

The Thermal Transformation of Hydrated Ferric Oxides

By G. BUTLER and H. C. K. ISON

(*Metallurgy Division, National Physical Laboratory, Teddington*)

THE ferric oxides of iron are interesting in having four hydrated forms, α -, β -, γ -, and δ -FeOOH.¹ The α - and γ -forms occur in nature as the minerals goethite and lepidocrocite, respectively. Both these forms, and occasionally β -FeOOH, are found in the products of the corrosion of iron and steel in aqueous media.

The thermal transformation of these oxides has been studied by heating samples for one week at temperatures in the range 50—200° in a series of thermostats utilising the thermal gradient along a metal bar.² The oxides were heated in the absence and presence of water in small ignition tubes open to the air or sealed after the addition of a drop of water respectively. The changes in composition were followed by X-ray analysis.

α -FeOOH was prepared by the rapid oxidation of a solution of ferrous hydrogen carbonate,³ β -FeOOH by the hydrolysis of a solution of ferric chloride at elevated temperature,⁴ γ -FeOOH by the controlled oxidation of ferrous chloride⁵ and δ -FeOOH by the rapid oxidation of ferrous hydroxide⁶ prepared by anodic dissolution of pure iron under deaerated conditions.

In the Figure the relative amounts of the

different oxide phases are plotted as a function of temperature. In all cases the final product at 200° is haematite, α -Fe₂O₃. In air the transformation of the hydrated oxides took place at temperatures in the range 145—180° which are considerably lower than some of those reported by other workers.^{1,7} Francombe and Rooksby⁷ found that the dehydration of α -FeOOH in air started at 230°, 20% of the water being lost in a half-hour's heating, and the transformation to haematite was complete at 270°. With the δ -form substantial dehydration to α -Fe₂O₃ was observed on heating at 150° for 2 hours, conversion being complete at 240°.

Bernal¹ found that β -FeOOH rapidly lost water on heating in air, 13% being lost at 230°, while γ -FeOOH was converted into a mixture of γ - and α -Fe₂O₃ at 200° and to α -Fe₂O₃ at 250°. In the case of δ -FeOOH, although α -Fe₂O₃ was present at 120—130°, the original hydrated oxide persisted up to 180° and transformation was only complete at 200°. In our work α -FeOOH appeared as an intermediate phase, although the evidence for this relies largely on the presence of the (110) line which still persists at low intensity at 200°.

¹ J. D. Bernal, *Schweizer Archiv.*, 1960, 69; J. D. Bernal, D. R. Dasgupta, and A. L. Mackay, *Nature*, 1957, **180**, 645; *Clay Min. Bull.*, 1959, **4**, 15.

² G. Butler, *J. Sci. Instr.*, 1963, **40**, 545.

³ W. H. Albrecht, *Ber.*, 1929, **62**, 1475.

⁴ O. Kratky and H. Nowotny, *Z. Krist.*, 1938, **A**, **100**, 356.

⁵ L. A. Welo and O. Baudisch, *Phil. Mag.*, 1934, **17**, 754.

⁶ O. Glemser and E. Gwinner, *Z. anorg. Chem.*, 1939, **240**, 163.

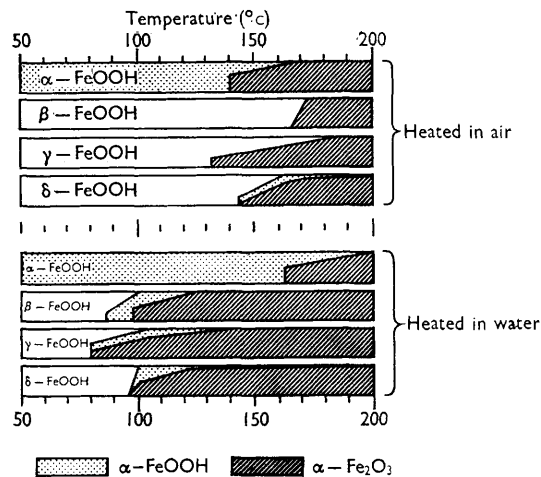
⁷ M. H. Francombe and H. P. Rooksby, *Clay Min. Bull.*, 1959, **4**, 1.

The most striking observation is the much lower transformation temperatures observed on heating the β -, γ -, and δ -hydrated oxides in water as compared with those found in air. This is consistent with observations that β -FeOOH is transformed to α -Fe₂O₃ if boiled with water for 6 days,¹ and that in the presence of water the change was complete after only 2 hours at 150°.⁷

At 100° in water the stable phases are clearly α -FeOOH and α -Fe₂O₃. This is in agreement with experiments on the corrosion of iron in boiling solutions, these two phases being found in the product and not γ -FeOOH, the main constituent of rust at ambient temperature. In the presence of water the first transformation is to the most stable hydrate, α -FeOOH. This is presumably formed by dissolution of the hydrated oxides and reprecipitation as goethite in a less ordered crystalline state which is transformed into haematite more easily than goethite prepared at ambient temperature.

At 200° haematite is the only stable ferric oxide, a confirmation of the results found by X-ray

examinations of corrosion products from boilers operating at 200°.



(Received, April 23rd, 1965.)