

**DIFFERENTIAL SCANNING CALORIMETRY STUDIES ON
AGED IRON(III) - CHROMIUM(III) - HYDROXIDE
COPRECIPITATES^{† §}**

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DSC measurements in air from 20 to 800° are reported on aged iron(III)-chromium(III) coprecipitated hydroxides (with Fe³⁺:Cr³⁺ wt % ratios of 9:1, 7:3, 1:1, 3:7 and 1:9). A comparison of the DSC profiles of aged coprecipitates with the thermal behaviour of freshly precipitated and well characterized samples provided information on the modification occurring in the structure and reactivity of the coprecipitates on prolonged aging.

The mechanism of crystallization of coprecipitated Fe(III)-Cr(III) hydrogels on aging in the mother liquor was studied by Zolotovskii *et al.* [1]. They showed that, upon aging, the coprecipitates break up, with a breakaway of the primary polymeric particles of the minor component, and

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with subsequent formation of a mixture of secondary crystals of the individual Fe(III) and Cr(III) hydroxides or oxides. The growth of the secondary crystals was shown to proceed in accordance with a mechanism of oriented accretion or vice versa.

In recent studies [2] on the structural and thermal characterization of coprecipitated iron(III)-chromium(III) hydroxides, we observed the similar existence of an inhomogeneous microstructure in the coprecipitates, identifiable with the presence of individual protoferrihydrite and chromium trihydroxide phases. These component phases tend to merge together on gradual heating, and result in nucleation and crystallization of α -Cr₂O₃, followed by that of α -Fe₂O₃ with formation rhombohedral α -Fe₂O₃-Cr₂O₃-type solid solutions as the final phase, discernible by a strong exothermic crystallization effect with a peak temperature in the range 410° to 520°. Amongst the very many parameters which influence the physical and structural properties of the coprecipitates (such as the pH of precipitation, the reactants used, the concentrations of the reactants, the temperature of precipitation, the method of addition of the reactants, the degree of stirring, the method of washing, the aging time in wet and dry states, and the extent of drying (time and temperature)), the aging of the coprecipitates was deemed to be a crucial step during the synthesis of these systems and in determining their reactivity and thermal stability.

The present work, as a continuation of previous studies, reports new results on the characterization by means of DSC, of coprecipitates aged at room temperature for a period of 5 years. A comparison of the thermal behaviour of the aged coprecipitates with that of freshly prepared samples, revealed the influence of the aging time on the microstructure and reactivity of the coprecipitates.

Experimental

Coprecipitated iron-chromium hydroxides with Fe:Cr weight per cent ratios of 9:1, 7:3, 1:1, 3:7 and 1:9 were prepared by slowly adding 1 M sodium hydroxide (A. R.) solution to rapidly stirred and freshly prepared mixtures of Fe(III) chloride and Cr(III) chloride solutions, till the pH at the end of precipitation and that of the suspension was \approx 7. The coprecipitates were washed with double-distilled water until free from electrolyte, air-dried at 60° in an electric oven for 24 hours, and then stored in a desiccator.

The aged specimens were obtained by aging the dried coprecipitates in a desiccator at room temperature for 5 years. Thermal analysis of the freshly prepared coprecipitates was carried out with a derivatograph (MOM, Budapest) from room temperature to 1000° in air, at a rate of 10 deg per minute. The initial coprecipitates and the annealed products obtained on heating them at different temperatures were examined by means of powder XRD, electron microscopy (TEM), IR spectroscopy and Mössbauer resonance spectroscopy. Some of the results of these studies have been published elsewhere [2].

DSC measurements on the aged coprecipitates were performed in air over the temperature range 300-1073 K, at a heating rate of 5 deg min⁻¹, by using a DSC 111-G apparatus (Setaram, France). The coprecipitated sample mass was in each case 25 mg, and calcined alumina was used as reference. Calibrations were performed via the melting points and enthalpies of melting of high-purity metals. The error in the ΔH measurements is estimated to be $\leq 0.2\%$ and the error in the temperature is ≤ 0.5 deg.

Results and discussion

Table 1 summarizes the results of DSC measurements on the aged samples. DSC curves of the coprecipitates and of iron(III) hydroxide and

Table 1 Exothermic crystallization temperatures and heats of crystallization of bulk α -Cr₂O₃, corundum phase α -Fe₂O₃.Cr₂O₃ solid solutions, and α -Fe₂O₃ from DSC curves of aged samples of chromium hydroxide, coprecipitated Fe-Cr hydroxides, and iron(III) hydroxide

Sample No.	Composition Fe:Cr weight % ratio	Onset temperature °C ± 0.5 deg	Peak temperature °C ± 0.5 deg	Heat of crystallization $-\Delta H$, ± 0.2 J/g
1	0:10 (chromium(III) hydroxide)	387	393	84
2	1:9	407	423	141
3	3:7	393	407	78
4	1:1	421	613	85
5	7:3	543	575	74
6	9:1	498	529	93
7	10:1 (iron(III) hydroxide)	366	374	129

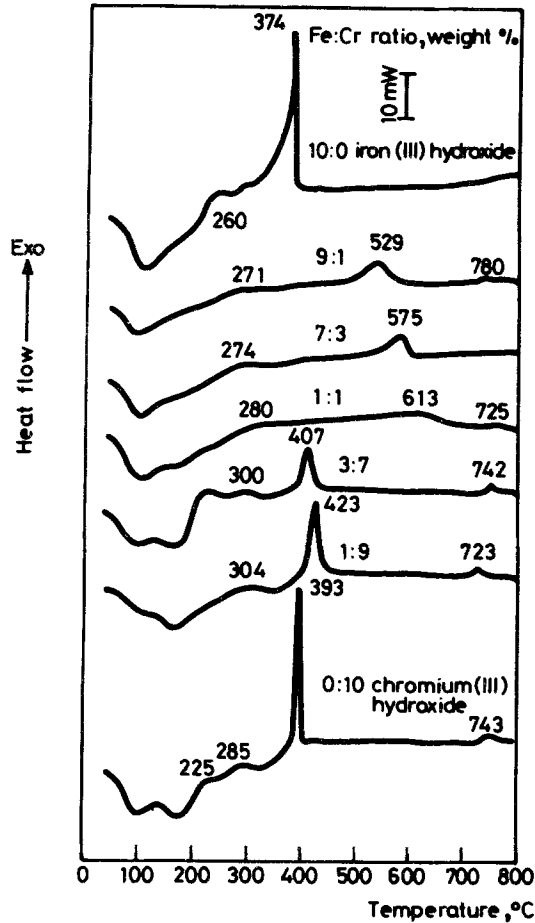


Fig. 1 DSC curves of samples aged for 5 years

chromium(III) hydroxide, each aged at room temperature for 5 years, are depicted in Fig. 1. Figure 2 presents a DSC curve, traced on a different scale, for sample 4, so as to give a better resolution of the thermal effects involved. Thermal (DTA and TG) curves obtained for the freshly prepared coprecipitates are shown in Fig. 3. Figures 4 and 5 display the variation in the heat of crystallization and in the temperatures of crystallization, corresponding to the formation of corundum phase solid solutions from the

aged coprecipitates, as a function of their composition (expressed in terms of the chromium content by weight per cent in the initial precursors).

Below, we discuss the thermal curves of freshly prepared and aged samples in the light of information available from detailed microstructural studies.

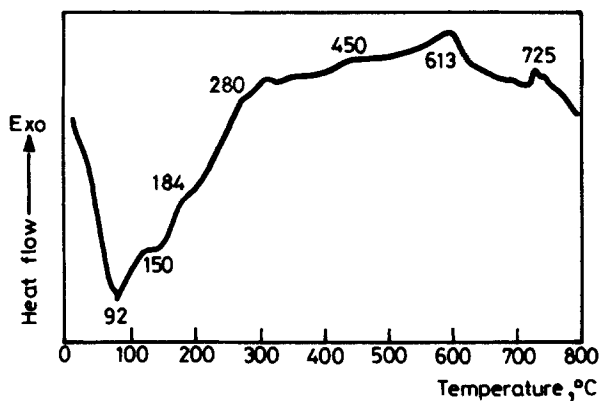


Fig. 2 DSC curve of aged sample 4 (Fe:Cr ratio = 1:1) with a better peak resolution

1. Study of aged iron(III) hydroxide and chromium(III) hydroxide precipitates

For freshly precipitated iron(III) hydroxide, Van der Giessen [4] has shown that dehydration and recrystallization are quite separate processes, which respectively give rise to the usual endothermic effect with a peak in the range of 140° to 200° and a strong exothermic effect with a peak between 360° and 450° in their differential thermal curves. Similar thermal behaviour is displayed by natural protoferrihydrite specimens and its synthetic analogues [5, 6]. Displacement of water ligands due to aging of the precipitate may be expected to result in its partial or complete transformation into goethite (α -FeOOH) or akaganeite (β -FeOOH) and/or hematite (α -Fe₂O₃) to different extents. This, along with an increased microporosity of the precipitate due to aging on early dehydration, would be expected to create a two or three-phase structure with local inhomogeneities due to the creation of anionic vacancies and cavities. Indeed, aging causes the following changes in the thermal features of the aged iron(III) hydroxide:

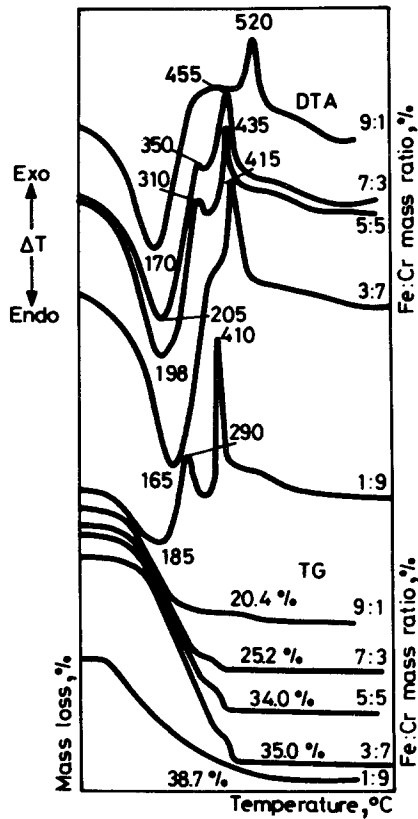


Fig. 3 DTA and TG curves of freshly prepared coprecipitates

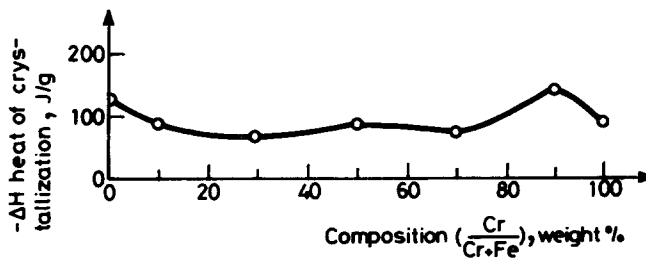


Fig. 4 Variation in $-\Delta H$ (crystallization) with composition in aged coprecipitates

(i) The single broad endothermic effect corresponding to the dehydration of the freshly prepared hydroxide is associated with another, weak but distinct endothermic effect with a peak at relatively high temperature, e.g. 276°, corresponding to the removal of water due to the dehydroxylation of goethite [7, 8] in the aged samples.

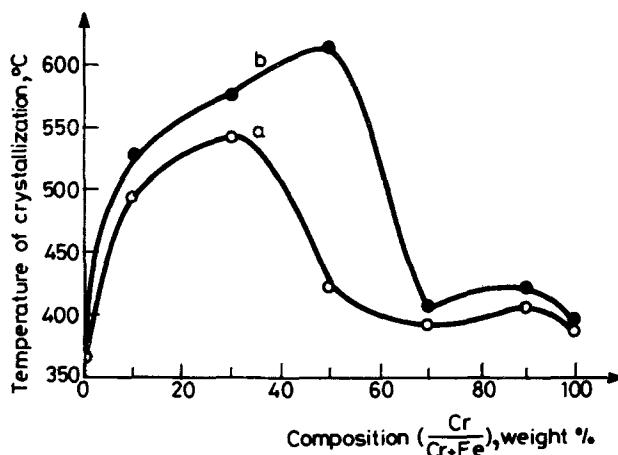


Fig. 5 Variation in temperatures of crystallization with composition in aged coprecipitates. Curve (a) indicates the onset temperature at which crystallization just starts. Curve (b) refers to the peak temperatures at which the effect attains its maximum

(ii) The sharp exothermic effect corresponding to the well-known glow phenomenon and crystallization of α -Fe₂O₃ may be considerably modified in its intensity and breadth, depending on the defect microstructure and surface area of the aged precipitate. The temperature of crystallization to α -Fe₂O₃ is also altered, depending on the size of the particles and the degree of continuity of the local microstructure. The immediate precursors of hematite obtained from goethite decomposition have been noted by Wolska [9] as protohematite and hydrohematite, with their nominal formulae given by Fe_{2-x/3}(OH)_xO_{3-x} with $1 \geq x > 0.5$ (for protohematite) and $0.5 \geq x > 0$ (for hydrohematite). Similar intermediate phases have been identified by Saraswat *et al.* [16, 17] during the thermal transformation of iron(III) oxide hydrate precipitates.

In the present study the DSC curve of sample 7 of aged iron(III) hydroxide is characteristic of finely divided protoferrihydrite as a major phase [5, 6], along with a small fraction of goethite, which gives a separate

weak endotherm at 260° (Fig. 1, Table 1), corresponding to its transformation to the pseudohematite phase [8, 9, 16, 17].

For chromium hydroxide precipitates, Carruthers *et al.* [10] have observed a complex structure in the low-temperature endothermic peak, having superimposed on it two exothermic peaks at about 230 and 280°, giving an appearance that might be mistaken for three endothermic peaks. The exothermic peak at 230° has been shown to correspond [10, 11] to the partial hydrothermal conversion of the precipitate to the orthorhombic α -CrOOH phase. Further, the effect at 200-300° is associated with the occurrence of the exothermic oxidation of Cr³⁺ species to Cr⁴⁺-Cr⁶⁺ mixed valency compounds (e.g. CrO₃, CrO₂ and Cr₂O₅), etc., predominantly in the surface layers of the precipitate.

At temperatures above 200°, the loss in area of the calcined samples is associated with the oxidation-reduction cycle Cr³⁺ → Cr⁶⁺ → Cr³⁺ in air, and it results eventually in the formation of crystalline α -Cr₂O₃ [12] with a surface structure that is not perfected till the calcination temperature is above 900°.

In conformity with these findings, the DSC curve of aged chromium hydroxide (Fig.1) shows a broad endotherm, intersected by two weak and distinct exothermic effects, peaking at 225 and 285°. These correspond [10, 12] to partial hydrothermal conversion of the precipitate to α -CrOOH and its surface oxidation to Cr⁴⁺-Cr⁶⁺ compounds, respectively.

Further, a sharp exotherm with a peak at 423°, corresponding to the crystallization to α -Cr₂O₃, is indicative of the fact that, even after aging, the precipitate largely retains its finely divided form and interparticle continuity, and the coherence of the precipitate is not much disrupted on aging. A weak exothermic signal peaking at 743° is identifiable with the stiffening of the network for a fraction of the sample on aging, causing its crystallization to α -Cr₂O₃ to occur at higher temperature. A similar effect has been reported for aged chromia gels by Fahim *et al.* [13]. This effect persists in some of the aged coprecipitates, as well.

2. Studies on freshly prepared coprecipitates

Before we deal with the DSC results on aged coprecipitates, it would be in place to examine briefly the thermal (TG - DTA) behaviour of freshly precipitated coprecipitates. Primarily the observed increase in mass loss for coprecipitates with increasing chromium component is in conformity with the absorption of a significant amount of water in the more polymeric amorphous structure of the chromium hydroxide component. The large uptake of

water in chromium hydroxide is to be associated with the availability of a larger population of coordinatively unsaturated chromium ions [11] in the chromium hydroxide, which has a high surface area, and therefore greater affinity for water ligands. This may be better seen from a consideration of the bulk compositions of the hydroxides: $\text{Cr}_2\text{O}_3 \cdot 4.4\text{H}_2\text{O}$ [14] and $\text{Fe}_2\text{O}_3 \cdot 2.2\text{H}_2\text{O}$ [15]. A microstructural characterization of the coprecipitates using electron microscopy [2] indicated that:

(i) Mixing of the iron hydroxide component coarsens the $\alpha\text{-Cr}(\text{OH})_3$ phase. This favours its transformation to $\alpha\text{-CrOOH}$ and decreases the oxidation of Cr^{3+} to $\text{Cr}^{4+}\text{-Cr}^{6+}$ mixed valency phases. It is known [10] that the occurrence of $\text{Cr}^{4+}\text{-Cr}^{6+}$ species in the surface layers facilitates the rearrangement of the lattice at a faster pace, thereby causing an early crystallization of microcrystalline $\alpha\text{-Cr}_2\text{O}_3$, later manifested by the exothermic peak associated with the glow phenomenon.

Also, the smaller ionic radius of Fe^{3+} ion, with its harder acid character and stronger affinity towards oxygen as compared with that of Cr^{3+} ion, coupled with different states of dispersion and activation of component phases, results in a delayed and diminished oxidation of Cr^{3+} ion to $\text{Cr}^{4+}\text{-Cr}^{6+}$ ions, which in turn delays crystallization of the corundum phase to higher temperature in comparison with that observed for chromium hydroxide alone.

(ii) A protective chromium oxide layer formed on the iron hydroxide component, on the other hand, creates an island-like structure, thereby preventing the particles from coalescing, and stabilizing the protohematite and hydrohematite phases. This observably retards their transformation to corundum phase solid solutions.

This quelling of reactivity through "mutual retardation" is discerned for all the coprecipitates. With increasing incorporation of the iron ion component, the crystallization temperature is shifted by as much as 110 deg for the sample with composition $\text{Fe}:\text{Cr} = 9:1$, as compared to that with composition $\text{Fe}:\text{Cr} = 1:9$ (Fig. 3). Further, a continuous broadening of the exothermic effect occurs in parallel with this retardation, indicating that an increasingly inhomogeneous and stiffened network develops in the coprecipitates with increasing iron component, which shows that their crystallization to corundum phase solid solutions occurs rather sluggishly.

In their extensive studies on freshly prepared iron-chromium trihydroxide gels obtained by adding NH_4OH to mixtures of iron nitrate and

chromium nitrate solutions (followed by oven-drying of the samples at 110°), Bhattacharya *et al.* [7, 8] have demonstrated that a maximum mutual protective action against crystallization (marked by an exothermic peak at 550° (DTA) and a maximum surface area of 291.8 m²/g (B.E.T.)) is exhibited by the gel containing 40 mole % Cr₂O₃ and 60 mole % Fe₂O₃. In the present study, however, due to the different preparation parameters used, a rather different trend is discerned, showing the maximum protective action against crystallization in the coprecipitate with Fe:Cr wt % ratio = 9:1 (Table 2).

Table 2 (a) Mass loss (from TG) and exothermic crystallization peak temperature (from DTA) of initial coprecipitates

Sample No.	Composition, Fe:Cr wt. % ratio	Mass loss, %	Crystallization temperature, °C
1	1:9	38.7	410
2	3:7	35.0	415
3	1:1	34.0	435
4	7:3	25.2	455
5	9:1	20.4	520

Table 2 (b) Crystallization temperature and heat of crystallization of α -Fe₂O₃ and α -Cr₂O₃, determined by DTA on freshly prepared iron and chromium hydroxides prepared by ammonical hydrolysis of the nitrates followed by drying in an airoven at \approx 120° (after Natarajan *et al.* [3])

Sample	Crystallization temperature, °C		- ΔH , kJ/mol
	Starting temperature	Peak temperature	
Chromium(III) hydroxide	390	410	51.16
Iron(III) hydroxide	260	335	133.76

3. Studies on aged Fe(III)-Cr(III) hydroxide coprecipitates

DSC curves for the aged coprecipitates show the following changes as compared with the thermal features of freshly prepared samples:

1. The endothermic effect corresponding to the initial removal of water appears to be split into a twin peaked doublet and shows different degrees of asymmetry, depending on the initial microstructure of the aged coprecipitates. This may be an indication of the presence of phases with different individual chemical compositions, such as goethite, protoferrihydrite, rhombohedral α -CrOOH, and α -Cr(OH)₃ mixed or demixed to different extents. The existence of a single phase inhomogeneity, e.g. the partitioning of

bulk and surface components having an identical chemical composition (with creation of microporosity on the removal of water from coprecipitates on aging) or built up of an amorphous phase on the surface of bulk particulate coprecipitates, may also cause such asymmetry, due to the inequivalence of the bond energies of water and hydroxy groups in different regions.

2. The exothermic effects occurring at 225° and 285° for the bulk aged chromium hydroxide, corresponding to the partial hydrothermal conversion of the chromium hydroxide component into orthorhombic α -CrOOH and surface oxidation CrO₂, CrO₃ phases, are modified to different degrees due to different interactions in the coprecipitates on aging. The removal of water would be expected to create microporosity, with substantial or negligible modifications of the surface, which would in turn account for these subtle but distinct changes upon aging. The nucleation and primary crystallization of the α -Fe₂O₃ and α -Cr₂O₃ phases above 200°, following these events, would also be governed by the nature of the surfaces and morphology of the precursor phases formed below 200°. Thus, isolated primary particles of iron hydroxide precipitates with a flaky aggregate structure would result in a porous metastable relic oxide on dehydration, while chromium hydroxide, with a highly amorphous polymeric structure with very fine particles constituting the precipitate, on dehydration would end up in a denser and highly microporous network for the oxides formed on dehydration. Corresponding to the transformation of part of the iron hydroxide on aging into goethite, α -FeOOH, a weak endothermic effect with variable intensity also appears in the range 260-320° in the DSC curves of the aged coprecipitates.

3. The exothermic effect peaking in the range 407° to 613° in the DSC curves of the aged coprecipitates shows $-\Delta H$ crystallization varying from -141 to -74 J/g, corresponding to the release of energy on recrystallization and the formation of corundum phase solid solutions. This energy was stored by the relic oxide phases formed during their primary nucleation and crystallization. In freshly prepared coprecipitates, the crystallization temperature rises from 410° (for Fe:Cr = 1:9) to 520° (for Fe:Cr = 9:1) and the width of the endothermic peak increases with increasing iron hydroxide component, presumably due to an increasing surface area and porosity associated with iron hydroxide-rich samples.

The aged samples qualitatively show a similar trend, but with several striking changes in both their temperatures and heats evolved on crystal-

lization, which are to be accounted for by the substantial modifications in the microstructure of the coprecipitates on aging. The aging of xerogels in general is known to lead to a higher microporosity and a hardening of the network with the removal of water [19]. Electron microscopic (TEM) examination indicated that the aging of coprecipitates resulted in a partial demixing of the constituents, thereby modifying the microstructure and homogeneity. Heating of these aged coprecipitates was shown to result in primary nucleation and crystallization of the individual oxides.

In an earlier DSC study [18], we have shown that the different breadths of the exothermic effect corresponding to the transformation $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ originate from differences in the particle size distribution of the samples. A similar effect occurs here. Thus, a broad exotherm for coprecipitates is observed for the oxides, resulting from their dehydration prior to their exothermal crystallization, which have a broad size range. A narrow size distribution of the crystallizing phases is again indicated by observation of a sharp exotherm (Figs 1 and 2).

Demixing and independent crystallization of the individual iron and chromium oxides in aged samples with Fe:Cr = 1:1, 7:3 and 9:1 therefore lead to a very broad exotherm. This corresponds to the slow process of ordering and recrystallization states characterized by wide differences in their local coordinations and surface structures.

As compared with the values of $-\Delta H$ of crystallization for the freshly precipitated chromium hydroxide and iron hydroxide, a sharp decrease in $-\Delta H$ occurs on aging in these samples, which is largely to be accounted for by the substantial loss in their original surface area.

In view of the small ionic radius and hard acid character, the Fe^{3+} ion is substitutionally incorporated into the chromium hydroxide lattice during the process of coprecipitation [2]. However, this solubility is limited and for samples with a higher iron hydroxide content, i.e. other than with Fe:Cr = 1:9, the iron hydroxide component exists only as colloiddally mixed with chromium hydroxide. The incorporation of iron into chromium hydroxide would result in an initial higher uptake of structural water (see Table 2). Loss of this excess, strongly held structural water would create higher disorder than occurs in bulk chromium hydroxide alone. The vacancies, lattice imperfections and higher porosity thus created would lead to an observably large heat of crystallization at a temperature higher than that observed for chromium hydroxide. The observed DSC data on the aged coprecipitate (Fe:Cr = 1:9) are in conformity with these features.

In the sample with Fe:Cr = 3:7, displacement of the water on aging results in a partial demixing of the components. Thus, iron hydroxide and iron-doped chromium hydroxide separate out and nucleate into the individual oxides. The surface of the mixture of these oxides being less than that in the preceding case, it releases a lower amount of exothermic energy at a lower temperature, leading to the formation of corundum phase α -Fe₂O₃.Cr₂O₃ solid solution.

In the sample with composition Fe:Cr = 1:1, aging results in still further demixing, giving iron hydroxide and iron-doped chromium hydroxide. Divergence of the DSC curve from the baseline, starting from 400° and peaking at \approx 450°, corresponds to the partial crystallization of an iron-containing chromium oxide phase and the nucleation of largely amorphous iron oxide. A broad exotherm centred at 613°, with a slightly higher $-\Delta H$ of crystallization; (corresponds to the highly amorphous and inhomogeneous structure of the phases; which need a higher temperature for recrystallization) into homogeneous α -Fe₂O₃.Cr₂O₃ solid solution. For samples with Fe:Cr = 7:3 and 9:1, a similar demixing of the component phases occurs. In the former, the chromium oxide phase interacts creating an island-like structure, thereby promoting the amorphous character of the iron oxide. This results in a higher temperature of transformation than that observed for pure iron hydroxide, and a much higher $-\Delta H$ is to be expected. This is indeed the case if we take into account the definite contribution made through the exothermic effect, reflected in the divergence of the DSC curve from the baseline starting at temperatures as low as 300°, to the $-\Delta H$ of 85 J/g determined uniquely from the exothermic peak centred at 613°.

In the sample with Fe:Cr = 9:1, the further relative lack of interaction of the chromium hydroxide component in the aged coprecipitate results in a still less amorphous structure than that in the preceding sample. This results in crystallization at a lower temperature, with a $-\Delta H$ of crystallization approaching that of bulk α -Fe₂O₃, considering the contribution made to the exothermic DSC curve through the weak exothermic effects shown via the divergence of the curve from the baseline, observed as early as at 300°.

In conclusion, the demixing and hardening of the aged coprecipitates results in striking modifications in their microstructure, in terms of the attendant interactions occurring between the components and the surface states and bulk structures of the metastable and stable oxides formed therefrom. In particular, the differences observed in the temperatures and heats of recrystallization $-\Delta H$ to corundum phase α -Fe₂O₃.Cr₂O₃ solid solutions, studied by DSC measurements, have shown a reasonable relationship and

systematic evolution between the thermal characteristics observed and the microstructure anticipated for these systems using a host of characterization techniques. Such relationships, which are not fortuitous, and which are far from complete in this initial study, should be a useful guide for controlling the microstructure and reactivity in iron-chromium mixed oxide systems and in studying the order-disorder and homogeneity-inhomogeneity problem in these mixed oxides, often prepared by using wet chemical methods [20, 22] or via the processing of mixed salt precursors [21].

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Zusammenfassung – Es werden DSC-Messungen an gealterten kofällten Eisen(III) - Chrom(III) - hydroxiden (mit $\text{Fe}^{3+}:\text{Cr}^{3+}$ Gewichtsanteilen von 9:1, 7:3, 1:1, 3:7 und 1:9) im Temperaturbereich von 20 bis 800° beschrieben. Ein Vergleich der DSC-Profile von gealterten Kofällungen mit dem thermischen Verhalten frisch gefällter und gut definierbarer Proben lieferte Informationen über die Veränderungen in Struktur und Reaktivität der Kofällungen bei längerem Altern.