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Anisotropic x-ray line broadening in goethite-derived haematite

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Abstract. The non-uniform x-ray line broadening in goethite-derived haematite has been investigated by Rietveld structure refinements and transmission electron microscopy (TEM). Mechanisms reported in the literature for this phenomenon are critically discussed. Based on the structure refinements of whole x-ray diffraction patterns and TEM measurements of various goethite-derived haematites, we demonstrate that the non-uniform x-ray line broadening effect is caused by the platelike shape of the haematite crystals.

Iron oxides are widespread in nature and are important industrial products, being used, for example, in inorganic dyes and as magnetic recording media [1]. Among them, goethite, α -FeOOH, and haematite, α -Fe₂O₃, are two of the most stable minerals. Goethite is an abundant mineral in nature and haematite is the oldest known iron oxide mineral and widespread in soils and rocks. It is well known that α -FeOOH can transform into α -Fe₂O₃ through dehydration. The transformation is especially important since it influences the subsequent reaction steps in the production of magnetic recording materials. With respect to the reaction process, much attention has been paid to two problems: one is the mechanism of the transformation and the other is the non-uniform x-ray diffraction peak broadening of haematite. As to the former, after intensive investigations by various techniques [2–11], it has been understood that the conversion of goethite to haematite without any intermediate phase is facilitated by the common anion framework shared by these two compounds while cations rearrange. Three unit cells of goethite form one unit cell of haematite. Thereby, the volume contracts by a factor of 0.62 as a result of a contraction factor of 0.25 in the [100] direction and an elongation factor of 1.012 in the [010] direction and of 1.037 in the [001] direction [7]. Haematite crystals are separated by pairs of slit-shaped nanopores (approximately 0.8 nm wide) at the initial stage of the decomposition. The topotactic relationship between goethite and haematite has been established [4]: α -FeOOH(100) \parallel α -Fe₂O₃(001) and α -FeOOH(001) \parallel α -Fe₂O₃(010), where the hexagonal three-index system of the haematite lattice is used. However, to the latter, the non-uniform x-ray diffraction peak broadening of haematite, i.e., 012, 104, 024, 116, 018 and 214 peaks are broader than 110, 113 and 300 peaks, is still a subject of debate although many models have been suggested in the last four decades [2–15]. Here we report the origin of this phenomenon through Rietveld structure refinements of whole x-ray diffraction patterns for various goethite-derived haematites. Mechanisms reported

in the literature for this phenomenon are critically discussed. We demonstrate that the non-uniform x-ray line broadening phenomenon in goethite-derived haematite is caused by the platelike shape of haematite crystals. This explanation can be also applied to other α -MOOH-derived α -M₂O₃ (M: metal element) systems.

Before tackling the origin of the non-uniform line broadening phenomenon, different explanations reported may be surveyed. Rooksby [11] proposed the existence of a sub-unit, common both to goethite and haematite, that suffers only a little disturbance when goethite transforms into haematite on heating. The Bragg peaks of those with interplanar spacings (d values) nearly equal for goethite and haematite in this sub-unit are sharp. This model could not explain why the 104 peak ($d = 0.270$ nm) in the goethite-derived haematite is broad because a 130 peak ($d = 0.269$ nm) exists in goethite. Lima de Faria [3] pointed out that this phenomenon could be ascribed to stacking faults, which causes a broadening for Bragg peaks of $h - k \neq 3n$ planes in crystals with a hexagonal structure. On the other hand, the $l = 3n$ planes would not be affected. Nakajima *et al* [14] also suggested that the cation sublattice in γ -FeOOH-derived γ -Fe₂O₃ is divided into small domains with stacking faults. Watari *et al* [6] further performed XRD, TEM and HRTEM studies and interpreted this as a morphological effect due to the twin formation in the process of topotactic dehydration transformation. The obverse and reverse twin components have the common oxygen arrangement but have different cation stacking sequences of abcabc... for one component and acbacb... for the other. The $l \neq 3n$ reflections belonging to either the observe or reverse variant are seriously broadened because of the very small component size, while the $l = 3n$ reflections common to both twin components remain sharp because of coherency at the twin boundary. However, these two models (stacking faults and twin formation) could not explain the experimental observation of the broadening of the 116 peak in haematites. Furthermore, Yamaguchi and Takahashi [12] associated the non-uniform broadening with an incomplete displacement of the iron ions. If this is true, the integrated intensities of (104) and (110) planes would vary in samples heated at different temperatures, which conflicts with experimental results observed, i.e., no variation in intensities of these reflections in the samples annealed at various temperatures [6, 15]. Naono *et al* [7] experimentally observed the formation of nanopores between goethite-derived haematite crystals. They suggested that the nanopores were the cause of the broadening. However, no correlation between the non-uniform line broadening and nanopores was established. Duvigneaud and Derie [13] and da Costa and de Jesus Filho [15] qualitatively illustrated that this phenomenon can be explained by the shape effect of the goethite-derived haematite. However, a quantitative explanation of this phenomenon is still lacking. This is the subject of the present report.

Synthetic goethite crystals were hydrothermally prepared by mixing 1.1 mole Fe(NO₃)₃ with 4.3 mole KOH. The suspensions were stored at ambient temperature for 20 days and then the samples were washed three times with distilled water by centrifugation until pH \approx 7 was reached. They were dried at 110 °C for 2 hours and finally were gently ground. X-ray powder diffraction, transmission electron microscopy and energy dispersive analyses of the powder revealed a single goethite phase with an acicular morphology along the [001] direction (c -axis). For the dehydration process, the acicular goethite powders were heated in a porcelain dish in an electric furnace with the temperature controlled to ± 5 K. Heat treatments were carried out in air at four temperatures: 440, 620, 710 and 900 °C, for 30 minutes and then furnace cooled. X-ray powder diffraction measurements were performed in Bragg–Brentano scattering geometry with a Philips PW1820/3711 diffractometer using Cu K α radiation, in which a graphite monochromator and an automatic divergence slit were used. The data were collected in the 2θ range of 20–130° with a step size of 0.02° and a counting time of 30 s

Table 1. The residual R , the lattice parameters, a and c , and average dimensions of crystallites along a and c axes, D_a and D_c , for haematites derived from goethite at different annealing temperatures.

Annealing temperature (°C)	R (%)	a (Å)	c (Å)	D_a (nm)	D_c (nm)	D_a/D_c
440	8.0	5.0364(8)	13.7504(20)	39.9(3)	8.7(2)	4.59
620	7.2	5.0351(5)	13.7451(11)	51.4(4)	14.3(2)	3.59
710	7.1	5.0339(4)	13.7428(9)	64.3(9)	20.9(4)	3.08
900	7.8	5.0336(4)	13.7447(8)	122.1(40)	50.9(14)	2.40

per step. Transmission electron microscopy (TEM) measurements of the goethite-derived haematite samples were performed using a Philips EM430 TEM.

The Rietveld refinements were carried out with a modified LHMP1 program [16]. The profile function used was the Voigt function (i.e., a convolution of a Gaussian and a Lorentzian), in which the Lorentzian component depends on the crystallite sizes along a and c axes. The parameters, U , V and W , defining the full width at half maximum of the Gaussian component $(U \tan^2 \theta + V \tan \theta + W)^{1/2}$, were kept constant through all of the refinements to avoid any correlation to the Lorentzian component and to facilitate the comparison of the crystallite dimensions obtained from the different data sets. A total of 19 parameters were refined for all data sets. The parameter set comprised a scale factor, six parameters for the background, one zero point, one preferred orientation parameter, unit cell parameters, fractional atomic co-ordinates, thermal parameters for iron and oxygen, and the occupancy factor of the iron site while the occupancy factor of the oxygen site is fixed.

Figure 1 shows Rietveld structure refinements of four haematite samples obtained by heating acicular goethite at 440, 620, 710 and 900 °C for 30 minutes. All refinements converged to small residual R values listed in table 1, in which the lattice parameters and average dimensions of crystallites along a and c axes, D_a and D_c , for haematites derived from goethite at different annealing temperatures are also listed. The occupancy factor at the iron position, P_{Fe} , against the dimension of crystals along c axis is shown in figure 2. The analysis using the Williamson–Hall method [17] indicates that the effect of microstrain on the line broadening is negligible in these haematites studied. The non-uniform line broadening phenomenon is clearly illustrated in figure 3, in which the full widths at half maximum (FWHMs) for different planes were plotted as a function of $\tan(\theta)$ for the samples annealed at four temperatures. It is clear that the FWHMs of the peaks with $l = 0$ are much smaller than those of the peaks with $l = 2n$. This effect decreases on increasing the annealing temperature. The FWHM of a given hkl peak is inversely proportional to the mean coherence length (D) perpendicular to the (hkl) plane: the larger the FWHM, the smaller the D . It should be stressed that the 116 peak is obviously broader than the 300 peak in the samples annealed at low temperatures, which is opposite to the normal line-broadening effect, i.e., high-angle reflections should be broader than low-angle reflections. The integrated intensity ratio of (104) to (110) planes remains almost constant, 1.9 ± 0.1 , in the samples annealed at various temperatures. These observations are consistent with the data reported in the literature [3, 6, 7, 12–15], which allow us to exclude twin formation [6], stacking fault [3, 14] and incomplete displacement of the iron ions [12] as the main factors for the non-uniform line broadening phenomenon observed in the goethite-derived haematite. The lattice parameters are also different in the haematite crystallites obtained by heating goethite at different temperatures. They decrease with increasing temperature except for the value of c in the sample annealed at 900 °C. The average dimension of haematite crystals along the c axis is much smaller than that along the a axis while the ratio of D_a/D_c decreases with

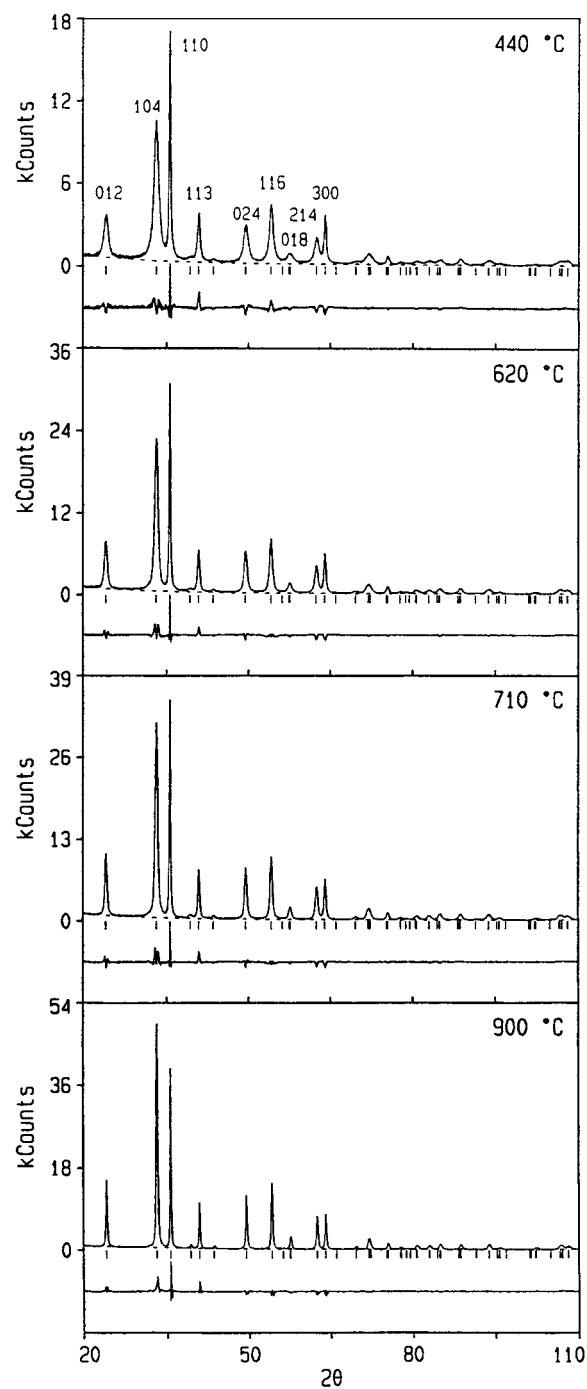


Figure 1. Rietveld structure refinement profiles of the x-ray powder diffraction data for four haematite samples obtained by heating goethite at 440, 620, 710 and 900 °C. In the upper field of each plot, the experimentally observed pattern is shown. Below that the background is also plotted as a dashed line in this field. The difference pattern (observed minus calculated patterns) is plotted in the lower field. In the intermediate field the positions of the possible Bragg reflections are indicated as a series of short vertical bars corresponding to the crystalline α -Fe₂O₃ phase.

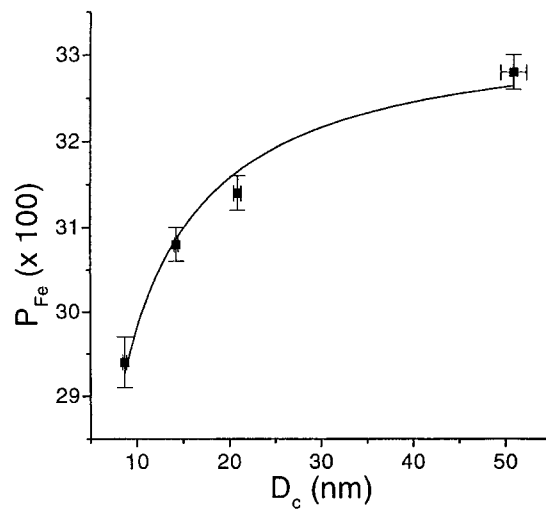


Figure 2. The cation occupancy factor, P_{Fe} , in the goethite-derived haematite crystallites as a function of the dimension along the c axis, D_c . The solid line is the best fit curve following $P_{Fe} = 1/3 - (0.35 \pm 0.03)/D_c$ with standard deviation of 1.078 and relevancy of 0.989. Note that the full cation occupancy is $P_{Fe} = 1/3$.

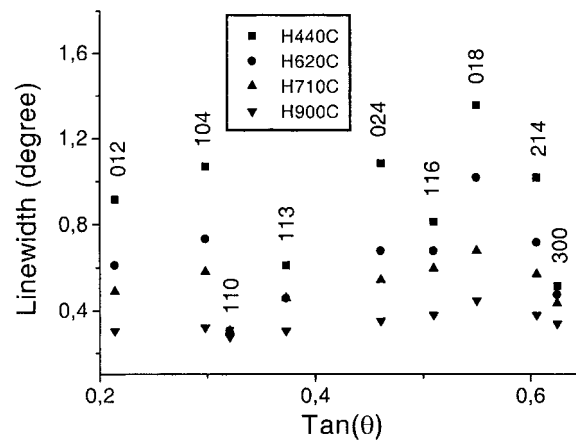


Figure 3. The full widths at half maximum (FWHMs) for different planes plotted as a function of $\tan(\theta)$ for the samples annealed at four temperatures.

increasing annealing temperature. This indicates a preferential development of platy crystals in the x - y plane (plate diameter), whereas development in the z direction (plate thickness) is strongly impeded. The cation occupancy factor depends on the annealing temperature and follows $P_{Fe} = 1/3 - 0.35/D_c$. For a platy crystal, the smaller the plate thickness, the larger the ratio of surface atoms to the total atoms in the crystal. The relationship between the cation occupancy factor and the plate thickness implies a surface layer with high concentration of cation vacancies. Furthermore, TEM studies of these samples confirm that nanopores are formed in the samples annealed at low temperatures and a sintering effect of nanopores occurs in the samples annealed at high temperatures, consistent with the data reported by Naono *et al* [7]. They found that haematite crystals are separated by nanopores along the [001] axis

and perpendicular to the needle axis [010]. The dimension of haematite crystals along the [001] direction is smaller than that along the [010] direction, confirming the shape of the goethite-derived haematite crystals determined by the Rietveld structure refinements.

On the basis of Rietveld structure refinements of full x-ray diffraction patterns and TEM measurements for various goethite-derived haematites, we conclude that the non-uniform x-ray line broadening effect in goethite-derived haematite is indeed caused by the shape effect of the haematite crystals. Due to the formation of nanopores, the growth of haematite crystals along the *c* axis was impeded in the samples annealed at low temperatures, resulting in a platelike shape of the haematite crystals. With increasing annealing temperature, nanopores sintered and D_a and D_c increased while D_a/D_c decreased. Consequently, the non-uniform line broadening effect decreased.

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References

- [1] Cornell R M and Schwertmann U 1996 *The Iron Oxides* (Weinheim: VCH)
- [2] Bernal J D, Dasgupta D R and Mackay A L 1959 *Clay Miner. Bull.* **4** 15
- [3] Lima de Faria J 1963 *Z. Kristallogr.* **119** 176
- [4] van Oosterhout G W 1967 *J. Inorg. Nucl. Chem.* **29** 1235
- [5] Derie R, Ghodsi M and Calvo-Roche C 1976 *J. Therm. Anal.* **9** 435
- [6] Watari F et al 1979 *J. Solid State Chem.* **29** 137
Watari F et al 1979 *J. Solid State Chem.* **29** 417
Watari F et al 1982 *Phys. Status Solidi a* **73** 215
Watari F et al 1983 *J. Solid State Chem.* **48** 49
- [7] Naono H et al 1980 *J. Colloid Interface Sci.* **73** 406
Naono H et al 1987 *J. Colloid Interface Sci.* **120** 439
- [8] Paterson E and Swaffield R 1980 *J. Therm. Anal.* **18** 161
- [9] Rendon J L et al 1983 *J. Colloid Interface Sci.* **92** 508
- [10] Schwertmann U 1984 *Thermochim. Acta* **78** 39
- [11] Rooksby H P 1960 *Silicates Industriels* **25** 335
- [12] Yamaguchi T and Takahashi T 1982 *J. Am. Ceram. Soc.* **65** C-83
- [13] Duvigneaud P H and Derie R 1980 *J. Solid State Chem.* **34** 323
- [14] Nakajima K, Hirotsu Y and Okamoto S 1987 *J. Am. Ceram. Soc.* **70** 321
- [15] da Costa G M and de Jesus Filho M F 1992 *J. Mater. Sci.* **27** 6116
- [16] Howard C J and Hill R J LHMP: a computer program for Rietveld analysis of fixed wavelength x-ray and neutron powder diffraction patterns AAEC (now ANSTO) Report M112, Lucas Heights Research Laboratory (1986)
- [17] Williamson G K and Hall W H 1953 *Acta Metall.* **1** 22