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Synthesis and characterization of γ-Fe_2O_3 — a magnetic tape material

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Abstract. Acicular $FeC_2O_4 \cdot 2H_2O$ was precipitated from glycerol and starch media. Thermal decomposition of this oxalate in dry and moist nitrogen yielded primarily FeO and Fe_3O_4 respectively. Characterization was attempted through DTA, TG, x-ray diffraction, TEM and magnetization studies. It was found that the oxalate can be completely decomposed to Fe_3O_4 in moist nitrogen ($P_{H_2O} \sim 35$ torr) at 775 K and then oxidised by dry air to acicular γ-Fe_2O_3 at 575 K. The resulting material has saturation magnetization ($\sim$ 70 emu/g), coercive field ($\sim$300 Oe) and squareness ratio ($\sim$ 0·60-0·65), which values art comparable with those of the commercial samples.

Keywords. γ-Fe_2O_3; magnetic tape materials; synthesis of γ-Fe_2O_3; magnetization.

1. Introduction

Single domain acicular γ-Fe_2O_3 is an important material used as recording medium in applications such as magnetic tapes and other information storage devices like drums and discs. The present annual demand for this oxide is about 25 MT and is met through import (Patil 1977). Considering this growing demand it is imperative to intensify import substitution efforts through setting up viable production units, for which the necessary competence and infrastructure presumably exists in our country, optimizing conditions for the existing preparative conditions and developing new cheaper methods of synthesis. Commercially γ-Fe_2O_3 is manufactured through the reaction route

$$\alpha\text{-FeOOH} \xrightarrow{\text{dehydration}} \alpha\text{-}Fe_2O_3 \xrightarrow{\text{reduction}} Fe_3O_4 \xrightarrow{\text{oxidation}} \gamma\text{-}Fe_2O_3.$$

However, an alternative method *via* thermal decomposition of ferrous oxalate dihydrate, $FeC_2O_4 \cdot 2H_2O$, has shown more promise. Venkatesh Rao *et al* (1974) observed that the hydrated oxalate containing traces of moisture can be decomposed in air under the ambient of its own gaseous products at 575 K to give γ-Fe_2O_3. However the decomposition is highly exothermic so that local oxidative heating leads to unavoidable contamination with α-Fe_2O_3. In this

paper it will be shown that proper manipulation of experimental conditions can give a high yield of tape-quality material with appropriate physical and magnetic characteristics. Since only spherical particles result from aqueous solutions, results of precipitation of the oxalate from other new media such as glycerol and starch have been discussed.

2. Experimental

For the synthesis of $FeC_2O_4 \cdot 2H_2O$, aqueous solution method of Bevan and Brown (1966) was modified in the sense that equal volumes of glycerol and water or saturated solution of starch and water were employed as precipitating media. For characterization, DTA, TG, x-ray diffraction, TEM and hysteresis loop tracer techniques were employed. DTA curves were recorded in UHP nitrogen and in the presence of moisture on a Mettler thermal analyser using $\sim$ 100 mg of the sample at a heating rate of 8°/min and a gas flow rate of 150 ml min. Isothermal decomposition studies were made by passing a slow stream of UHP nitrogen containing moisture, over the sample placed in a tubular furnace and held at selected temperatures. The products were identified by x-ray powder diffraction using CoK_α ($\lambda = 1{\cdot}79021$ Å) radiation on a Philips diffractometer PW 1501. The magnetic characteristics such as saturation magnetization (σ_s), remanent magnetization (σ_s) and coercive field (H_c) were measured on a hysteresis loop tracer described by Likhite *et al* (1965). TEM photographs on a Philips EM 301 unit determined the size and acicularity of $FeC_2O_4 \cdot 2H_2O$ and γ-Fe_2O_3 particles.

3. Results and discussion

3.1 *Decomposition of $FeC_2O_4 \cdot 2H_2O$ (glycerol medium)*

Seshan (1980) has reported DTA, TG, DTG curves for $FeC_2O_4 \cdot 2H_2O$ in air and in UHP nitrogen and concluded that (i) α-Fe_2O_3 results on heating in air, (ii) primarily FeO in dry nitrogen and (iii) primarily Fe_3O_4 in moist nitrogen. The step (iii) involving formation of Fe_3O_4 is crucial; in dry conditions water vapour escapes quickly and is unavailable for reaction, while in the presence of high partial pressure of water vapour, dehydration and subsequent steps occur at higher temperatures at which formation of α-Fe_2O_3 is facilitated. In order to determine optimum partial vapour pressure of water (P_{H_2O}) the samples were maintained at 520, 570 and 620 K respectively for 30 min each in a flowing gas atmosphere of appropriate mixtures of nitrogen and water vapour. Table 1 summarizes the results of the decomposition. It will be noted that at 570 K the decomposition to γ-Fe_2O_3 gets completed (corresponding to 56% mass loss). The values of σ_s, H_c and σ_r/σ_s under $P_{H_2O} = 30$ and 35 torr compare favourably with those of standard commercial samples ($\sigma_s = 74$ emu/g, $H_c = 270$ Oe, $\sigma_r/\sigma_s = 0{\cdot}65$).

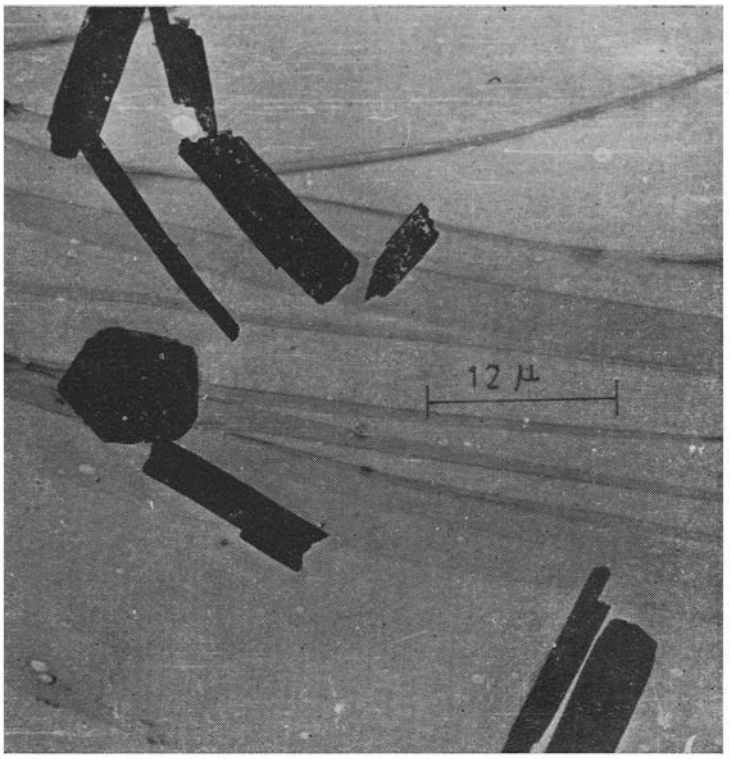

Figure 1. TEM hotograph of acicular $FeC_2O_4 . 2H_2O$ (starch medium).

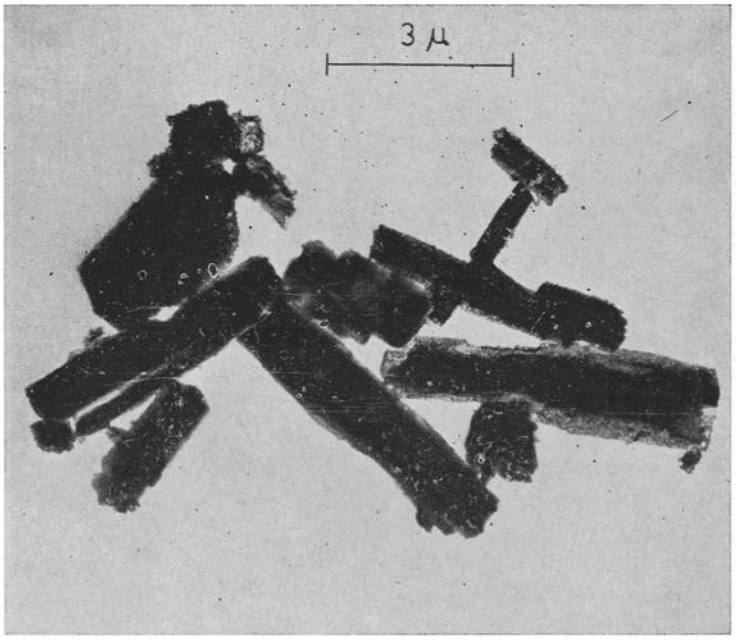

Figure 3. TEM photograph of acicular γ - Fe_2O_3.

3·2 *Decomposition of* $FeC_2O_4 \cdot 2H_2O$ *(starch medium)*

Since glycerol is costly, a cheaper starch medium was used for precipitating the acicular oxalate (figure 1). DTA curves in dry UHP nitrogen and nitrogen plus moisture ($P_{H_2O} = 35$ torr) were recorded (figure 2). In the absence of moisture dehydration occurred at 720 K corresponding to primarily FeO (mass loss = 60% and non-magnetic). Similarly, in the presence of water vapour, dehydration took place at a higher temperature ($\sim$ 495 K), as expected, and decomposition to Fe_3O_4 (mass loss = 60% and strongly magnetic) occurred around 710 K. The above findings indicate that $FeC_2O_4 \cdot 2H_2O$ should be heated in nitrogen and moisture ($P_{H_2O} \sim$ 35 torr) at least up to 775 K at which Fe_3O_4 has been completely formed. Apparently the oxidation of Fe_3O_4 to γ-Fe_2O_3 can be carried out at this stage. Therefore, dry air was introduced in the DTA apparatus for about 30 min when the temperature reached 775 K and was held constant there. An exothermic peak was observed, which corresponded to α-Fe_2O_3 (mass loss = 56% and non-magnetic). Thus it appears that this process is unsuitable for the production of γ-Fe_2O_3.

In another set of experiments, after the oxalate had been decomposed in nitrogen and moisture ($P_{H_2O} \sim 35$ torr) to Fe_3O_4 by heating up to 775 K, the DTA apparatus was steadily cooled to 575 K and dry air introduced isothermally for about 30 min. A similar exothermic peak corresponding to the same mass loss (= 56%, i. e. Fe_2O_3) was observed; however the product was highly magnetic and on analysis through x-ray and magnetic measurements was found to be γ-Fe_2O_3. Following the same heating and cooling schedule the reaction was now carried out in a reactor on a larger scale (yield $\sim$ 10 g) and

Table 1. Isothermal decomposition of $FeC_2O_4 \cdot 2H_2O$ (glycerol medium) under partial different pressures of water vapour.

Temperature (K)	Mass loss (%)	Saturation magnetization σ_s (e.m. u./g)	Coercive field H_c(Oe)	Squareness ratio σ_R/σ_s
P_{H_2O} = 30 torr				
520	46	19·7	188	0·28
570	56	68·0	300	0·50
620	56	54·0	300	0·32
P_{H_2O} = 37 torr				
520	44	15·4	130	0·20
570	56	69·2	300	0·50
620	56	47·6	300	0·30
P_{H_2O} = 150 torr				
520	45	24·4	109	0·30
570	56	50·0	140	0·36
620	56	28·0	125	0·33

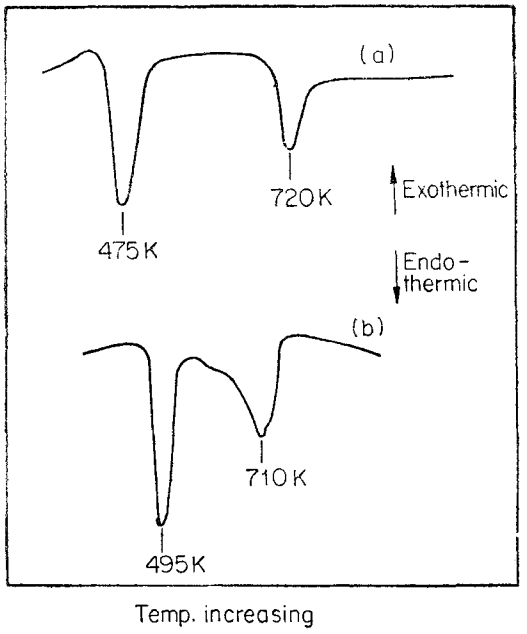

Figure 2. DTA curves for $FeC_2O_4 \cdot 2H_2O$ in (a) UHP nitrogen (b) UHP nitrogen containing water vapour ($P_{H_2O} \sim 35$ torr).

the resulting product was found to have appropriate acicularity (figure 3) and magnetic characteristics ($\sigma_s = 70$ emu/g; $H_c = 300$ Oe; $\sigma_R/\sigma_s = 0{\cdot}60$).

4. Conclusions

Acicular ferrous oxalate dihydrate, $FeC_2O_4 \cdot 2H_2O$ can be precipitated from glycerol and starch media, decomposed completely to Fe_3O_4 in moist nitrogen ($P_{H_2O} \sim 35$ torr) at 775 K and then oxidized by dry air to acicular γ-Fe_2O_3 at 575 K. The resulting material possesses magnetic properties comparable with those of commercial samples.

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