THERMAL REACTIONS OF INORGANIC HYDROXY-COMPOUNDS UNDER APPLIED ELECTRIC FIELDS

IV. DEHYDRATION OF AMORPHOUS IRON(III)HYDROXIDE

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The effect of electric fields on the thermal dehydration of amorphous hydrated iron(III) oxide under oxidizing, inert and reducing atmospheres was studied by X-ray diffractometry. In oxidizing and inert atmospheres, the transformation to α-Fe_2O_3 was enhanced by electric fields, especially at the negative electrode. The crystallite size of the product was also greatest at the negative electrode. Both results are explained in terms of the migration of protons to the negative electrode, where they subsequently form water which acts as a nucleating agent for the crystalline phase. In reducing atmospheres the formation of Fe_3O_4 and FeO at the expense of Fe_2O_3 is facilitated by electric fields, particularly at the negative electrode. Possible reaction mechanisms are considered, and the role of protons in stabilizing defect-spinel intermediates and products is discussed.

In previous papers [1, 2] it was reported that the dehydroxylation of compounds such as $Mg(OH)_2$ and kaolinite ($Al_2Si_2O_5(OH)_4$) occurs at lower temperatures and with decreased activation energies when carried out under the influence of d.c. electric fields. Similar effects have been observed in studies on the dehydration of pseudoboehmite (a poorly crystalline hydrous aluminium oxyhydroxide), in which both the reaction rate and crystallite size of the product are increased under the influence of d.c. electric fields [3]. On the other hand, electrolysis was found to have little or no effect on the dehydroxylation of crystalline $Al(OH)_3$ [2]. The question therefore arises as to whether the crystallinity of the reactant hydroxide is an important factor in determining the role of applied electric fields in dehydration and dehydroxylation reactions. A study of the effect of electrolysis on the thermal decomposition of a fully amorphous hydrated material would provide useful additional information on this matter.

A further interesting question which has not so far been addressed in electrolysis studies concerns the behaviour of variable-valence compounds in the vicinity of the electrodes, in particular, whether oxidation or reduction might be initiated or facilitated by the electric field.

One compound whose study could provide information on both these questions is amorphous iron III hydroxide. Previous workers [4] have reported that this compound dehydrates progressively to form amorphous Fe_2O_3 which exothermically crystallizes in the α-form at about 270° under reduced pressure [5], or 430°

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in air [6]. Gas evolution studies at reduced pressures [5] suggest that the step-wise dehydration proceeds with the formation of amorphous intermediate hydrates of definite composition. The crystallization of α-Fe_2O_3 occurs before dehydration is complete, but previous workers are vague as to whether the crystallized product is a hydrated oxide (Berg et al. [5] describe it as the hemihydrate 2 $Fe_2O_3.H_2O$), or a mixture of the anhydrous oxide with an amorphous hydroxide [6] (the latter suggestion apparently follows from the observation that a final small weight loss occurs at about 940° in air [6]). As with all thermal studies of iron compounds, strict atmosphere control is essential, although no previous work has been reported on the effect of the oxygen potential of the reaction atmosphere on the products of the dehydration. For this reason, the present studies were carried out under oxidizing, inert and reducing conditions.

Experimental

Materials. The amorphous hydrous oxide was precipitated with ammonia from solutions of ferric nitrate heated to 60°. Vigorous stirring and an excess of ammonia ensured the suppression of basic salts. The product was washed well at the filter and oven dried at 60°. X-ray examination did not reveal any crystalline phase. Thermogravimetry in air at a heating rate of 2.5°/min showed a two-stage weight loss, the first plateau at 400° corresponding to a 23.5% weight loss, with a further loss of 1.7% up to 1000°.

The theoretical weight loss for the reaction

$$2 \text{ Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3 \text{ H}_2\text{O} \tag{1}$$

is 25.23%, but the agreement between this and the observed total weight loss may be merely fortuitous.

Electrolysis experiments. The electrolyses were carried out in two types of cell. Those in air and oxygen-free-nitrogen were made in a boat-type cell described elsewhere [7], while those in H_2/N_2 were made in an X-ray electrolysis cell used in conjunction with a Stone XR−6 X-ray furnace attachment which allowed simultaneous X-ray examination of the products [8]. The X-ray cell is more convenient for studies of the present nature, but the sample thickness ($\sim$2 mm) is much smaller than in the boat-type cell ($\sim$5 mm) and in the present system, arcing occurred under air and nitrogen atmospheres in the thinner samples. The X-ray cell could therefore only be used for experiments in H_2/N_2 atmospheres, which appeared to suppress arcing in the samples, possibly by changing the sample resistance.

The experiments in nitrogen were performed by packing the cell tightly with the sample powder, placing the platinum mesh upper electrode in position and introducing the assembly into a tube furnace inside a fused quartz tube through

which the flowing gas atmosphere (2.5 ml·s^{-1}) had been established. The experiments in air were similar except that the atmosphere was static. The electrolysis voltage was obtained from a Brandenburg model 475R EHT power supply. Experiments were performed at temperatures between 100 and 700° with the top electrode at both negative and positive polarity. Control experiments were also made without the electric field. After electrolysis, the cell was withdrawn from the furnace, cooled under the gas atmosphere, and the layer of sample immediately adjacent to the electrode taken for X-ray examination.

The electrolysis technique in the X-ray cell was slightly different, the sample being rapidly heated to the required temperature under the flowing gas atmosphere, the electrolysing voltage established, and the X-ray diffractometer set to scan over the region of interest after the appropriate electrolysis time lapse. The sample temperature was then raised, and the procedure repeated. The total electrolysis time at each temperature was similar to that used in the boat-cell experiments (0.5 h). The temperature calibration of the X-ray cell was established using the known expansion characteristics of the MgO lattice, as previously described [8].

X-ray analytical technique. The samples taken from the boat-cell for room-temperature X-ray examination were analyzed for Fe_2O_3 using 10% by weight of rutile as an internal standard. The samples were also examined for all other possible iron-oxygen phases, but apart from very small traces of maghemite (γ-Fe_2O_3) at lower temperatures, no other phase was detected. The crystallite size of the α-Fe_2O_3 was estimated from the X-ray line width of the 104 peak ($d = 2.69$ Å) by the standard procedure [9].

The X-ray analytical method for the experiments in the X-ray cell was complicated by the presence of at least three phases, and the nature of the experiment, which prevented the use of an internal standard. The best compromise was to measure the absolute intensities of the major peak of each phase, making an approximate conversion to relative percentages by comparison with the intensities of the pure phases measured under the same conditions. This conversion to phase percentages assumes that the calibration curve for each phase is linear over the composition range of interest, as is certainly the case with α-Fe_2O_3. The method also assumes that the X-ray beam intensity and disposition of the sample in the beam is constant for each experiment. Since only one sample is used for each set of experiments, the results should be reasonably internally comparable, despite slight changes in the disposition of the sample caused by shrinkage during dehydration.

Results and discussion

Oxidizing and inert atmosphere

Plots of percentage α-Fe_2O_3 are shown as a function of the reaction temperature for oxidizing and inert atmospheres in Figs 1 and 2, respectively.

Under both atmospheres the greatest percentage of crystalline product is formed at the negative electrode at all temperatures, consistent with the behaviour of

of other proton-containing systems [3, 10]. The percentage of crystalline phase at the positive electrode, although less than at the negative electrode, is greater than in the unelectrolyzed control, except at higher temperatures in flowing nitrogen. The fact that the crystallization of Fe_2O_3 is sensitive both to electric
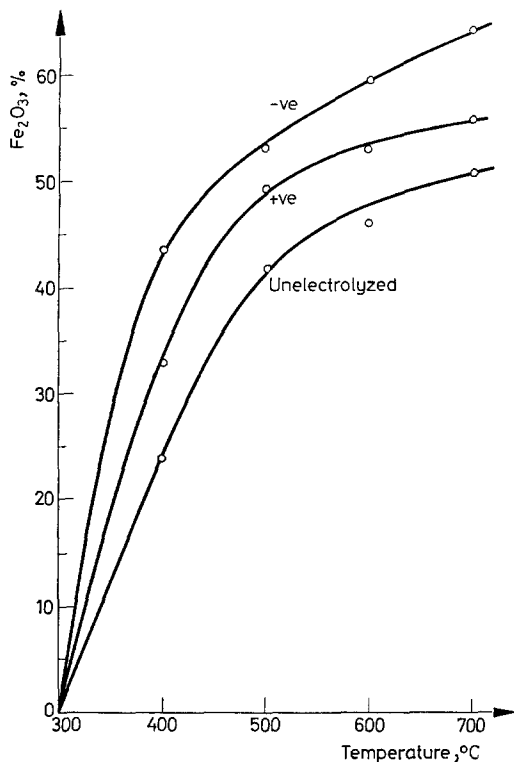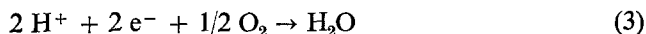

Fig. 1. Development of α-Fe_2O_3 from amorphous iron(III) hydroxide as a function of temperature in static air atmosphere. Field strength $= 1.6 \times 10^5$ V/m, Reaction time $= 0.5$ h

fields and the nature of the atmosphere (i.e. whether flowing or static) suggests that the crystallization process requires the removal of a certain amount of hydration water for its initiation, but also that the presence of a certain amount of residual water is beneficial (probably to assist nucleation processes in the reactant). The unelectrolyzed reaction can be written:

$$Fe_2O_3 \cdot 3 H_2O \rightarrow Fe_2O_3 \cdot nH_2O + (3 - n)H_2O \qquad (2)$$
$$\text{(amorphous)} \qquad \text{(crystalline)}$$
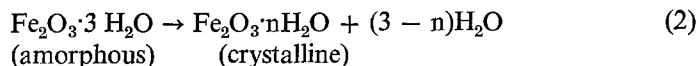
Under electric fields, protons from the hydration water will migrate to the cathode, where, under oxidizing conditions, the following electrode reaction would be expected:

$$2 H^+ + 2 e^- + 1/2 O_2 \rightarrow H_2O \qquad (3)$$

A competing electrode reaction involving iron can also be written:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{4}$$

Comparison of the standard electrode potentials for reactions (3) and (4) indicate that the standard free energy associated with reaction (3) is $- 237.2$ kJ/mole, whereas that for reaction (4) is only 74.3 kJ/mole. Thus, the formation
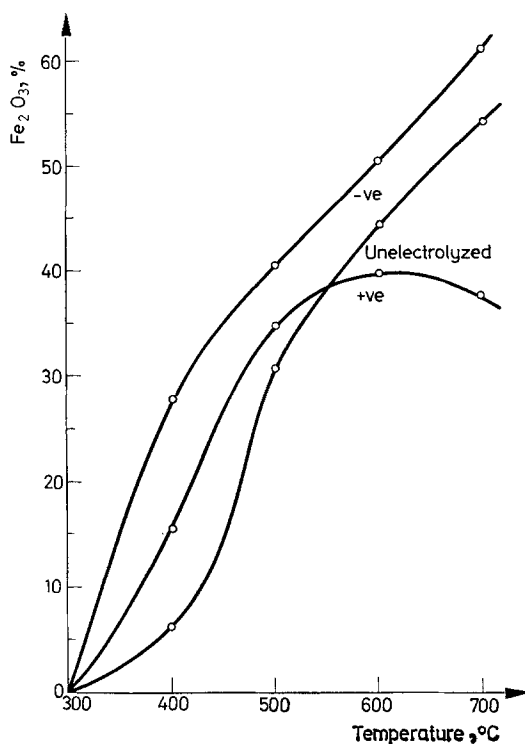

Fig. 2. Development of α-Fe_2O_3 from amorphous iron(III) hydroxide as a function of temperature in flowing oxygen-free-nitrogen (2.5 ml $\cdot$ s^{-1}). Field strength = 1.6×10^5 V/m, Reaction time = 0.5 h

of water should be the preferred cathodic reaction under these conditions. It should be noted that migration of protons to the cathode implies depletion of this species from other regions of the sample, leading to enhanced dehydration throughout the bulk. The increased water concentration in the immediate vicinity of the cathode will, however, enhance nucleation of the crystalline phase in that region.

The results obtained under flowing inert atmospheres (Fig. 2) require comment. The effect of the field will again be to assist migration of protons to the cathode, where they will be discharged as water:

$$H^+ + OH^- \rightarrow H_2O \tag{5}$$

However, this is not an electrode reaction, and can occur anywhere within the sample bulk; the increased concentration of protons at the cathode merely increases the probability that reaction (5) will occur in that region. True electrolytic water formation (reaction 3) depends on the availability of oxygen, and is therefore, of limited significance under inert conditions.
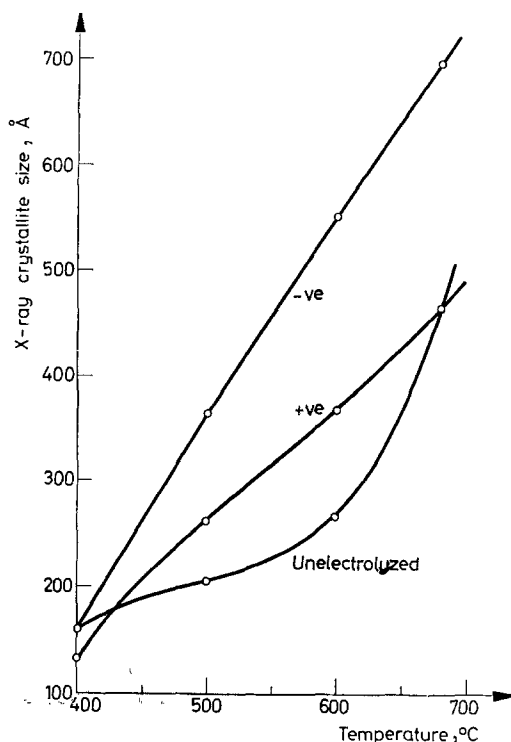

Fig. 3. X-ray crystallite size of α-Fe$_2$O$_3$ as a function of temperature in static air atmosphere. Field strength $= 1.6 \times 10^5$ V/m, Reaction time $= 0.5$ h

The decreased degree of crystallization observed at the anode under flowing nitrogen might be explained in terms of the depletion from that region of water vapour required for nucleation, by the combined action of the electrolysis process and the flowing atmosphere. At higher temperatures, both the efficiency of the thermal processes leading to dehydration and the mobilities of the residual protons are increased. Depletion of water vapour from the anode, reinforced by the action of the flowing atmosphere, should interfere with the nucleation of crystalline Fe$_2$O$_3$ at the anode under these conditions.

Results of the crystallite size determinations of the product are shown in Figs 3 and 4 for oxidizing and inert atmospheres respectively.
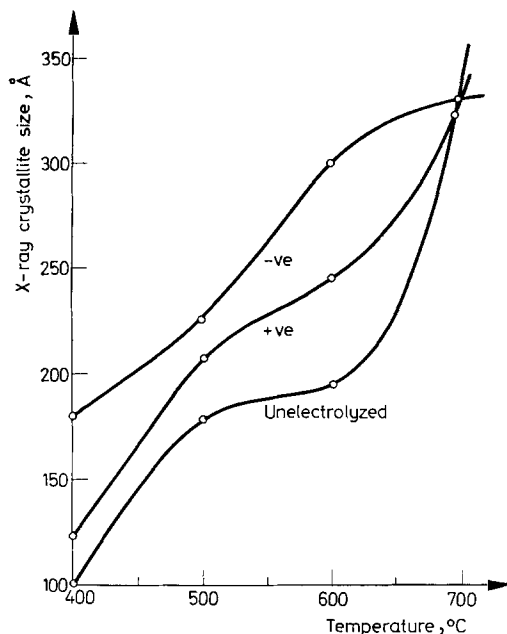

Fig. 4. X-ray crystallite size of α-Fe$_2$O$_3$ as a function of temperature in flowing oxygen-free-nitrogen (2.5 ml $\cdot$ s^{-1}). Field strength = 1.6× 10^5 V/m, Reaction time = 0.5 h

The following points emerge:

(i) In all cases the crystallite sizes increase with temperature as would be expected.

(ii) The crystallites at the cathode are generally larger than those in the unelectrolyzed samples.

(iii) Crystallite growth in inert flowing atmospheres is retarded by comparison with static air atmospheres, especially at the cathode.

These results are fully consistent with a crystallite growth mechanism in which water vapour plays an essential role, probably by proton attack on metal–oxygen bonds. Similar observations have been made in other protonated oxides, e.g. Mg(OH)$_2$ [8].

The efficiency of the electrolysis process in promoting crystallization and grain growth appears to be in no way reduced by the amorphous nature of the starting material. It may be that the movements of migrating species are less hampered where there are no rigid structural units to impose a structural "memory" on the system, as is probably the case with crystalline Al(OH)$_3$ [2].

Reducing atmospheres

The results for reducing atmospheres are shown in Fig. 5, from which it is seen that electrolysis under these conditions markedly influences the phase composition of the samples at various temperatures. Moreover, although the electrolyzed results at the anode and cathode are formally similar, the temperatures at which the various phases appear and disappear differ significantly at the two electrode faces.
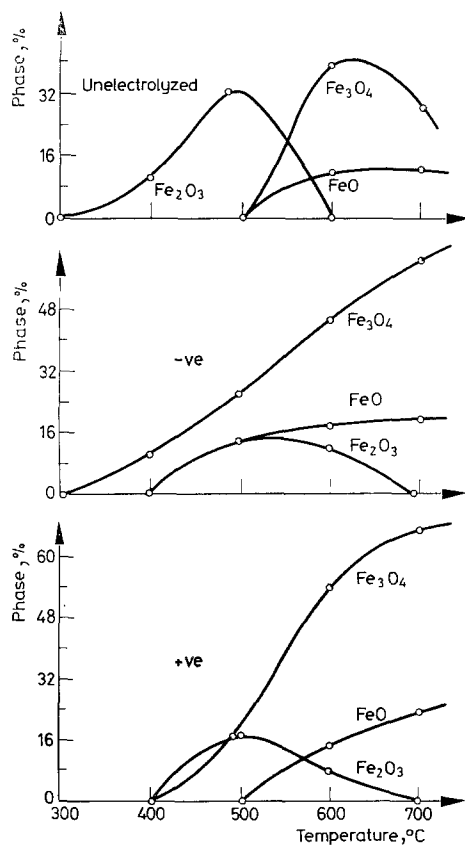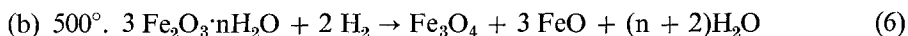

Fig. 5. Development of oxide phases from amorphous iron(III) hydroxide as a function of temperature in flowing H_2/N_2 (5%/95%) atmosphere (2.5 ml · s^{-1}). Field strength = = 5.0× 10^5 V/m. Reaction time at each temperature = 0.5 h

The unelectrolyzed results (Fig. 5A) show that hematite is the first phase to be formed, appearing at similar temperatures to the experiments in oxidizing and inert atmospheres. At higher temperatures (750°) some reduction sets in, with magnetite (Fe_3O_4) and wustite (FeO) being formed at the expense of hematite. The formation of the mixed-valence oxide magnetite is more pronounced at lower
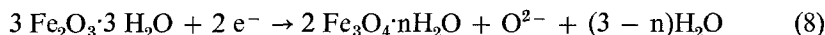
temperatures, but at higher temperatures, further reduction results in an increase of wustite at the expense of magnetite. These results may be summarized as follows:

(a) 300°. Dehydration according to equation (2).

(b) 500°. $3 Fe_2O_3 \cdot nH_2O + 2 H_2 \rightarrow Fe_3O_4 + 3 FeO + (n + 2)H_2O$ $\qquad$ (6)

(c) 600°. $Fe_3O_4 + H_2 \rightarrow 3 FeO + H_2O$ $\qquad$ (7)

Under electrolysis, reduction occurs at the anode simultaneously with the crystallization of hematite, while at the cathode, the appearance of the reduced phase precedes the formation of hematite by at least 100°. Moreover, the appearance of the fully reduced oxide wustite occurs at the cathode at temperatures at least 100° lower than at the anode. Thus, the reduction processes occurring under reducing atmospheres are markedly accelerated at the cathode, suggesting that at this electrode, chemical reduction is reinforced by electroreduction (Eq. 4). The primary crystallization appears to be preceded (or accompanied) by reduction:

$$3 Fe_2O_3 \cdot 3 H_2O + 2 e^- \rightarrow 2 Fe_3O_4 \cdot nH_2O + O^{2-} + (3 - n)H_2O \qquad (8)$$

The appearance of a small amount of Fe_2O_3 at $\sim 500°$ is probably due to the increase at that temperature of the dehydration rate, which temporarily exceeds the rate of reduction; at higher temperatures Fe_3O_4 and/or FeO is formed at the expense of this Fe_2O_3. This cathodic electroreduction should proceed irrespective of whether the Fe_2O_3 formed at 500° is hydrated or not.

At the anode, the electrode reaction is in opposition to the effect of the atmosphere. Figure 5 shows, however, that the nett result at this electrode is very similar to the result in the absence of the field (Fig. 5A), suggesting that electro-oxidation is a second-order effect compared with the atmospheric reduction. It should be noted, however, that Fe_3O_4 is formed under anodic electrolysis conditions at temperatures at least 100° lower than in the unelectrolyzed control. One possible explanation might be the effect of the field on the anion structure of the reactant and product phases. The hematite formed initially in the unelectrolyzed control has a hexagonal array, whereas the defect spinel phase Fe_3O_4 formed under electrolysis either preferentially (as at the cathode) or concomitantly (as at the anode) has a cubic oxygen lattice. The energy involved in the transformation of the oxygen lattice from the hexagonal to cubic can be estimated as follows:

At 550°, the free energy of the reaction

$$3 Fe_2O_3 \rightarrow 2 Fe_3O_4 + 1/2 O_2 \qquad (9)$$
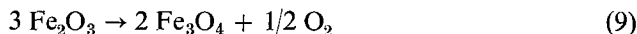
is $+122.5$ kJ/mole, from standard thermodynamic tables. This energy includes the energy involved in the reduction of two moles of Fe^{3+} to Fe^{2+}, the oxidation of one mole of oxide ion to oxygen, and the difference between the lattice energies

of the hexagonal and cubic oxide phases. The energy involved in Fe^{3+} reduction (at room temperature) is, from the standard electrode potential, known to be -148.6 kJ/mole, but the energy involved in oxide ion oxidation is harder to estimate. An approximate idea of this value is given by the room-temperature heat-of-formation, giving an estimate for the enthalpy of the reaction

$$O^{2-} - 2\,e^- \rightarrow 1/2\,O_2 \qquad (10)$$

of -949 kJ/mole [11]. The energy of the overall redox step is therefore about -1100 kJ/mole. The difference between this energy and that of reaction (9) approximately represents the change in lattice energy when the hexagonal-to-cubic transition occurs. The difference in lattice energies between these two phases is large (600 kJ/mole Fe_3O_4), and reflects a preference for the hexagonal phase, in the absence of a field. From energetic considerations it therefore appears that the effect of electrolysis on the anion structure is more likely to be due to the reduction of the iron, which necessitates a structural change, than to the effect of the field on the anions themselves. However, the above calculations refer to anhydrous systems, and the situation may be rather different in the presence of protons, which can stabilize defect spinel structures [12]. Bearing in mind that small amounts of maghemite (a defect spinel containing only Fe^{3+}) were found in the lower-temperature samples reacted in air, it seems possible that even in non-reducing situations, the reaction proceeds via spinel phases, which can be proton stabilized at the cathode (and conversely, destabilized at the anode by electrolysis of protons away from that region). If, under reducing conditions, anodic destabilization of maghemite is accompanied by reduction of some Fe^{3+} to form the more stable Fe_3O_4, this would explain both the lack of maghemite and the increased Fe_3O_4 content observed at the anode at lower temperatures in H_2/N_2 atmospheres.

Conclusions

1. In both oxidizing and inert atmospheres, the thermal crystallization of amorphous hydrated iron III oxide to α-Fe_2O_3 is enhanced by applied electric fields, particularly at the cathode The crystallite size of the α-Fe_2O_3 is greatest at the cathode, under both oxidizing and inert conditions.

2. These results are consistent with the effects of electrolysis of protons to the negative electrode, where they re-combine with hydroxyl ions to form water. This water assists both the nucleation of the crystalline phase and the growth of crystallites in the cathode region.

3. In reducing atmospheres, electric fields promote the formation of Fe_3O_4 and FeO at the expense of Fe_2O_3. The relative phase concentrations and formation temperatures are different at the negative and positive electrodes. At the cathode, electrolysis reinforces the effect of the atmosphere, leading to the formation of

Fe_3O_4 during initial dehydration; whereas at the anode, electrolysis tends to oppose atmospheric reduction.

4. Electric fields may also influence changes in the anion lattice which accompany reduction, by proton stabilization of defect spinel structures at the cathode (or destabilization of these structures at the anode).

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References

1. K. J. D. MacKenzie, J. Thermal Anal., 5 (1973) 5.
2. K. J. D. MacKenzie, J. Thermal Anal., 5 (1973) 19.
3. K. J. D. MacKenzie, Thermochim. Acta, 16 (1976) 1.
4.a. G. F. Huttig and H. Garside, Z. Anorg. Chem., 179 (1929) 49.
4.b. E. Ya. Rode, Zh. Russ. Fiz. Khim. Obshch., 62 (1930) 1443.
5. L. G. Berg, K. P. Pribylov, V. P. Egunov and R. A. Abdurakmanov, Russ. J. Inorg. Chem., 14 (1969) 1211.
6. E. P. Tsymbal, S. I. Smyshlyaev and L. M. Dvornikova, Russ. J. Inorg. Chem., 15 (1970) 1635.
7. K. J. D. MacKenzie, Trans. J. Brit. Ceram. Soc., 74 (1975) 121.
8. K. J. D. MacKenzie and P. J. Melling, Thermochim. Acta, 9 (1974) 389.
9. I. F. Guilliatt and N. H. Brett, J. Brit. Ceram. Soc., 6 (1969) 56.
10. K. J. D. MacKenzie, R. Smits and P. J. Melling, Trans. J. Brit. Ceram. Soc., 73 (1974) 185.
11. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, N. Y., 1962, p. 270.
12. K. J. D. MacKenzie, Trans. J. Brit. Ceram. Soc., 72 (1973) 209.

Résumé — L'effet d'un champ électrique sur la déshydratation thermique de l'oxyde de fer(III) hydraté amorphe a été étudié par diffractométrie des rayons X, dans des atmosphères oxydante, inerte et réductrice. En atmosphères oxydante et inerte, le champ électrique facilite la transformation en α-Fe_2O_3, en particulier à l'électrode négative. La taille des cristaux formés est également plus élevée à l'électrode négative où il se forme de l'eau qui agit comme agent de nucléation de la phase cristalline. En atmosphère réductrice, le champ électrique facilite la formation de Fe_3O_4 et FeO, aux dépens de Fe_2O_3, en particulier à l'électrode négative. On considère les mécanismes de réaction possibles et on discute le rôle des protons sur la stabilisation des produits et des intermédiaires défauts-spinelles.

Zusammenfassung — Der Einfluß eines elektrischen Feldes auf die thermische Dehydratisierung des amorphen hydratisierten Eisen(III)oxids in oxidierenden, inerten und reduzierenden Atmosphären wurde durch Röntgendiffraktometrie untersucht. In oxidierenden und inerten Atmosphären wurde die Umwandlung zu α-Fe_2O_3 durch elektrische Felder gefördert, besonders an der negativen Elektrode. Die Form der Kristallite des Produkts war ebenfalls an der negativen Elektrode am größten. Beide Ergebnisse werden durch die Proteinwanderung zur negativen Elektrode erklärt, wo diese Wasser bilden, das für die kristalline Phase als Keimbildner fungiert. In reduzierenden Atmosphären wird die Bildung von Fe_3O_4 und FeO auf Kosten von Fe_2O_3 durch elektrische Felder besonders an der negativen Elektrode erleichtert. Mögliche Reaktionsmechanismen werden erörtert und die Rolle der Protonen bei der Stabilisierung defekt-spineller Zwischenstufen und Produkte besprochen.

Резюме — С помощью рентгено-диффрактометрии изучено влияние электрического поля на термическую дегидратацию гидроокиси железа(III) в окислительной, инертной и восстановительной атмосфере как среде. В окислительной и инертной атмосферах превращение до α-Fe_2O_3 увеличивалось электрическим полем, особенно на отрицательном электроде. Размеры кристаллитов этого продукта были наибольшими также на отрицательном электроде. Оба результата были объяснены на основе миграции протонов к отрицательному электроду, где они впоследствии образуют воду, которая действует как кристаллизационное средство для кристаллической фазы. В восстановительной атмосфере образование Fe_3O_4 и FeO за счет Fe_2O_3 облегчается электрическим полем и особенно на отрицательном электроде. Рассмотрен возможный механизм реакций и обсуждена роль протонов в стабилизации промежуточных продуктов с дефектной шпинельной структурой, а также конечных продуктов.