COMPARATIVE INVESTIGATION OF SEVERAL TYPES OF γ-Fe₂O₃ FERRO-POWDERS BY THE METHODS OF THERMAL ANALYSIS

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Commercial γ–Fe₂O₃ ferro-powders obtained by the sulphate technology, have been compared by means of thermal analysis. Depending on the technology, each type of γ–Fe₂O₃ was found to be characterized by certain thermal transformation sequence. Thermal analysis and data systematisation allowed to find criteria for the qualification of γ–Fe₂O₃ particles. LKN ferropowders were found to have more disbalanced surface properties and chemical composition than PERK and GX ferro-powders.

Keywords: ferro-powders, non-isothermal DSC, DTA, TG

Introduction

Needle-shaped γ-Fe₂O₃ is widely used as a working layer of powder carriers for magnetic recording. The successive four-step scheme of the α-FeOOH (goethite) to γ-Fe₂O₃ transformation is the main route for ferromagnetic iron oxide preparation [1]. The hematite (Fe₂O₃) to magnetite (Fe₃O₄) reduction is the most crucial step from a material quality point of view. As concerns the chemistry, the magnetite preparation process is based on the reaction of deposition of iron protoxide salts (FeSO₄, FeCl₂, etc.) from solution by alkaline reagents. The chemical components of the technology determine the admixture composition in the final product, namely soluble and insoluble sulphates, chloride ions, etc. [1, 6]. The shape of the γ-Fe₂SO₃ particle is determined by the shape of the iron oxide monohydrate, and may at best be preserved after further processing. One of the main requirements placed upon the γ-oxide microparticles is minimum contamination and distortion of their surface [1].

Maghemite (γ-Fe₂O₃; cubic lattice) is transformed exothermally into the hexagonal α-phase in the temperature interval 673–973 K, with a calorific effect of

up to 200 J/g [2–5]. The γ-α phase transition temperature and corresponding calorific effect are known to be strongly dependent on the prior chemical, thermal and mechanical processing [2, 4, 8–10]. The influence of different factors on this transformation has been investigated in several papers by means of both isothermal [6] and non-isothermal methods [2, 4, 8, 10]. In the present paper we report a comparative investigation by means of non-isothermal methods (DSC, DTA and TG), of several commercial ferro-powders obtained by sulphate technology.

Experimental

The types of ferro-powders were as follows: Perk-20 (Czechoslovakia), GX-1104 (Japan), LKN-83 uncompressed, LKN-83 compressed and LKN-M-82. The last three types of powders are produced in the USSR. The abbreviations used in the text are as follows: Perk, GX, LKN(1), LKN(2), LKN(3). The average size of the particles was 0.6–0.8 μm for Perk and GX, and 0.4–0.6 μm for LKN. The shape-factor is 4–6 for all types of powders. The samples were investigated without any previous treatment.

For thermal analysis, the following apparatus was used: a DSM2M scanning calorimeter in the temperature interval 323–773 K, a DSC-7 calorimeter (Perkin-Elmer) in the temperature interval 313–973 K and a Q-1500D derivatograph (Hungary) in the temperature interval 293–973 K. All experiments were performed in ambient air. The sample weight was 20–60 mg for DSC and 800 mg for thermal analysis. The powder heat treated at 973 K, similar to that positioned in the working unit, was used as standard in experiments on the derivatograph. The heating rate was 10–20 deg/min for DSC and 5 deg/min with the derivatograph. Zinc (T_{ml}=689 K, ΔH_{ml}=7.24 kJ/mole) and lithium sulphate (T_{ml}=848 K, ΔH= 260.4 J/g) were used as standards for quantitative estimation of the calorific effects.

DTA curves were recorded with a sensitivity of $7.2 \cdot 10^{-2}$ deg/mm in two steps. First, the initial sample curve was obtained. The furnace was then cooled and a second measurement was performed for determination of the base line position. Nevertheless, it was not possible to eliminate the uncertainty in the base line position completely. Its degree of reliability was determined in the derivatograph sensitivity regime of 20 mg on 250 mm of diagram film. P=0.16 mg or $2 \cdot 10^{-2}$% of the initial weight (P=800 mg) was considered to be reliable.

Results and discussion

All ferro-powders were prepared by the sulphate method, but there were some differences in technology: Perk was synthesized through lepidocrisite (γ-

FeOOH), while the others were synthesized through goethite (α-FeOOH, needle-shaped). Perk was subjected to antiagglomeration treatment with phosphoric acid. LKN(2) was mechanicaly disaggregated, and LKN(3) was treated with an organic phosphorus compound in the goethite step for antiagglomeration purposes.
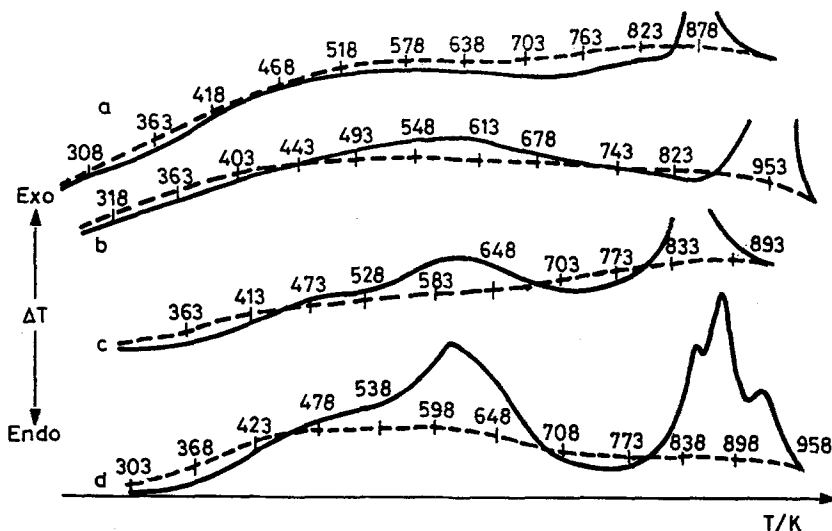

Fig. 1 DTA curves of ferropowders: a) Perk, b) GX, c) LKN(1), d) LKN(3)

Comparison of the DSC and DTA data for the ferro-powders shows that several heat-absorbing and heat-evolving processes take place during heating from room temperature to $T_{\gamma-\alpha}$ (Fig. 1, Table 1). 1. In the case of the Perk ferro-powder, a non-monotonous endothermic effect is observed up to the γ-α phase transition (Fig.1, Table 1). The DSC and DTA data reveald that the γ-α phase transition is recorded as a single narrow exopeak at 898 K (Table 2). The TG curve decreases monotonously from 303 K to 873 K (Fig. 4). In the γ-α phase transition region, a slight increase in sample weight (less than 0.02%) takes place.

For the GX powder, an exoprocess is observed in the temperature interval up to 773 K (Figs 1 and 2). The γ-α phase transition occurs at 958 K (Fig. 2, Table 2). The TG data (Fig. 4, Table 3) indicate a monotonous weight loss up to 958 K. There is no weight change in the γ-α phase transition region The weight decreases above he exotransition, possibly due to reduction processes.

As observed previously, the Perk γ-α phase transition proceeds very rapidly in a narrow temperature interval. According to the data in [6] and [8], this ferro-powder has a high degree of dispersion, and it is chemically and crystallographically homogeneous. The α-phase embryos grow rapidly on the γ oxide particle surface, occupying the whole particle volume. Though the γ-α phase transition of GX samples exhibits a greater temperature interval than that for Perk (Tables 1

Table 1 Summarized DSC and DTA results of γ-Fe_2O_3 ferropowders

Powders type	Type of transformation: endo., exo.	Calorific effect temperature interval/ K	Value of effect/ $J \cdot g^{-1}$
Perk	endo.	up to $\gamma - \alpha$	110–120
	exo.	863–943, $\gamma - \alpha$	90–100
GX	endo.	303–453	10– 15
	exo.	453–673	10– 15
	endo.	befor $\gamma - \alpha$	10– 15
	exo.	883–993, $\gamma - \alpha$	100–115
LKN (1)	endo.	303–433	10– 15
	exo.	433–693	20– 25
	endo.	befor $\gamma - \alpha$	10– 15
	exo.	803–923, $\gamma - \alpha$	100–115
LKN (2)	endo.	303–433	15– 20
	exo.	433–683	25– 30
	endo.	befor $\gamma - \alpha$	5– 10
	exo.	773–893, $\gamma - \alpha$	100–110 125–135*
LKN (3)	endo.	303–433	15– 20
	exo.	433–733	30– 35
	endo.	befor $\gamma - \alpha$	5– 10
	exo.	773–973, $\gamma - \alpha$	90–100

* -after preliminary heating up to 753 K

and 2), the surface state of this material seems to be slightly disturbed and in an equilibrium state. The $T_{\gamma-\alpha}$ enhancement and α-phase growth velocity decrease are possibly caused by the particle morphology [6, 8]. The exoeffect in the range 453–723 K, which is observed for GX and LKN powders (Fig. 2, Table 1), is probably caused by processes of surface state reconstruction (SSR) with excess energy release. The SSR includes different chemical transformations of admixtures, and the mechanical and chemical dissipation of surface defect energy [8, 10]. In this temperature region, a phase transition for aggregates and non-needle-shaped parti- cles is possible [9]. If one estimates the general inhomogeneity and

nonbalance of material, by the corresponding calorific effect, then the contribution to the integral γ-α transformation heat is imperceptible for Perk and not significant for GX.
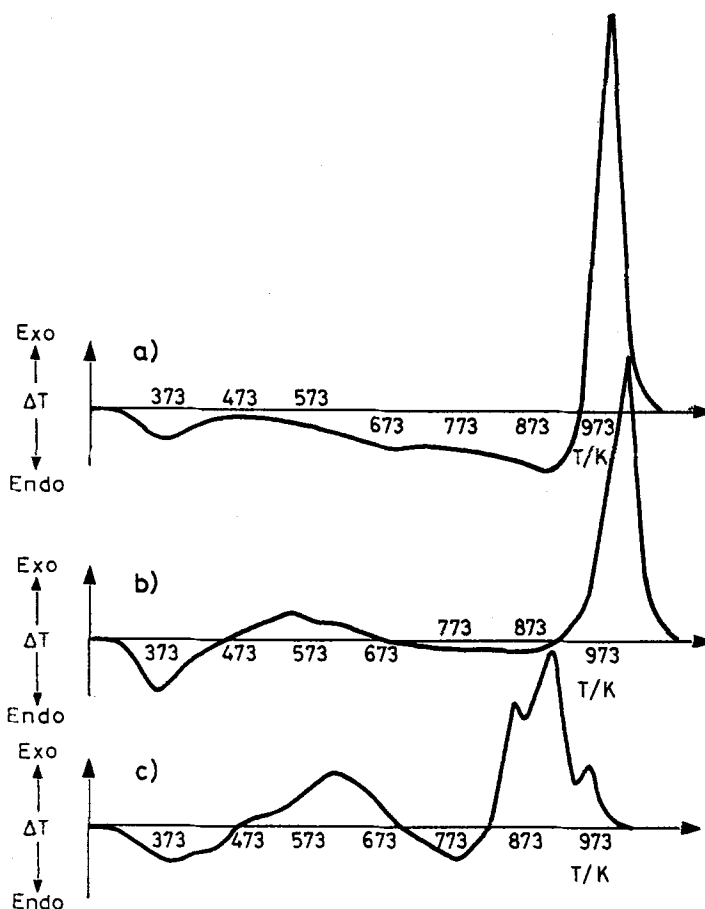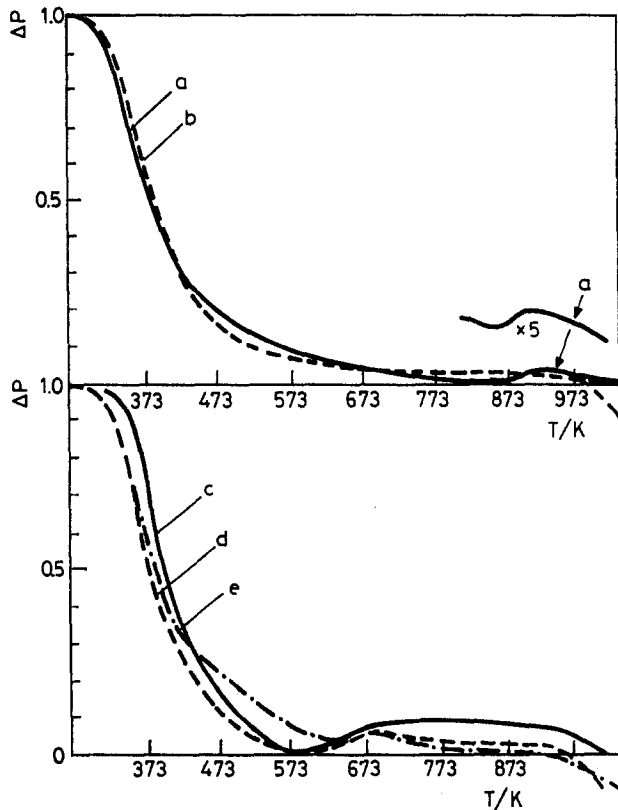

Fig. 2 DSC curves of ferro-powders: a) Perk, b) GX, c) LKN(3)

The TG data reveal that the Perk and GX powder surfaces contain 0.8–1.0% by weight of water (storage under usual conditions); dehydration proceeds in a wide temperature interval (Fig. 4). Water physically adsorbed on iron oxide is known to be removed at 423–453 K [11, 12], with not large activation energies (~20 kJ/mole) and calorific effects close to those of water evaporation and ice sublimation (~45 kJ/mole). From the TG results, it can be concluded that the main part of the water is adsorbed physically, and full dehydration from the Perk and

Table 2 Thermal analysis results (DTA) of the ferropowders γ–$Fe_2O_3 \rightarrow \alpha$–$Fe_2O_3$ phase transition

Powders	Exoeffect parameters		
type	$T_{max.}$, K	$T_{1/2}$, K	$-\Delta H$, J / g
Perk	898	13	90–100
GX	958	30	100–115
LKN (1)	863	30	100–115
LKN (2)	853	37	100–110
LKN (3)	853, 883, 923		90–100

Comment: $T_{1/2}$ – exopeak width on the half of its height. Three overlapping exoeffects are registered for LKN (3), with distance between the first one and the last one being 70 K.

Fig. 3 Mass loss curves (P) in arb. units of ferropowders: a) Perk, b) GX, c) LKN(1), d) LKN(2), e) LKN(3)

GX powder surfaces is completed in the γ-α phase transition region, i.e. there is a wide energy distribution of surface adsorbing centers.

The endothermic process observed for LKN(1) samples from the starting point of heating is transformed into an exoeffect below 453 K (Fig. 2, Table 1). To judge from the exopeak shape, the contribution to heat release gives two overlapping processes, which are completed up to 733–753 K with a simultaneous calorific effect of ΔH=30–35 J/g. For the sample previously annealed at 393 K, an endotherm starts already from 373 K, and the subsequent exoeffect reaches 40 J/g, due to the compensational influence of the decrease in the reaction of opposite sign.

DTA also reveals a wide (up to 473 K) endothermic effect and a following asymmetric exopeak (Fig. 2). The γ-α phase transition parameters are given in Table 2.
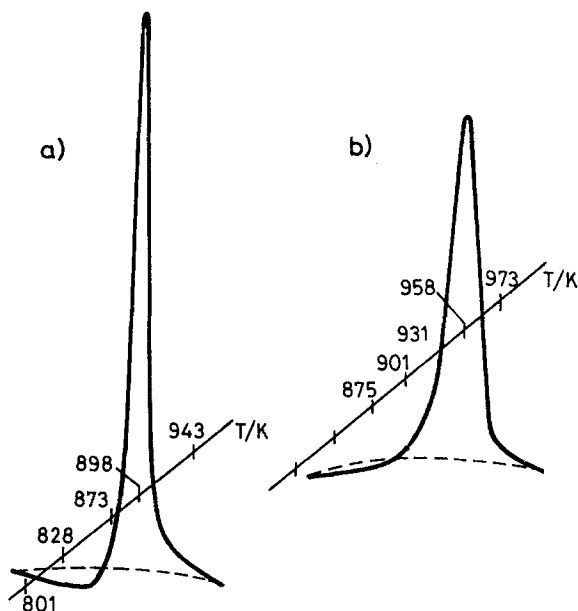

Fig. 4 DTA dates on phase transitions of ferropowders: a) Perk, b) GX

A distinguishing feature of the TG curves of LKN powders is a weight increase, starting before the γ-α phase transition (Fig. 4, Table 3). In general, the same results are obtained for LKN (2) (Fig. 2, Tables 1–3).

The DSC and DTA data on LKN(3) samples show that in the temperature interval 423–733 K several successive exoreactions take place with the simultaneous heat release of 25–35 J/g. From 313 K to 423 K, a dehydration endotherm

Table 3 TG results of ferropowders

Powders type	Overal weight loss at T_f-α		Weight loss (ΔP) in % from ΔP					Temperature of weight enhancement	Weight increment	
			at 423	in 423–673	in 673–873	on 973 K				
	mg	in % from P	K	K	K	mg %	from P	beginning/K	mg	% P
Perk	6.8	0.85	68	30	2	–	–	893	0.16	0.02
GX	8.0	1.00	70	27	2	0.50	0.062	–	–	–
LKN(1)	4.64	0.58	65	35	–	0.23	0.03	623	0.32	0.04
LKN(2)	5.6	0.70	75	25	–	0.28	0.035	623	0.24	0.03
LKN(3)	9.44	1.02	65	35	–	0.47	0.06	623	0.56	0.071

Comment: Initial samples weight P=800 mg; Heating rate 5 deg/min

is registered (Fig. 2). The LKN(3) γ-α phase transition is represented by a three-step sequence of exoeffects (Figs 1 and 2).

The LKN(3) samples lose weight up to 623 K (Fig. 4, Table 3), and then increase by 0.05% of the starting weight. Taking into account this TG peculiarity, it can be concluded that LKN(3) dehydration is completed at about 673 K. The smoothness of the TG curve of this powder differs from the others. Above 423 K, the rate of weight loss is approximately constant, i.e. two regions can be distinguished in the TG curve, with different dehydration velocities.

The thermal analysis data show that the LKN ferro-powders have the following features distinctive from those of Perk and GX. The endothermal dehydration processes below 423–453 K are more pronounced (Fig. 2, Table 1). Exothermal SSR proceeds intensively, with one or several calorific effects, having a value in the interval 25–35 J/g (Table 1). From 573–623 K, these materials gain weight (Fig. 4, Table 3), i.e. they absorb oxygen due to surface chemical processes.

It is obvious that, besides the endothermal dehydration reaction, which occurs in general on OH group recombination, several exothermal SSR processes take place on the γ-oxide surface. The only exception is Perk, for which an intermediate exoeffect is not observed. The basis of these processes, if part of the general energetic nonbalance is not taken into consideration, is the interaction of admixtures with other admixtures and with surface OH groups. Under the conditions of a sulphate excess, as the most obvious consequence of the LKN powder preparation technology, oxidizing and hydrolytic reactions occur in ambient air and in the presence of water [13]. During these reactions, the formation and exothermal recrystallization of amorphous Fe_2O_3 with subsequent SO_3 release is not excluded. During sulphate ion dissociation, which is accelerated by proton formation on the oxide particle surface, oxygen takes part in the Fe(III) – Fe(II) recovery reaction or in the dehydration reaction. This depends on the acidity or the degree of alkalinity of the hydrated surface.

It should be noted that the region of weight increase of LKN samples coincides with the interval of exothermal processes and corresponds to almost complete dehydration, i.e. it corresponds to active surface center unblocking. It may be presumed that the oxygen deficit in the γ-oxide particle surface layer is predetermined by the last step in the technological process: air oxidation of Fe_3O_4 to γ-Fe_2O_3 during heat treatment at 533 K [1]. A certain compensation of the deficit is possible due to subsequent dehydration. It can also occur as a result of interactions between admixtures and the surface. There is a possibility of magnetite oxidizing iron traces or FeO [1]. During the oxidation of Fe_3O_4 to γ-Fe_2O_3, the oxide weight increases by 3.46% according to the stoichiometry $Fe_{1.33} \rightarrow FeO_{1.5}$. Among the investigated samples, the maximum weight increase was observed for LKN(3): 0.071% (Table 3). To a crude approximation, this corresponds to 0.02% of magnetite in γ-Fe_2O_3.

As for the γ-α phase transition itself, the most complex mode is observed for LKN(3), and the lowest temperature (853 K) for LKN(2), which is mechanically

disaggregated. It is possible that there is a certain heterogeneity on the surface or in the volume of LKN(3) particles which determines the γ-α process kinetics. This heterogeneity may be a result of the use of a phosphorus organic modifier in the goethite step. Such a modification leads to the formation of phosphate and/or carbide inclusions or surface centers, which hamper α-phase embryo growth. Even a defect distribution of identical type would influence the reaction kinetics in the same way it would accelerate or decelerate the process. The heterophase state can influence the kinetics in different ways, due to diffusion inhibition of the topotactic transformation.

The investigated materials have one more special feature. The DSC and DTA data demonstrate endothermal effects immediately before the γ-α phase transition (Figs 1 and 2, Table 1).

It is possible that the oxides are ordered in the sense of a cation and vacancy distribution at octahedral lattice positions [4]. In this case, processes of γ-α lattice disordering and reformation occur practically simultaneously, but an opposite signs of ΔH [4]. After preliminary heat treatment of LKN(2) samples at 753 K, the transition ΔH is higher (Table 1). There is another explanation, if one takes into consideration the small values of the corresponding effects for Perk and GX samples. SSR in LKN samples proceeds in a more complex way and with larger calorific effects. As a result, powder particle defection increases after the corresponding exoprocesses. Thus, 'pseudomelting' or diffusion disordering of the lattice components proceeds in the surface layer on the γ-oxide particle surface as soon as α-phase embryos appear.

The TG data show that Perk and GX ferro-powders lose water continuously up to the γ-α phase transition. In the LKN samples, dehydration is possibly over at 623–673 K. A more definite conclusion is hardly possible, because in this temperature region the powder weight increases, the latter masking the further process trend. Thermal analysis of ferro-powder dehydration becomes complicated, because above 423 K it is hard to distinguish calorific effects applying to the water loss itself. Up to 423–453 K, the endothermic effects (DSC and DTA) are not determined precisely, and besides their values do not exceed 20 J/g. For a more detailed investigation of the dehydration kinetics of commercial ferro-powders, other methods are needed. Nevertheless, the initial dehydration heat approximation shows that LKN powders are more hydrophilic and contain more physically adsorbed water than Perk and GX.

Conclusion

Thermal analysis results on several ferro-powders obtained by sulphate technology show that each type of oxide is characterized by a specific sequence of calorific transformation, with individual distribution and heat release or absorp-

tion. The main processes are dehydration, surface state reconstruction and γ-α phase transformation.

The quantity and value of the exothermal calorific effects prior to the γ-α phase transition were minimum for the following optimal parameters of the γ-oxide: crystal structure and surface, shape, size, morphology, chemical composition and hydrophobicity. Perk and GX ferro-powders correspond more to these demands than LKN powders. The latter might be classified as 'defective' in the sense of the surface properties and chemical composition disbalance.

It is considered that the further systematization of the thermal analysis data on commercial ferro-powders will point to more definite quantitative criteria of the perfection of their preparation technology.

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Zusammenfassung — Mittels Thermoanalyse wurden kommerzielle, mit der Sulfattechnologie erhaltene γ-Fe_2O_3 Ferropulver untereinander verglichen. In Abhängigkeit von der Technologie kann jeder γ-Fe_2O_3-Typ durch gewisse thermische Umwandlungsfolge charakterisiert werden. Thermoanalyse und Datensystematisierung ermöglichten es, Kriterien zur Qualifizierung von γ-Fe_2O_3 Partikeln zu finden. Man fand, daß LKN Ferropulver mehr unausgewogene Oberflächeneigenschaften und chemische Zusammensetzungen besitzt als PERK- und GX-Ferropulver.