

THE INFLUENCE OF WATER VAPOUR ON THE CONVERSION OF α - TO γ -Fe₂O₃

W. WEISWEILER,

Institute of Technical Chemistry, University of Karlsruhe, Federal Republic of Germany

and

M. IQBAL,

Department of Chemistry, University of Engineering and Technology, Lahore

Abstract. An attempt has been made to study the significance of water vapour in the conversion of α -Fe₂O₃ (hematite) to pure phase γ -Fe₂O₃ (maghemite or γ -hematite) which represents the information carrier for magnetic tape recording. A gas mixture of 10 v/o carbon monoxide and 90 v/o nitrogen instead of conventional hydrogen/nitrogen gas mixture was used as a reducing agent for α -Fe₂O₃ to Fe₃O₄ (magnetite). Subsequently Fe₃O₄ was oxidized by dry air to produce γ -Fe₂O₃. Air oxidation of freshly reduced active magnetite forms pure phase γ -Fe₂O₃ while that of altered magnetite (which was exposed to atmospheric conditions and has developed α -Fe₂O₃ nuclei on its surface) results in the formation of a mixture of α - and γ -Fe₂O₃. In the presence of water forming reducing gases, γ -Fe₂O₃ was obtained at switching temperatures (*i.e.* changing over from reducing to oxidizing atmosphere) of 190-280°, whereas in the absence of water a smaller temperature range of 240-80° was found. The results suggest that the presence of water vapour is not a necessary condition in the production of γ -Fe₂O₃.

Introduction

The production of γ -Fe₂O₃ (maghemite) has become extremely important due to the increased use of magnetic tapes. γ -Fe₂O₃ is ferromagnetic as compared to α -Fe₂O₃ which is paramagnetic. Recently chromium dioxide has been tried as an alternate material. Out of the numerous techniques^{1, 2} available for the production of γ -Fe₂O₃, the dehydration of goethite (γ -FeOOH) at 220-50° in 2-24 hr. or the direct oxidation of aqueous solutions should be mentioned. Hematite (α -Fe₂O₃) is at first converted to magnetite (Fe₃O₄) by heating it in a reducing atmosphere and is then oxidized to maghemite (γ -Fe₂O₃). None of the known techniques³ leads to the production of pure phase γ -Fe₂O₃ except the reduction of hematite to active magnetite followed by an instantaneous air oxidation⁴. The conversion rate is dependent on a number of parameters like input material, technique applied, surface area, water content and thermal treatment. According to David and Welch⁵ magnetite is oxidized to maghemite only in the presence of water. Similar observations have been previously made by other investigators^{6, 7} while Aharoni *et al.*⁸ considered γ -Fe₂O₃ a mixture of two solid solutions of α -Fe₂O₃ with regular imperfections on one hand and H-ferrite on the other. Elder⁹ found that the oxidation of Fe₃O₄ (particles smaller 1 μ m dia.) in dry oxygen atmosphere of 220° after 1 hr.

leads only to α -Fe₂O₃. On the contrary in air and water vapour high percentage of γ -Fe₂O₃ will be obtained in addition to α -Fe₂O₃. The effect of water as a catalyst for this conversion is not very clear till today. Therefore for the production of pure phase γ -Fe₂O₃ 10% CO and 90% N₂ will be used as the reduction gas instead of 10% H₂ and 90% N₂,⁴ so that the formation of water as a by-product is eliminated.

Experimental

The starting material, α -Fe₂O₃ (Merck, Darmstadt) in powder form p. a., was placed in thin layer in an alumina boat and then put inside a tubular furnace. The sample was heated to 750° for 1 hr. (Fig. 1) and maintained at this temperature for several min. The heating was switched off and the furnace cooled. In between the pre-determined temperature range of 160 to 310°, the water-free reducing CO-atmosphere was suddenly converted to an oxidizing one, which was also free of water vapour. This temperature range of air oxidation has been proved to be effective in our previous investigation.⁴ The analyses of the reacted samples with respect to α -Fe₂O₃ (input material or undesired product), Fe₃O₄ (intermediate product), and γ -Fe₂O₃ (final product) were performed with the help of precision X-ray scattering. The following important reflexes were used as detailed in the Table.

TABLE. IMPORTANT X-RAY REFLEXES (HKL) OF IRON OXIDES (WITHOUT INTERMEDIATE PHASES),⁴ Cu K α -RADIATION RELATIVE INTENSITIES I/I_0 ALONG WITH LATTICE SPACINGS.

Substance	hkl	d, Å	I/I_0
Fe ₃ O ₄	311	2,53	100
	440	1,49	40
	220	2,97	30
	111	4,85	8
γ -Fe ₂ O ₃	311	2,52	100
	440	1,48	53
	220	2,95	34
	110	5,90	2
α -Fe ₂ O ₃	104	2,703	100
	110	2,52	70
	116	1,70	36

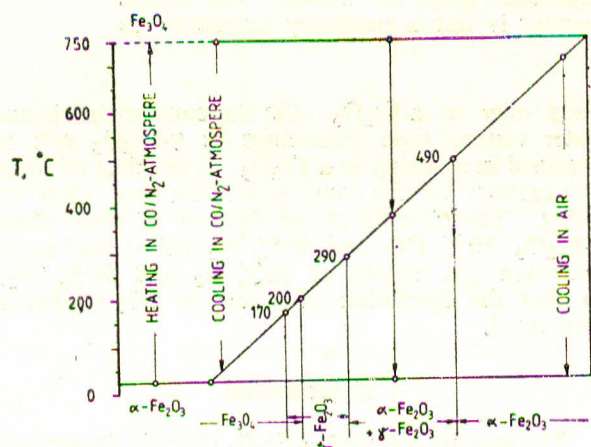


Fig. 1. Scheme of the reactions performed. Reduction of the starting material α -Fe₂O₃ by heating it in CO/N₂-atmosphere leads to Fe₃O₄ at 750°. Fe₃O₄ is cooled to certain temperatures (on the diagonal in the diagram) where the reducing atmosphere is switched to an oxidizing one. The reaction products are shown on the abscissa.

With the applied Cu-K α -radiation the (220)-reflex, whose intensity is fairly acceptable, was found to be optimal in order to separate Fe₃O₄ and γ -Fe₂O₃ which crystallize in the same spinel lattice. Care has to be taken to see that no α -reflex coincides.

Results and Discussion

The intensities of the X-ray reflexes obtained under identical operating conditions are taken as a measure of the quantity of phases present. Abscissa

in Fig. 2 represents the switching temperature from reducing to oxidizing conditions. As expected, the

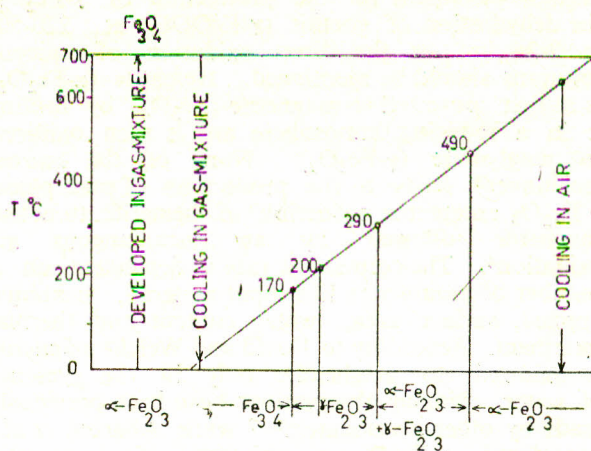
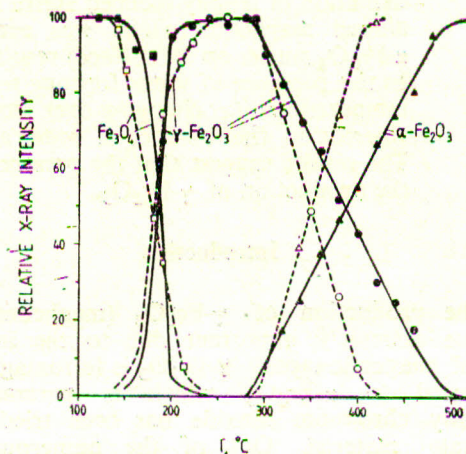
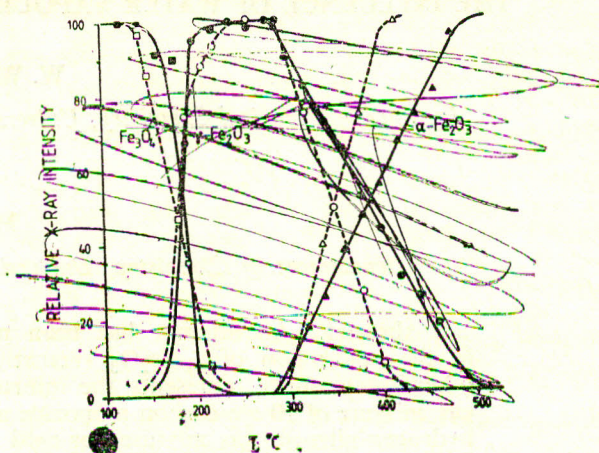


Fig. 2. Developed phases (γ - and α -Fe₂O₃) after reduction of α -Fe₂O₃ to active Fe₃O₄ which is oxidized in air. The ordinate represents the amount of phases, the abscissa shows the switching temperature from reducing to oxidizing atmosphere. Full line: water containing H₂/N₂-atmosphere, Dotted line: dry CO/N₂-atmosphere.

reduction of haematite in CO-contained atmosphere under suitable conditions leads to pure-phase magnetite without the formation of measurable amounts of wuestit Fe_{1-x}O or elemental Fe. As the reducing force of CO is smaller than that of H_2 , a longer heating time is required. In comparison with the previous reduction experiments in H_2 -contained atmosphere and subsequent air oxidation, a pure phase ferrimagnetic γ - Fe_2O_3 of recording tape quality is obtained by using CO-gas instead of H_2 , but the formation range has been contracted from 190-280° to 240-80°. This may be due to the absence of water formation as the case with is H_2 -reduction. On switching temperatures higher than the above mentioned range the quantity of undesired paramagnetic α - Fe_2O_3 is expected to be increased. Although γ - Fe_2O_3 is thermodynamically unstable as compared to α - Fe_2O_3 it will no more transform at room temperature, once it is formed. On the basis of the experiments conducted in the CO-contained atmosphere one concludes that water vapour plays no negative role in the production of γ - Fe_2O_3 by the reduction process using H_2 . But nothing can be mentioned as regards the long time stability of the maghemite so obtained, while cobalt is added as a stabilizing agent for maghemite in industry. Elder⁹ suggested that the removal of water in γ - Fe_2O_3 causes a conversion to the α -phase because bondings in the spinel lattice are broken and cation defects increase. This will happen above 450°. It is proposed that 1 H-atom per 10-20 cations will be included and an O-anion is substituted by OH^- resulting in the Brutto formula $(\text{Fe}_{20}^{+++} \square 4) (\text{OH})_4 \text{O}_{28}$ where \square represents a vacancy. The corresponding water free oxide is written as $(\text{Fe}_{21} \frac{1}{3} \square 2 \frac{1}{3}) \text{O}_{32}$.

A description of the proposed mechanism for the conversion of Fe_3O_4 to γ - Fe_2O_3 is just described by one of the authors.⁴ The formulation does not need the presence of water :

(a) With the assumption of an inverse spinel lattice :

$\text{Fe}_3\text{O}_4 \triangleq [\text{Fe}_8^{+++}]$ tetrahedric $[\text{Fe}_8^{++}\text{Fe}_8^{+++}]$ octahedric O_{32}^{--}

$\rightarrow \gamma\text{-Fe}_2\text{O}_3 \triangleq [\text{Fe}_8^{+++}]$ tetr. $[\text{Fe}_5^{+++1/3} \square 2 \frac{2}{3} \text{Fe}_8^{+++}]$ oct. O_{32}^{--}

(b) With the assumption of a normal spinel lattice :

$\rightarrow \gamma\text{-Fe}_2\text{O}_3 \triangleq [\text{Fe}_5^{+++1/3} \square 2 \frac{2}{3}]$ tetr. $\text{Fe}_8^{+++} \text{Fe}_8^{++}$ oct. O_{32}^{--}

The experiments of Weisweiler and Alavi⁴ have ascertained that this method for the production of γ - Fe_2O_3 can as well be applied on a commercial scale.

Acknowledgments

Financial assistance given by the International Seminar of the University of Karlsruhe (supported by DAAD and UNESCO) and leave for one of the authors by the University of Engineering and Technology, Lahore, are gratefully acknowledged.

References

1. S. Hilpert, J. Beyer, Ber. Deutsche Keram. Ges., **44**, 1608 (1911).
2. M. A. Geith, Amer. J. Sci., **250**, p. 677 (1952).
3. M. Camras, U. S. Pat. **2**, 694,656 (1954), in D. J. Craik (ed.), *Magnetic Oxides*, (London: Wiley, vol. 2, Chap. 12, "Oxides for Magnetic Recording") (1975).
4. W. Weisweiler and M. Alavi, Ber. Deutsche Keram. Ges., **54**, p. 268 (1977).
5. J. David and A. J. E. Welch, Trans. Farad. Soc., **52**, p. 1642 (1956).
6. F. H. Healey, J. J. Chessick and A. V. Fraioli, J. Phys. Chem., **60**, p. 1001 (1956).
7. E. J. W. Verwey, Z. Krist. **91**, p. 65 (1935).
8. A. Aharoni, *et al.*, J. Phys. Solids, **23**, p. 542 (1962).
9. T. Elder, J. Appl. Phys., **36**, p. 1012 (1965).