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Synthesis of gamma ferric oxide by direct thermal decomposition of ferrous carbonate

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Abstract

Ferrous carbonate was precipitated from the reaction of ferrous sulfate and sodium carbonate in an aqueous medium. The precipitate was calcined at different heating rates (2, 5 and 10 °C/min, respectively) up to 500 °C and the iron oxides produced were found to be magnetic. X-ray diffraction studies indicated the presence of gamma ferric oxide as a major phase in all the cases. It was found that wet precipitates, faster heating rate and short residence time in the furnace produced gamma ferric oxides with better magnetic properties (coercivity of around 360 Oe and saturation magnetization of 64 emu/g). The effect of aging time of ferrous carbonate precipitates on the magnetic properties was also studied. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gamma ferric oxide (γ-Fe_2O_3) is a ferrimagnetic material that finds wide use as magnetic storage media in audio and video recording. Numerous methods of synthesis abound in literature yielding gamma ferric oxide characteristic to the precursor and preparation techniques [1]. The well-established method of synthesis consists of a three-step process, producing acicular particles of alpha ferric oxide from alkali precipitation of ferrous salts followed by its tapotactic reduction to magnetite, and then controlled oxidation of magnetite to acicular gamma ferric oxide [2]. It is shown that gamma ferric oxide prepared by this technique exhibit enhanced coerciv-ity due to its shape anisotropy and particle size. Aerosol pyrolysis techniques are being employed nowadays to produce sub-micrometer gamma ferric oxide powders, wherein at the first instance, a fine amorphous intermediate is produced followed by heat treatment to achieve complete crystallization [3,4]. With the advent of sputtering techniques, thin films of gamma ferric oxide are formed in presence of controlled partial pressures of argon and oxygen. They show high coercivities of the order of 600–700 Oe because of the uniform micro-crystals of gamma ferric oxide [5]. Efforts to prepare gamma ferric oxide by single step calcination are found successful in the case of organic iron salts like ferrous oxalate [6], ferrous hydrazine carboxylate [7] and ferrous acetate [8]. However, the prohibitive cost of the reagents is a compelling factor to look for simple iron precursors. The present investigation describes

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the synthesis of gamma ferric oxide from the direct thermal decomposition of ferrous carbonate precipitated from ferrous sulfate and sodium carbonate solutions.

2. Experimental

Electrolytic iron powder (99.9%) and stoichiometric quantities of sulfuric acid (Analar) were reacted to produce ferrous sulfate (0.90 M) stock solution. An aliquot of the stock was diluted and hot (70 °C) sodium carbonate (0.50 M) solution was added as a thin stream with constant stirring until the pH became 9.5. The precipitated ferrous carbonate was filtered and washed with warm distilled water to remove the excess alkali and sodium sulphate. The wet precipitate was transferred to a silica crucible and calcined using a 'Thermolyne' 54500 programmable furnace. Three different heating rates viz., 2, 5 and 10 °C/min were used up to a temperature of 500 °C. Experiments were also conducted to study the effect of soaking time of the samples at 500 °C and 'aging time' of the precipitates before calcinations on the magnetic properties. The air-dried precipitates were calcined and studied under similar conditions. In each case, the calcined iron oxide powder was washed thoroughly with hot water and dried at 110 °C for 6 h. The X-ray diffraction studies were carried out with Philips Diffractometer. The vibration sample magnetometer (EG&G Princeton Applied Research) was used to evaluate the coercivity and saturation magnetization of the samples. FT-IR Spectra (Perkin-Elmer) and scanning electron microscopy were used additionally to characterize the iron oxide powders.

3. Results and discussion

The initial amount of sodium carbonate was used to neutralize the free acid and at a pH of 6. The light green precipitate formed was stable. With addition of more alkali, the precipitation was complete at a pH of 9.5. From the pC–pH diagram (Fig. 1) of Fe^{2+}–$FeCO_3$–$Fe(OH)_2$, it can be seen that the solid phase below 10.5 is $FeCO_3$ and $Fe(OH)_2$ formed at this pH is reprecipitated as $FeCO_3$ [9]. The hatched portion in Fig. 1 indicates the area of precipitation chosen for the experiments where only $FeCO_3$ is formed. Table 1 gives the phase composition of the iron oxide samples (S-1–S-10) prepared at different heating rates (2, 5 and 10 °C/min) under different soaking time (0, 30 and 60 min). In all the cases, the temperature of calcination was set at 500 °C (except S*-7). X-ray diffraction analysis indicates that faster
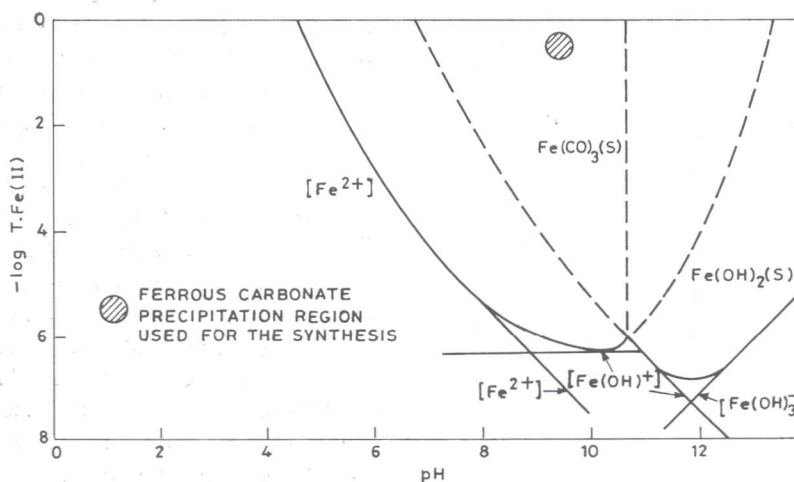

Fig. 1. The pC–pH diagram of Fe^{2+}–$FeCO_3$–$Fe(OH)_2$ system (adapted from Ref. [9]).

Table 1
Experimental conditions for the preparation of iron oxide samples from ferrous carbonate and their X-ray diffraction analysis

Sample code	Heating rate (up to 500 °C), °C/min	Soaking time (at 500 °C), min	Phase composition	Remarks
S-1	2	0	γ-Fe_2O_3 + α-Fe_2O_3	Weak diffraction lines of α-Fe_2O_3
S-2	2	30	γ-Fe_2O_3 + α-Fe_2O_3	Slightly strong diffraction lines of α-Fe_2O_3
S-3	2	60	γ-Fe_2O_3 + α-Fe_2O_3	Stronger diffraction lines of α-Fe_2O_3
S-4	5	0	γ-Fe_2O_3	Sharp diffraction lines of γ-Fe_2O_3
S-5	5	30	γ-Fe_2O_3 + α-Fe_2O_3	Weak diffraction lines of α-Fe_2O_3
S-6	5	60	γ-Fe_2O_3 + α-Fe_2O_3	Slightly strong diffraction lines of α-Fe_2O_3
S-7	10	0	γ-Fe_2O_3	Distinct diffraction lines of γ-Fe_2O_3
S*-7	10	0	Fe_3O_4	Distinct diffraction lines of Fe_3O_4
S-8	10	30	γ-Fe_2O_3	Distinct diffraction lines of γ-Fe_2O_3
S-9	10	60	γ-Fe_2O_3 + α-Fe_2O_3	Weak diffraction lines of α-Fe_2O_3
S-10	10	0	α-Fe_2O_3	Distinct diffraction lines of α-Fe_2O_3

S*-7—product intermediate removed at 350 °C, dried at 110 °C in nitrogen gas for 2 h.
S-10—ferrous carbonate precipitate dried at 110 °C for 2 h before calcinations.

heating rate promotes the formation of gamma ferric oxide (S-4, S-7 and S-8) whereas slow heating rate produces gamma ferric oxide with alpha ferric oxide (S-1). It is also clear that the increase in soaking time enhances the formation of alpha ferric oxide (S-2, S-3, S-5, S-6, and S-9). In order to study the reaction mechanism, a reaction product was taken out at 350°C (10 °C/min). It was a sticky moist black mass and dried at 110 °C in nitrogen stream to produce a black powder that was confirmed to be magnetite (S*-7). The ferrous carbonate dried at 110 °C (2 h) on heating (10 °C/min) produced the non-magnetic alpha ferric oxide (S-10). Fig. 2 shows the XRD patterns of samples S-3, S-5, S*-7, S-7 and S-10. Fig. 3 shows the effect of heating rate and soaking time on the magnetic properties (coercivity, H_c and saturation magnetization, σ_s) of the iron oxides produced from direct thermal decomposition at 500 °C. It was noted that iron oxide samples S-4, S-7 and S-8 exhibited better coercivity (324, 363 and 323 Oe) and saturation magnetization (56.5, 64.0 and 58.5 emu/g) when compared with samples S-1, S-2, S-3, S-5, S-6 and S-9. Fig. 4 shows the hysteresis curve for gamma ferric oxide (S-7). From the investigation, it is clear that rapid heating of ferrous carbonate is essential to produce phase pure gamma ferric oxide with good magnetic properties. Similar rapid heating was adopted to prepare gamma ferric oxide from ferrous oxalate dihydrate that was decomposed directly at 300 °C in 15–20 min [6]. Also, the soaking

time has a marked influence on the magnetic properties owing to the formation of alpha ferric oxide, and hence, lower coercivity and saturation magnetization
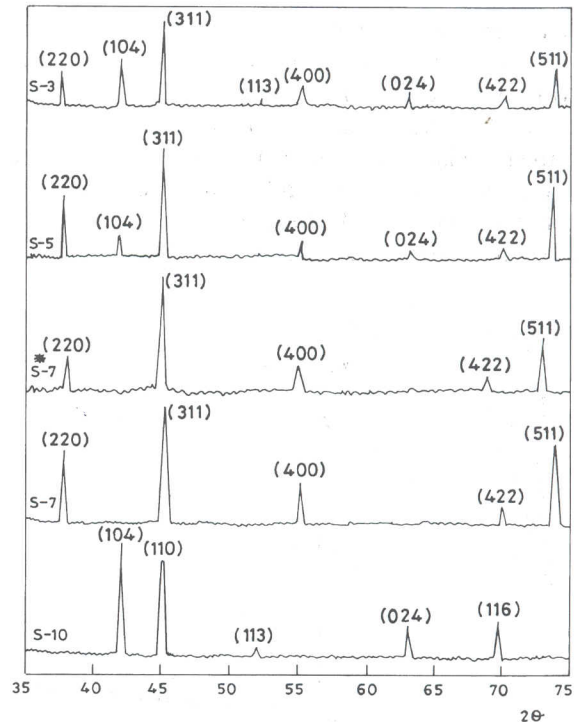

Fig. 2. X-ray diffraction pattern of iron oxide samples: S-3 (γ-Fe_2O_3 + α-Fe_2O_3); S-5 (γ-Fe_2O_3 + α-Fe_2O_3); S*-7 (Fe_3O_4); S-7 (γ-Fe_2O_3); and S-10 (α-Fe_2O_3).

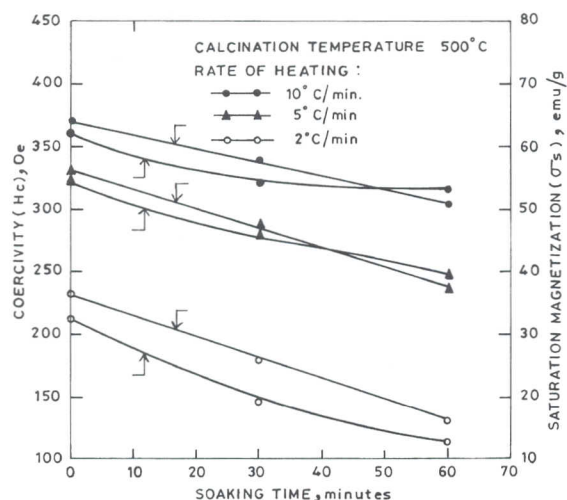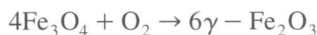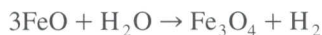Fig. 3. Effect of heating rate and soaking time on the magnetic properties (H_c and σ_s) of iron oxide samples prepared from thermal decomposition of ferrous carbonate.

netite is not violent enough to produce alpha ferric oxide. The sequence of reactions can be written as:

$$FeCO_3 \cdot XH_2O \rightarrow FeO \cdot XH_2O + CO_2$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

$$4Fe_3O_4 + O_2 \rightarrow 6\gamma - Fe_2O_3$$

The significance of water vapour in the synthesis of gamma ferric oxide has been documented in several instances [10–12]. When the wet cake of ferrous carbonate was dried at 110 °C (2 h), a brownish yellow powder was produced that on subsequent calcinations (500 °C, 10 °C/min) produced the non-magnetic alpha ferric oxide. This shows that only wet precipitates on immediate calcinations could produce gamma ferric oxide. It was observed that wet ferrous carbonate precipitates standing in air turned yellowish due to the slow onset of oxidation from ferrous to ferric state. A series of experiments were carried out to study the effect of such aging time of the precipitates on the magnetic properties (H_c and σ_s) of the ferric oxides prepared from them. Fig. 5 shows that the coercivity (H_c) and saturation magnetization (σ_s) values drastically reduced with aging time due to the conversion of ferrous carbonate hydrate to ferric oxy hydroxide (α-FeO · OH). The extent of oxidation is initially high and falls down with time, indicating that the reaction is probably diffusion-controlled. Methods of gamma ferric oxide synthesis based on the oxidation of ferrous carbonate to produce goethite are reported in the

values. Based on the results, the formation of gamma ferric oxide can be explained on the basis that ferrous carbonate undergoes rapid thermal decomposition to produce wustite (predominantly FeO phase with some magnetite) that is oxidized to magnetite in presence of water vapour. The magnetite undergoes further oxidation to form gamma ferric oxide. Moreover, the evolution of carbon dioxide along with water vapour should be beneficial in reducing partial pressure of oxygen such that the oxidation of mag-
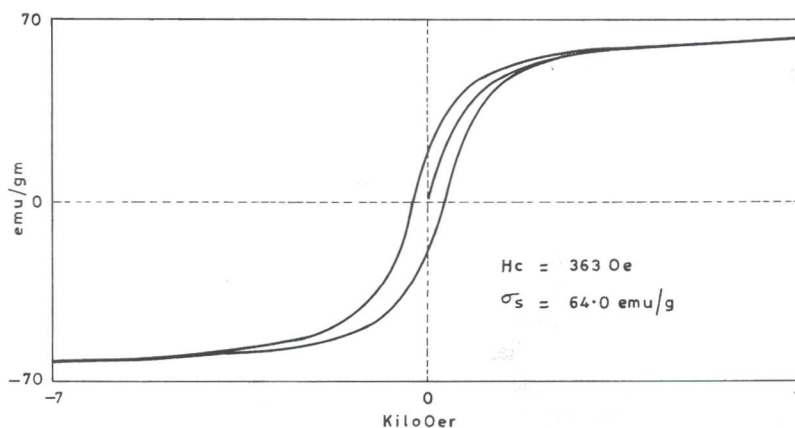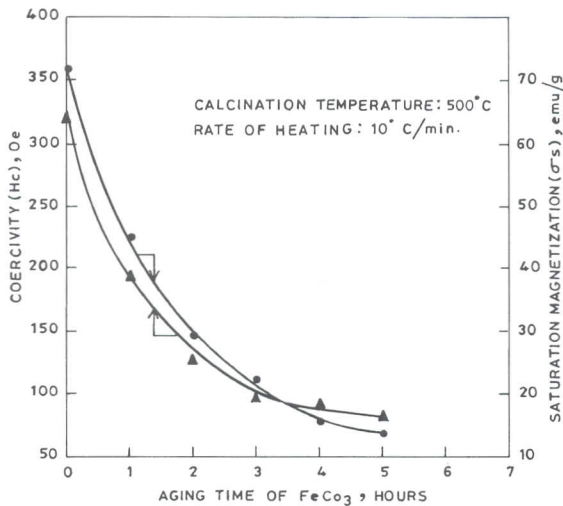

Fig. 4. Hysteresis loop of gamma ferric oxide (S-7).

Fig. 5. Effect of 'aging time' of the ferrous carbonate precipitate on the magnetic properties (H_c and σ_s) of the iron oxide samples synthesized from them.

Fig. 7. SEM photograph of gamma ferric oxide (S-7).

literature [13,14], but they involve multiple steps like dehydration, reduction and oxidation processes. Fig. 6 shows the FT-IR spectra of samples S-7 and S-10. It can be seen that S-7 shows bands at 465, 585 and 632 cm^{-1} that are characteristic of gamma ferric oxide. There are also bands at 3443 and 1643 cm^{-1}, indicating the presence of water molecules and carbonate residue, respectively. S-10 shows bands at

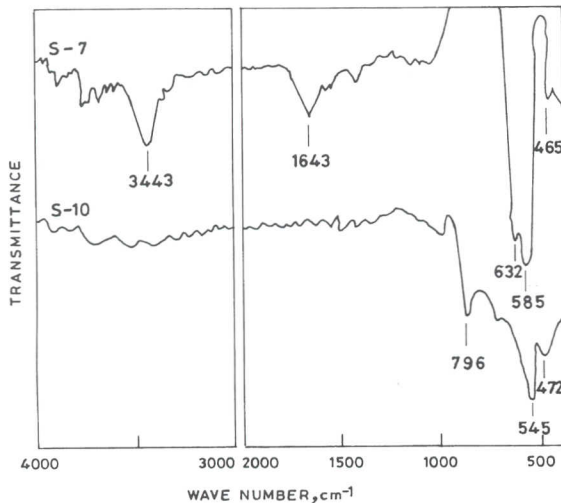472, 545 and 796 cm^{-1} that are characteristic of crystalline alpha ferric oxide. The scanning electron micrograph of gamma ferric oxide powder (S-7) is shown in Fig. 7. The particles are non-acicular and agglomerated.

Acknowledgements

Fig. 6. FT-IR spectra of iron oxides S-7 (γ-Fe$_2$O$_3$) and S-10 (α-Fe$_2$O$_3$).

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