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DSC STUDY OF WATER ELIMINATION FROM THE COPRECIPITATED FERRITE POWDERS

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Abstract

The differential scanning calorimetry (DSC) technique was used to analyse the thermal effects and the irreversible processes associated with the dehydration of manganese ferrite powders coprecipitated from aqueous solution of salts obtained by simultaneous dissolution of MnO_2 and $FeSO_4\cdot 7H_2O$.

Keywords: coprecipitation, dehydration, DSC, ferrites, manganese iron mixed oxide

Introduction

The presence of water in coprecipitated oxide powders is a consequence of the precipitation mechanism and of the water chemisorption as a tendency of surface metal cations to complete their coordination.

The coprecipitation occurs through the condensation of neutral complex species, $[M^{z+}(H_2O)_{z-x}(OH)_x]^0$ and $[M^{z+}(OH)_z]^0$, which exist in aqueous solution of salts at basic pH values [1]. Depending on temperature and time of aging in solution, the coprecipitated ferrite powders contain variable amounts of water molecules and OH^- groups under various forms: coordinated water (aqua- and hydroxo-complexes), constitutional water (hydroxides and oxyhydroxides), lattice water, absorbed water into the pores and physically or chemisorbed water on the particle surface [2, 3].

Based on the IR bands, one can state that there are some similarities between the water types from these coprecipitated ferrite powder [3] and those from zeolites prepared by sol-gel method [4]. In zeolites, part of the framework atoms form ligands with water molecules and assume an octahedral coordination. Such interactions may account for the relatively strong interaction of water with the materials framework, the liberation of this water occurs at about 126°C [5, 6]. Water molecules, which form

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these ligands, provide sites for adsorption of further water molecules through the formation of hydrogen bonds and facilitate the build up of a limited and disordered three-dimensional water structure. This water is lost between 25 and 100°C [6]. In the case of the coprecipitated ferrite powders, during precipitation and aging, part of the coordinated water from the complex precursors is gradually lost, a part of it turns into M–OH–M and M–O–M bridges forming the framework of the spinel structure, and part of it remains. The residual water molecules and OH^- groups facilitate the adsorption of further water molecules.

In the case of oxide powders, the water surface chemisorption is accompanied by the surface hydroxylation, which determines a structuring effect on the adsorbed water molecules, via hydrogen bond [1, 7–8].

In order to complete our previous results concerning the dehydration of coprecipitated mixed oxide powders [3, 9], differential scanning calorimetry investigation of coprecipitates generating manganese ferrite were carried out.

Experimental

The ferrite powders were coprecipitated at ambient and 95°C and aged at 95°C (Table 1), without air bubbled and without stirring during aging. The coprecipitation was performed by adding a 15% solution of NaOH to a 2 N solution of cations obtained through simultaneous dissolution of stoichiometric (Fe:Mn=2:1) amounts of MnO_2 and $FeSO_4 \cdot 7H_2O$ in presence of H_2SO_4 [9].

Table 1 Experimental conditions for samples preparation

Sample symbol	Precipitation temperature/°C	Aging temperature/°C	Aging duration/min
S_1	20	non-aged	non-aged
S_2	20	95	10
S_3	95	95	10
S_4	95	95	120

Sample S_2 was obtained by fast immersing a part of coprecipitate S_1, together with the mother solution, and keeping it for 10 min in a water bath at 95°C. After coprecipitation (sample S_1) and maturation (samples S_2–S_4), the powders were filtered, washed and air-dried at ambient temperature for 48 h. All the samples were kept in air at ambient temperature.

DSC analyses were performed in purified Ar atmosphere at a heating rate of 2 K min^{-1} using a Perkin Elmer differential scanning calorimeter DSC7 and a suitable amount of sample (~30 mg).

Results and discussion

TG analysis of the ferrite coprecipitated powders [3] indicate considerable mass losses, depending on the temperature and time of aging ~30% for sample S_1, ~19% for sample S_2, ~9% for sample S_3 and ~4% for sample S_4. In the temperature range 20–300°C, about 90% of these mass losses occur without the superposition of Mn^{2+} oxidation. As shown by DTG and DTA curves [3, 9], this overall process results from a succession of single steps with partial superposition. As in the samples there are no other volatile components (the coprecipitates do not contain 'green rust' or ammonium salts), the mass losses are to be assigned exclusively to the water losses, as confirmed by mass spectrometry [3].

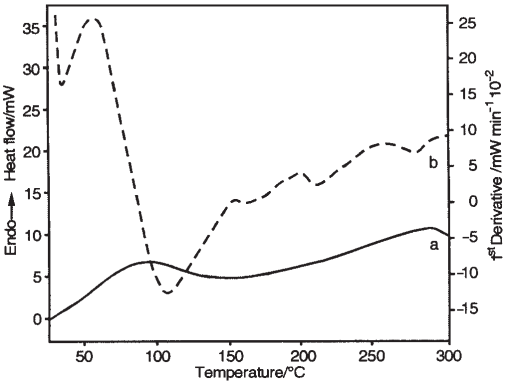

Fig. 1 (a) DSC and (b) 1^{st} derivative DSC curves of sample S_1

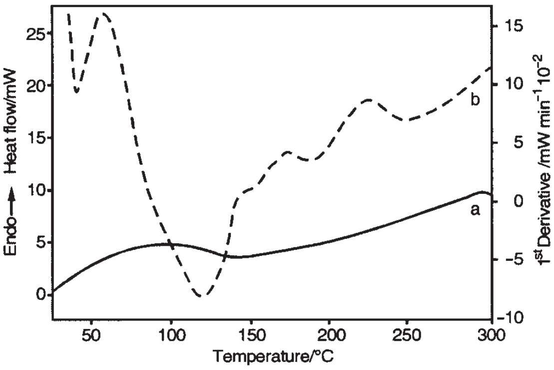

Fig. 2 (a) DSC and (b) 1^{st} derivative DSC curves of sample S_2

DSC curves of the samples S_1–S_4 (Figs 1–4) show two endothermic peaks in the ranges 20–120 and 120–300°C respectively. It seems evident to consider that the first peak corresponds to the elimination of the physically adsorbed water molecules with various degrees of structuration via hydrogen bonds. The lower the temperature of coprecipitation is, the higher the temperature is, at which the first peak is shifted (samples S1 and S2 with respect to samples S_3 and S_4). The second peak corresponds to the elimination of the lattice water and the water from the pores, these phenomena being superposed. In the case of the second peak, the superposition of some slight exothermic processes in the range 200–250°C can be observed if the temperature and time of aging increases. These phenomena are more obvious for the sample S_4 with low amount of water and correspondingly with low endothermic effect associated to its elimination (curve a in Fig. 4) and for the sample reheating (curves b in Figs 3 and 4).

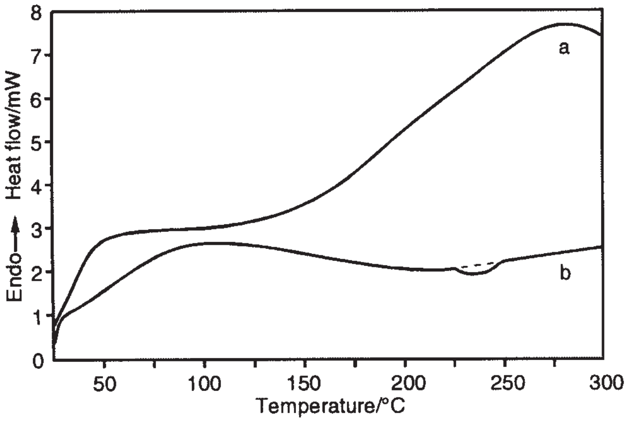

Fig. 3 DSC curves of sample S_3, a – at the first heating and b – at the reheating

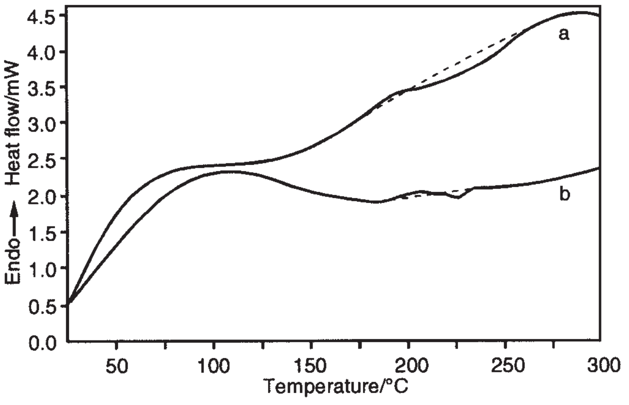

Fig. 4 DSC curves of sample S_4, a – at the first heating and b – at the reheating

The exothermic peak between 225 and 250°C on the DSC curves is associated with a slight mass loss and by weak exothermic peaks on the TG and DTA curves [3]. It corresponds to the microstructure changes associated with the elimination of water from the micropores. Its removal is accompanied by a decrease of the number of point defects, by the formation of (111) and (422) planes and by a slight increase of the crystallites size [3], it follows that bridges M–O–M are realized. These bridges contribute to the elimination of the pores and lead to the increase of crystallite size and healing of the point defects. The 1st derivatives of DSC curves of S_1 and S_2 samples (Figs 1 and 2) clearly show that if until ~150°C an endothermic effect is recorded, at higher temperatures this is partly compensated by exothermic ones. The 'toothed' form of DTA curves in these temperature range [3] evidences this competition. The phenomenon could be assigned to the breaking and reforming of bonds corresponding to the release of the water and the formation of M–O–M bridges. This confirms that during calcination in air at temperatures higher than 200°C, the removal of water is accompanied by a slight spinel lattice reorganization and relaxation. The observation agrees with the X-ray diffraction and IR spectra data. The lower the water amount from powder is, the more extended the exothermic effect corresponding to the structuration of the lattice is.

During maturation in solution, the mechanism of water elimination from the powders always determines the increase of their crystallization degree. The amount of water form the precipitates decreases due to the elimination of the proton from the coordinated water molecules and OH groups; the oxygen ions remain the framework generators. The proton elimination is facilitated by the existence in aqueous liquid phase of a three-dimensional disordered lattice of hydrogen bonds which settle up permanent statistic connections for fast proton transfer. The transfer needs low activation energy and explains the easy formation and growing of ferrite crystallites in solution.

When the oxide powders are separated from the aqueous solution, the hydrogen bond lattice is limited and reduced to the residual water molecules and hydroxyl groups coming from the coordination sphere of cations as well as to the adsorbed water molecules. This lattice is not continuous depending on the number and position of H_2O and OH^- in the precipitate structure, i.e. on its maturation step in solution. By heating the coprecipitation in air, the release of water and hydroxyl ions from the spinel lattice occurs by proton transfer for enough H_2O molecules and OH groups, in powders with a large amount of water. Two neighbors water molecules with different values of the coordination energy can behave differently, one more strongly bounded by the cation as an acid and the other as base. When the water is released through breaking of M–OH and M–OH_2 coordinative bonds, it determines some microstructure disorders. The high specific area of these powders facilitates surface reaching and water release.

In order to show the irreversible processes accompanying the water release from the coprecipitates, we repeated DSC analysis with the same samples, which were removed and cooled in the ambient atmosphere, after the first heating. The difference between two curves representing the measurements taken from the first and the second heating (Figs 3 and 4) is illustrated by the curves in Fig. 5. From this figure, two endothermic irreversible peaks at ~55 and 270°C, with:

$$\Delta H^0_{55°\text{C}}=33.8\ \text{J g}^{-1} \text{ and } \Delta H^0_{270°\text{C}}=405.9\ \text{J g}^{-1} \text{ for sample } S_3,$$

$$\Delta H^0_{55^\circ\mathrm{C}}=19.1\ \mathrm{J\ g^{-1}}\ \text{and}\ \Delta H^0_{270^\circ\mathrm{C}}=210.4\ \mathrm{J\ g^{-1}}\ \text{for sample}\ \mathrm{S_4}.$$

can be evidenced. These values do not correspond to single processes but to complex processes resulted by superposition of the release of more water types associated with some irreversible microstructural changes. The first peak corresponds most probably to the release of the structured water molecules at the powder surface. It seems that the non or less aged coprecipitated oxide samples contain structured physically adsorbed water molecules which are evolved at a maximum rate at ~55°C. The structuring effect on the water molecules at the powder surface depends on the formation of an OH^- chemisorbed layer. Its existence is due to the coordination non-saturation of the surface cations i.e. to the lattice defects.

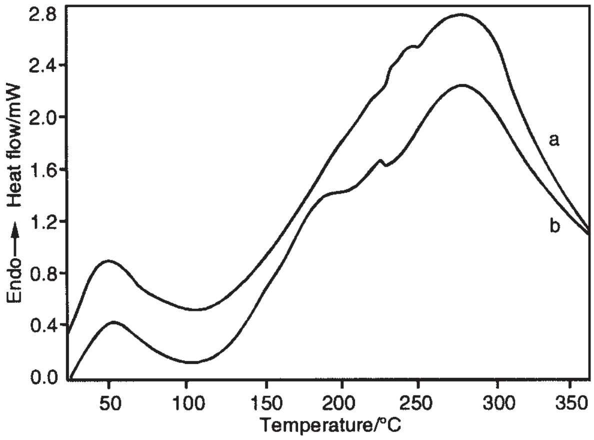

Fig. 5 The difference between two DSC curves recorded for the first and the second heating of samples a – S_3 and b – S_4

The second irreversible endothermic peak is associated to complex processes; it corresponds mainly to the release of lattice and pores water and to a less extent of the constitution water. The thermal effect associated to the second endothermic peak is ten times higher than that associated to the first peak although it corresponds to the release of a ~ four times lower amount of water. Obviously, the water released in this temperature range is more strongly bound. Its release occurs with breaking of M–OH bonds and generation of M–O–M bridges. These are irreversible processes which satisfy cation coordination and determine pores stopping up.

Conclusions

At the dehydration of coprecipitated manganese ferrite powders, two endothermic irreversible peaks at ~55 and ~270°C were observed.

The first peak corresponds most probably to the release of the structured water molecules at the powder surface. The second peak corresponds to the irreversible release of the lattice and pores water, which determines pores elimination and a slight spinel lattice structuration and relaxation.

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