Journal of Thermal Analysis, Vol. *17 (1979) 495–500*

THERMAL TRANSFORMATIONS OF THE ORIGINALLY AMORPHOUS $Zn^{II}_xFe^{III}_{1-x}(OH)_{3-x}$ SYSTEM

W. WOLSKI and J. KACZMAREK

Magnetochemistry Department of Adam Mickiewicz University, Poznan, Poland

(Received January 22, 1979)

On the basis of X-ray identification and studies of magnetic properties, it has been found that coprecipitated hydroxides of iron(III) and zinc(II) transform, after being boiled in distilled water, into a mixture of hydrated oxides, the ferromagnetic modification of iron(III) oxide, γ-Fe_2O_3, being responsible for the ferromagnetic behaviour of the mixture. The highest specific magnetization value is obtained for the stoichiometry $ZnO : Fe_2O_3 = 0.275 : 0.725$.

Since for spinel stoichiometry, $Zn(OH)_2/2\ Fe(OH)_3$, the magnetic property drops to near zero, formation of zinc ferrite cannot be excluded. However, the poor crystalline shape of this phase, as usually happens when the technique adopted here is involved, does not allow direct confirmation of the existence of that phase by diffraction methods.

Coprecipitation at room temperature of iron(III) and Zn(II) hydroxides yields gelatinous amorphous flakes, in spite of the crystalline character of $Zn(OH)_2$. When the system is stored at moderately elevated temperatures or boiled under reflux in distilled water, according to some authors it is transformed into a crystalline oxide, namely the corresponding zinc ferrite, $ZnFe_2O_4$ [1–3].

Our investigations on systems involving other divalent cations suggested a rather more complicated picture of alterations, until the thermally stable phase, i.e. the spinel ferrite, MFe_2O_4, was reached [4, 5].

Results given below indicate that examinations with appropriate identification methods of ageing products covering the whole range of stoichiometries and not just that of the spinel, $Zn(OH)_2$:2 $Fe(OH)_3$, reveal some distinctive features of this system, manifesting for some specific stoichiometry the presence of a metastable ferromagnetic iron oxide, maghemite.

Experimental

An aqueous solution of the nitrates (0.25 *M*) of iron(III) and zinc(II), mixed in ratios appropriate for the planned composition and in quantities sufficient for a total yield of hydroxide mixture of approximately 2 g (calculated as oxides), was alkalified with 1 *M* sodium hydroxide, added under agitation until pH = 8.4 was reached.

In series "A" the precipitated mixture of amorphous hydroxides was thoroughly washed from accompanying ions, then placed in conical flasks, supplemented with distilled water to approximately 200 ml and boiled for 5hrs under reflux. The samples were dried in air and subjected to further examinations. In series "B" the hydroxides precipitated in a similar manner were first boiled and only then washed from ions.

The preparations were chemically analyzed and examined by means of X-ray diffraction using a TUR-M-61 X-ray diffractometer, with CoK_α.

Measurements of the specific magnetization at 25° were carried out on a magnetic balance for ferromagnetics designed in our laboratory. Samples exhibiting maximum specific magnetization were heated for 24 hrs at 50° intervals in the range 100–700° and identified as above.

Results and discussion

After being boiled under the conditions described amorphous Fe(III) hydroxide is transformed, in accordance with previous observations [6, 7], into a two-phase system (Fig. 1, diffr. 1), i.e. goethite (α-FeOOH) with the strongest (011) and (111) peaks (at 4.17 Å and 2.43 Å, respectively), and hydrohematite (α-$Fe_2O_3 \cdot x\,H_2O$) characterized by the remaining peaks (those with interplanar distances d = 2.68 Å and 2.51 Å occur in both phases under examination).

As is seen from pattern 2, for the composition ZnO : Fe_2O_3 = 0.1 : 0.9 the goethite phase disappears, leaving only hydrohematite. Higher ZnO concentrations hamper the crystallization almost completely, so that hydrohematite disappears as

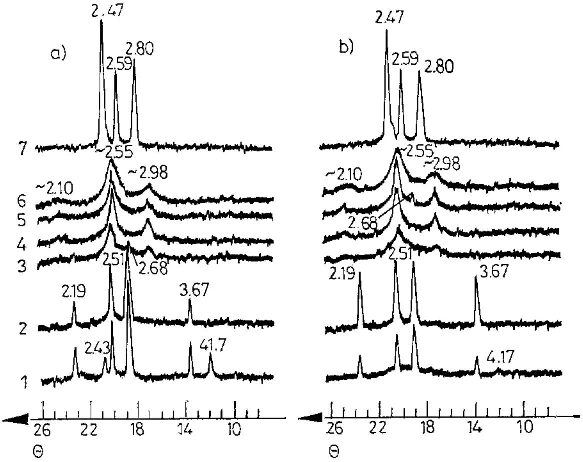

Fig. 1. X-ray patterns of the ageing products of coprecipitated hydroxides $Zn(OH)_2/Fe(OH)_3$ with the stoichiometry ZnO : Fe_2O_3 = (1) 0.000 : 1.000; (2) 0.100 : 0.900; (3) 0.200 : 0.800; (4) 0.275 : 0.725; (5) 0.300 : 0.700; (6) 0.500 : 0.500; (7) 1.000 : 0.000

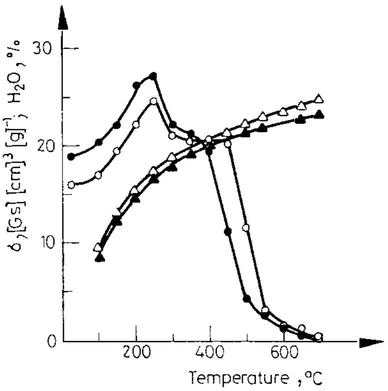

Fig. 2. Specific magnetization ($\sigma_{25°}$) and loss of water of the preparation with the stoichiometry ZnO : Fe_2O_3 = 0.275 : 0.725 as a function of heating at various temperature. Curves with empty points — series *A*; curves with shaded points — series *B*

well. The best then crystallized sample stems from the ratio ZnO : Fe_2O_3 = 0.275 : : 0.725 (pattern 4), though we might expect this to happen in the vicinity of spinel stoichiometry, ZnO : Fe_2O_3 = 0.5 : 0.5, as is the case with other cations [4, 5].

The broad peak at $d \approx 2.95$ Å should be related to the (220) plane, the higher one at $d \approx 2.53$ Å to the (311) plane, and the small one at $d \approx 2.10$ Å to the (400) plane, characteristic for $ZnFe_2O_4$, ferrite or maghemite. The fact that at such low temperatures the crystalline spinel phases are in the form of small crystallites makes it impossible here to make use of minute differences in parameters between MFe_2O_4 and γ-Fe_2O_3 ($\approx$ 0.05 Å).

Preparations with the ZnO : Fe_2O_3 ratio = 0.275 : 0.725, heated at elevated temperatures, yield magnetization curves (Fig. 2). Which can be interpreted as follows: due to the occurrence of maghemite formed during ageing, the magnetization initially increases at the cost of water loss and growth of crystallites, giving a maximum at 250° (in both washed-boiled and boiled-washed preparations). In the range 250–300° σ decreases, demonstrating the metastable nature of γ-Fe_2O_3, however, this trend is stopped and instead of transformation into the antiferromagnetic α-Fe_2O_3, as would be the case without the presence of ZnO, stabilization by zinc ions takes place, the phase being maintained up to 500° for the preparation first washed and then boiled, and up to approx. 450° for the sample prepared in the reverse order. Heating at higher temperatures causes a rapid loss of magnetization, because of the formation of zinc ferrite and α-Fe_2O_3.

Taking into account that the sample of original composition ZnO : Fe_2O_3 = = 0.275 : 0.725, after being boiled and dried in air, contains approx. 25 % H_2O and a considerable amount by weight of ZnO, the specific magnetization found should be recognized as very high, though somewhat smaller than for the quantitative transformation of amorphous $Fe(OH)_3$ into γ-Fe_2O_3. Figure 3 displays the crystalline phase state of the sample (washed-boiled) with this ratio ZnO : Fe_2O_3 =

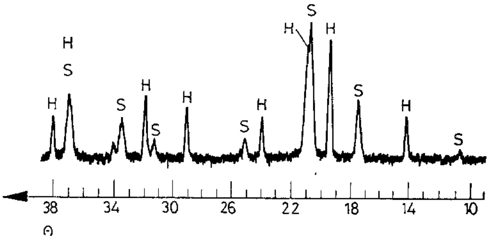

Fig. 3. X-ray pattern of a preparation with the stoichiometry ZnO : Fe_2O_3 = 0.275 : 0.725, heated at 550°. S = spinel phase; H = hematite phase

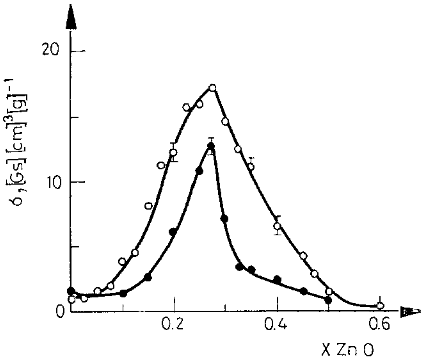

Fig. 4. Specific magnetization ($\sigma_{25°}$) of the ageing products $Zn(OH)_2/Fe(OH)_3$ as a function of the ZnO ratio. Curves with empty cricles — series A; curves with shaded circles — series B. Vertical lines show the range of the average deviation of a single determination from the mean for 10 measurements

= 0.275 : 0.725, heated at 550°; it is seen that only at temperatures > 500° does zinc ferrite start to be identifiable. The peak at $\theta \approx 20°48'$ is in fact the superposition of two peaks: d_{311} = 2.53 Å at 20°42′ of zinc ferrite and d_{110} = 2.51 Å at 20°48′ of hematite. There are thus visible two phases, *viz.* hematite and a spinel phase, this time without accompanying ferromagnetic properties.

In Fig. 4, where the specific magnetizations are presented as a function of ZnO content, the sharpness with which the sample reaches its maximum indicates just how favourable for the direction of ageing towards γ-Fe_2O_3 is this particular stoichiometry ZnO : Fe_2O_3 = 0.275 : 0.725. For samples with spinel stoichiometry (0.5 on the concentration axis), in both washed- boiled and boiled–washed cases the magnetization drops nearly to zero, while X-ray diffraction reveals almost the same pattern as that with the highest value of σ.

The small crystallites, causing extensive broadening of the lines, wreck any hopes of resolving all three lines recorded into those belonging to zinc ferrite and those belonging to maghemite (Fig. 1, diff. 4).

On the basis of X-ray analysis and studies of the magnetic properties of the samples for the whole range of $xZn(OH)_2(1-x)Fe(OH)_3$, Table 1 presents the identified crystalline phases formed during artificial ageing.

The transformations observed in the system $Zn_xFe_{1-x}(OH)_{3-x}$ may be regarded as due to the action of Zn^{2+} ions on the originally amorphous iron hydroxide, $Fe(OH)_3$, and might be interpreted in the following way: small concentrations of Zn^{2+} liquidate one of the two crystalline forms into which pure amorphous $Fe(OH)_3$ passes, i.e. goethite. In the neighbourhood of $x = 0.2$, hydrohematite, well crystallized in lower concentrations, cannot bear the presence of zinc ions in these quantities and forms a poorly crystallized α-Fe_2O_3 phase. Simultaneously, badly crystallized maghemite appears, with the highest yield at $x = 0.275$. From then on the formation of zinc ferrite prevails up to $x = 0.5$. At higher concentrations, $ZnFe_2O_4$ is accompanied by ZnO, which for $x = 0.8$ is the only crystalline phase to be identified with certainty, although it is still possible to record traces (in terms of X-ray identification) of $ZnFe_2O_4$. At $x > 0.8$ the highest-intensity line (311) in the diffractogram of this phase approaches the level of the background noise, thus leaving ZnO as the only phase to represent the crystalline system for ZnO : $Fe_2O_3 > 0.8$.

Table 1

Crystalline phases after artificial ageing of $Zn_x^{II}Fe_{1-x}^{III}(OH)_{3-x}$

x	series A	series B
0.0	α-Fe_2O_3, α-FeO (OH)	α-Fe_2O_3, α-FeO (OH)
0.1	α-Fe_2O_3	α-Fe_2O_3
0.2	γ-Fe_2O_3, α-Fe_2O_3, (x)	very small crystallites of γ-Fe_2O_3, traces of α-Fe_2O_3, (x)
0.3	γ-Fe_2O_3, (x)	γ-Fe_2O_3, traces of α-Fe_2O_3, (x)
0.4	γ-Fe_2O_3, (x)	γ-Fe_2O_3, α-Fe_2O_3, (x)
0.5	$ZnFe_2O_4$, γ-Fe_2O_3 (in small amounts)	$ZnFe_2O_4$, γ-Fe_2O_3 (in small amounts)
0.6	decreasing $ZnFe_2O_4$ phase	
0.7	increasing amount of ZnO	
0.8	ZnO traces of $ZnFe_2O_4$	ZnO traces of $ZnFe_2O_4$
0.9	ZnO	ZnO
1.0	ZnO	ZnO

(x) = presence of $ZnFe_2O_4$ not excluded

References

1. H. Forrestier and J. Longuet, Compt. Rend., 208 (1939) 1729.
2. T. Takada and M. Kiyama, ICF*, 6A1. 1, 1970.
3. V. Chalyi, Ukr. Khim. Zh., 25 (1959) 285.
4. W. Wolski and U. Politańska, Zh. Prikl. Khim., 38 (1965) 667.
5. W. Wolski, Monatsh. Chem., 104 (1973) 1276.
6. U. Schwertmann and W. Fischer, Z. Anorg. Allgem. Chem. 346 (1966) 137.
7. U. Schwertmann, Z. Anorg. Allgem. Chem. 298 (1959) 337.

* ICF = International Conference on Ferrites (Japan).

Résumé — L'identification aux rayons X et l'étude des propriétés magnétiques montrent que les hydroxydes coprécipités de fer (III) et zinc (II) se transforment, après ébullition dans l'eau distillée en un mélange d'oxydes hydratés, la modification ferromagnétique de l'oxyde de fer (III), γ Fe_2O_3 étant responsable du comportement ferromagnétique de ce mélange. On obtient la valeur la plus élevée de la magnétisation spécifique pour le rapport stoechiométrique $ZnO : Fe_2O_3 = 0.275 : 0.725$.

Etant donné que pour la stoechiométrie du spinelle: $Zn(OH)_2/2\,Fe(OH)_3$, le ferromagnétisme tombe à une valeur proche de zéro, on ne peut pas exclure la formation de ferrite de zinc. Cependant, la forme mal cristallisée de cette phase, obtenue généralement, ne permet pas de confirmer directement l'existence de cette phase par les méthodes de diffraction.

Zusammenfassung — Aufgrund von röntgenographischen Untersuchungen und von magnetischen Messungen wurde festgestellt, daß die beim Kochen gemeisam gefällter Hydroxide $Zn(OH)_2/Fe(OH)_3$ im Wasser entstehenden hydratisierten Oxide ferromagnetische Eigenschaften besitzen, die durch Anwesenheit von γ-Fe_2O_3 bedingt sind.

Die höchste spezifische Sättigungsmagnetisierung weist ein Präparat mit einer Stöchiometrie $ZnO : Fe_2O_3 = 0.275 : 0.725$ auf.

Bei spineller Stöchiometrie: $Zn(OH)_2/2\,Fe(OH)_3$, fallen die magnetischen Eigenschaften bis in die Nähe des Nullwertes herab. Man kann daher die Entstehung von Zinkferrit nicht ausschließen. Eine eindeutige röntgenographische Bestätigung dieser Phase ist durch die schlechte kristalline Form dieser Phasen, welche meistens bei einer solchen präparativen Technik entstehen, nicht möglich.

Резюме — На основании рентгено-диффракционного исследования и изучения магнитных свойств, было найдено, что соосажденные гидроокиси железа(III) и цинка(II) после нагревания до кипения в дестиллированной воде превращаются в смесь гидроокисей, содержащих ферромагнитную модификацию окиси железа(III), γ—Fe_2O_3, которая ответственна за ферромагнитные свойства этой смеси. Наиболее высокое значение удельного намагничивания получено для стехиометрического состава $ZnO : Fe_2O_3 = 0.275 : 0.725$. Поскольку стехиометрический состав шпинели: $Zn(OH)_2/2Fe(OH)_3$ и магнитное свойство которой почти падает до нуля, тогда не может быть исключено образование феррита цикла. Однако, слабо выраженная кристалличность этой фазы, не позволила прямо подтвердить методом диффракции образование феррита цинка.