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SIMULTANEOUS THERMOMAGNETIC AND DILATOMETRIC MEASUREMENTS IN A STUDY OF THE Fe_2O_3 METASTABLE TRANSFORMATION

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Simultaneous measurements of variations in magnetic and dilatometric properties were successfully used to detect the phase transition occurring during the thermal treatment of iron(III) oxide microcrystals. The increase of the compacting pressure, i.e. the increase of the interparticular number, favours the irreversible $\gamma \rightarrow \alpha$ transition. An unusual phase of iron(III) oxide, different from the γ-phase, has been unambiguously demonstrated. Its stability seems to be improved by the surface energy excess due to the highly-divided state.

The properties and reactivity of a finely-divided powder are well known to depend on its preparation process. Moreover, it is obvious that the more the raw material is divided, the greater is the possibility of its transformation. Consequently, the characterization of such a powder is of paramount importance and requires of necessity the use of several accurate methods, in particular thermal analysis. Iron(III) oxide is not only one of the most important active ingredients in magnetic recording devices, but is also used as a catalyst in industrial processes. Ultrafine iron(III) oxide particles may be obtained in a flame-supported reaction [1]. Depending on the preparative conditions, the morphological and structural properties of these particles may differ widely. In order to follow the evolution of these properties, an original apparatus was used to record simultaneously very fine dimensional and magnetic variations [2, 3].

The aim of this work is to detect possible modifications occurring during the thermal treatment of samples prepared at high temperature and quenched.

Experimental procedures

Iron(III) oxide is prepared from iron(III) chloride, the vapour of which is carried by an oxygen or nitrogen stream towards an oxygen–hydrogen flame. The reactor and the particle formation mechanism have been described previously [1]. The flame temperature, mass flow rate and residence time of the reactive species in the flame

may be controlled, so as to govern the size (from 10 to 100 nm) and the crystalline structure of the oxides. In hot flames (3000 K) γ-iron(III) oxide is obtained. The X-ray powder diagrams are recorded at room temperature on a PW 1700 Philips diffractometer using Cu K_α radiation ($d = 1.5405$ Å) filtered out with a curved graphite monochromator. In hot flames (3000 K) γ-iron(III) oxide is obtained. X-ray powder diagram is shown in Fig. 1. All the reflexions of the cubic spinel structure are present and extra lines indicate the vacancy ordering characteristic of the γ-phase. The particles are monocrystalline or twinned; their morphology has already been studied [4]. In cold flames (1500–2000 K) the crystalline structure is more complex: the X-ray diffraction patterns (Fig. 2) exhibit essentially the 104 reflexion of haematite, the other reflexions of this phase are weak and some extra reflexions may be attributed to the dzeta phase [5].

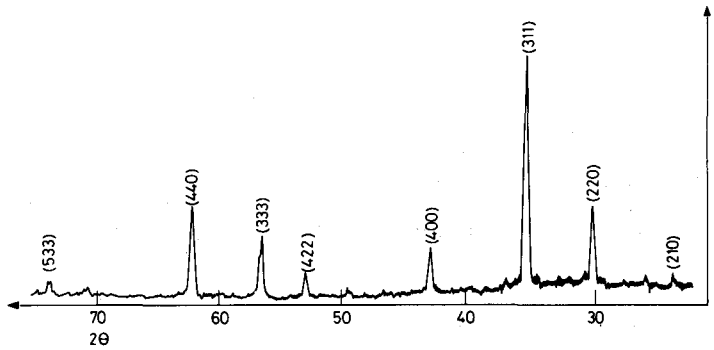

Fig. 1 X-ray diagram of γ-Fe_2O_3 prepared in a hot flame (3000 K)

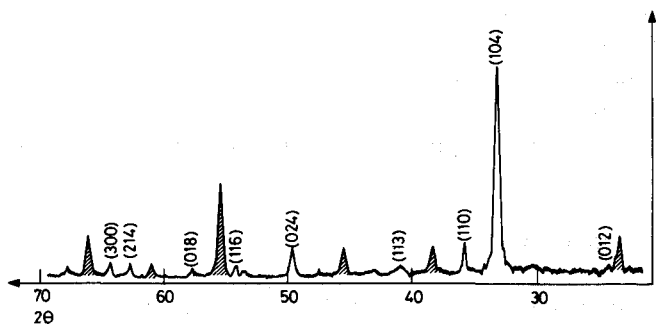

Fig. 2 X-ray diagram of Fe_2O_3 prepared in a cold flame (1500 K). Dotted peaks refer to the dzeta phase. Indexing of the other reflexions is based on hexagonal cell of α-Fe_2O_3

Figure 3 shows γ-iron(III) oxide particles which are facetted. The mean diameter calculated from the B.E.T. specific surface area is 39 nm, in good agreement with the crystalline size (36 nm) determined from the X-ray line broadening. Typical micrography of iron(III) oxide particles prepared in a cold flame is shown in Fig. 4. The particles are polyhedral and the mean diameters of the three samples are 28 nm, 23 nm and 19 nm, respectively, also in agreement with the crystallite sizes.

Small cylindrical compacts are formed from these samples and put in the axial zone of a platinum coil wound around the sample holder of an optoelectronic dilatometer [2, 3]. The magnetic permeability variations of the samples induce corresponding coil impedance variations, which are easily measured.

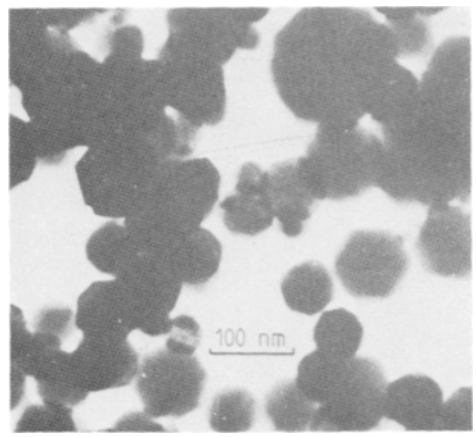

Fig. 3 Micrography of γ-Fe_2O_3 particles. $S_{BET} = 32\ m^2 \cdot g^{-1}$

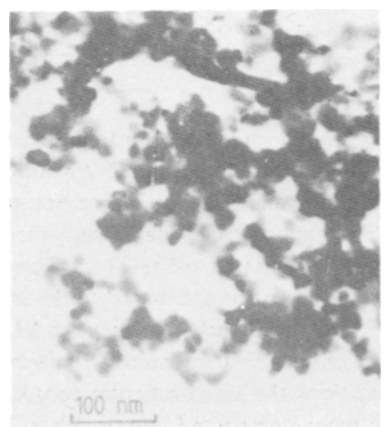

Fig. 4 Micrography of Fe_2O_3 particles prepared in a cold flame. $S_{BET} = 54\ m^2 \cdot g^{-1}$

Results and discussion

This study deals with the thermal evolution occurring before the actual sintering of iron(III) oxide powder (above 870 K). Thermal curves were recorded at a heating rate of 7 degree min^{-1} in air.

The γ form of iron(III) oxide is a metastable phase. The $\gamma \rightarrow \alpha$ transformation occurs between 670 and 870 K, depending on the physicochemical properties of the studied material. In the case of small microcrystalline particles, the $\gamma \rightarrow \alpha$ transition begins at 700 K when the compacting pressure of the samples is $2600 \cdot 15^5$ Pa, and at 730 K when the compacting pressure is $900 \cdot 10^5$ Pa (Fig. 5). Simultaneously with the

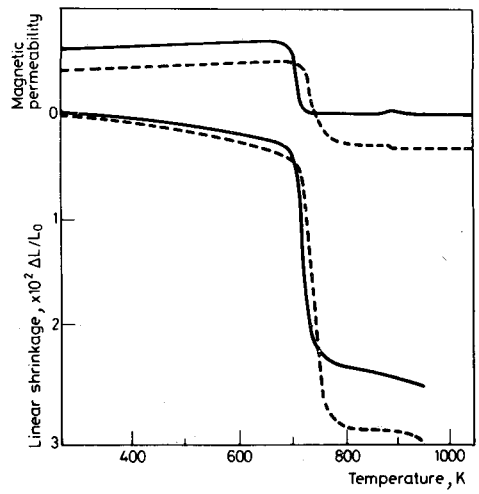

Fig. 5 Simultaneous thermomagnetic and thermodilatometric curves of γ-iron(III) oxide samples compacted under different pressures. Fe_2O_3 32 $m^2 \cdot g^{-1}$, ——— $2600 \cdot 10^5$ Pa, – – – – $900 \cdot 10^5$ Pa

decrease in magnetic permeability, a linear shrinkage occurs, corresponding essentially to the cell contraction associated with the $\gamma \rightarrow \alpha$ transition. A part of this shrinkage may be due to the particle rearrangement involving occupation of the interparticular space. The extent of this rearrangement decreases when the initial density of the compact increases. The Curie point of α-Fe_2O_3 appears at 900 K in the magnetic curves. The compaction effect must be attributed to the increase of the interparticular number per mass unit. By taking a packed sphere model, the interparticular contact point number per particle, or coordination number, may be obtained from the relative density. Under these conditions the interparticular contact per mass unit is increased by a factor of 10 for the more compacted sample. Thus, it appears that these contact zones act as nucleation sites.

In the case of particles obtained in cold flames, the presence of the γ-phase cannot be detected in the X-ray diagrams. Samples with different surface areas have been studied. In each case a decrease of the magnetic permeability associated with an abrupt linear shrinkage is observed (Fig. 6). These simultaneous variations must be

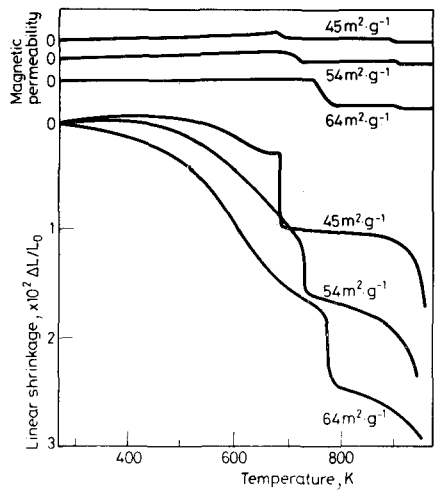

Fig. 6 Simultaneous thermomagnetic and thermodilatometric curves of iron(III) oxide samples with different specific surface area

attributed to a phase transition. The extent of magnetic and dilatometric variations are weaker than those observed for the $\gamma \rightarrow \alpha$ transition. The transition temperature increases when the particle size decreases. The initial phase seems characteristic of a highly-divided state and is stabilized by surface energy. The X-ray diagrams obtained just before this transition (610 K) does not change with respect to the initial diagram (Fig. 2). Just after this transition (750 K) the relative intensities and the positions of the reflexions correspond exactly to those of haematite. Hence, the initial phase of the particles prepared in cold flames cannot be considered as the α-phase, but as a metastable phase which turns to haematite between 700 and 770 K, depending on the particle size.

References

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Zusammenfassung – Der bei der thermischen Behandlung von Eisen(III)oxid-Mikrokristallen vor sich gehende Phasenübergang wurde mit Erfolg durch gleichzeitige Messungen der Veränderungen der magnetischen und dilatometrischen Eigenschaften detektiert. Die Vergrösserung des Verdichtungsdruckes, d.h. die Vergrösserung der Interpartikularzahl begünstigt den irreversiblen $\gamma \rightarrow \alpha$ Übergang. Eine ungewöhnliche, von der γ-Phase verschiedene Eisen(III)oxid-Phase wurde eindeutig nachgewiesen, deren Stabilität durch den auf den hochdispersen Zustand zurückzuführenden Oberflächenenergieüberschuss erhöht zu werden scheint.

Резюме – Совмещенные измерения изменений магнитных и дилатометрических характеристик были успешно использованы для обнаружения фазового перехода, происходящего во время термической обработки микрокристаллов окиси трехвалентного железа. Увеличение уплотняющего давления благоприятствует необратимому $\gamma \rightarrow \alpha$ переходу. Однозначно установлена необычная фаза окиси трехвалентного железа, отличающаяся от γ-фазы. Стабильность этой фазы увеличивается избыточной поверхностной энергией, обусловленной высокоделящимся состоянием.