

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can never be produced without the presence of some H<sup>+</sup> (and accordingly Fe<sup>2+</sup>, for the charge balance).

## 2. Development of texture

The reaction in question is directed by the initial lattice and hence leads to a highly oriented product, unless the water vapour pressure rises to a point allowing nucleation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The reaction happens within the solid; it is topochemical. Since the movements of the ions involved follow two lattice dimensions of the initial  $\gamma$ -FeOOH, it may even be called topotactic, although we feel that we then stretch that concept to its very limits.

The reflections of the final  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are, at closer inspection, selectively broadened. This may be attributed to different crystallite dimensions in the according directions, or else to a disorder phenomenon. As we have already mentioned, the Fe<sup>3+</sup> ions have scarcely time and occasion to arrange themselves; i.e. along a four-fold screw axis in the proper sequence ... □ □ Fe □ □ Fe ... (on the so-called "lithium sites" of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> lattice). Under such conditions the 400 and 440 reflections of the cubic pseudocell are less affected than pyramid reflections, let alone the tetragonal supercell reflections which do not appear at all in our case.

In conclusion we may say that with respect to all these manifold ordering processes necessary to form fully crystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>\*, it is clearly impossible to go all along the reaction from  $\gamma$ -FeOOH single crystals to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> single crystals and the total disruption of the initial crystal into tiny bits of disordered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is a necessity.

## 3. Kinetics

While the measured time law is, within the experimental error, compatible with the first order law (F1) as well as with diffusion controlled mechanisms (D1, D2, D3, D4), we can rule out all mechanisms leading to a sigmoid function. From this evidence alone it would be futile to speculate about the proper mechanism. The electron microscopical pictures, however, lead without any doubt to the conclusion that nucleation occurs all over the crystal at random. It is possible, or even probable, that the sluggish end part is directed by another law, namely by diffusion of H<sub>2</sub>O molecules out of the polycrystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. This does not show in the decomposition curves, and the reduced time plots of diffusion controlled reactions are very similar to each other anyway.

We should like to point out, finally, that the electron micrographs give us the means to rule out the nomenclature "monocrystal with mosaic texture" as the new phase appears in places quite far apart from each other, and as new interfaces are formed.

\*Actually Fe<sub>64</sub>O<sub>96</sub> or  
 $\{Fe_{24}^{\text{Tetrahedral}} [Fe_{36}^{\text{Octahedral}} (Fe_4^{\text{Li-sites}} \square_8^{\text{Li-sites}})] O_{96}\}$

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## REFERENCES

- 1 R. Giovanoli and R. Brüttsch, *Chimia*, 28 (1974) 188.
- 2 W. Feitknecht, *Pure Appl. Chem.*, 9 (1964) 423.
- 3 K. J. Gallagher, W. Feitknecht and U. Mannweiler, *Nature*, 217 (1968) 1118.
- 4 J. D. Bernal, D. R. Dasgupta and A. L. Mackay, *Nature*, 180 (1957) 645.
- 5 D. R. Dasgupta, *Ind. J. Phys.*, 35 (1961) 401.
- 6 H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures*, Wiley & Co., New York, 1954, p. 1959.
- 7 B. Delmon, *Rev. Inst. Franç. Pétr. & Ann. Combust. Liq.*, 18 (1963) 471.
- 8 K. J. Gallagher, in G. M. Schwab (Ed.), *Reactivity of Solids*, Proc. 5th I.S.R.S. Munich 1964, Elsevier, Amsterdam, 1965, p. 192.
- 9 V. Šatava and F. Škvára, *J. Amer. Ceram. Soc.*, 52 (1969) 591.
- 10 H. G. Wiedemann, A. V. Tets and H. P. Vaughan, presented 21st Feb. 1966, *Conference on Analytical Chemistry and Applied Spectroscopy*, Pittsburgh.
- 11 S. F. Bartram, in E. F. Kaelble (Ed.), *Handbook of X-Rays*, McGraw-Hill, New York, 1967, pp.17-19.
- 12 R. Schrader and G. Büttner, *Z. Anorg. Chem.*, 320 (1963) 205.