Mechanothermal Solid-state Synthesis of Cobalt(II) Ferrite and Determination of its Heat Capacity by MTDSC

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Cobalt ferrite ($CoFe_2O_4$) has been synthesized by a solid-state mechanothermal process, and its molar heat capacity has been determined. A stoichiometric mixture of $CoC_2O_4 \cdot 2H_2O$ and $FeC_2O_4 \cdot 2H_2O$ was subjected to a combination of mechanical activation (by high-energy milling) and thermal activation (by annealing at temperatures between 300 and 700 °C). The process was followed by thermogravimetric analysis and high-temperature X-ray powder diffraction. It has been shown that $CoFe_2O_4$ forms at all temperatures, though with different degrees of crystallization, while Co_3O_4 and Fe_2O_3 are the only products formed when starting from unmilled mixtures. The molar heat capacity of $CoFe_2O_4$ has been determined in the temperature range 60 – 400 °C by MTDSC. It has been shown that the molar C_P values of $CoFe_2O_4$ samples produced at $T \geq 500$ °C are close to each other while those of the samples produced at 300 and 400 °C are lower. Furthermore the $CoFe_2O_4$ samples prepared at $T \geq 500$ °C show very similar microstructures.

Key words: Cobalt Ferrite, Modulated Temperature Differential Scanning Calorimetry (MTDSC), Heat Capacity, Mechanochemistry

Introduction

Cobalt ferrite belongs to a family of AFe_2O_4-type spinel ferrites where A is a divalent metal. Ferrites have several practical applications as magnetic [1] and refractory materials [2], in medical diagnostics [3] and as catalysts [4]. Several synthetic routes have been devised to prepare $CoFe_2O_4$. Paike *et al.* [5] synthesized spinel cobalt ferrite by the coprecipitation method using tetramethyl-, tetraethyl-, and tetrabutyl-ammonium hydroxide as precipitating agents. It has been shown that the degree of crystallinity depends on the thermal decomposition temperature and also on the bulkiness of the cation of the occluded organic base. Garcia Cerda *et al.* [6] prepared a metal-citrate-silica gel from metal salts, citric acid and tetraethylorthosilicate by the sol-gel method. The gel was dried at 100 °C and then calcined at temperatures between 600 and 1000 °C to obtain powder samples. Liu *et al.* [7] prepared $CoFe_2O_4$ nanoplatelets and nanoparticles by a facile hydrothermal treatment of an aqueous solution of cobalt dodecyl sulfate, $FeCl_3$ and NaOH at 120 °C. Cote *et al.* [8] produced $CoFe_2O_4$ *via* the reaction of ferric nitrate and cobalt nitrate with sodium hydroxide. The reaction was carried out in water at temperatures ranging from 200 to 400 °C and pressures of 25 MPa. Yan *et al.* [9] utilized the combustion method to prepare $CoFe_2O_4$ from a stoichiometric mixture of the nitrates of Co and Fe by using glycine as fuel.

Kasapoglu *et al.* [10] proposed a microwave-assisted combustion synthesis of $CoFe_2O_4$ with urea as a fuel. The synthesis takes only a short time (≈ 15 min) at 1000 °C. The thermolysis of organic precursors was also used for the synthesis of $CoFe_2O_4$. Randhawa *et al.* [11] investigated the thermal decomposition of a cobalt tris(malonato)ferrate(III) trihydrate precursor $Co_3[Fe(CH_2C_2O_4)_3] \cdot 3H_2O$ from ambient temperature to 600 °C in static atmosphere and succeeded in obtaining $CoFe_2O_4$ at a temperature (380 °C) much lower than that of the ceramic method provided the excess CoO is removed by treatment with 2 N nitric acid. Cobalt ferrite nanoparticles have also been prepared by the combination of chemical coprecipitation, mechanical alloying and subsequent heat treatment to reduce milling time and contamination effects [12].

The present work reports a solid-state synthesis process of $CoFe_2O_4$ starting from stoichiometric mixtures of $CoC_2O_4 \cdot 2H_2O$ and $FeC_2O_4 \cdot 2H_2O$ subjected to a combination of mechanical activation (by high-energy milling) and thermal activation (by annealing at T between 300 and 700 °C). Furthermore the molar heat capacity of $CoFe_2O_4$ obtained at the mentioned temperatures has been determined by modulated temperature differential scanning calorimetry (MTDSC) in the temperature range $60 - 400$ °C.

Results and Discussion

On samples of the mechanically activated mixtures dynamic (10 K min^{-1}) simultaneous TG/DSC measurements were performed up to 600 °C in static air.

Fig. 1 shows the TG/DSC curve of a sample of a milled mixture. The mean mass value attained at the maximum temperature is $M_{600 °C} = 42.6 \pm 0.1$ %, significatively lower than the value expected for the formation of a mixture CoO-Fe_2O_3 or of $CoFe_2O_4$ (43.2 %). This fact can be explained by taking into account that, during high-energy milling, volatile impurities were absorbed by the mixture. These volatile impurities are then released during heating of the milled mixtures. From the experimental mass value attained at 600 °C it can be easily calculated that ≈ 1.4 % by mass of volatile impurities is absorbed during milling.

The DSC curve shows that a very sharp exothermic DSC peak sets in when the endothermic thermal effect due to the dehydration of the mixture is nearly over. This exothermic peak is over at ≈ 300 °C, and its mean enthalpy is -2104 ± 120 J g^{-1} corresponding to -1158 ± 66 kJ. The same thermal protocol was applied to samples of the two metal oxalates after they had been subjected to mechanical activa-
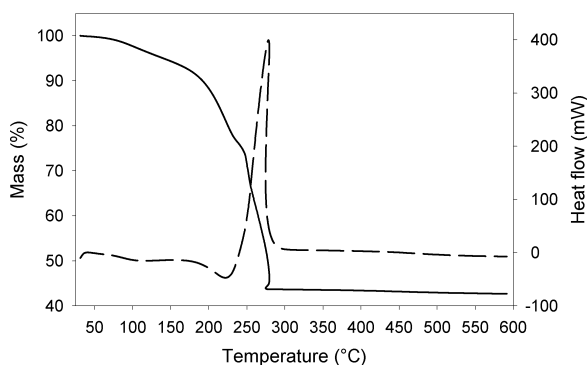

Fig. 1. TG (full line)-DSC (dashed line) of a sample of a milled mixture (10 K min^{-1}; static air).
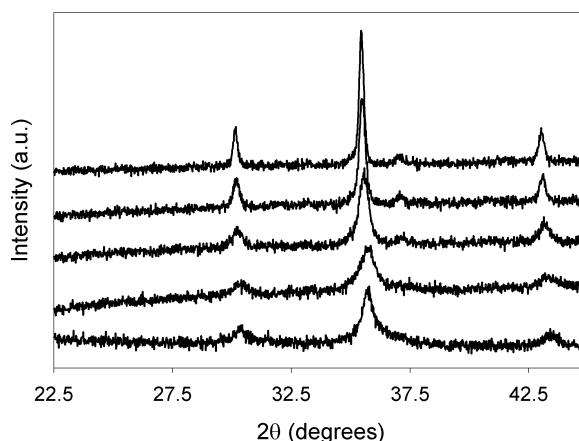

Fig. 2. HT-XRPD powder patterns of a milled mixture heated (10 K min^{-1}; static air) at temperatures from 300 °C (lower curve) up to 700 °C (upper curve) in steps of 100 °C.

tion by high-energy milling under the same conditions as adopted for the mixture. The DSC thermograms of the two oxalates show, below the decomposition stage, exothermic peaks with associated enthalpies of -280.7 ± 5.5 kJ [Co(II) oxalate] and -283.9 ± 2.9 kJ [(Fe(II) oxalate], respectively. By taking into account the decomposition enthalpies of the two oxalates, the value expected for the decomposition enthalpy of the mixture is -848.5 kJ. Confronted with the experimental value of -1158 kJ, it appears that an enthalpic excess of ≈ -310 kJ is released during the stage of the decomposition of the mixture that is likely due to the reaction between the formed oxides CoO and Fe_2O_3 to yield $CoFe_2O_4$. Indeed the XRPD powder patterns of the residuals recovered at the end of the TG/DSC measurements performed up to 600 °C only showed the reflections of $CoFe_2O_4$.

The results of the TG/DSC measurements indicate that $CoFe_2O_4$ begins to form at temperatures as low as 300 °C. Therefore, in order to establish the extent of $CoFe_2O_4$ formation as the temperature increases, an X-ray powder diffraction experiment was carried out on a sample of a milled mixture which was heated (10 K min^{-1}, static air) up to 700 °C and recording the XRPD patterns at 300, 400, 500, 600 and 700 °C. The relevant patterns are shown in Fig. 2.

The peaks characteristic of the constituent oxides (CoO, Co_3O_4, Fe_2O_3) are absent in the patterns recorded at all the temperatures, and the patterns only show very broad peaks characteristic of $CoFe_2O_4$. By increasing the temperature, other peaks characteristic
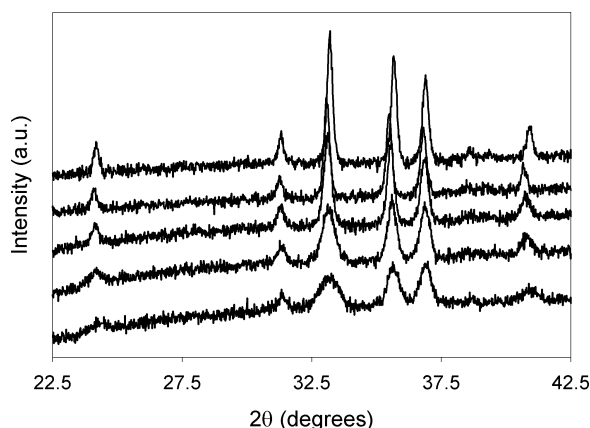
Fig. 3. HT-XRPD powder patterns of a physical mixture heated (10 K min^{-1}; static air) at temperatures from 300 °C (lower curve) up to 700 °C (upper curve) in steps of 100 °C.

of CoFe$_2$O$_4$ appear, and their intensity gradually increases. For sake of comparison the same experiment was conducted on a sample of the physical mixture. The results are reported in Fig. 3. Here the only peaks present are those characteristic of the constituent oxides (*i. e.* Co$_3$O$_4$ and Fe$_2$O$_3$).

Therefore, on the basis of the results of the HT-XRPD diffraction patterns, we attempted to synthesize CoFe$_2$O$_4$ starting from mixtures mechanically activated and subjecting them to thermal annealing for 8 h at temperatures of 300, 400, 500, 600 and 700 °C. The relevant powder patterns are shown in Fig. 4. It can be seen that all the peaks characteristic of CoFe$_2$O$_4$ are
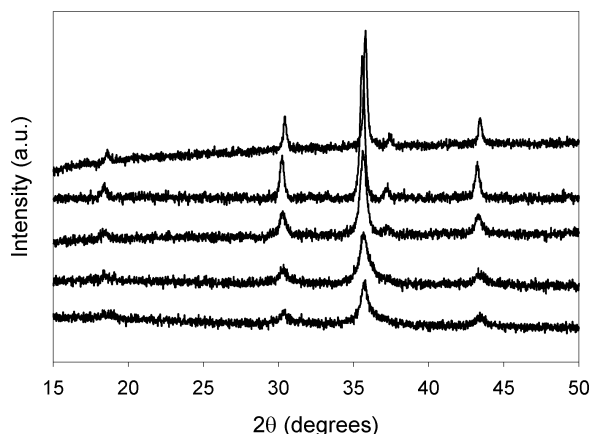

Fig. 4. XRPD powder patterns of samples of a milled mixture heated (10 K min^{-1}; static air) for 8 h at temperatures of from 300 °C (lower curve) up to 700 °C (upper curve) in steps of 100 °C.

Table 1. TG data on mechanically activated samples. $M_{\text{iso,in}}$ and $M_{\text{iso,fin}}$ are the mass-% reached respectively at the beginning and at the end of the annealing period (8 h) at T_{iso} between 300 and 700 °C. $M_{1000\,°C}$ is the mass-% reached at the end of the ramp at 1000 °C appended at the isothermal stage.

T_{iso} (°C)	$M_{\text{iso,in}}$ (%)	$M_{\text{iso,fin}}$ (%)	$M_{1000\,°C}$ (%)
300	44.0 ± 0.1	43.6 ± 0.1	42.3 ± 0.1
400	44.2 ± 0.1	43.6 ± 0.1	42.9 ± 0.1
500	43.6 ± 0.1	43.1 ± 0.1	42.7 ± 0.1
600	43.1 ± 0.1	42.5 ± 0.1	42.4 ± 0.1
700	42.9 ± 0.1	42.3 ± 0.1	42.2 ± 0.1

present only in the samples annealed between 500 and 700 °C.

The thermal treatment performed on the milled mixture (8 h at temperatures between 300 and 700 °C) was followed by recording the mass signal. Furthermore, at the end of the isothermal period, a heating ramp up to 1000 °C (10 K min^{-1}, static air) has been appended. Table 1 reports the % mass value recorded at the beginning and at the end of the 8 h isothermal stage ($M_{\text{iso,in}}$, $M_{\text{iso,fin}}$) and at 1000 °C ($M_{1000\,°C}$). The following considerations can be proposed: a) the mass loss recorded at the isothermal stage is lower at 300 °C (-0.4%) while it is about the same ($\approx -0.6\%$) at the other temperatures; b) for $T_{\text{iso}} > 300$ °C, the mass value attained at the end of the different isothermal periods decreases with increasing T_{iso}; c) the values of $M_{\text{iso,fin}}$ become indistinguishable (within the standard deviations) in the case of the samples annealed for 8 h at 600 and 700 °C; d) in the case of the mixtures annealed for 8 h at 600 and at 700 °C, the mean $M_{\text{iso,fin}}$ values are indistinguishable, within the standard deviations, from the mean mass values attained at 1000 °C.

Clearly, the mass loss process is over within the isothermal stage only in the case of the runs performed at 600 and 700 °C while a mass loss process takes place after the 8 h isothermal stage performed at 300 °C, 400 °C and, to a lesser extent, at 500 °C. At first sight such a mass loss process could be the reduction of Co$_3$O$_4$ to CoO.

However there are two arguments against this hypothesis: a) the mass loss of the mixture annealed for 8 h at 300 °C is significantly higher than expected if the reaction Co$_3$O$_{4(s)} \rightarrow 3$CoO$_{(s)}$ + 1/2 O$_{2(g)}$ occurs; b) the XRPD patterns of all the samples annealed at $T_{\text{iso}} \leq 500$ °C do not show evidence of Co$_3$O$_4$ or of CoO. Another possible explanation of the mass loss process (for $T_{\text{iso}} \leq 500$ °C) could be the oxidation of the graphite that originates from the carbon deposition
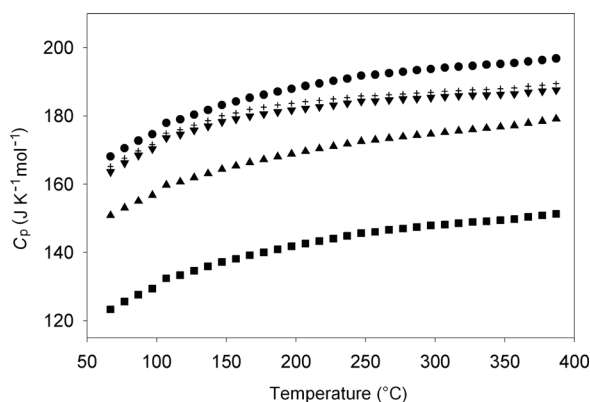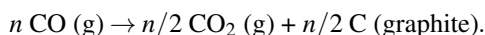
Fig. 5. Molar C_P determined by MTDSC of milled mixtures annealed for 8 h at 300 °C (squares); 400 °C (triangles); 500 °C (lozenges); 600 °C (horizontal bars); and 700 °C (circles).

(a)

(b)

(c)

Fig. 6. SEM micrographs taken on a $CoFe_2O_4$ sample prepared from the milled mixture of oxalates of Co(II) and Fe(II) subjected to an 8 h annealing at 500 °C (a), 600 °C (b) and 700 °C (c).

from the CO released during the decomposition of the oxalates according to the reaction:

$$n \, CO \, (g) \rightarrow n/2 \, CO_2 \, (g) + n/2 \, C \, (graphite).$$

The molar heat capacity of the samples obtained from annealing the milled mixtures has been determined by MTDSC. The values are shown in Fig. 5.

It can be seen that the data of the samples prepared by annealing the activated mixture at temperatures between 500 and 700 °C are superimposable while the data of the samples annealed at lower temperatures (300 and 400 °C) are lower.

The relevant data have been fitted as a function of temperature by the second order polynomia listed in the following:

$$300\,°C : \; C_p = 105.16 + 0.1864T - 0.0002T^2$$
$$400\,°C : \; C_p = 129.87 + 0.2056T - 0.0003T^2$$
$$500\,°C : \; C_p = 153.2 + 0.1976T - 0.0003T^2$$
$$600\,°C : \; C_p = 152.47 + 0.2179T - 0.0003T^2$$
$$700\,°C : \; C_p = 151.73 + 0.1971T - 0.0003T^2$$

It can be concluded that the heat capacity data of $CoFe_2O_4$ samples prepared by annealing the milled mixture at temperatures between 500 and 700 °C can be represented, as a function of temperature, by the relationship:

$$C_p = (152.5 \pm 0.6) + (0.2042 \pm 0.0097)T - 0.0003T^2$$

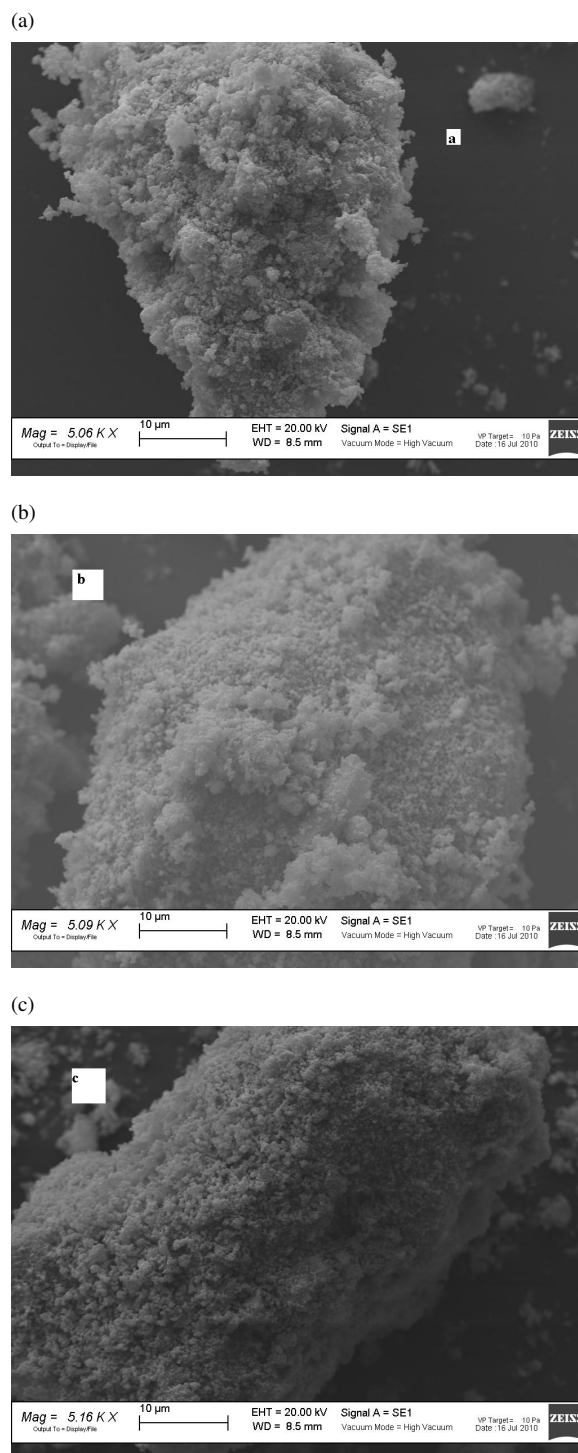The cobalt ferrite samples prepared by the mechanothermal treatment that were annealed at 500, 600 and

700 °C show, beside very similar C_p values, also a similar microstructure as it can be seen from the SEM micrographs taken under similar conditions (Figs. 6a, b, c).

Conclusion

It has been demonstrated that $CoFe_2O_4$ can be synthesized starting from a mixture of Co(II) and Fe(II) oxalate dihydrates provided it is mechanically activated by high-energy milling before being held isothermally (for 8 h) at temperatures as low as 300 °C. Only a mixture of the constituent oxides (Co_3O_4 and Fe_2O_3) is obtained when starting from mixtures where the mechanical activation step has been skipped. Evidence of reaction between the constituent oxides in the milled mixture has also been obtained by DSC and XRPD experiments. Molar heat capacity data on $CoFe_2O_4$ samples prepared by annealing samples of the milled mixture for 8 h at temperatures of 300, 400, 500, 600 and 700 °C have been determined: it has been shown that very similar values of C_p as a function of temperature (in the 60 – 400 °C temperature range) are recorded for the samples prepared by annealing the mixture at $T \geq 500$ °C. Also these samples showed, in SEM micrographs, very similar microstructures.

Experimental Section

The starting chemicals [$CoC_2O_4 \cdot 2H_2O$ (purity 99+ %) and $FeC_2O_4 \cdot 2H_2O$ (purity 99+ %)] were purchased from Aldrich Chimica (Italy). Physical mixtures of molar ratio Fe/Co = 2.0 were prepared by weighing the appropriate amounts of precursors and by dry milling the powders in an agate mortar. The mechanically activated mixtures were prepared by dry milling lots of 1 g of the physical mixtures.

The powders were put into zirconia jars (12.5 mL) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with 4 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 7 : 1). The mill was operated at 500 rpm (rotation speed) for 8 h.

TG/DSC measurements were performed with a TG-DSC Q600 simultaneous TG/DSC analyzer (TA Instruments Inc., USA). Samples of $\approx$ 50 mg of the mixtures were placed into alumina cups and heated (10 K min^{-1}, air flow 100 mL min^{-1}) from 25 °C up to 600 °C.

Samples of both physical and milled mixtures heated at 10 K min^{-1} were examined by XRPD. The XRPD patterns were recorded at 300, 400, 500, 600, and 700 °C. The relevant patterns were recorded in step scan mode (position-sensitive detector: step width 0.015°, 2s/step , 40 kV, 40 mA, $2\vartheta =$ $15 - 50°$, CuK_α radiation) with an X-ray powder diffractometer (Bruker D5005).

Milled mixture samples were put into alumina boats and heated in air at 10 K min^{-1} up to 300, 400, 500, 600, and 700 °C for 8 h; the samples were examined by X-ray powder diffraction. The milled samples were subjected to the same thermal treatment while following the sample mass on a thermobalance (TG Q5000 by TA Instruments Inc., USA).

The specific heat capacity of these very same samples were determined by MTDSC (Q2000, T_{zero} technology, TA Instruments Inc., USA). The samples ($\approx$ 30 mg) were placed in a hermetically closed aluminum pan and heated at 5 K min^{-1} (nitrogen flow of 50 mL min^{-1}, oscillation period 60 s; oscillation amplitude ± 0.8 °C) whereby the true reversing heat capacity was measured. The data given are the means of at least 15 runs. Before the measurements, the instrument was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions. A calibration constant of 1.0943 ± 0.0075 was obtained. SEM microphotographs were collected on gold-sputtered samples with a Zeiss EVO-MA10 scanning electron microscope.

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