

Preparation and characterisation of γ -Fe₂O₃ as tape recording material

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Abstract. Optimum conditions for the preparation of tape recording quality γ -Fe₂O₃ by the thermal decomposition of ferrous oxalate dihydrate have been established. Formation of the intermediate Fe₃O₄ which is most important in forming γ -Fe₂O₃ takes place only in the presence of water vapour. Various stages of decomposition have been characterised by DTA, TG, DTG, and x-ray powder diffraction. The method for the preparation of acicular γ -Fe₂O₃ that matches very well with the commercial tape recording material has been developed.

Keywords. γ -Fe₂O₃; tape recording material; preparation.

1. Introduction

Over the last five decades, γ -Fe₂O₃ has been the most widely used material for magnetic tapes. It has an ideal combination of such parameters as saturation magnetisation (σ_s), coercive force (H_c) and remanence (σ_r) that makes it an excellent recording material (Smit 1971). Generally, it is used in the form of single domain particles of acicular shape for a good signal-to-noise ratio on recording. Commercially it is obtained from goethite (α -FeOOH) as follows:



The formation of Fe₃O₄ is the most important step and the conditions are stringent. An alternative method for the preparation of γ -Fe₂O₃ from FeC₂O₄·2H₂O is reported here. Although Tsyrnorchki and Peshev (1961) have reported the formation of γ -Fe₂O₃ by heating ferrous oxalate dihydrate in low oxygen partial pressures, no information is available of the reaction conditions (also Peshev and Tsyrnorchki 1961). The mechanism of formation of γ -Fe₂O₃ has been investigated and a method has been developed for obtaining acicular γ -Fe₂O₃ with desired properties for magnetic tapes.

2. Experimental methods

$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was prepared as a fine yellow crystalline powder by the method of Bevan and Brown (1966). DTA, TG and DTG curves were recorded in air and also in nitrogen on a Mettler thermal analyser using 10 mg of the sample at a heating rate $8^\circ\text{C}/\text{min}$ and gas flow rate 150 ml/min. For isothermal decomposition studies in air, a known mass of the oxalate was maintained at selected temperatures for 6 hr in an air oven, while similar studies in nitrogen were conducted by passing a slow stream of UHP nitrogen over the sample placed in a tubular furnace. The products were identified by x-ray powder diffraction using $\text{CoK}\alpha$ radiation on a diffractometer PW 1501. Infrared spectra were recorded on Perkin Elmer 237 in nujol and the magnetic properties were measured on a hysteresis loop tracer described by Likhite *et al* (1965). Nitrogen gas used was of UHP quality supplied by Indian Oxygen Ltd.

3. Results and discussion

3.1 Thermal analyses of ferrous oxalate dihydrate

The DTA, TG and DTG curves for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are shown in figures 1 and 2. The TG curve shows a continuous mass loss in the temperature range 445–545 K (total mass loss 55% corresponding to the formation of Fe_2O_3). The DTA curve in air shows an endotherm at 463 K due to dehydration and two exotherms at 518 and 633 K. The first exotherm corresponds to oxidative decomposition to give Fe_2O_3 and the second exotherm was assigned to a structural change as the TG did not show any mass change in this region. DTA in nitrogen showed two endotherms (475 and 720 K) with a total mass loss of 60% corresponding to the formation of FeO . Broadbent *et al* (1967) also observed two endotherms but identified the product as a mixture of Fe, FeO and Fe_3O_4 .

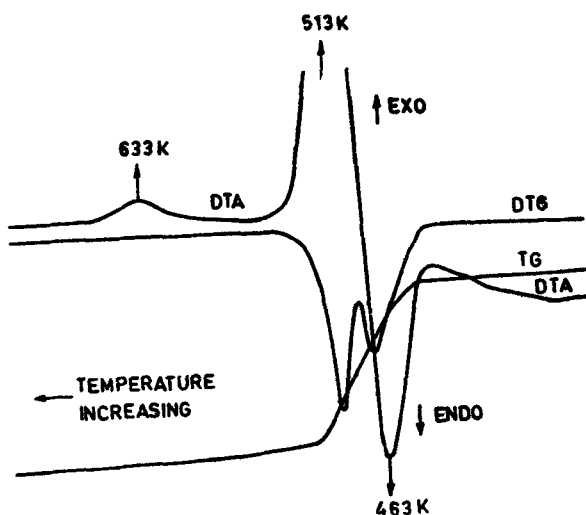


Figure 1. DTA, TG and DTG curves for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air.

The results of isothermal decomposition studies in air at various temperatures are summarised in table 1. The decomposition is nearly complete at 475 K (mass loss $\sim 54\%$) which was confirmed from IR spectra of the samples which did not show absorption due to water and carbonyl groups in samples heated above 475 K. The decomposition, however, starts at a much lower temperature, even at 445 K mass loss (37.4%) is much higher than expected for dehydration alone (20%). X-ray data indicate that the DTA peak at 633 K is due to the transformation of a non-crystalline form of α -Fe₂O₃ to a crystalline state. In none of these experiments we could notice the formation of γ -Fe₂O₃.

3.2 Preparation and characterisation of γ -Fe₂O₃

It was reported by David and Welch (1956) that the presence of water vapour is essential in obtaining γ -Fe₂O₃ from magnetite. In our experiment, about 50 g of moist FeC₂O₄·2H₂O was heated in a large porcelain dish at 575 K for 20 minutes. The dish was taken out and the content was stirred well to obtain dull reddish-brown

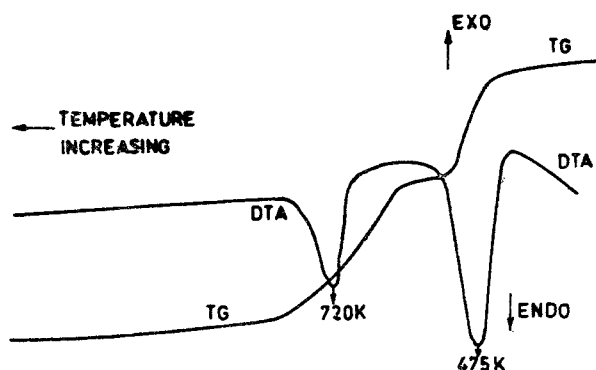


Figure 2. DTA and TG curves for FeC₂O₄·2H₂O in UHP nitrogen.

Table 1. Isothermal decomposition of FeC₂O₄·2H₂O in air

Temp (K)	Time of heating (hr)	Mass loss (%)	3450 OH(H ₂ O)	IR data (cm ⁻¹) 1615 CO	810 OH(H ₂ O)	X-ray data corresponds to	Colour of product
373	6	..	P	P	P	FeC ₂ O ₄ ·2H ₂ O	Yellow
423	6	3.4	P	P	P	"	Yellow
443	6	37.4	A	P	A	Non-crystalline Powder	Dark red Brown
473	6	53.8	A	V.W.	A	"	"
503	6	55.5	A	A	A	"	"
573	6	55.5	A	A	A	α -Fe ₂ O ₃	Red brown
623	6	55.5	A	A	A	α -Fe ₂ O ₃	"

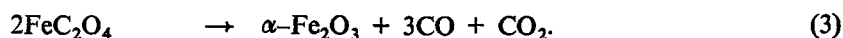
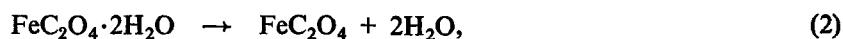
P—Present; A—Absent; V.W.—Very Weak

powder of γ -Fe₂O₃, the x-ray and magnetic data for which are given in table 2. The magnetic properties compare very well with commercial material used in magnetic tape.

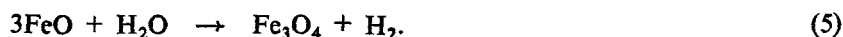
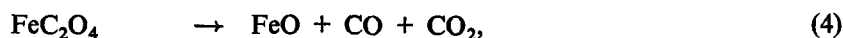
In order to obtain the optimum conditions for the preparation of γ -Fe₂O₃ with desired property, the effect of the partial pressure of water on the decomposition of FeC₂O₄·2H₂O has been studied. For this purpose, the sample was flushed with UHP nitrogen and then nitrogen containing water vapour at a definite partial pressure was introduced and the sample was heated isothermally. After the reaction was over, the nitrogen supply was replaced by air and the furnace was switched off. The properties of the product γ -Fe₂O₃ are given in table 3. The samples obtained at 575 K and $p_{\text{H}_2\text{O}}$ at 30 and 37 torr gave the best results. The particles were spherical in shape (~ 600 Å) (figure 3a) and the coercive force (~ 300 Oe) indicates single domain nature of the particles as there is no contribution from shape anisotropy.

3.3 Steps involved in the formation of γ -Fe₂O₃

The results show that FeC₂O₄·2H₂O decomposes in air as



However, in an atmosphere of nitrogen containing water vapour, FeC₂O₄ reacts as follows:



Formation of Fe₃O₄ is the most crucial step in obtaining γ -Fe₂O₃ by its oxidation. In dry conditions, water vapour from dehydration quickly escapes and is not available

Table 2. X-ray and magnetic data for γ -Fe₂O₃ obtained by decomposition of moist FeC₂O₄·2H₂O

X-ray data			Magnetic data			
Reported d' value	Intensity	Present investigation 'd' value	Intensity	Property	Reported	Present Investigation
2.95	S	2.94	S	Coercive force	250-300 Oe	250 Oe
2.51	VS	2.69 (α -Fe ₂ O ₃)	W			
2.08	S	2.50	VS	Saturation magnetisation	74 emu.g ⁻¹	70 emu.g ⁻¹
1.82	S	2.07	M			
1.70	M	1.87	W	Ratio of remanence to saturation	0.67	0.6
1.60	S	1.70	M			

VS—Ver strong; S—Strong; M—Medium; W—Weak.

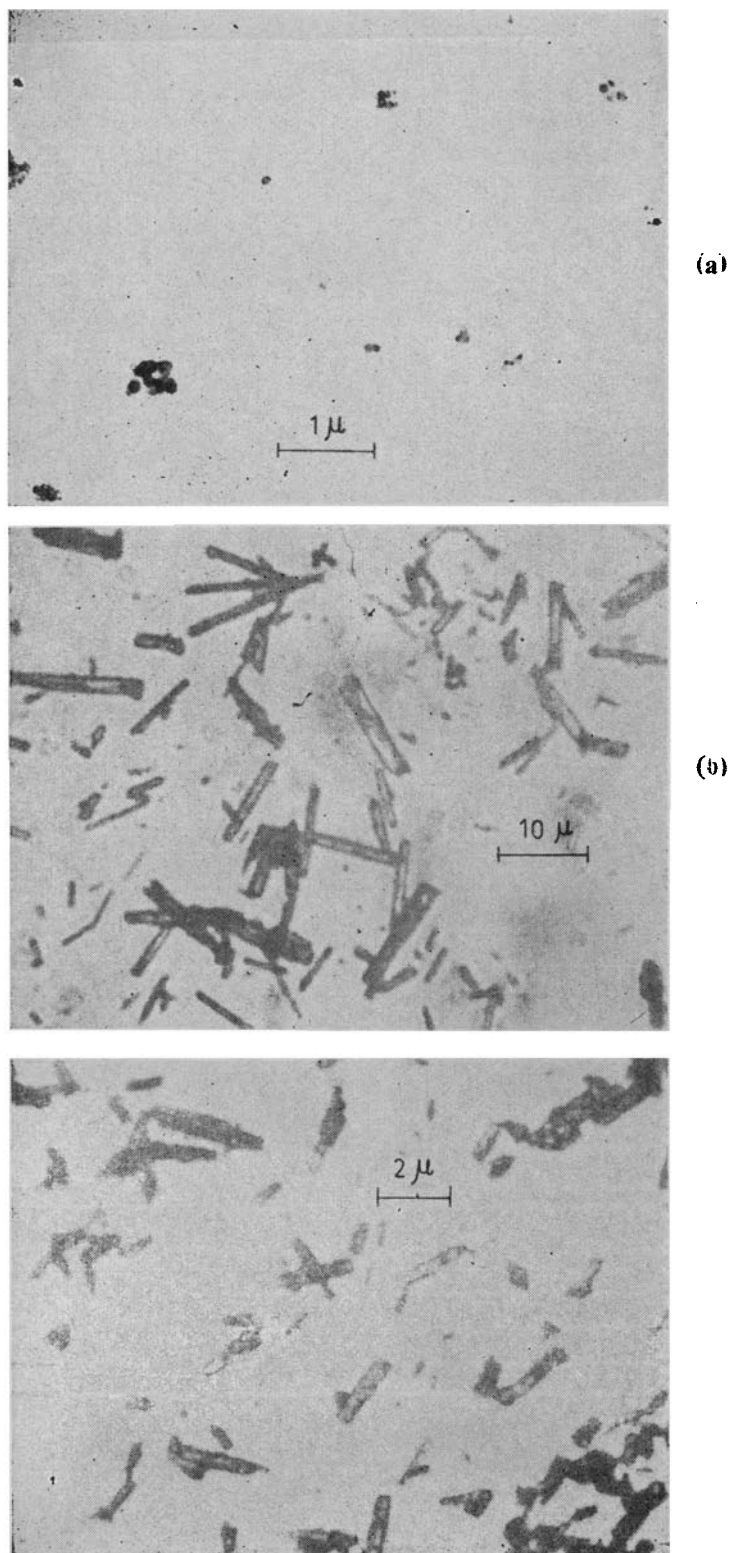


Figure 3. TEM photographs: (a) γ - Fe_2O_3 particles; (b) acicular $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals; (c) acicular γ - Fe_2O_3 .

Table 3. Properties of the products of thermal decomposition of $FeC_2O_4 \cdot 2H_2O$ under various conditions.

Temp. K	Time (h)	$P_{H_2O} = 30$ torr				$P_{H_2O} = 37$ torr				$P_{H_2O} = 150$ torr			
		Weight loss %	H_c Oe	σ_s emu.g ⁻¹	$\frac{\sigma_r}{\sigma_s}$	Weight loss %	H_c Oe	σ_s emu.g ⁻¹	$\frac{\sigma_r}{\sigma_s}$	Weight loss %	H_c Oe	σ_s emu.g ⁻¹	$\frac{\sigma_r}{\sigma_s}$
470	1/2	32	33	32
520	"	46	188	19.7	0.28	44	130	15.4	0.20	45	109	24.4	0.30
570	"	55	300	68.0	0.5	55	300	69.2	0.5	55	140	50.0	0.36
620	"	55	300	54.0	0.32	55	300	47.5	0.3	55	125	28.0	0.33

Table 4. Properties of acicular γ -Fe₂O₃.

γ -Fe ₂ O ₃	Shape	Coercive force (Hc) (Oe)	Saturation magnetisation σ_s (emu.g ⁻¹)	Squareness ratio σ_r/σ_s
Present investigation	Acicular	300	70.5	0.60
Commercial sample	Acicular	270	74.0	0.65

for reaction. In high $P_{\text{H}_2\text{O}}$, the dehydration and hence subsequent steps occur at higher temperature at which formation of α -Fe₂O₃ is facilitated. Thus an optimum partial pressure of water vapour is necessary to get Fe₃O₄ which is then oxidised to γ -Fe₂O₃.

3.4 Preparation of acicular γ -Fe₂O₃

It has been reported in the literature that acicular metal carboxylates can be prepared by precipitating them from a solution containing complexing agents like glycerol (Berkowitz and Schuele 1968). We have prepared acicular FeC₂O₄·2H₂O using the method of Bevan and Brown (1966), with the exception that the precipitation was carried out in glycerol medium at 325 K. The needle-like crystals (figure 3b) were washed with hot water and then decomposed in air (see § 3.2) to obtain acicular γ -Fe₂O₃ (figure 3c), whose properties compare very well with the commercial sample (table 4).

For better economy, precipitation of FeC₂O₄·2H₂O was tried from a medium of saturated starch solution. This gave excellent acicular crystals with length-to-breadth ratio 10:1 without any loss in quality of the final product.

References

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