

## Investigation of the formation of nickel–zinc ferrite from coprecipitated oxalates

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### Abstract

Homogeneous solid-solution oxalates of  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  ions were synthesized by coprecipitation from acetate solutions using a special double-inlet technique and freeze drying of the precipitates. The mixed oxalates decomposed on heating to form ferrites with a spinel structure. The conditions of precipitation, the characteristics of the precipitates and the decomposition conditions affect phase formation and product characteristics. When preparing the oxalate precursor by dropwise addition of ammonium oxalate solution to a metal sulphate solution, as well as the ferrite, simple oxides are partially formed on decomposition. On decomposition of the substances prepared according to the method described here, however, the appropriate ferrite was formed as the sole phase.

The grain size distribution of the oxalate precursors can be widely influenced by the precipitation conditions. For finely dispersed initial powders, the grain size distribution and grain shape are extensively maintained during the decomposition process.

### INTRODUCTION

In addition to the widespread solid state reactions employed to produce high performance ferrite powders, various unconventional methods of powder preparation have also been investigated and evaluated [1–3]. These are chemical methods in which an intermediate product containing metal ions of the required stoichiometry is first synthesised; this is then converted into ferrite powder by a series of reactions taking place at elevated temperatures. Various authors have investigated the coprecipitation of metal oxalates from appropriately composed solutions in order to produce precursor compounds for ferrites of spinel structure,  $\text{MFe}_2\text{O}_4$  [4–6]. When the precipitate has the composition  $\text{MFe}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Ni}, \text{Co}$ ), according to Schuele [4] the ferrite is formed by a direct thermal decomposition reaction at  $400^\circ\text{C}$ . This is in contradiction to the results reported by Schröder [7] who identified together with  $\text{NiFe}_2\text{O}_4$ , a comparatively high proportion of  $\text{NiO}$  and some other phases in the analogously obtained decomposition products of  $\text{NiFe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ . From the TG investigations and magnetic measurements during the decomposition process, Schröder [7] concluded

that the decomposition of mixed oxalate is an apparently low temperature phenomenon, and that the spinel part of the invariably multiphase product depends on the extent of local superheating of the samples by exothermic effects.

Although other investigations on coprecipitation and decomposition of oxalates have recently been made [8,9], so far there is little information relating the conditions of precipitation, the characteristics of the precipitates and the decomposition conditions to the phase formation and product characteristics. For this reason, the following investigations should contribute to the further elucidation of these relations. The influencing factors not taken into account so far, for example the powder characteristics of the oxalate precursor, should also be considered. The investigations were made using coprecipitated oxalates of general composition  $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ .

## PREPARATION

To optimize the conditions, solid-solution oxalates were prepared as follows (preparation A). Freshly prepared 0.66 M metal sulphate solutions were added to ammonium oxalate solution under a nitrogen atmosphere at 60 °C. To avoid fractionation during the coprecipitation, a double-inlet technique was applied in which the solutions of metal ions and oxalate were mixed in the required stoichiometry using dosing pumps. For a quantitative precipitation, a 10% excess of ammonium oxalate is optimal. After precipitation, the mixture was stirred for 2 h, filtered, and the precipitate was dried at 100 °C. When these conditions are strictly observed, a precipitate of composition  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  in about 98.5% yield is obtained. Thus the residual ionic concentrations are  $[\text{Ni}^{2+}] = 0.18 \times 10^{-3}$ ,  $[\text{Zn}^{2+}] = 0.12 \times 10^{-3}$  and  $[\text{Fe}^{2+/3+}] = 2.6 \times 10^{-3} \text{ mol l}^{-1}$ . The residual ion concentrations were compensated by a systematic metal-ion excess in the initial solution. They are considerably higher than the values expected from the solubilities of the appropriate metal oxalates [10]. In addition to other factors which increase the solubility, the overwhelming cause of the high values is the high ionic strength of the starting solution. To counter this disadvantage, precipitations were made from metal acetate solutions using oxalic acid. According to Wickham [6], nearly quantitative solid-solution precipitates of  $\text{Co}^{2+}-\text{Ni}^{2+}-\text{Mg}^{2+}-\text{Fe}^{2+}$  oxalates are possible from solutions containing acetic acid.

Preparation B was performed as follows, by modifying the technique given in ref. 6. A measured amount of iron powder was heated in a twofold excess of 1.5–2.0 M acetic acid under a nitrogen atmosphere and stirred (until quantitative dissolution); then an appropriate volume of 0.4–0.5 M  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  acetate solution was added. The resulting solution was boiled and 3–5% excess of 1 M oxalic acid solution was added. After 1 h of

boiling, the precipitate was filtered, washed and dried at 100 °C. In this way, 99.8% precipitation is achieved. In another variant, preparation C, the variant B precipitate was frozen with liquid nitrogen together with the total mother solution and then freeze dried. The products of the various preparation techniques were heated at fixed temperatures between 300 and 1000 °C in a furnace exposed to air to convert them into ferrites. In the following description, the decomposition temperatures corresponding to the respective samples are indicated. In preference, samples of  $x = 0.5$  and  $x = 0.66$  in the formula were investigated.

#### THERMAL DECOMPOSITION OF SOLID SOLUTION OXALATES AND CHARACTERIZATION OF PRODUCTS

The thermal decomposition of solid solution oxalates proceeds in at least two separate steps observable by DTA. This is demonstrated in Fig. 1 where a solid solution of  $x = 0.5$  is shown as an example. When decomposed in air (Fig. 1(a)) and in  $N_2$  gas (Fig. 1(b)), the first reaction is the endothermic loss of the total water content (after pre-drying at 120 °C;  $n = 6$  in the formula). The subsequent decomposition in an oxidizing atmosphere is strongly exothermic; it represents a superposition of the decomposition reaction proper with the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  and of  $CO$  to  $CO_2$ . The pointed exothermic peak at 405 °C, clearly the result of the recrystallization of a

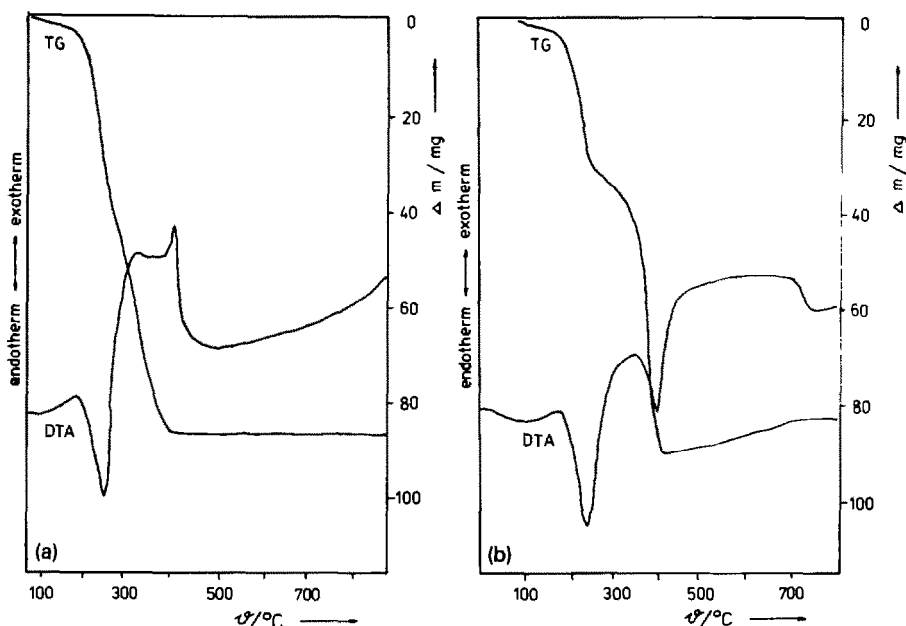


Fig. 1. Thermal analysis of  $Ni_{0.5}Zn_{0.5}Fe_2(C_2O_4)_3 \cdot 6H_2O$  (heating rate,  $10 K min^{-1}$ ): (a) air; (b)  $N_2$  gas.

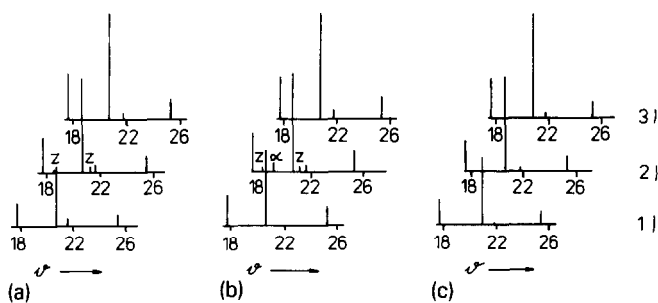


Fig. 2. Portions of schematic X-ray diffraction patterns of the decomposition products of solid solution oxalates ( $x = 0.66$ ): (a) and (b) preparation A; (c) preparation C. Conditions of decomposition: (a)-1, 3 h at 300 °C; (a)-2, 3 h at 900 °C after (a)-1; (a)-3, 3 h at 1100 °C after a-2; (b)-1, 3 h at 400 °C; (b)-2, 3 h at 750 °C after (b)-1; (b)-3, 3 h at 1000 °C after (b)-2; (c)-1, 3 h at 300 °C; (c)-2, 3 h at 500 °C after (c)-1; (c)-3, 3 h at 1100 °C after (c)-2.  $z = \text{ZnO}$ ,  $\alpha = \alpha\text{-Fe}_2\text{O}_3$ .

primary amorphous decomposition product owing to an unknown degree of overheating of the sample by reaction heat, cannot always be separately identified. Figure 1(b) shows that the actual oxalate decomposition is also endothermic. According to the literature [11], when nickel oxalate decomposes, the initial proportionately formed metallic nickel is gradually oxidized in a consecutive reaction by the traces of oxygen present. An indication of this is the small mass increase above 420 °C coupled with a slight exothermic effect (Fig. 1(b)).

Figures 2(a)–2(c) show positions of the X-ray diffraction powder diagrams for the decomposition products of differently prepared solid solution oxalates. Even following heating at 300 °C, the diagrams show peaks typical of nickel–zinc ferrites. Decomposition or subsequent heating to higher temperatures results in an increase in the peak intensities and a simultaneous decrease in the half-intensity width. The phase content of the products depends on the technique used to prepare the oxalate precursors.

In the decomposition product of a sample prepared according to variant A, in addition to ferrite of spinel structure, there are small amounts of simple oxides, recognized by the less intense peaks at  $\theta = 18.5$  and  $\theta = 21.2$ , which can be assigned to ZnO (Fig. 2(a)-2). Only after heating at 1100 °C is the ferrite the sole phase present (Fig. 2(a)-3). When varying preparation A and preparing the oxalate precursor, in accordance with ref. 5, by the gradual dropwise addition of ammonium oxalate solution to a metal sulphate solution, other phases become more apparent in the decomposed product at 750 °C (Fig. 2(b)-2). Again, after heating at 1000 °C, the ferrite is the only phase present (Fig. 2(b)-3).

When samples prepared by methods B and C are decomposed, irrespective of the decomposition temperature, the products yield X-ray patterns which show only spinel peaks (Fig. 2(c) 1–3). This emphasizes the advantage

of using coprecipitation from a solution of metal acetate with oxalic acid. This preparation clearly favours conditions for the deposition of homogeneous solid-solution crystals which decompose with direct formation of ferrites. The X-ray patterns do not indicate the formation of different spinel phases with increased  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$  content, as were identified in the preparation by solid-state reactions [12]. Their formation by oxalate decomposition requires further investigation [13].

#### POWDER CHARACTERISTICS

The grain size distribution of the coprecipitates can be comparatively strongly influenced by the reaction conditions during the precipitation process. This is shown by the  $d_{50}$  values listed in Table 1 for various methods of preparation (where 50% of the particles are of diameter  $d < d_{50}$ ). The largest grains are obtained by slow precipitation, e.g. using the double-inlet technique); small grains arise due to rapid fusion of the reactants or when alcohol is present in the reaction system. The relationship between the grain sizes of the precursor and the decomposition product is of interest. For finely dispersed initial powders of  $d_{50} < 10 \mu\text{m}$ , the grain size distribution is maintained during decomposition. The larger the starting powder crystallites, the more the grain size range shifts towards smaller values. At decomposition temperatures up to  $900^\circ\text{C}$ , the grain size changes slightly with decomposition temperature. Above  $1000^\circ\text{C}$ , sintering leads to coalescence of the grains and to an increase in the average grain size. Figure 3 shows the grain size distributions of an oxalate powder and of the respective decomposition products.

As can be deduced from Fig. 4, oxalate decomposition yields products of relatively large specific surface areas. The specific surface values suggest that either porous products or that many smaller primary grains are present than is reflected in the grain size distribution. This is understandable when the considerable gas release in the decomposition process is considered. With increasing temperature, the proportion of pores decreases, resulting in a

TABLE 1

$d_{50}$  Values for oxalate precursors and decomposition products ( $x = 0.66$ )

| Preparation variant      | $d_{50}$ ( $\mu\text{m}$ ) |                  |        |         |
|--------------------------|----------------------------|------------------|--------|---------|
|                          | Oxalate                    | Decomposition at |        |         |
|                          |                            | 400 °C           | 750 °C | 1000 °C |
| A (dropwise addition)    | 21.3                       | 16.5             | 15.0   | 16.2    |
| B (double-inlet)         | 27.2                       | 15.6             | 14.7   | 17.2    |
| B' (fusion, 25% ethanol) | 4.2                        | 4.8              | 5.7    | 7.0     |
| C (fusion, freeze dried) | 14.8                       | 13.0             | 12.3   | 13.0    |

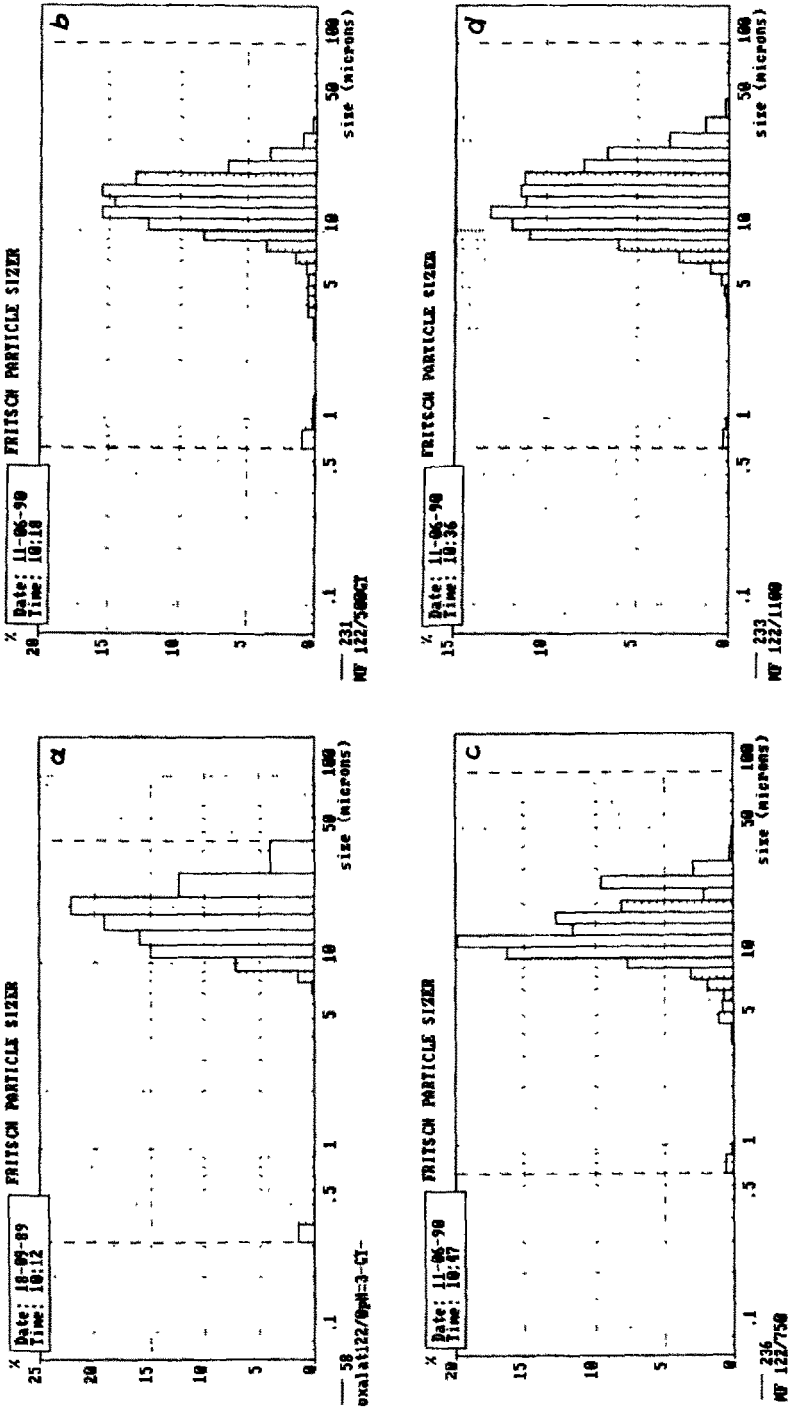


Fig. 3. Grain size distribution spectrum of an oxalate precursor prepared according to variant C: a, not decomposed; b, c and d, tempered at 500 °C, 750 °C and 1100 °C respectively.

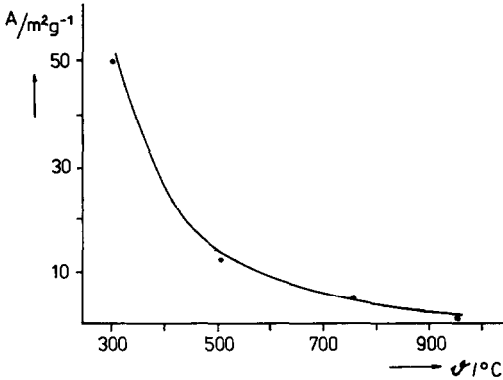


Fig. 4. Specific surfaces,  $A$ , against decomposition temperature (variant C,  $x = 0.5$ ).

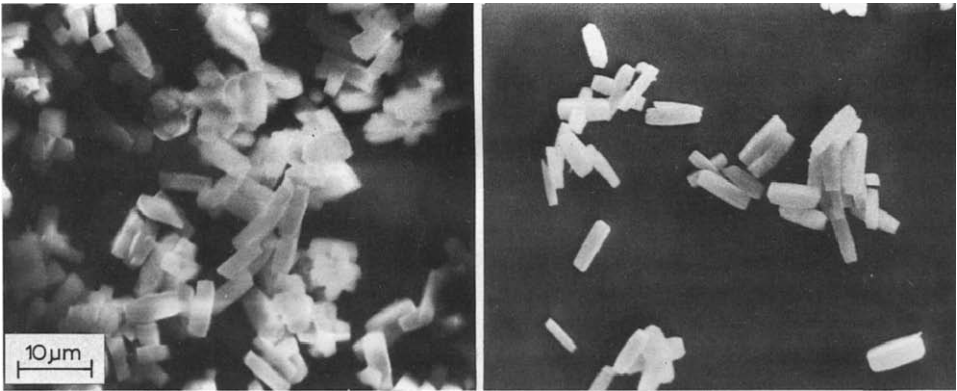


Fig. 5. Scanning electron micrographs, preparation variant B' (according to Table 1): (left) not decomposed; (right) decomposed at 400 °C.

decrease in the specific surface. The occurrence of pseudomorphy [14] is remarkable, and is especially visible for small grains. In addition the grain shape remains essentially unchanged during the decomposition process. This is demonstrated by the scanning electron micrographs shown in Fig. 5.

## CONCLUSIONS

From the results of the investigations discussed above, it can be stated that pure nickel-zinc ferrites are formed by direct reaction in the thermal decomposition of homogeneous  $\text{Ni}^{2+}\text{-Zn}^{2+}\text{-Fe}^{2+}$  solid-solution oxalates. However, in the synthesis of the appropriate oxalate precursors, a precipitation regime is required in which quantitative precipitation takes place with extensive fractionation. These conditions are successfully fulfilled by precipitation with oxalic acid from solutions of the appropriate metal acetates. By systematically achieving supersaturation by changing the rate of precipi-

tation, and by partially substituting water with an organic solvent, the grain size distribution of the oxalates and hence of the ferrites formed is widely variable.

Under the conditions mentioned above, the thermal decomposition of solid-solution oxalates to ferrite proceeds at a temperature which is extraordinarily low for solid state reactions. Even after thermal treatment at 750°C, the powders have attained more than 90% maximum crystallinity. This also coincides with the measurement of saturation magnetization, following different thermal pretreatments [13].

The more the precipitation conditions favour fractionation, the more the decomposition behaviour corresponds to that of intimate mixtures of individually precipitated metal oxalates, and the thermal decomposition products include simple oxides. In these circumstances, temperatures above 1000°C, typical for solid state reactions, are necessary for conversion to pure ferrites of spinel structure.

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