodispersed and single crystal goethite particles with small particle size, less than 60 nm, and high axial ratio, appropriate for their use as precursors for MP used in high density recording media. The method described in this paper is based on the hydrolysis of alkaline Fe^{III} suspensions in the presence of carbonate by a three-step procedure, (i) initial precipitation of ferrihydrite, (ii) ferrihydrite dissolution and nucleation of goethite, and (iii) growth of the goethite nuclei. Changing the temperature of heating achieved a separation of the two last stages. Moreover, the reagent concentration and the nature of the base used were systematically varied to investigate their effect upon the phase composition and morphological characteristics of the goethite. Finally, the experimental conditions for the preparation of uniform, small goethite particles were optimized and the crystallographic direction of the long particle dimension was determined. In addition, the mechanism of particle formation was also inferred.

Experimental

All chemicals were analytical grade reagents (ferric sulfate hexahydrate, sodium carbonate, and sodium hydroxide from Aldrich) and used without further purification. The solutions were prepared using doubly distilled water.

The preparation of the ferrihydrite was carried out by mixing in a screw-top polythene bottle, 50 ml of an aqueous 0.1 M $Fe_2(SO_4)_3\cdot 6H_2O$ solution and the required amount of 2.5 M NaOH solution to reach a [OH]/[Fe] molar ratio of 0.35. The resulting solutions were aged at 21 °C for 4 h and, after that, an appropriate amount of sodium carbonate (molar ratio $[CO_3]/[Fe] = 3.75$) or sodium hydroxide (molar ratio $[OH]/[Fe] = 0.75$) was added to raise the pH to about 10 and the volume was

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Table 1 Experimental conditions for the preparation of ferrihydrite and final phases identified by X-ray diffraction

Sample	Preparation conditions of ferrihydrite[a]							Final phase[b]
	$[Fe]_T$/M	$Base_1$	$[Base]_1/[Fe]$ molar ratio	pH_1	$Base_2$	$[Base]_2/[Fe]$ molar ratio	pH_2	
G	0.10	NaOH	0.35	1.4	Na_2CO_3	3.75	10.3	G
G_A	0.20	NaOH	0.35	1.1	Na_2CO_3	3.75	9.8	G
G_B	0.05	NaOH	0.35	1.6	Na_2CO_3	3.75	10.2	G + H
G_C	0.10	NaOH	0.50	1.8	Na_2CO_3	3.75	10.1	G
G_D	0.10	NaOH	0.10	1.2	Na_2CO_3	3.75	9.6	H
G_E	0.10	NaOH	0.35	1.4	NaOH	0.75	10.4	G
G_F	0.10	Na_2CO_3	0.35	1.8	Na_2CO_3	3.75	10.1	G + H

[a]The subscripts 1 and 2 correspond to the two stages in the preparation of the ferrihydrite described in the Experimental section, and subscript T denotes the total iron concentration. [b]By XRD: G and H correspond to goethite and hematite phases, respectively.

made up to 100 ml. Finally, the ferrihydrite was aged in two stages: at 40 °C for 2 days and at 60 °C for 3 days. The bottles were shaken occasionally each 24 h. All samples were filtered, washed several times with water to eliminate impurities, and dried at 100 °C for 24 h.

Following the procedure described above, the reagent concentrations and the nature of the base were changed to determine their effect upon the product formation. A detailed description of the experimental conditions used is shown in Table 1. Aliquots of sample G were collected at different times of ageing to follow goethite formation. In addition, in order to study the effect of the ferrihydrite ageing in only one step, a sample was prepared in the same base conditions as sample G but with the temperature of heating fixed at 60 °C for the 5 days.

Phase identification was carried out by X-ray diffraction (XRD; Philips PW1710) using Cu-Kα radiation. The size and shape of the goethite particles were examined by transmission electron microscopy (TEM; JEOL 2000 FXII microscope). Average particle size ($D \pm$ SD) was taken from the electron micrographs by measuring around two hundred particles and the polydispersity was characterized.[21] Additional high-resolution TEM (HRTEM) was used to characterize the goethite samples. The surface area was measured by BET method in a CG2000 instrument at liquid nitrogen temperature based on gas desorption isotherm.

Results and discussion

Effect of the experimental conditions

The method here described is based on a modified route of the goethite preparation method proposed by Atkinson *et al.*,[16] based on the hydrolysis of iron(III) nitrate in alkaline medium. Two important modifications are proposed in this work and are represented in Fig. 1: (a) the use of sodium carbonate to control the hydroxyl ion concentration (pH = 10) in order to obtain more uniform conditions, and (b) the separation of the goethite formation stage into two steps by heating at 40 °C for 48 h and at 60 °C during the remaining time. In this way, the nucleation and growth of the goethite particles are expected to be somewhat separated, providing the maximum number of initial goethite nuclei in the first 48 h to produce smaller and more uniform final particles.

The experimental conditions used in the preparation of the ferrihydrite precursor had a strong effect on the resulting precipitate (Table 1). The XRD patterns for the different samples described in Table 1 are shown in Fig. 2. It was observed that a pure hematite phase appears at a low [OH]/[Fe] molar ratio during the first stage of the ferrihydrite precipitation (sample G_D). It seems that low hydroxyl species concentration favours hematite growth.[19,22] Therefore, in order to obtain only goethite particles several restrictions must be considered in this system, such as the use of iron salt concentrations equal to, or higher than, 0.1 M and [OH]/[Fe] ratios higher than 0.35. In addition, to obtain pure goethite, the presence of NaOH during the first stage seems to be essential (Table 1). It should also be mentioned that when NaOH was used in the second stage instead of carbonate, goethite was always obtained, the size of which being dependent on the [OH]/[Fe] ratio. Thus, particles smaller than 300 nm in length, were obtained for an [OH]/[Fe] ratio of around 0.75, which gave rise to a pH of around 10.

The TEM micrographs (Fig. 3) showed different particle sizes and degrees of homogeneity for the pure goethite samples. The mean particle length and width together with the polydispersity degree for these samples are given in Table 2. In addition, the particle length and width distributions are represented in the insets in Fig. 3. Samples G and G_E present high

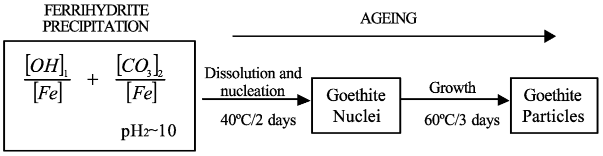

Fig. 1 Experimental scheme for the preparation of goethite particles.

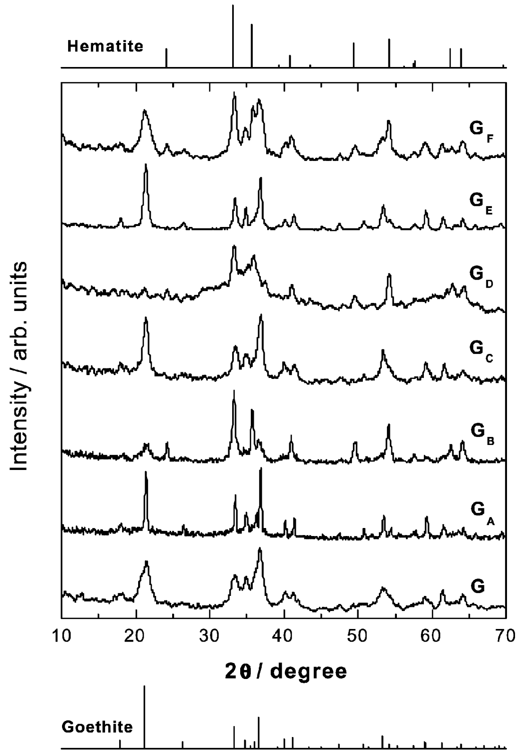

Fig. 2 X-Ray diffraction patterns for goethite samples synthesized according to the experimental conditions given in Table 1 and the diffraction patterns identifying hematite and goethite phases.

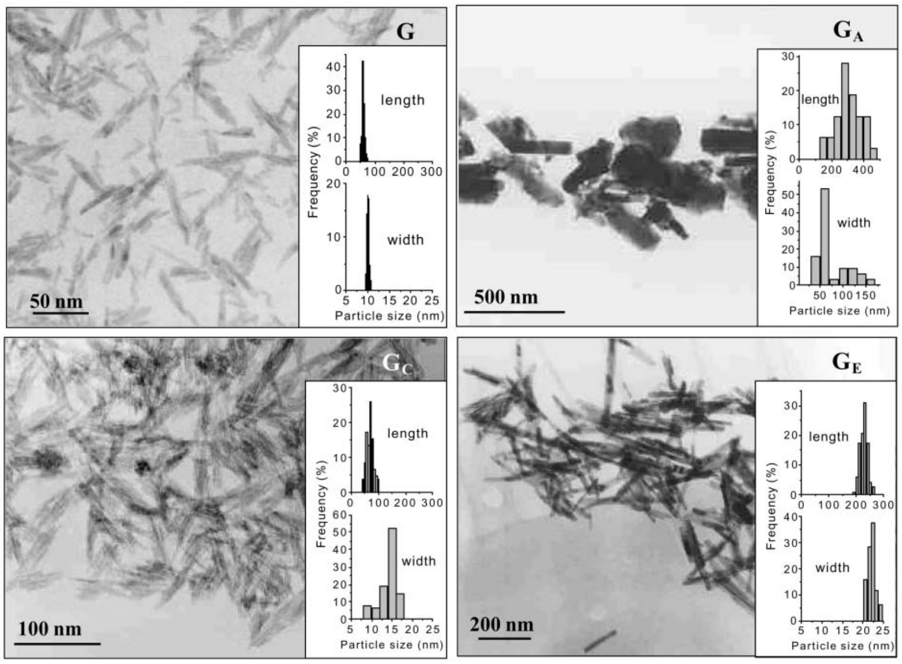

Fig. 3 TEM pictures of the goethite particles obtained according to Table 1. The insets show the size distribution (length and width) of the acicular goethite particles.

Table 2 Particle length and width and degree of polydispersity calculated from TEM for the goethites from the different preparations (Table 1)[a]

	TEM			Polydispersity	
Sample	L/nm	w/nm	L/w	SD/L	SD/w
G	60(5)	10(1)	6	0.08	0.1
G_A	300(80)	74(34)	4	0.27	0.46
G_C	70(14)	14(2)	5	0.20	0.14
G_E	230(14)	22(2)	10	0.06	0.09

[a] L, length; w, width; L/w, axial ratio; and SD, standard deviation. Numbers in parentheses correspond to SD.

morphological homogeneity with polydispersity degrees smaller than 0.1, which means that they are rather monodispersed.[21] However, sample G_A, prepared with a higher iron salt concentration, presents the largest particles, although quite irregular in shape and size (Fig. 3). High iron concentrations have been reported to slow down the hydrolysis process, which decreases the number of initial nuclei leading to larger particles.[16] On the other hand, sample G_C, obtained at an [OH]/[Fe] ratio higher than 0.35, has similar particle sizes to sample G but a higher degree of polydispersity (Table 2).

The crystallite size of the monodispersed samples (G and G_E) was calculated using the Scherrer equation[23] from the full width at half maximum of the (020) reflections, which have been related to the particle width in the case of acicular goethite.[24] The obtained values, 9.9 ± 0.2 nm and 21.5 ± 0.4 nm for samples G and G_E, respectively, indicate that, in both cases, the particles are formed by single crystals according to the dimensions observed by TEM (Table 2). Supporting this result, Fig. 4 shows a high-resolution electron image for sample G, which illustrates the texture of the goethite particles along the (110) planes. It suggests that the 001 crystallographic axis is along the longest particle dimension, in accordance with the goethite crystal habit of growth.[25]

It can be concluded that during the initial stage, high iron(III) and OH^- concentrations lead to heterogeneous goethite particles (samples G_A and G_C), while low iron(III) and OH^- concentrations favour the hematite phase formation (samples G_B and G_D). In the same way, when sodium hydroxide was changed to sodium carbonate in the first stage (sample G_F), the effect is similar to that observed with low OH^- concentration and the presence of the hematite phase was identified.

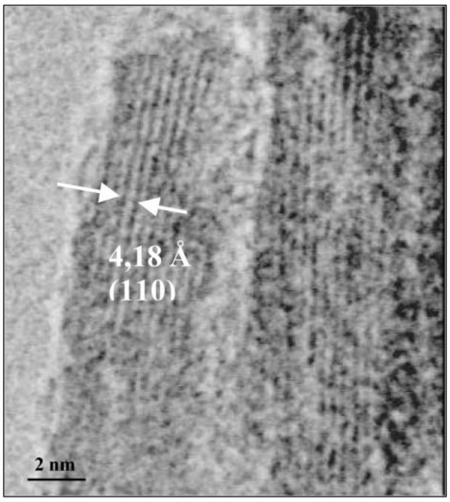

Fig. 4 HRTEM of sample G showing the particle texture along the (110) plane.

The second modification proposed in this work concerns the two temperatures used for goethite particle nucleation and growth. The use of a lower initial temperature (40 °C) is expected to give rise to an increase in the supersaturation due to a decrease in the iron salt solubility and therefore, to an increase in the number of initial goethite nuclei, which leads to smaller particles.[16] In fact, when the temperature was fixed at 60 °C during the whole reaction, goethite particles with low uniformity and large sizes, 300–500 nm in length, were obtained (data not shown). A temperature of 40 °C seems to be high enough to promote ferrihydrite dissolution and goethite nucleation. However, at this temperature, the growth rate of the particles relative to the nucleation rate must be small. A further increase of the temperature up to 60 °C allows the growth of the nuclei, leading to a very uniform solid favored

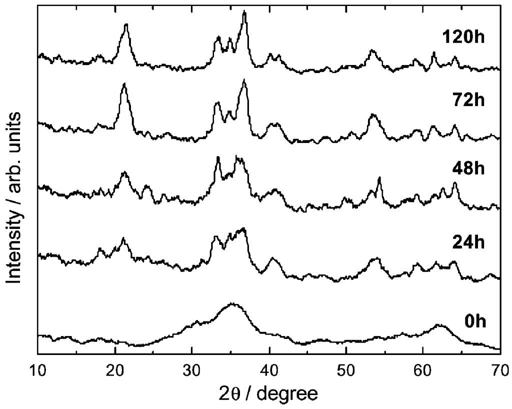

Fig. 5 X-Ray diffraction patterns of sample G during the growth stage.

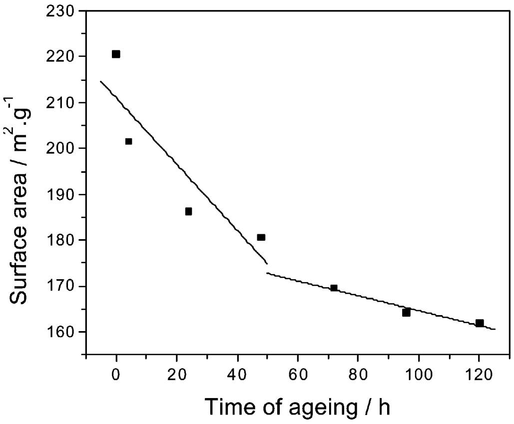

Fig. 7 Surface area evolution during the ageing period.

by the better incorporation of the remaining product at high temperature, in which Ostwald ripening could even be taking place at such a temperature.[26]

Mechanism of formation

The formation mechanism of monodispersed goethite particles was investigated for sample G using XRD (Fig. 5) and TEM (Fig. 6) during the goethite nucleation and growth, *i.e.* after sodium carbonate addition. The base addition induces a rapid hydrolysis and the formation of 2-line ferrihydrite (Fig. 5, 0 h). At this stage, the TEM micrograph showed the presence of aggregates, consisting of spherical particles of around 3–5 nm in diameter, typical of ferrihydrite (Fig. 6, 0 h). Goethite formation was already observed at 4 h by TEM (data not shown) and clearly detected by XRD at 24 h (Fig. 5). The TEM results showed that the size of the goethite particles at this step is ~20 nm, too big to be considered as nuclei. This result means that during the heating at 40 °C there is not only nucleation but also some slow growing of the initial nuclei giving rise to primary goethite particles (Fig. 6, 24 h), probably due to dissolution of ferrihydrite. The constant OH^- concentration due to the presence of carbonate ions seems to be responsible for the constant dissolution rate of the ferrihydrite and, consequently, for a homogeneous goethite nucleation process.

The ageing temperature was increased after 48 h from 40 °C to 60 °C promoting the total dissolution of the ferrihydrite and resulting in a further growth of the goethite primary particles, as it can be observed by the increase in the XRD peak intensities (Fig. 5). In agreement with this result, the TEM micrograph after 72 h of heating showed the presence of a large number of acicular goethite particles of around 60 nm in length together with few smaller particles of 20–30 nm and some ferrihydrite aggregates (Fig. 6). Finally, the growth of the goethite particles was finished after 120 h resulting in monodispersed particles of 60 ± 5 nm in length. The presence of a broad particle size distribution during the ageing period (72 h) indicates that several nucleations took place and the final uniformity could be achieved thorough a self-sharpening growth process where the small particles grow more rapidly than the larger ones.[26] Moreover, simulations have showed that monodispersed solids can be formed, even though the nucleation extends over a measurable time when the particle growth rate is slow relative to the nucleation rate.[27]

Surface area measurements show a greater decrease in specific surface area during the heat treatment at 40 °C in

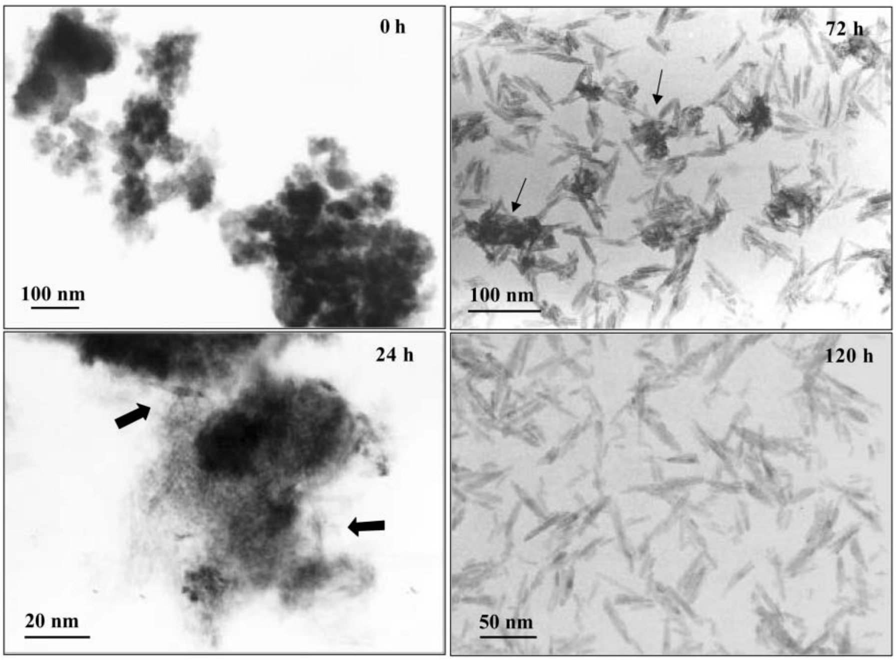

Fig. 6 TEM pictures of the sample taken at different times during the growth stage, indicating ferrihydrite (narrows arrows) dissolution and goethite (wide arrows).

comparison to the decrease when heating at 60 °C (Fig. 7). This result suggests that most of the ferrihydrite, which is a high surface area phase, is mainly dissolved during the first 48 h, according to Fig. 6. In the next stage, at 60 °C, besides the small amount of ferrihydrite, the growth of the goethite particles does not seem to make a significant contribution to the surface area decrease. The final goethite particles have a surface area of 162 $m^2 g^{-1}$. This value is larger than those found for goethite particles of 100 nm in length (~ 60 $m^2 g^{-1}$)[13] and it is in agreement with that for a small particle size.

Conclusions

Monodispersed and single crystal acicular goethite particles of small particle size and high axial ratio can be prepared by hydrolysis of alkaline Fe^{III} solutions in the presence of sodium carbonate through a three-step process, which attempts to separate the goethite nucleation and growth stages. The [OH]/[Fe] molar ratio and the nature of the alkaline medium used in the preparation of the ferrihydrite have a strong influence on the final goethite particle size and axial ratio. The use of sodium hydroxide leads to monodispersed goethite particles with an axial ratio of up to 10 and lengths of 230 nm, while the use of sodium carbonate can give rise to uniform particles of axial ratio up to 6 and lengths of 60 nm. The mechanism of goethite particle formation consists of the initial ferrihydrite dissolution and goethite nuclei formation followed by the growth of the goethite nuclei in the presence of the carbonate species, which keeps the pH constant during the reaction thereby giving rise to more uniform particles.

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