

## THE INFLUENCE OF WATER VAPOUR ON THE CONVERSION OF $\alpha$ - TO $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>\*

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An attempt has been made to study the significance of water vapour in the conversion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) to pure phase  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite or  $\gamma$ -hematite) which represents the information carrier for magnetic tape recording. A gas mixture of 10% carbon monoxide and 90% nitrogen instead of conventional hydrogen/nitrogen gas mixture was used as a reducing agent for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> (magnetite). Subsequently Fe<sub>3</sub>O<sub>4</sub> was oxidized by dry air to produce  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Air oxidation of freshly reduced active magnetite forms pure phase  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> while that of altered magnetite (which was exposed to atmospheric conditions and has developed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nuclei on its surface) results in the formation of a mixture of  $\gamma$ - and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. In the presence of water forming reducing gases,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was obtained at switching temperatures (i.e. changing over from reducing to oxidising atmosphere) of 190–280° whereas in the absence of water a smaller temperature range of 240–280°, was found. The results suggest that the presence of water vapour is not a necessary condition in the production of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

### INTRODUCTION

The production of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) has become extremely important due to the increased use of magnetic tapes.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is ferromagnetic as compared to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> which is paramagnetic. Recently chromium dioxide (CrO<sub>2</sub>) has been tried as an alternate material. Out of the numerous techniques [1,2] available for the production of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the dehydration of goethite ( $\gamma$ -FeOOH) at 220–250° in 2–24 hr or the direct oxidation of aqueous solutions should be mentioned. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is at first converted to magnetite (Fe<sub>3</sub>O<sub>4</sub>) by heating it in a reducing atmosphere and is then oxidized to maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). None of the known techniques [3] leads to the production of pure phase  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> except the reduction of hematite to active magnetite followed by an instantaneous air oxidation [4]. 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 Welch [5] magnetite is oxidized to maghemite only in presence of water. Similar observations have been previously made by other investigators [6,7] while Aharoni *et al.* [8] considered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a mixture of two solid

solutions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with regular imperfections on one hand and H-ferrite on the other. Elder [9] found that the oxidation of Fe<sub>3</sub>O<sub>4</sub> (particles smaller than 1  $\mu$ m dia) in dry oxygen atmosphere of 220° after 1 hr leads only to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. On the contrary in air and water vapour high percentage of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> will be obtained in addition to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The effect of water as a catalyst for this conversion is not very clear till today. Therefore for the production of pure phase  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> 10% CO and 90% N<sub>2</sub> will be used as the reduction gas instead of 10% H<sub>2</sub> and 90% N<sub>2</sub> [4], so that the formation of water as a by product is eliminated.

### EXPERIMENTAL

The starting material  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Merck, Darmstadt/W. Germany) in powder form *p.a.* was placed in thin layer in an alumina boat and then put inside a tube 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 160–310°, the waterfree-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

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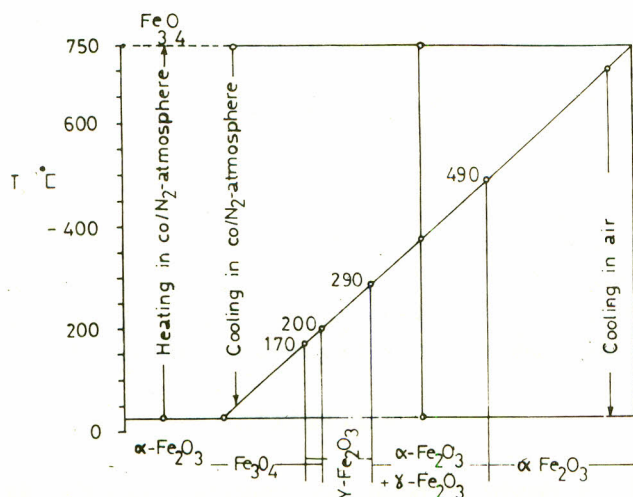


Fig. 1. Scheme of the reactions performed. Reduction of the starting material  $\alpha$ - $\text{Fe}_2\text{O}_3$  by heating it in  $\text{CO}/\text{N}_2$ -atmosphere leads to  $\text{Fe}_3\text{O}_4$  at  $750^\circ\text{C}$ .  $\text{Fe}_3\text{O}_4$  is cooled to certain temperatures (on the diagonal in the diagram) where the reducing atmosphere is switched to an oxidizing one. The reaction products are shown on the abscissa.

effective in our previous investigations [4]. The analyses of the reacted samples with respect to  $\alpha$ - $\text{Fe}_2\text{O}_3$  (input material or undesired product),  $\text{Fe}_3\text{O}_4$  (intermediate product), and  $\gamma$ - $\text{Fe}_2\text{O}_3$  (final product) were performed with the help of precision X-ray scattering. The following important reflexes were used (Table 1).

With the applied  $\text{Cu K}\alpha$ -radiation the (220)-reflex, whose intensity is fairly acceptable, was found to be optimal in order to separate  $\text{Fe}_3\text{O}_4$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$  which crystallize in the same spinel lattice. Care has to be taken to see that no  $\alpha$ -reflex coincide.

## 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 reduction of hematite in  $\text{CO}$ -contained atmosphere under suitable conditions leads to pure-phase magnetite without the formation of measurable amounts of wuestit  $\text{Fe}_{1-x}\text{O}$  or elemental  $\text{Fe}$ . As the reducing force of  $\text{CO}$  is smaller than that of  $\text{H}_2$ , longer heating time is required. In comparison to the previous reduction experiments in  $\text{H}_2$ -contained atmosphere and subsequent air oxidation, a pure phase ferrimagnetic  $\gamma$ - $\text{Fe}_2\text{O}_3$  of recording tape quality is obtained by using  $\text{CO}$ -gas instead of  $\text{H}_2$ , but the formation range has been contracted from  $190$ – $280^\circ$  to  $240$ – $280^\circ$ . This may be due

Table 1. Important X-ray reflexes (hkl) of iron oxides (without intermediate phases [4],  $\text{Cu K}\alpha$ -radiation relative intensities  $I/I_0$  along with lattice spacings  $d$ .

substance	hkl	$d, \text{\AA}$	$I/I_0$
$\text{Fe}_3\text{O}_4$	311	2,53	100
	440	1,49	40
	220	2,97	30
"	111	4,85	8
	<hr/>		
$\gamma$ - $\text{Fe}_2\text{O}_3$	311	2,52	100
	440	1,48	53
	220	2,95	34
"	110	5,90	2
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$\alpha$ - $\text{Fe}_2\text{O}_3$	104	2,703	100
	110	2,52	70
"	116	1,70	36

to the absence of water formation as it is the case with  $\text{H}_2$ -reduction. At switching temperatures higher than the above mentioned range the quantity of undesired paramagnetic  $\alpha$ - $\text{Fe}_2\text{O}_3$  is expected to be increased. Although  $\gamma$ - $\text{Fe}_2\text{O}_3$  is thermodynamically unstable as compared to  $\alpha$ - $\text{Fe}_2\text{O}_3$

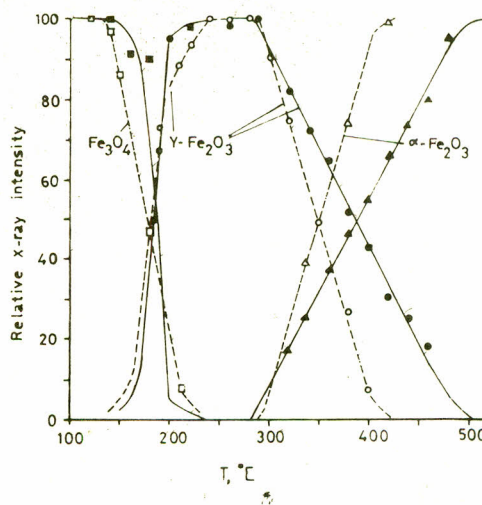


Fig. 2. Developed phases ( $\gamma$ - and  $\alpha$ - $\text{Fe}_2\text{O}_3$ ) after reduction of  $\alpha$ - $\text{Fe}_2\text{O}_3$  to active  $\text{Fe}_3\text{O}_4$  which is oxidized in air. The ordinate represents the amount of phases, the abscissa shows the switching temperature from reducing to oxidizing atmosphere. Full line: water containing  $\text{H}_2/\text{N}_2$ -atmosphere, dotted line: dry  $\text{CO}/\text{N}_2$ -atmosphere.

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 can come to the conclusion that water vapour plays no negative role in the production of  $\gamma$ - $\text{Fe}_2\text{O}_3$  by the reduction process using  $\text{H}_2$ . 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. Elder [9] suggested that the removal of water in  $\gamma$ - $\text{Fe}_2\text{O}_3$  causes a conversion to the  $\alpha$ -phase because bondings in the spinel lattice are broken and cation defects increase. This will happen above  $450^\circ$ . It is proposed that 1 H-atom per 10–20 cations will be included and an O-anion is substituted by  $\text{OH}^-$  resulting in a 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  $(\text{Fe}_{21}^{1/3} \square_2^{1/3})\text{O}_{32}$ .

A description of the proposed mechanism for the conversion of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  is just described by one of the authors [4]. The formation do not need the presence of water:

(a) with the assumption of an inverse spinel lattice  $\text{Fe}_2\text{O}_4 \triangle \text{Fe}_8^{+++}$  tetrahedric  $\text{Fe}_8^{++}\text{Fe}_8^{+++}$  octahedric  $\text{O}_{32} \rightarrow \gamma\text{-Fe}_2\text{O}_3 \triangle [\text{Fe}_8^{+++}]$  tetr.  $[\text{Fe}_5^{++} \frac{1}{3} \square_2 \frac{2}{3} \text{Fe}_8^{+++}]$  oct.  $\text{O}_{32}$

(b) with the assumption of a normal spinel lattice  $\rightarrow \gamma\text{-Fe}_2\text{O}_3 \triangle [\text{Fe}_5^{+++} \frac{1}{3} \square_2 \frac{2}{3}]$  tetr.  $\text{Fe}_8^{+++} \text{Fe}_8^{++}$  oct.  $\text{O}_{32}$

The experiments of Weisweiler and Alavi [4] have ascertained, that this method for the production of  $\gamma$ - $\text{Fe}_2\text{O}_3$  can as well be applied in a commercial scale.

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