ON THE THERMAL DECOMPOSITION OF [Fe$_2$NiO(CH$_3$COO)$_6$(H$_2$O)$_3$]·2H$_2$O

H. Langbein and P. Eichhorn

DEPARTMENT OF CHEMISTRY, TECHNICAL UNIVERSITY, DRESDEN, GERMANY

The heteronuclear μ-oxoacetate with the composition [Fe$_2$NiO(CH$_3$COO)$_6$(H$_2$O)$_3$]·2H$_2$O decomposed on heating, forming nickel ferrite NiFe$_2$O$_4$ and (depending on the decomposition conditions) in part other solid phases. H$_2$O, CH$_3$COOH, acetone and CO$_2$ were also formed in the decomposition. A reaction scheme is given for the decomposition. The products were porous powders with grain diameters between 3 and 10 μm. On increase of the temperature of decomposition from 300 to 800 °C, the BET surface area and the surface area of the pores decreased, but only a small alteration in grain size was observed. As a result of thermal treatment in the temperature region abone 800°C, larger aggregates of grains were formed in sintering processes.

On addition of an acetate solution, mixed acetato complexes are precipitated as relatively poorly soluble compounds from solutions of Fe(III) salts and salts of bivalent metal ions M(II) (M = Fe, Co, Ni, Mn, Zn) [1, 2]. The decisive structural element is an M$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$ unit, with oxygen at the centre of an equilateral triangle and metal ions at the vertices, as in the cations of the respective Fe(III)$_3$ and Cr(III)$_3$ compounds [3, 4].

In connection with the synthesis of ferrites with spinel structure MFe$_2$O$_4$, we are interested in the conditions of preparation and thermal decomposition of the μ–oxoacetates of composition [Fe(III)$_2$M(II)O(CH$_3$COO)$_6$(H$_2$O)$_3$]·nH$_2$O (I).

In these compounds, the metal ion stoichiometry of the spinel is already present. However, the Fe(III)/M(II) ratio in the complex acetates depends considerably on the reaction conditions in the synthesis, and even products with very different metal ion stoichiometries give identical X–ray powder diffraction diagrams, except for small differences in the d values.

Generally, for the synthesis of solid compounds with a Fe(III)/M(II) stoichiometry of 2:1, a simultaneous excess of M(II) and acetate component during the precipitation process is required. However, for $M^{II} = Ni^{II}$ or Fe^{II}, the precipitation of products of composition I could be attained by using solutions with a 2:1 metal ion stoichiometry [5]. The thermal decomposition of complex acetates of type I has already been investigated by various authors [6-9]. The decomposition takes place in several steps between room temperature and about 300°, forming the corresponding oxides. However, there are different statements on the decomposition mechanism. Therefore, in the investigation of the thermal decomposition of $[Fe_2NiO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O(II)$, we set out to characterize in detail the decomposition and the possibility of influencing this process, in order to draw conclusions concerning the direct formation of nickel ferrite from the precursor acetato compound. This included characterization of the decomposition product with regard to solid-state chemistry.

Experimental

For quantitative determination of the decomposition products CO_2 and CH_3COOH, a definite sample quantity was heated to the desired temperature in a glass tube, and the gas evolved was passed in a N_2 stream into a known quantity of NaOH solution. CO_2 and CH_3COOH were completely absorbed. The NaOH excess was back-titrated by means of HCl, with phenolphthalein as indicator. To determine the CO_2 portion, an excess of HCl was added and, after expulsion of CO_2, the unreacted HCl was back-titrated with NaOH. The results of titration were confirmed by various measurements and the respective blank experiments.

X-ray phase analysis was performed with an HZG·1 instrument operated by a TUR M62 X-ray generator (iron-filtered Co-K_α radiation, $\lambda = 179.02$ pm). The specific surface area was determined by the BET method and was analyzed and assessed by the method of Haul and Dümbgen. For the thermal analysis, a Q-1500 D derivatograph (system Paulik–Paulik–Erdey) was used. Pore size analysis was performed with a 225 high-pressure porosimeter of the firm Carlo–Erba–Strumentazione*.

Grain size analysis was performed with a Partoscope F particle analyzer (MDZ granulometry and ZWG at the Dresden Technical University).

Results and discussion

Thermal decomposition of [Fe2NiO(CH3OO)6(H2O)3] · 2H2O

Figure 1 illustrates the results of thermal analysis of compound II. Two endothermic and one exothermic reactions are identifiable. Obviously, the latter includes several incompletely resolved partial reactions. The total mass loss of 62.2% coincides well with the mass loss to be expected theoretically for complete decomposition to the mixed oxide (62.8%). Although the results of the DTA, TG and DTG investigations coincide well with those of other authors, there are differences with respect to the interpretation of the decomposition, including the product formed. Yakubov *et al.* [6] describe a decomposition of acetato complexes where water and acetic acid are released. In [8], decomposition involving the splitting-off of H_2O, acetone and CO_2 is discussed.

In independent qualitative investigations, we found that when the complexes are thermally decomposed, water, acetic acid, acetone and CO_2 are formed. To clarify the reaction in greater detail, a known quantity of compound II was heated up to 300° in 20 min beginning from room temperature, in a dry nitrogen flow, and was then maintained at this temperature for 3 h. The decomposition products acetic acid and CO_2 were quantitatively determined titrimetrically (see Experimental), and the total mass loss was determined.

The data are summarized in Table 1. The difference between the total mass loss and the acetic acid and CO_2 formed can be assigned to the splitting-off of acetone and H_2O. CO_2 and acetone are produced in a molar ratio of 1:1. It is evident in Table 1 that for 1 mole of the initial compound about 2 moles each of acetic acid, CO_2 and acetone, are produced. The minor difference between the 6 acetate residues/mole initial compound found by C−H analysis and the 6.08 acetate residues found by titration is within the limit of error of the method of identification. The error mainly affects the figure determined by subtraction of the water molecules evolved on decomposition; hence, this figure seems to be somewhat low. When the sample is gradually heated up to 300°, the respective mass loss is determined and the decomposition products are analyzed, further statements on the decomposition can be made: up to 110°, even on prolonged tempering, only H_2O is

released (2–3 moles H_2O/mole compound II). When the temperature is increased up to 200°, after a tempering time of 5 h a stationary state is achieved, which correlates with the additional release of 2 moles of acetic acid and 1–2 moles of H_2O. Only at about 250° is CO_2 split off, together with the formation of acetone. The following reaction scheme can be assumed for the decomposition:
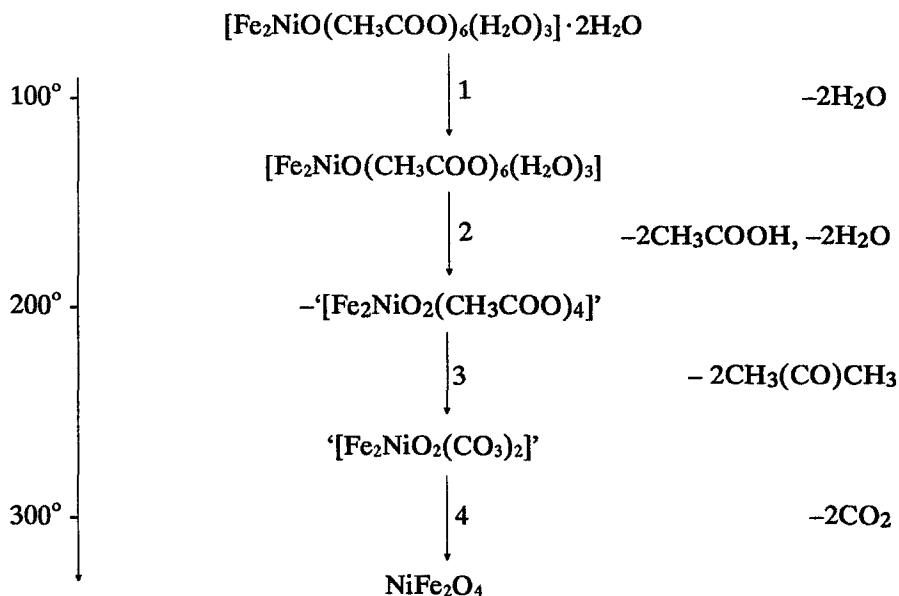
$$[Fe_2NiO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$$

100° —	↓ 1	$-2H_2O$
	$[Fe_2NiO(CH_3COO)_6(H_2O)_3]$	
	↓ 2	$-2CH_3COOH, -2H_2O$
200° —	$-'[Fe_2NiO_2(CH_3COO)_4]'$	
	↓ 3	$- 2CH_3(CO)CH_3$
	$'[Fe_2NiO_2(CO_3)_2]'$	
300° —	↓ 4	$-2CO_2$
	$NiFe_2O_4$	

Table 1 Procentual parts of decomposition products in the decomposition of II, total mass loss: 62.1%

	CH_3COOH	CO_2	Acetone	H_2O
%–part	19.8	14.0	18.4	9.9
mole/mole of II	2.08	2.0	2.0	3.43

Reaction steps 3 and 4 are not observed separately. Beginning at about 250°, a rapid decomposition of the intermediate occurs, forming acetone and CO_2. It is noteworthy that the quantitative ratios of the volatile decomposition products depend on the decomposition conditions. When the decomposition takes place in a humid atmosphere or in the presence of moisture in the stepwise decomposition, the CO_2 and acetone percentages decrease in favour of a greater quantity of acetic acid. When H_2O is present at above 200°, the hygroscopic intermediates are thermally hydrolyzed, and

acetic acid is evolved. The CH_3COOH proportion in the products can increase up to 4 moles per mole initial compound. This is used in the literature to explain discrepancies with regard to the main decomposition products.
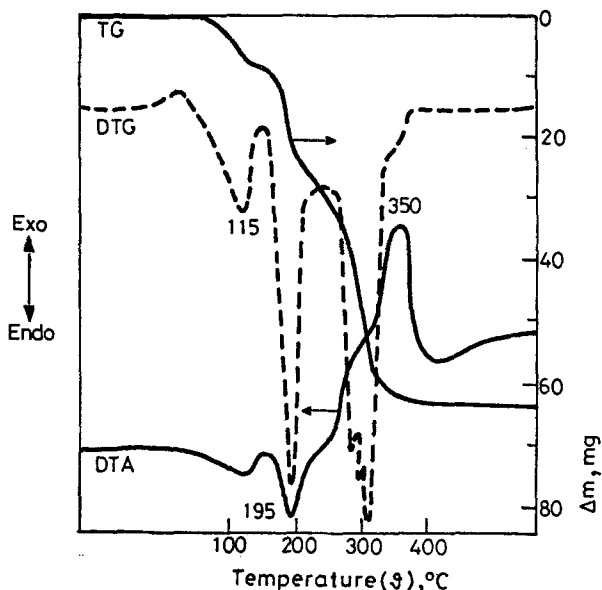

Fig. 1 Thermal analysis of $[Fe_2NiO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$ Sample mass: 100 mg, heating rate: 10 deg/min

X-ray characterization of decomposition products

Figure 2 presents sectors of X–ray powder-diffraction diagrams of decomposition products of the title compound obtained in various ways. After a 3-h tempering of compound II at 300°, the X–ray diffraction diagram shows peaks which can be assigned to the spinel structure (Fig. 2a–1). The following treatment at 600° and at 800° for 3 h, respectively, results in an increase in peak intensity, with a simultaneous decrease in the half-intensity width. Other phases are not detectable in the diagrams. The intensity ratios are consistent with the expected for values for $NiFe_2O_4$. When an intimate 2:1 mixture of iron(II) acetate and nickel acetate is decomposed under analogous conditions, after the 300° treatment, primarily the peaks of the simple oxides are detected (Fig. 2b–1). The following tempering at 600° results in intensified $\alpha–Fe_2O_3$ formation from $\gamma–Fe_2O_3$ and Fe_3O_4. Only at 800° is nickel ferrite increasingly formed from the simple oxides (Fig. 2b–3),

and even after a 3-h tempering at $1150°$ NiO and α–Fe_2O_3 are present, as identified by X–ray diffraction. This confirms the advantage of the decomposition of complex acetato compounds with regard to the direct formation of nickel ferrite at low temperature. It can be concluded from Fig. 2c that the extent of spinel formation at low temperature depends on the decomposition conditions. When compound II is immediately heated up to $600°$, α–Fe_2O_3 and NiO are formed in addition to $NiFe_2O_4$. The former two products are recognized by the excessive intensities of the spinel peaks at $\delta = 21.8°$ and $\delta = 25.4°$, resulting from superposition with NiO peaks. Even after only 10 min, a phase composition and crystallinity are obtained which change only slightly on prolonged tempering. Only after treatment at $1150°$ is a spinel obtained as sole phase (Fig. 2c–3).
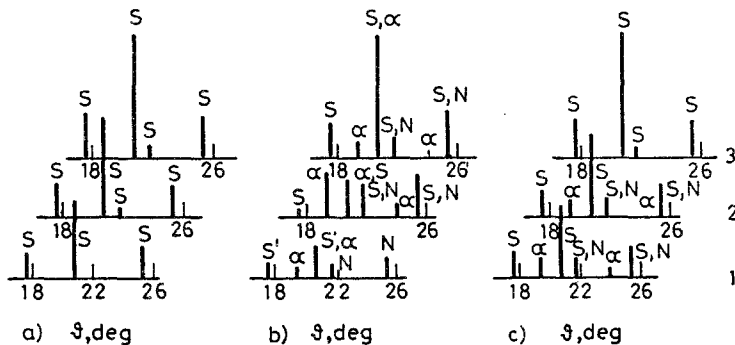
Fig. 2 Sectors of X-ray diffraction patterns of the decomposition products of II (a, c) and of a mixture $2\ Fe(CH_3COO)_2 + Ni(CH_3COO)_2 \cdot 4H_2O$ (b)

Conditions of decomposition:

a-1: 3 h 300 °C; a-2: 3 h 600 °C after a-1; a-3: 3 h 800 °C after a-2;

b-1: 3 h 300 °C; b-2: 3 h 600 °C after b-1; b-3: 3 h 800 °C after b-2;

c-1: 10 min 600 °C; c-2: 90 min 600 °C; c-3: 7 h 1150 °C after c-2;

From the investigations, it can be deduced that for the formation of pure nickel ferrites without other phases a longer tempering phase at between 300 and $400°$ is required. In this temperature range, there is a considerably disturbed lattice besides more amorphous products, and an ordering process where nickel ferrites are formed takes place. γ–Fe_2O_3 and Fe_3O_4 possibly occur proportionately, their peaks coinciding extensively due to their analogous structure with that of nickel ferrite. Ilie *et al.* [9] discuss Fe_3O_4 as an intermediate phase when $NiFe_2O_4$ is formed from acetato complexes. However, in this case, NiO is to be expected to an extent that we could not detect by X–ray investigation.

Characterization of powders

On decomposition of compound II at 300° in air, not compact, but porous powders are obtained, the surface areas of which, $A > 20 \text{ m}^2 \text{g}^{-1}$ were determined by the BET method. Subsequent tempering at higher temperature results in a considerable decrease in the BET surface area. On tempering for 3 h at 300°, up to 600° and then 800°, a change in the specific surface area from 24.3 $\text{m}^2 \text{g}^{-1}$ to 4.7 $\text{m}^2 \text{g}^{-1}$ and then 3.0 $\text{m}^2 \text{g}^{-1}$ is observed. From the cumulative pore volume curves presented in Fig. 3 and the variation in the surface area of the pores with the pore radius, the decrease in the specific surface area can be explained by the disappearance of pores with radii $r < 200$ nm. It can be deduced from hysteresis measurements that V_p for $r > 1000$ nm is predominantly interspace volume. Grain size distributions relating to powder volume or powder mass show maximum values for grain diameters of $d < 10 \, \mu\text{m}$ (Fig. 4). The insignificant shrinking of the grains when the temperature of decomposition is increased from 300 to 600° and then 800° correlates with the disappearance of small pores and the decrease in the specific surface area. The comparatively large increase in the medium
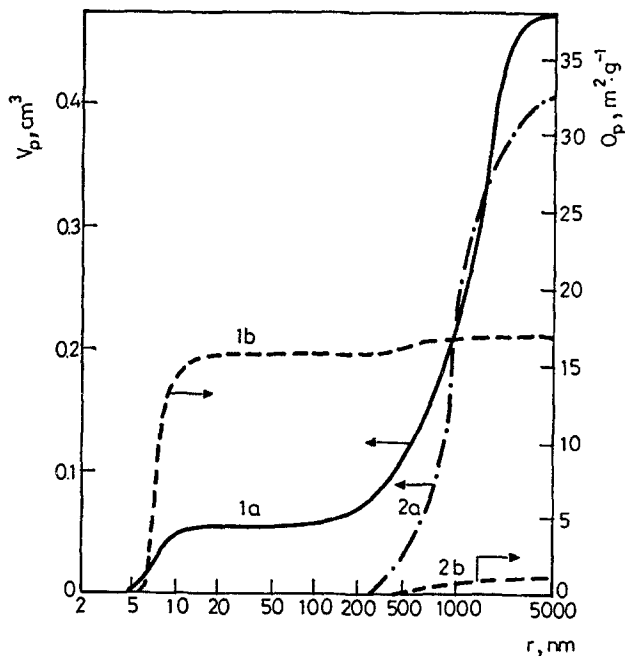

Fig. 3 Hg-high-pressure porosimetry of decomposition products of II; decomposition at a – 300 °C and b – 800 °C after a;
V_p...pore volume; O_p...pore surface

grain size with simultaneous broadening of the distribution curve after tempering treatment at 1150° is noteworthy. This is explained in Fig. 5, where scanning electronmicrograms of the tempered products are presented. The measured grain size diameters correlate well with the grain size distributions in Fig. 4. The particles remain extensively spherical up to a treatment temperature of 800°. From 800° onward, sintering processes begin, leading to smoother surfaces and irregular intergrowth.
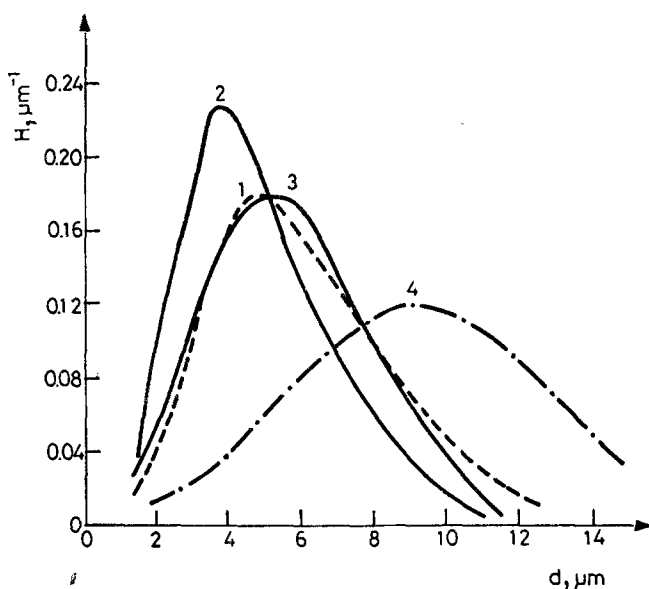

Fig. 4 Grain size distribution related to powder volume of decomposition products of II; conditions of decomposition: 1 – 300 °C; 2 – 600 °C after 1; 3 – 800 °C after 2; 4 – 1150 °C after 3; 3 h in each case

Conclusions

The above investigations on the thermal decomposition of acetato complex II show that preestablishment of the metal ion stoichiometry desired in the thermally decomposable precursor compound is advantageous for the synthesis of nickel ferrite at a temperature uncommonly low for solid-state reactions. However, a stoichiometry predefined at a molecular level is still not a sufficient condition. When rapid crystallization takes place after the decomposition, partial formation of the simple oxides cannot be excluded. However, this can be avoided by a slow ordering process in the primary
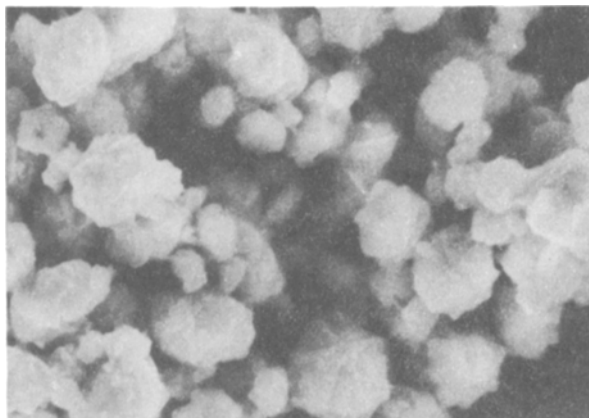
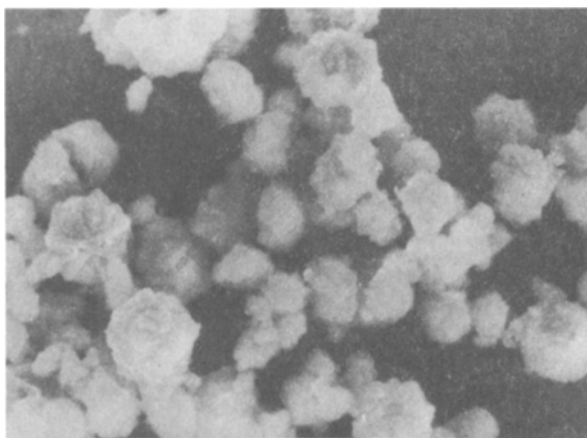Fig. 5–1 Scanning electron micrographes of samples 1–4 appropriate Fig. 4

Fig. 5–2 Scanning electron micrographes of samples 1–4 appropriate Fig. 4

amorphous or considerably disturbed oxidic decomposition product. This requires a slow decomposition process during slow heating of the precursor up to 300–400°. If there is insufficient dissipation of heat in the considerably exothermic decomposition steps above 200°, appreciable local overheating can occur, resulting in ignition of the product. Under certain circumstances, this results in the partial crystallization of α –Fe_2O_3. In this case, the formation of nickel ferrite as the only phase needs subsequent ignition at a high temperature typical of solid-state reactions.

The results are generally applicable to other MFe_2O_4 compounds as well. However, the relations are more complicated if favoured higher oxidation
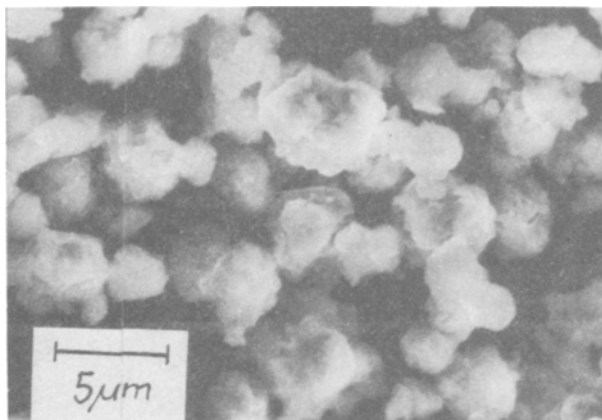
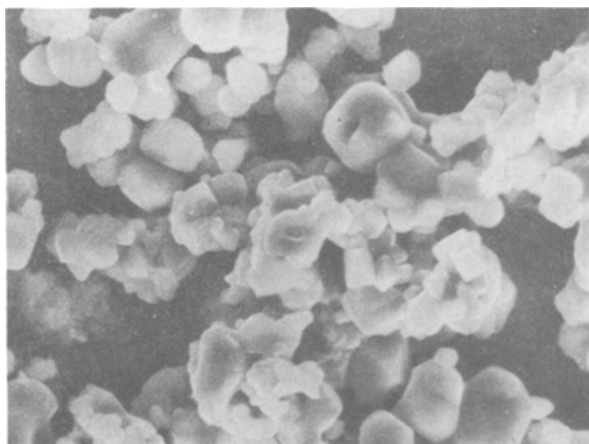Fig. 5–3 Scanning electron micrographes of samples 1–4 appropriate Fig. 4

Fig. 5–4 Scanning electron micrographes of samples 1–4 appropriate Fig. 4

numbers (e.g. for M = Mn or Fe) favour the occurrence of other phases. To make technically interesting ferrites of different M(II) ions, other ways must be found, because the syntheses of the respective mixed acetato complexes at justifiable expense are difficult to achieve with regard to the problems mentioned at the beginning.

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Zusammenfassung — Heteronukleare μ-Oxoazetate der Zusammensetzung $[Fe_2NiO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$ werden durch Erhitzen zersetzt, wobei Nickelferrite $NiFe_2O_4$ und - in Abhängigkeit von den Bedingungen der Zersetzung - mit einem Teil anderer fester Phasen gebildet wird. In der Zersetzungsreaktion werden auch H_2O, CH_3COOH, Azeton und CO_2 gebildet. Es wird ein Reaktionsschema für die Zersetzung angegeben. Die Produkte sind poröse Pulver mit einem Korndurchmesser zwischen 3 und 10 m. Wird die Zersetzungstemperatur von 300 auf 800°C erhöht, nimmt die BET-Oberfläche und die Porenoberfläche ab, wobei sich die Korngröße aber nur wenig verändert. Im Ergebnis der Wärmebehandlung im Temperaturbereich oberhalb 800°C werden durch Sinterprozesse größere Partikelaggregate gebildet.