Investigation on the formation of manganese–zinc ferrites by thermal decomposition of solid solution oxalates

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Abstract

Homogeneous solid solution oxalates of Mn(II), Zn(II) and Fe(II) were prepared by coprecipitation from metal acetate solution with oxalic acid, with the partial replacement of water by acetone as solvent. During the thermal decomposition of solid solution oxalates in a nitrogen atmosphere (10 ppm O_2) the oxygen partial pressure is considerably lowered by the mixture of $CO–CO_2$ produced. Under this condition a single phase ferrite of spinel structure is formed by thermal decomposition in the range 400–600°C with a short annealing time of 3 h. With annealing for a longer time in a nitrogen atmosphere (10 ppm O_2), α-Fe_2O_3 is formed as well as the spinel according to an extrapolated $p(O_2)$–θ diagram for manganese ferrite.

INTRODUCTION

To make high-performance ferrite powders, besides the prevalent solid state reactions, numerous unconventional methods have been investigated [1–3]. In many procedures, first a precursor compound with the intended metal stoichiometry is made, which in a subsequent calcination reaction is decomposed at temperatures $\theta < 600$°C to obtain the mixed oxide required.

A conceivable method to prepare ferrite powders is the coprecipitation and thermal decomposition of metal oxalates [4–6].

Investigations on making nickel–zinc ferrites by means of decomposition of oxalates revealed that characteristics of the coprecipitated product and the decomposition conditions exert a considerable influence on the properties of the decomposition product [7, 8].

Investigations into the low-temperature oxidation of $Mn_xFe_{3-x}O_4$ by thermal analysis methods show that manganese ferrite oxidatively decom-

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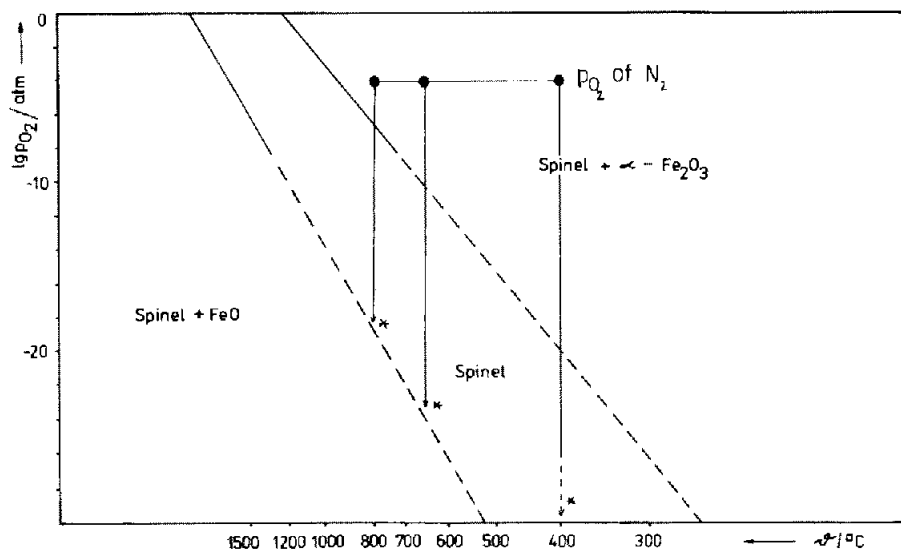
Fig. 1. $\lg p(O_2)$–θ diagram of the manganese ferrite. *Final $p(O_2)$ during the decomposition according to the calculation (see eqn. (4)).

poses above 600°C and α-Fe$_2$O$_3$ is formed [9]. Among other things, the reaction course depends on the oxygen partial pressure above the reaction system.

Michalk [10] determined by means of Mössbauer investigations that the oxidation of manganese(II) ions to manganese(III) ions and a change of sites in the spinel lattice AB$_2$O$_4$ precede the ferrite decomposition at about 500°C and at $p(O_2)$, (air) = 6 Pa.

The above discussed results can be assigned to a $p(O_2)$–θ diagram for manganese ferrite as indicated by Grisedski and Prilibko [11], extrapolating from the investigated high-temperature range to lower temperatures (Fig. 1).

In the present paper, the thermal decomposition of iron(II)–manganese(II)–zinc solid solution oxalates is investigated. The product arising is characterized with regard to its phase composition. The desired metal stoichiometry in the precursor is achieved by quantitative precipitation. This requires special conditions because of the known solubility data.

Decomposition turns out to be problematic, as divalent iron in the oxalate needs to be oxidized to the trivalent state, whereas the manganese should keep its oxidation state of 2+.

EXPERIMENTAL

Oxalates were prepared using a method indicated by Wickham [6].

A defined amount of iron powder, plus acetic acid (excess of 40%), was heated in nitrogen atmosphere until quantitative dissolution was reached.

Subsequently, the appropriate amounts of the metal acetates of zinc and manganese were added as required for the $Mn_{0.625}Zn_{0.285}Fe_{2.09}O_4$ stoichiometry; at this stage the total metal ion concentration was 0.67 mol l^{-1}. Afterwards, precipitation was carried out using oxalic acid solution either in acetone or in water.

After retreatment of 1 h at the boiling point, the precipitate was filtered off, washed and dried at 100°C. The resulting solid solution oxalate was decomposed in a nitrogen atmosphere (10 ppm O_2) in a tubular furnace and was annealed at different temperatures and for various periods of time.

The resulting complex oxides were characterized by X-ray powder diffraction analysis. The particle size distribution was measured by means of a laser particle sizer.

During the decomposition, the oxygen partial pressure was measured by a solid electrolyte cell.

RESULTS AND DISCUSSION

Oxalate precipitation

To obtain precise metal ion stoichiometry, it is necessary to achieve precipitation yields $\alpha > 0.995$ when the oxalate is precipitated. In agreement with published solubility data [12], when the individual oxalates are precipitated the lowest α values result for manganese.

To improve the yield of precipitation of the oxalates, there is the possibility of applying organic solvents of low dielectric constant. In Table 1 the dependence of the yield of precipitation on the presence of an organic solvent (acetone) is shown.

It becomes apparent that the yield of precipitation is improved with the inclusion of acetone in the solvent mixture. In addition, it may be stated that the yield of precipitation of a metal oxalate will be improved when

TABLE 1

Dependence of the yield of precipitation on the use of an organic solvent

Compound	pK_L [12]	α(metal) in water		α(metal) in 50% acetone	
Mn oxalate	5.3		0.875		0.980
Fe oxalate	6.7		0.975		0.995
Zn oxalate	7.56		1		1
Mn Fe oxalate	–	Mn	0.975	Mn	0.990
		Fe	0.980	Fe	0.995
Zn Fe oxalate	–	Zn	1	Zn	1
		Fe	0.985	Fe	1
Mn Zn Fe oxalate	–		–	Mn	0.996
				Zn	1
				Fe	1

precipitation is made together with less soluble metal oxalates forming solid solutions. The formation of solid solution oxalates of Mn(II), Zn(II) and Fe(II) was confirmed by X-ray investigations.

Maintaining the above mentioned precipitation conditions, it proved possible to obtain solid solution oxalates of the composition $Mn_{0.625}Zn_{0.285}$-$Fe_{2.09}(C_2O_4)_3 \cdot 2.2H_2O$ with yield of precipitation $\alpha > 0.995$ by precipitation from acetone–water solution.

For further characterization of the powder, the grain size distribution and particle shape of the coprecipitated oxalates are determined by means of a particle sizer or a scanning electron microscope (SEM) (Figs. 2a and 2b).
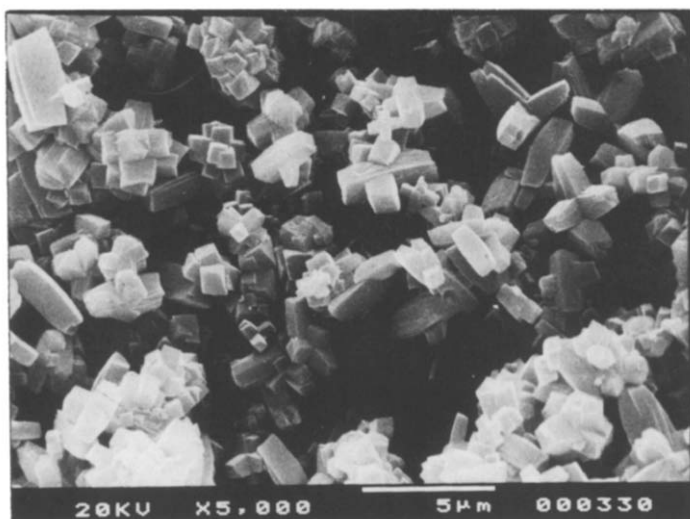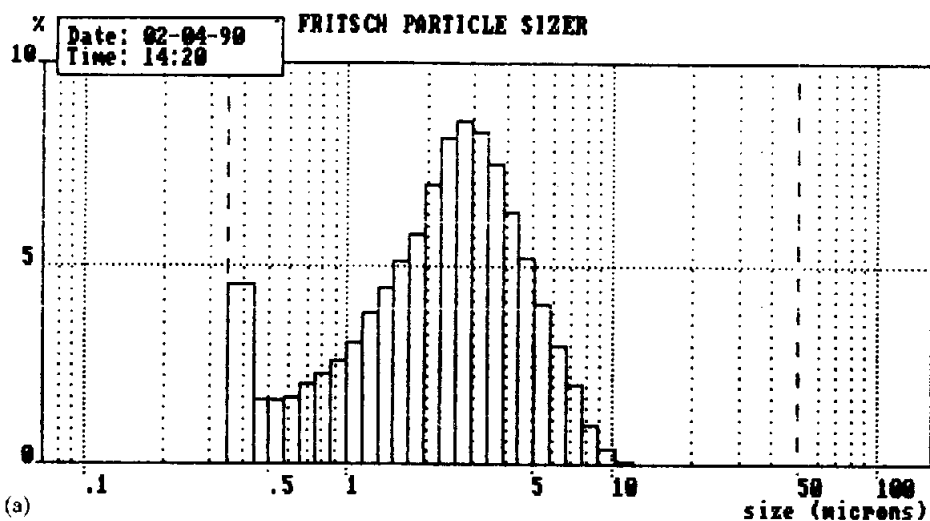

(a)

(b)

Fig. 2. (a) Particle size distribution of oxalate precursor $Mn_{0.625}Zn_{0.285}Fe_{2.09}(C_2O_4)_3 \cdot 2.2H_2O$, and (b) its scanning electron micrograph.

It can be seen that homogeneous solid solution oxalates of narrow grain size distribution and of typical crystal shape are formed.

As well as the improved yield of precipitation when acetone is added, the particle size of the solid solution oxalates is influenced also. With increasing acetone content, supersaturation in the solution obviously increases, and thus smaller particles result.

Thermal decomposition of the oxalates

In Fig. 3a and 3b, the decomposition curves of solid solution oxalates in air and nitrogen atmospheres are illustrated.

Decomposition proceeds in two discrete steps, as can be proved by DTA investigations. In a first step, in either an oxidizing or a nitrogen atmosphere, the oxalates are dehydrated. Oxalate decomposition in the second step takes place endothermically in a nitrogen atmosphere. In contrast, the decomposition in air is characterized by an exothermic effect; this can be explained by the oxidation of the initially formed CO to CO_2.
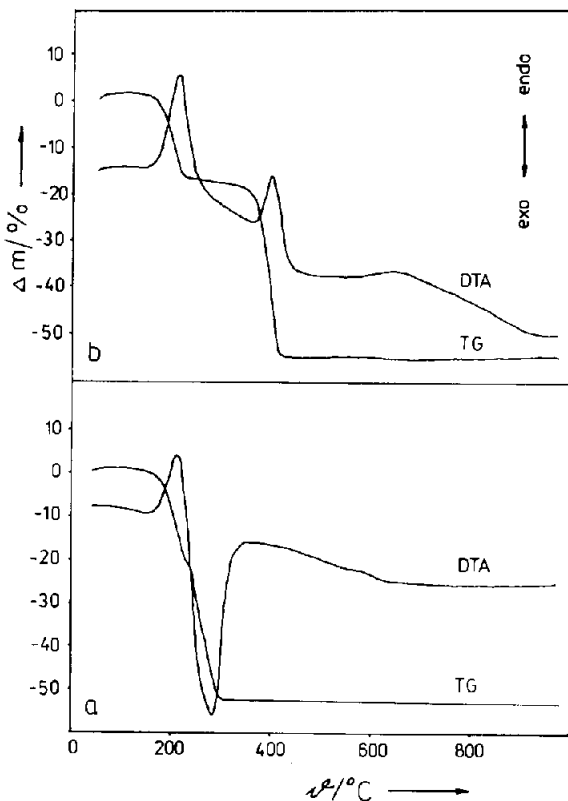

Fig. 3. Thermal analysis of $Mn_{0.625}Zn_{0.285}Fe_{2.09}(C_2O_4)_3 \cdot 2.2H_2O$ (heating rate $10 \: K \: min^{-1}$): (a) in air; (b) in nitrogen.
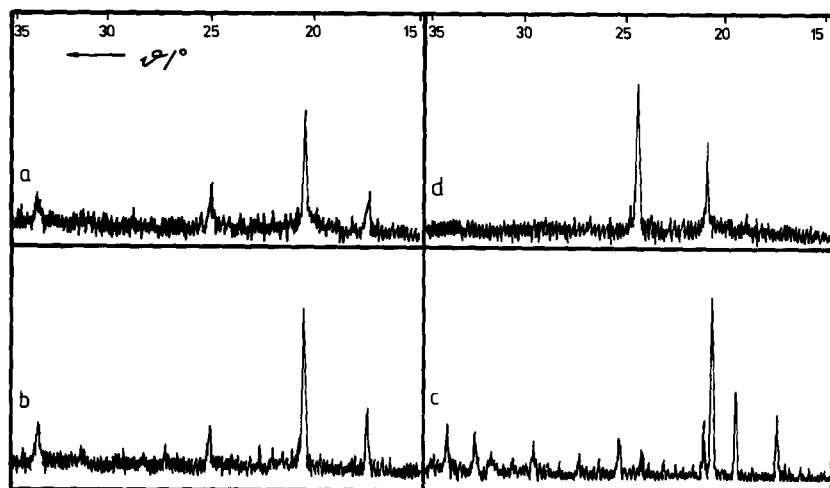
Fig. 4. X-ray diffraction diagrams of the decomposed products at (a) 400°C/3 h; (b) 650°C/3 h; (c) 650°C/24 h; (d) 800°C/3 h.

Differences in the decomposition temperatures in air and in a nitrogen atmosphere may be explained by overheating in the sample caused by CO oxidation.
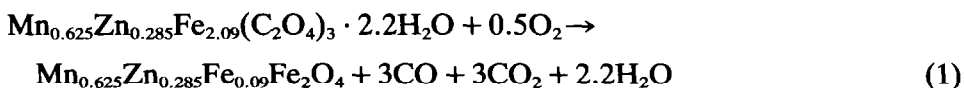
Figure 4 shows sectors of the X-ray powder diffraction diagram of the samples decomposed in a nitrogen atmosphere. Oxalates annealed in flowing nitrogen between 400 and 600°C show reflections that are typical of ferrites of spinel structure. Crystallinity increases with increasing decomposition temperature.

For powders annealed for 3 h above 650°C no remaining ferrite reflections can be identified. It is concluded from Mössbauer spectroscopic studies that all the iron is present in the oxidation state 2+. Obviously the oxidic phases produced form solid solutions of MnO–ZnO–FeO [14].

With very long annealing times (24 h) in a nitrogen flow, in the range 600–700°C, the formation of α-Fe$_2$O$_3$ and of a spinel phase results.

For the present, it is difficult to assign the results obtained to a $\lg p(O_2)$–θ diagram for Mn–Fe–O extrapolated to lower temperatures derived from [11] (Fig. 1). Assuming equilibrium conditions, at $p(O_2) = 10^{-4}$ atm in a range 400–700°C, α-Fe$_2$O$_3$ and a spinel phase should always coexist.

It was revealed by calculations that the residual oxygen in nitrogen at the usual flow rate of 1 l/h^{-1} is insufficient for the oxidation of Fe(II) to Fe(III) according to reaction (1) during 3 h

$$\text{Mn}_{0.625}\text{Zn}_{0.285}\text{Fe}_{2.09}(\text{C}_2\text{O}_4)_3 \cdot 2.2\text{H}_2\text{O} + 0.5\text{O}_2 \rightarrow$$

$$\text{Mn}_{0.625}\text{Zn}_{0.285}\text{Fe}_{0.09}\text{Fe}_2\text{O}_4 + 3\text{CO} + 3\text{CO}_2 + 2.2\text{H}_2\text{O} \tag{1}$$
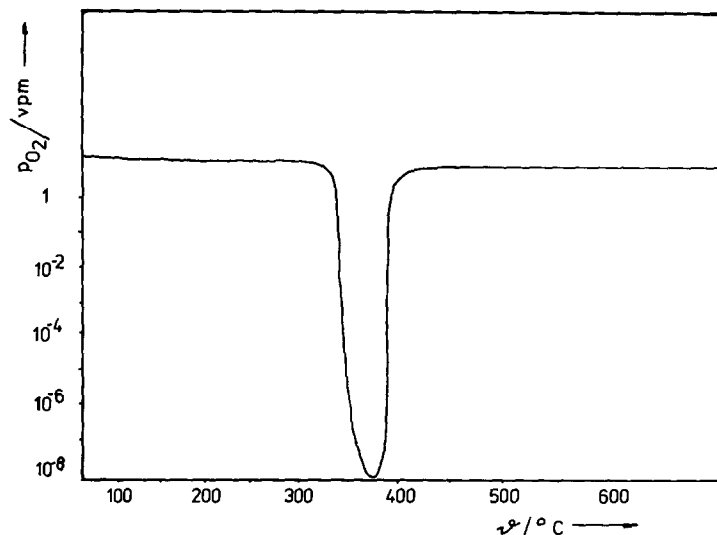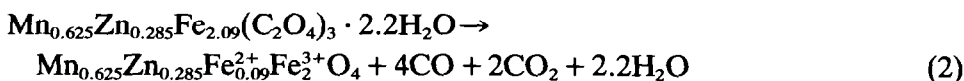
Hence it is supposed that the oxygen required for the oxidation of

Fig. 5. Measurement of oxygen partial pressure during the decomposition of $Mn_{0.625}Zn_{0.285}Fe_{2.09}(C_2O_4)_3 \cdot 2.2H_2O$ (heating rate $10\,K\,min^{-1}$).

Fe(II) originates from the system itself following a course described by reaction (2)

$$Mn_{0.625}Zn_{0.285}Fe_{2.09}(C_2O_4)_3 \cdot 2.2H_2O \rightarrow$$

$$Mn_{0.625}Zn_{0.285}Fe^{2+}_{0.09}Fe^{3+}_2O_4 + 4CO + 2CO_2 + 2.2H_2O \qquad (2)$$

With formation of the $CO-CO_2$ mixture, the resulting partial pressure of oxygen is determined on the basis of the temperature dependent equilibrium constant of the reaction (3).

$$CO + 0.5O_2 \rightarrow CO_2 \qquad (3)$$

This pressure is calculated according to eqn. (4)

$$\lg p(O_2) = 2 \lg p(CO_2)/p(CO) - \lg K_p \qquad (4)$$

For a $CO-CO_2$ ratio of 2:1, the resulting values are: at 400°C $p(O_2) = 10^{-35}$ atm and at 700°C $p(O_2) = 10^{-22}$ atm [13].

The decrease really obtained must surely be smaller. It should lie between the value calculated and that recorded at decomposition because, on the one hand, the complete appearance of equilibrium cannot be expected and, on the other hand measured value is equal to the equilibrium (3) for the solid electrolyte cell at a working temperature of 1000°C (Fig. 5).

Hence, in the range 400–650°C, with the $p(O_2)$ decrease, an area is reached in which the ferrite with spinel structure occurs as a single phase product when investigated by X-ray diffractometry. To gain knowledge about the structure in detail, Mössbauer spectroscopic investigations should be made.

With increasing decomposition temperature, the lower stability limit of the ferrite is finally achieved (Fig. 1). This means that, above 700°C and in presence of CO, Fe(II) is not oxidized to Fe(III) and mixed crystals of the system MnO–ZnO–FeO with the NaCl structure are formed. With longer annealing times in the N_2 flow, between 600 and 800°C, the phases occur which were expected in accordance with the $p(O_2)-\theta$ diagram, i.e. a spinel phase occurs in addition to α-Fe_2O_3 or the solid solution crystals α-Fe_2O_3–Mn_2O_3.

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