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THERMAL BEHAVIOR IN AIR OF IRON OXYHYDROXIDES OBTAINED FROM THE METHOD OF HOMOGENEOUS PRECIPITATION. PART I. GOETHITE SAMPLES OF VARYING CRYSTALLINITY

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ABSTRACT

Differential scanning calorimetry (DSC), thermogravimetry (TG) together with X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been employed to follow the structural and morphological changes in the thermal decomposition in air of goethite (α-FeOOH) samples of varying crystallinity. A clear relationship is noted between the starting goethite and hematite crystallinities. In the 280–600 ° C temperature range, the acicular hematite shows a nonuniform broadening process of the (104) and (110) X-ray lines, this process increased as the starting goethite crystallinity increased. Between 600 and 700 ° C a marked increase of the hematite crystallinity was observed, together with a change of acicular to spherical hematite particles.

INTRODUCTION

The dehydroxylation reaction that occurs on heating goethite in air has usually been observed on the differential thermal analysis (DTA) curve as a single clearly defined endothermic peak, in the temperature range 250–400 ° C, depending upon the particle size and crystallinity of the samples [1].

In some instances a double peak is obtained, and Derie et al. [2] indicated that the tendency for a double peak system to occur increases as the particle size decreases. They put forward the hypothesis of the formation on each grain of an impermeable hematite layer, that temporarily stops the dehydroxylation process of the internal part of the grain.

Spinzi and Nicolescu [3] pointed out two consecutive processes of structural water elimination according to the different parameters involved in the preparation of the iron oxides.

Schulze and Schwertmann [4] found that when the synthetic goethite is Al-unsubstituted, the dehydroxylation peak occurred between 220 and 360 ° C was often split into a double peak, the high-temperature component usually being the larger one of the two. The thermogravimetric data [5,6]

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show that the split endotherm corresponds to a brief decrease in the rate of weight loss from the sample, i.e. to a momentary decrease in the dehydroxylation rate. This conclusion agrees with the one pointed out by Derie et al. [2].

Recent research by Schwertmann and co-workers [7,8] concerning the DTA curves of goethite of varying crystallinity showed that these curves changed from a single low-temperature peak at 258–278 ° C, via a double peak, to a single, asymmetric high-temperature peak at 318–320 ° C. This shift suggested to them that two types of goethite can be proposed from the dehydroxylation behavior. So, the low-temperature dehydroxylation peak is attributed to a goethite of high *a* dimension of cell, and the high-temperature peak is attributed to the one of low *a* dimension.

Paterson and Swaffield [9] found a variation in the shape of the DTA and DSC curves for synthetic goethite. The increasing sophistication of thermal analysis, in particular differential scanning calorimetry, has enabled workers to distinguish three smaller peaks that are due to the dehydroxylation of singly, doubly and triply co-ordinated surface hydroxyl groups contained on the predominant (100) face of goethite. These authors studied the adsorption of various anions by goethite and its influence on surface hydroxyls reflected by changes in the DSC curves.

Koch et al. [10] have recently studied the effect on microcrystalline synthetic geothite samples of heating to 105 ° C. They concluded that heating led to no detectable changes in the unit-cell parameters or crystalline size; however, some of the X-ray diffraction lines were broadened due to an increase in microstrain in the (020) (110) and (120) crystallographic directions. After heating to 105 ° C the superferromagnetic transition temperature increased, showing that the desorption of water from the space between neighboring crystallites led to an enhanced magnetic coupling among them.

In a previous paper [11] we studied the influence of pH and aging time on goethite samples synthesized by the method of homogeneous precipitation. It was proposed that the crystallinity of the goethite increased with the two solution factors studied.

We describe in this paper the structural and textural changes occurring throughout the thermal decomposition in air of two goethite samples of different crystallinity. The study has been carried out by differential scanning calorimetry (DSC), thermogravimetry (TG), X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

EXPERIMENTAL

Sample preparation

Goethite samples were obtained from the method of homogeneous solution, as previously described [11].

Apparatus

X-ray powder diffraction

A Siemens diffractometer model D500 and a graphite monochromator K805, generating Cu K_α radiation, were used.

Transmission electron microscopy

An AEI EM6 microscope was employed. The samples were prepared by evaporation of the solid suspensions in water on a copper grid coated with a carbon film.

Thermal analysis (TG–DSC)

A Mettler TA 3000 analysis system with CTC10TA processor was employed. The weight of samples was about 20 mg; heating rate 10 °C min^{-1}; air stream and alumina crucibles were utilized.

RESULTS AND DISCUSSION

Thermal analysis

Two different types of thermal behavior were observed, according to the crystallinity of goethite samples; the behavior corresponding to the poorly crystallized goethite (30, 45 and 60 min aged), and that corresponding to the better crystallized one (75, 90 and 300 min aged). The TG and DSC curves of each group were identical in shape; therefore, in this paper we present the thermal study of two goethite samples aged 45 and 90 min.

TG curves

Figures 1 and 2 show the TG curves. As can be seen, from 25 to 470–530 °C there is a continuous weight loss due to the volatilization of the total water of the samples. At about 170 °C (Fig. 1) and at 150 °C (Fig. 2), an inflection is observed, which reveals the difference between the adsorbed water and that which is structurally bound. The amount of adsorbed water, for all synthetic goethite series, ranged from 2.5 to 6.6% w/w, and the amount corresponding to structural OH lost ranged from 11.1 to 12.1% w/w (See Table 1 in ref. 11). This latter loss is more than the theoretical weight loss of 10.1%. In comparison, from the TG analysis of goethite samples of varying crystallinity Schwertmann et al. [8] found a structural OH content ranging from 10.3 to 12.0% w/w. Paterson and Swaffield [9] reported a weight loss of 11.8% for a synthetic goethite. According to these authors, the difference between the theoretical value of 10.1% and the experimental one, probably reflects (a) an excess hydroxyl content due to protonation of surface oxide ions, and (b) the contribution of water co-ordinated to exposed iron(III) ions at the crystal edges.

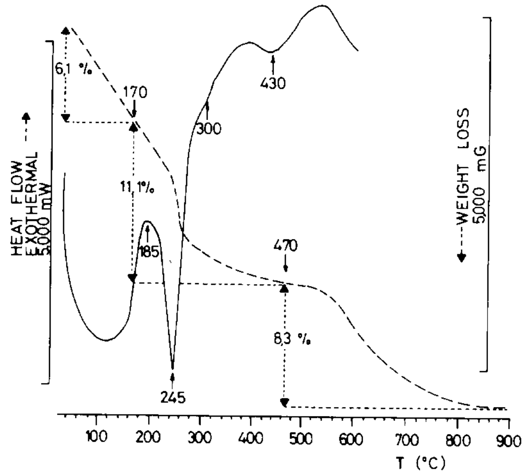

Fig. 1. TG and DSC curves of a goethite sample aged for 45 min.

Between 470–530 and 900 ° C a second weight loss was noted due to SO_3 volatilization. The SO_4 amount decreased from 9.6 to 1.3% w/w with increasing crystallinity of the samples (See Table 1 in ref. 11).

DSC curves

The endothermic and exothermic effects shown on the DSC curves were identified by XRD analysis of samples heated to the temperatures corresponding to before and after each peak.

On the DSC curve of the goethite poorly crystallized sample (Fig. 1), a large and broad endothermic peak appeared between 25 and 185 ° C, corresponding to the loss of adsorbed water (6.1%). The DSC curve of the

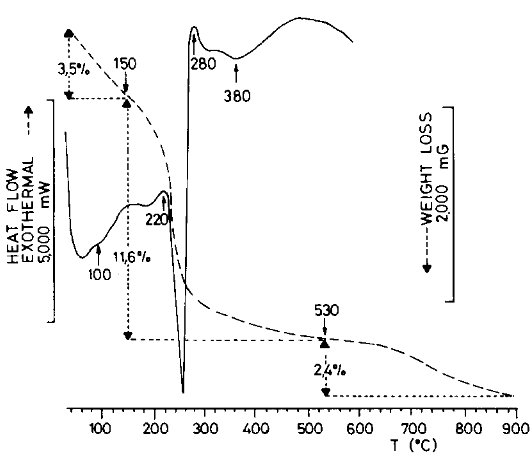

Fig. 2. TG and DSC curves of a goethite sample aged for 90 min.

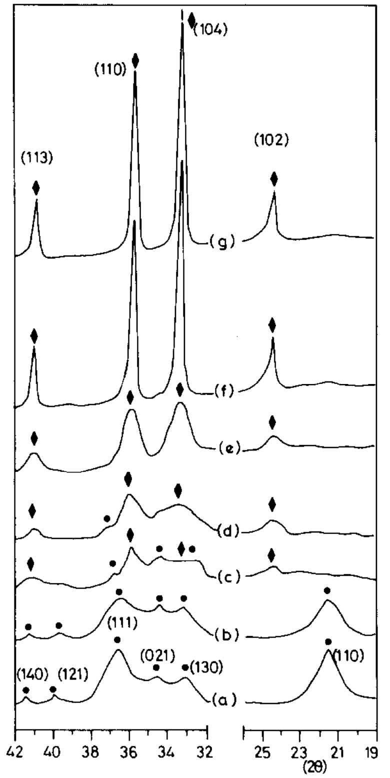

Fig. 3. X-ray diffraction patterns of goethite (aged for 45 min) heated at different temperatures: (a) unheated, (b) 185, (c) 245, (d) 300, (e) 600, (f) 700 and (g) 900 ° C. ●, α-FeOOH; ◆, α-Fe_2O_3.

goethite better crystallized sample (Fig. 2) in this low temperature region (25–220 ° C) showed an endothermic effect with two shoulders at 100 and 200 ° C. This peak is significantly different in shape from and less intense than that of the poorly crystallized goethite. The XRD analysis at 220 ° C only gave the goethite diffraction pattern, but its lines were broder and less intense than the ones of unheated goethite [compare Fig. 3(b) with Fig. 3(a) and Fig. 4(b) with Fig. 4(a)]. This indicates an increase of the goethite crystal disorder, due, we believe, to the stabilization of the goethite lattice by adsorbed water molecules, and the removal in part of the free surface structural OH ions.

The consensus of most studies of the thermal decomposition of α-FeOOH is that goethite is stable and unaffected by heating at temperatures below 100 ° C. Heating to temperatures above 100 ° C has generally been used for the determination of the amount of adsorbed water [4]. Fey and Dixon [12] reported that heating a sample of pure goethite at 110 ° C in air or in vacuo, resulted in an increase of the crystallite size, as determined from the

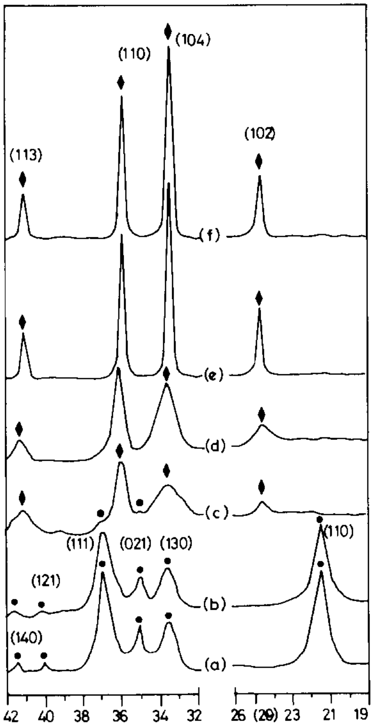

Fig. 4. X-ray diffraction patterns of goethite (aged for 90 min) heated at different temperatures: (a) unheated, (b) 220, (c) 280, (d) 600, (e) 700 and (f) 900 °C. ●, α-FeOOH; ◆, α-Fe_2O_3.

broadening of the X-ray powder diffraction profile, and they proposed that the observed changes were caused by a decrease in the amount of adsorbed water. However, Koch et al. [10] observed no changes in the crystallite size of goethite samples heated to 105 °C.

The dehydroxylation is shown by a sharp endothermic peak at 245 or 255 °C depending on the crystallinity of the sample. The small exothermic effect that appears after the dehydroxylation peak is due to an amorphous → crystalline hematite transformation; however, the XRD results at this point indicate poor hematite crystallization. Also impurities of the goethite phase can be seen [see Figs. 3(c), 3(d) and 4(c)]. In this respect, Mackenzie and Berggren [1] pointed out that the continuous diffusion of molecular water from the goethite structure leaves a residue which rapidly nucleates into α-Fe_2O_3 prior to the occurrence of the exothermal peak which represents the final development of α-Fe_2O_3 from the already existing protohematite. This agrees with the XRD analysis of the sample heated at 245 °C (before the exothermic peak) [Fig. 4(c)], where the hematite diffraction pattern is observed.

A weak and broad endothermic peak at about 430 or 380° C is followed by a weak and broad exothermic one. The first one may correspond to the loss of residual OH, and second one to a better hematite crystallization, as can be deduced from the XRD analysis at 600° C [see Figs. 3(e) and 4(d)].

According to Paterson and Swaffield [9], the dehydroxylation of synthetic goethite shows a principal peak at 260° C with three small shoulders at 180, 210 and 235° C, which correspond to the dehydroxylation of the surface hydroxyls singly, doubly and triply co-ordinated). These shoulders can be totally eliminated by adsorption of divalent sulfate anions which function as bidentate ligands and replace two adjacent surface hydroxyl groups. These authors also consider that the stability of the surface hydroxyls will be further enhanced by the additional hydrogen bonding of bidentate sulfate species to other surface hydroxyls and oxide ions. So, in addition to the weight losses representing dehydration and dehydroxylation a third weight loss occurred just before the SO_4 decomposition, due to the breaking of the bonding between the surface hydroxyls and sulfate species. From this point of view, in the case of the poorly crystallized goethite with a content of 6.1% w/w of adsorbed water and 8.3% w/w of SO_4 anions, a part of the surface hydroxyls will be replaced by the SO_4 anions and the adsorbed water molecules will be co-ordinated to the iron(III). Thus, the loss of free surface OH is overlapped by the great endothermic band corresponding to the loss of adsorbed water molecules. However, the better crystallized sample of goethite (SO_4 2.4%, H_2O 3.5%) has more free surface OH ions and less adsorbed water; therefore, two shoulders can be detected on the low-temperature endothermic peak at 100 and 200° C, probably due to the loss of the above mentioned surface hydroxyl groups.

X-ray analysis

It is well known that during the dehydration of goethite hematite is formed in a close orientation relationship with the original goethite, the *a*, *b*, *c* axes of the orthorhombic cell of goethite becoming *c*, *a* and (110) directions of the pseudohexagonal cell of hematite. This transformation has been studied extensively [13–25].

The poorly crystallized hematite formed from the dehydroxylation of goethite has been named "protohematite" by Mackenzie [1] and Yariv and Mendelovici [26]. Wolska [27] proposed the name of "hydrohematite" for a hematite in which OH^- ions of the goethite were substituted for O^{2-} ions in the lattice. In order to counterbalance the resulting decrease in negative charge, the author suggested that some divalent iron (8%) must be present in the structure. But, on the contrary, Rendon and Serna [23] were in disagreement with that point of view, because divalent iron ions were not detected in the Mössbauer spectroscopic analysis of various hematite samples.

A nonuniform broadening of the powder lines of hematite is often observed. As this effect decreases on further heating, some authors [13,17,18] believe that this nonuniform broadening is correlated with some crystal imperfections, strains or faults occurring at low temperature. This phenomenon has also been attributed to the difference in grain size and crystallinity of the starting materials. Naono and Fujiwara [21] related the nonuniform broadening to the presence of slit-shaped micropores in acicular hematite. However, Duvigneaud and Derie [22] and Rendon et al. [25] pointed out that the nonuniform broadening is ascribed to the shape anisotropy of the particles, since this phenomenon is negligible in spherical particles, and nonuniform broadening remains in acicular particles after heating at 600 ° C prior to the sintering process which affects the particle lath morphology.

Figures 3 and 4 show the XRD analyses made at different goethite heating steps. The hematite diffraction pattern begins to appear at 245 and 280 ° C. The poor hematite crystallinity can be seen, since the lines are broad and of low intensity [see Figs. 3(c) and 4(c)]. This hematite crystallinity increases with temperature, especially between 600 and 700 ° C [compare Fig. 3(e) with Fig. 3(f), and Fig. 4(d) with Fig. 4(e)].

This marked change in crystallinity has not been previously reported by Rendon et al. [25]. On the contrary, these researchers observed a gradual increase of the hematite crystallinity with temperature. We think that these different behaviors are seen because the SO_4 ions stop the gradual process of hematite crystallization. So, at 700 ° C when the SO_4 anions are rarely present in the samples (as can be seen on the TG curves in Figs. 1 and 2), the hematite crystallinity is very good. In the 700–900 ° C temperature range, the hematite crystallinity does not change significantly [see Figs. 3(f), 3(g), 4(e) and 4(f)].

It should be mentioned that the crystallinity of the hematite formed at low temperatures depends on the crystallinity of the original unheated goethite samples [compare Fig. 3(d) with Fig. 4(c)].

A nonuniform broadening process similar to the one mentioned above can be observed; thus the (110) reflection is sharper than the one (104) [see Figs. 3(d), 4(c) and 4(d)]. This phenomenon disappears at 700 ° C when both an interparticle sintering and a change from acicular to spherical forms take place in the hematite particle morphology. This is in agreement with the previously reported results of Duvigneaud and Derie [22] and Rendon et al. [25].

Note how the nonuniform broadening process increases when the crystallinity of the starting goethite increases [compare Figs. 3(d) and 3(e) with Figs. 4(c) and 4(d)].

Electron microscopic analysis

According to previous morphological studies [21–23,25], two different hematite morphologies can be observed during the thermal decomposition of

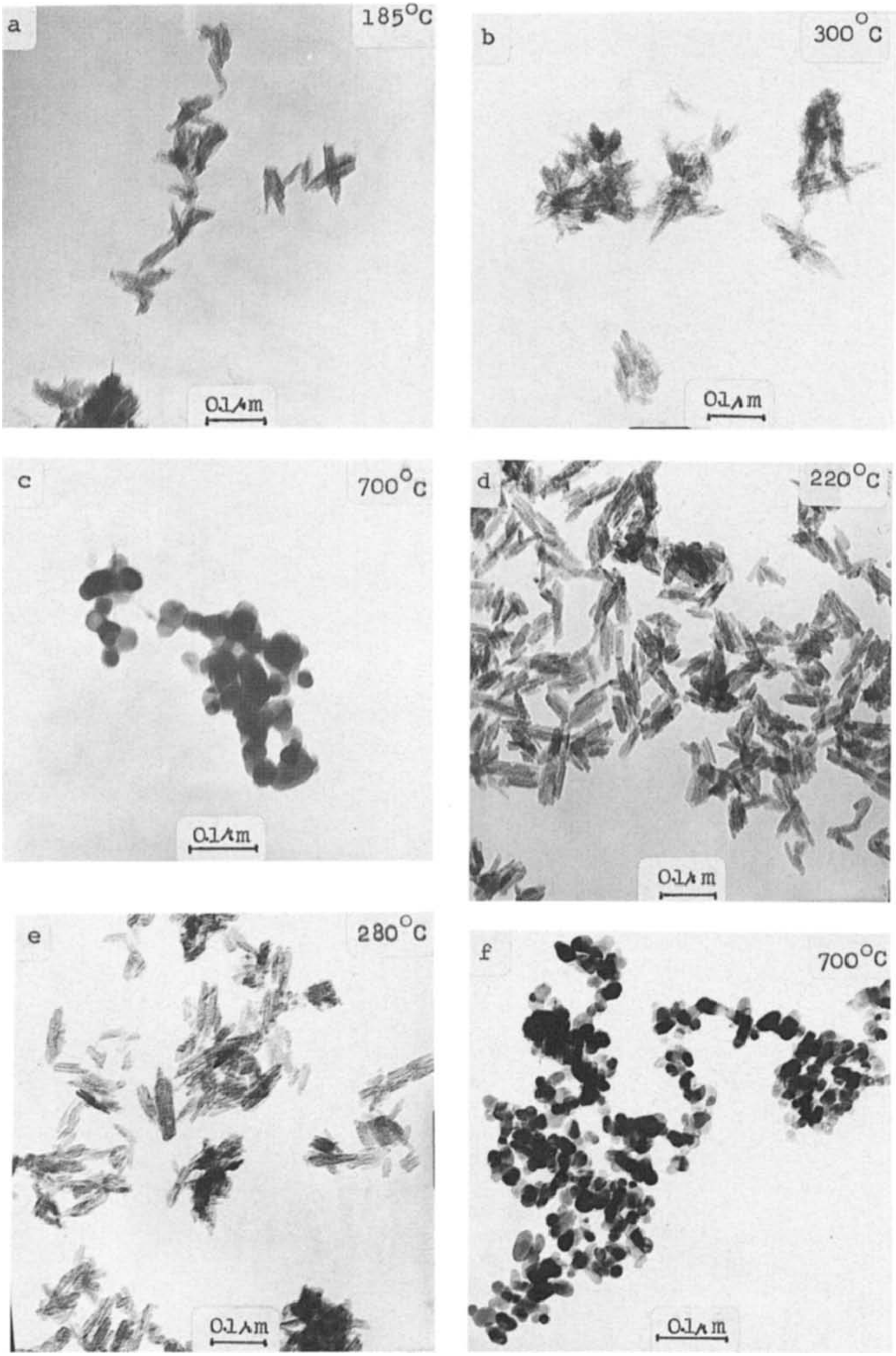

Fig. 5. Transmission electron micrographs. Goethite (aged for 45 min) heated at: (a) 185, (b) 300 and (c) 700 °C. Goethite (aged for 90 min) heated at: (d) 220, (e) 280 and (f) 700 °C.

acicular goethite samples: acicular and spherical forms. Both morphologies are strongly related, the acicular one with the formation of micropores and mesopores, the spherical one with the interparticle sintering and disappearance of porosity.

Rendon et al. [25] and Naono and Fujiwara [21] noticed that between 200 and 250 ° C slit-shaped micropores are formed along the elongated direction of the lath-shaped hematite microcrystals. In the 300–600 ° C interval, an internal sintering occurs within the microcrystals transforming the micropores into closed spherical mesopores. Above 600 ° C, interparticle sintering takes place and no valuable porosity is detected, the morphology of hematite particles at this temperature was spherical.

Figure 5 shows the transmission electron micrographs corresponding to goethite samples heated at different temperatures. The slit-shaped micropores can clearly be seen in samples heated to 300 ° C, the hematite particles presenting an acicular morphology. At 700 ° C, the morphology of the hematite particles became homogeneous spherical, and the porosity had not totally disappeared. Several porous nearly-spherical areas were observed where the interparticle sintering takes place [see Fig. 5(f)]. In contrast, above 600 ° C Rendon et al. [25] found a heterogeneity in size and shape of hematite particle, and no remarkable pore structure was reported by these researchers.

The size of the spherical particles of hematite at 700 ° C decreased as the starting goethite crystallinity increased [compare Fig. 5(f) with Fig. 5(c)].

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