Journal of Thermal Analysis, Vol. 9 (1976) 435–440

DTA STUDY OF THE DEHYDRATION OF SYNTHETIC GOETHITE αFeOOH

R. DERIE, M. GHODSI and C. CALVO-ROCHE

Université Libre de Bruxelles Faculté des Sciences Appliquées
Service de Chimie Industrielle–Chimie des Solides, Belgium

(Received June 2, 1975; in revised form October 27, 1975)

The shape of DTA endothermic peak, associated with the dehydration of goethite FeOOH into hematite, depends strongly on the size of the goethite particles. With samples of low specific surface, two distinct peaks were observed. The dehydration process of a low-specific surface goethite was followed by X-ray diffraction and low-temperature nitrogen adsorption. The results are in good agreement with the hypothesis of the formation of an impermeable hematite layer on each grain which temporarily stops the dehydration process of the internal part of the grain.

Synthetic goethite is usually prepared by slow oxidation of an aqueous suspension of iron(II) hydroxide by air bubbling, either in alkaline medium, or in the presence of an excess of iron(II) sulfate in solution.

By undergoing the following reactions:

$$\begin{array}{ll} 2\,\alpha\mathrm{FeOOH} \rightarrow \alpha\mathrm{Fe_2O_3} + \mathrm{H_2O} & (\mathrm{ca}\ 250^\circ) \\ 3\,\alpha\mathrm{Fe_2O_3} + \mathrm{H_2} \rightarrow 2\,\mathrm{Fe_3O_4} + \mathrm{H_2O} & (\mathrm{ca}\ 300^\circ) \\ 4\,\mathrm{Fe_3O_4} + \mathrm{O_2} \rightarrow 6\,\gamma\mathrm{Fe_2O_3} & (\mathrm{ca}\ 250^\circ) \end{array}$$

goethite is transformed into maghemite, γFe_2O_3, which is the commonest magnetic material for recording tape applications. If the transformation reactions are made in mild temperature conditions (not above 300°), the acicular form of the goethite particles remains unaltered in the final maghemite. The first of these reactions, the dehydration of goethite into hematite, never gives a simple endothermal DTA peak: in some cases the peak is unusually broad, in other cases, two more or less distinct peaks are observed. No satisfactory explanation of this anomaly can be found in the literature. The present work is a systematic study of the influence of the particle size on the dehydration process, as followed by DTA and X-ray diffraction.

Experimental

A series of samples of different specific surfaces have been chosen among the industrial products available, and among some goethites made in the laboratory. All these products were thoroughly washed with warm water, in order to eliminate most of the sulfate ions adsorbed on the surface.

The specific surfaces of the samples were determined using a classical laboratory-made BET apparatus. In order to characterize the porosity of partially dehydrated products, the complete nitrogen adsorption-desorption isotherms were also determined in some cases.

DTA experiments were made using a laboratory-made thermoanalyzer with a Mettler sample-holder, and in the following conditions: sample weight 200 mg; heating rate ~2°/min; sample environment: stream of dry nitrogen.

X-ray diffraction experiments were made on the Philips PW 1051 diffractometer using the Cu K_α line; iron fluorescence radiation is eliminated by means of a single-crystal monochromator.

Results

Figure 1 reproduces the DTA curves obtained with five samples whose specific surfaces are comprised between 24 m^2/g and 81 m^2/g. One observes a continuous evolution of the shape of the DTA curves as a function of the specific surface. The small particle-size goethites give broad endothermal dehydration peaks, whereas the large particle-size ones give two distinct peaks. The values of the mean particle diameters indicated in Fig. 1 have been calculated from the specific surfaces assuming that the particles are cylindrical and have the theoretical density

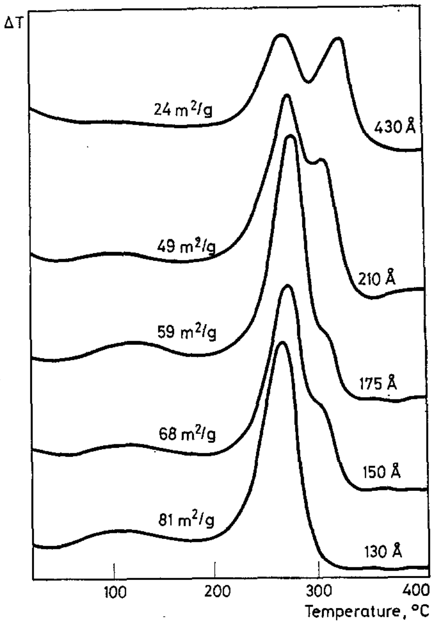

Fig. 1.

(4.25 g/cm^3). This is obviously not exact, since the size distribution of the particles is rather large, but gives a correct order of magnitude that we were able to verify by electron microscopy.

The DTA curve of the lowest specific surface sample being most typical, a systematic study of its dehydration process was carried out by means of a quenching method. DTA was stopped and the sample quenched in air at the temperatures corresponding to the points A, B, C, D, E, F, G and H on the DTA curve of the Fig. 2 (respectively 214, 235, 250, 266, 286, 379, 500 and 793°).

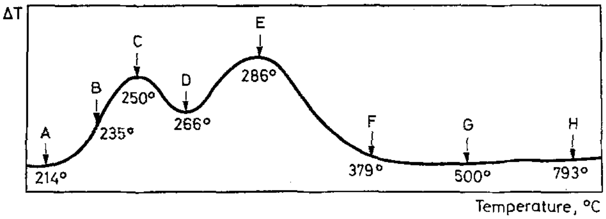

Fig. 2

After weighing, the samples were examined by X-ray diffraction; the specific surfaces were also measured. The results are summarized in Table 1.

Table 1

Sample	Quenching temperature, °C	Mass loss, %	Specific surface B.E.T., m^2/g	X-ray analysis G = goethite H = hematite
Initial goethite	—	—	24.0	G
A	214	2.44	29.5	G
B	235	2.55	32.1	G
C	250	4.17	45.2	G+H
	266	5.90	59.5	G+H
	286	7.22	71.5	H+G
	379	11.33	54.4	H
G	500	11.94	24.9	H
H	793	13.05	6.8	H

The interpretation of diffraction spectra is difficult, since most of the d-spacings are quite similar for the two crystal structures (for instance, the determination of hematite must be made using the (012) line, at 3.66 Å, whose relative intensity is only 25%). All the lines appearing in the intermediate stages C, D, E, can be indexed in the goethite or in the hematite lattices. The broadening of the hematite lines, at the end of the dehydration (stage F) is comparable to that of the initial goethite lines, and corresponds roughly to the dimension of the crystallites determined by electron microscopy: very probably, the goethite particles are monocrystalline, just as the final hematite ones. Obviously, no amorphous or poorly crystallized state is formed during the dehydration (as is the case for the dehydration of brucite): the reason for this could be the similarity of the two crystal structures and the simple relations between the cell parameters, as was pointed out for the first time by Goldsztaub [1].

The nitrogen adsorption isotherms of the samples A, B, F, G and H are of the non-porous solid type; the isotherms of samples C, D and E of the microporous solid type.

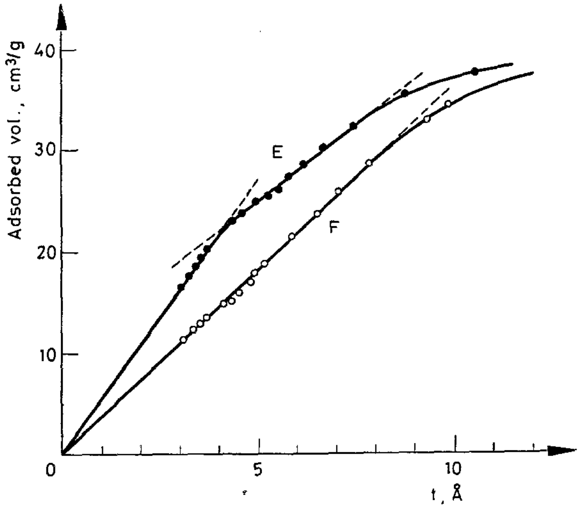

Fig. 3

This appears clearly on the "*t*-curves" calculated according to de Boer [2] and Lecloux [3]. The *t*-diagram of the samples E and F are reproduced on the fig. 3: the diagram of sample F is perfectly linear, indicating a non-porous solid; the diagram of sample E is composed of two linear parts, the first one corresponding to the adsorption on the whole surface (external surface + pores), and the second part to the adsorption on the external surface alone, the pores being filled with nitrogen. This filling occurs when the adsorbed nitrogen layer is about 4–5 Å, the dimension of the micropores being 8–10 Å (also for the samples C and D). The second linear part of the *t*-diagram allows calculation of an "external" specific surface, excluding the surface of the pores: the values obtained for samples C, D and E are 30, 37 and 47 m^2/g respectively. The maximum of the B. E. T. surfaces of table 1 may thus be attributed to the formation of the micropores, which are the "cracks" through which the dehydration water escapes. The gradual increase of the "external" specific surface, from sample A to sample F is attributed to the increasing roughness of the particles, easily observable by electron microscopy.

Discussion and conclusions

The thermal phenomena associated with goethite dehydration depend strongly on the specific surface of the sample namely on the mean particle size. The dehydration process has been carefully studied on a low specific surface sample presenting two well-separated DTA dehydration peaks. No trace of an intermediate compound has been found by X-ray diffraction; micropores (less than 10 Å) are formed during the process, and disappear once the transformation into hematite is achieved. From the evolution of the diffraction spectra, it may be concluded that no amorphous phase is formed during the transformation: this could result from the close relations existing between the two crystal structures.

There are then two possible explanations of the two more or less separated dehydration steps on the DTA curves:

a) The first dehydration step could lead to an intermediate product, a "water-containing hematite", as described by Lima de Faria in his important work on the dehydration of natural goethite and diaspore [5]. This intermediate is characterized by a periodic variation of the structure factor, along the c-axis (the periodicity of the superstructure so formed is about 32 Å), caused by an unequal repartition of Fe^{3+} ions and remaining protons between the close-packed oxygen layers. Those layers being parallel to the axis of the initial goethite needles, it is possible that for small particles having a diameter of only two or three times the periodicity of the superstructure, the water-containing hematite should not be stable, and the dehydration should occur in one step.

b) The first dehydration step could be the formation of an hematite layer around the grains. Owing to the close structural relations between hematite and goethite [1] this layer should strongly adhere to the unaltered goethite, and, once thick enough, should sufficiently impede the diffusion of water outside the grain, to stop the dehydration process.

With increasing temperature, the second dehydration step should then begin once the internal pressure in the grain becomes high enough to cause cracks (diffusion paths) to appear in the external hematite layer.

This view has been suggested by Blazek [4] and is supported both by our nitrogen adsorption measurements and by the evolution of DTA curves with the specific surface of the samples. If the goethite grains are very small, the relative importance of the first dehydration step becomes greater, and the second DTA peak vanishes. Moreover, the microporosity appearing during the dehydration process could have its origin in the high internal pressure in the goethite cores of the grains, which causes microcracks to appear in the external impervious hematite layer, enabling water vapour to escape. This microporosity vanishes once the dehydration is complete.

References

1. S. GOLDSZTAUB, Compt. Rend. Acad. Sci. Paris, 193 (1931) 533.
2. J. H. DE BOER, B. LINSEN, T. J. OSINGA, J. Catalysis, 3 (1964) 268.
3. A. LECLOUX, Mémoires Soc. Roy. Sciences Liège 6e s. T. 1 fasc. 4, (1974) 169.
4. A. BLAZEK, Thermal Analysis, Van Nostrand-Reinhold, London p. 180.
5. J. LIMA DE FARIA, Z. Kristallogr. Kristallgeom., 119 (1963) 176.

RÉSUMÉ — La déshydratation de la goethite de synthèse se marque en ATD par un phénomène endothermique plus ou moins dédoublé, ce dédoublement étant fonction de la dimension des particules de l'échantillon. La déshydratation d'une goethite de faible surface spécifique a été suivie par diffraction de rayons X et par adsorption d'azote à basse température sur des échantillons refroidis brutalement en cours d'ATD. C'est l'hypothèse de la formation sur chaque grain d'une couche externe d'hématite, bloquant temporairement la diffusion de la vapeur d'eau vers l'extérieur, qui se trouve le plus en accord avec les résultats expérimentaux.

ZUSAMMENFASSUNG — Die Form des mit der Entwässerung von Goethit FeOOH zu Hämatit verbundenen endothermen DTA-Peaks hängt stark von der Grösse der Goethit-Partikel ab. Bei Proben von kleiner spezifischer Oberfläche wurden zwei scharfe Peaks beobachtet. Der Entwässerungsprozess eines Goethits von kleiner spezifischer Oberfläche wurde durch Röntgendiffraktion und Stickstoff-Adsorption bei niedrigen Temperaturen verfolgt. Die Ergebnisse sind in guter Übereinstimmung mit der Hypothese nach welcher eine undurchdringliche Hämatitschicht auf jedem Körnchen gebildet wird, die den Entwässerungsvorgang im inneren des Körnchens vorübergehend stoppt.

Резюме — Вид эндотермического пика ДТА, связанный с дегидратацией готита FeOOH до гематита, сильно зависит от размера частиц первого. Для образцов низкой удельной поверхности наблюдали два различных пика. Процесс дегидратации готита с малой удельной поверхностью был прослежен с помощью диффракции рентгеновых лучей и низкотемпературной адсорбции азота. Полученные результаты находятся в хорошем согласии с гипотезой об образовании на каждой грануле готита непроницаемого слоя гематита, который временно приостанавливает процесс дегидратации внутренней части гранулы.