The combined effect of mechanical and thermal energy on the solid-state formation of $NiFe_2O_4$ from the system $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$

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Abstract

Spinel-type ferrites MFe_2O_4 (M = Ni, Zn, Mn, Co, Mg) are among the most important magnetic materials and they are prepared mostly by solid-state reaction at elevated temperatures. We proposed in the past [V. Sepelak, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Mmenzel, F.J. Litterst, S.J. Campbell, K. Becker, J. Phys. Chem. C 111 (2007) 502612; S. Bid, P. Sahu, S.K. Pradhan, Physica E 39 (2007) 175] a mixed synthetic route that uses both mechanical and thermal energy. In the present work the strategy is applied to the preparation of $NiFe_2O_4$ starting from mixtures of $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$ subjected to both mechanical and thermal annealing. TG/DSC measurements allowed to obtain information on the reaction mechanism and also a ΔH for the reaction between the constituent oxides yielding $NiFe_2O_4$ in good agreement with the deduced from the data of $\Delta G°$ versus T. The XRPD of the samples recovered after the TG/DSC runs shows the reflexions of $NiFe_2O_4$ only when starting from milled mixture. $NiFe_2O_4$ can be prepared by thermal treatment of physical mixtures $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H2O$–$10FeC_2O_4 \cdot 2H_2O$ by 36 h at 1100 °C. On the contrary 12 h at 400 °C yield XRPD-phase pure $NiFe_2O_4$. Samples of $NiFe_2O_4$ obtained from the milled mixture show a surface area that decrease by increasing the synthesis temperature from 400 °C to 700 °C. On the basis of measurements of molar thermal capacity, it is demonstrated that $NiFe_2O_4$ can be obtained by a 12 h annealing at 450 °C of the mechanically activated mixture.

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1. Introduction

Spinel ferrites MFe_2O_4 (M = Ni, Zn, Mn, Co, Mg) are among the most important magnetic materials and have been widely used for various applications. In particular Ni ferrite powders ($NiFe_2O_4$) have been extensively investigated for several applications such as ferrofluids, catalysts, microwave devices and magnetic materials [1–3].

Usually $NiFe_2O_4$ powders are prepared by solid-state reaction method and this approach requires heating at very high temperatures for long periods of time so that the energy consumption is high and the production rate quite limited. For these reasons, alternative routes have been searched for. So,

for example, the synthesis of powder of Ni ferrite has been accomplished by a self-propagating high-temperature synthesis [4] and, moreover, several wet chemical methods have been developed to synthesize oxide ceramic powders to improve their properties. Indeed hard- and soft-magnetic ultrafine ferrite powders have been synthesized using a combination of coprecipitation and mechanical milling [5] and low-temperature synthesis of $NiFe_2O_4$ has been performed by hydrothermal methods [6–8]. Furthermore Rashad and Fouad [9] synthesized Ni ferrite powders from fly ash via a chemical synthesis route (coprecipitation method) where the precursor had to be treated at $T > 800$ °C for 2 h to obtain $NiFe_2O_4$. Again nickel ferrite powders were synthesized by pulse wire discharge method and characterized for their magnetic properties [10].

It has however to be noted that these methods have also drawbacks: high pH sensitivity, stringent drying conditions, complex

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equipment and expensive precursors [11]. To circumvent these problems the preparation of $NiFe_2O_4$ has been performed by direct milling of equimolar mixtures of NiO and Fe_2O_3: it has been recently demonstrated that, by milling these mixtures for times between 1 h and 20 h, nanometric $NiFe_2O_4$ could be obtained [12,13].

As an attempt to take opportunity of the advantages of the conventional ceramic method (simple equipment, no stringent drying condition, no expensive precursors) and to do away with its main drawbacks (very high temperature, lack of microstructural homogeneity), we developed a "mixed" synthetic route to some technologically important ferrites such as $BaFe_{12}O_{19}$ [14] and $ZnFe_2O_4$ [15]. In this sense we used starting mixtures of precursors (metal, metal carbonates and metal oxalates) that are of low cost and not very sensitive to air moisture and subjected them, prior to the annealing stage, to mechanical activation by high-energy milling. We were able to show that the mechanical activation reduces the temperature and duration of the thermal activation (annealing) and that such a mechanical–thermal preparation succeeds in obtaining the desired compound with interesting magnetic properties [14,15].

In the present work, we applied the same synthetic strategy to nickel ferrite starting from mixtures of $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ and $FeC_2O_4\cdot2H_2O$.

2. Experimental

2.1. Starting chemicals and sample preparation

The starting chemicals were purchased from Aldrich Chimica (Italy): $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ (purity 99+%) and $FeC_2O_4\cdot2H_2O$ (purity 99.9%).

TG measurements have been performed on samples of the precursors $FeC_2O_4\cdot2H_2O$ and $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$. In the case of $FeC_2O_4\cdot2H_2O$ the mean residual mass attained at 400 °C is $44.63 \pm 0.01\%$ that is in good agreement with the value expected (44.38%) for Fe_2O_3 formation and the mean residual mass attained at 600 °C from $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ is $58.79 \pm 0.17\%$ that is much lower than that expected (63.56%) for the formation of NiO.

This experimental expected difference can be explained by allowing for the fact that $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ has converted during storage at room temperature to $2NiCO_3\cdot2Ni(OH)_2\cdot Ni(OH)HCO_3\cdot4H_2O$: in this case the expected value of the residual mass becomes 58.34% that is close to the mean experimental value attained at 600 °C ($58.79 \pm 0.17\%$). Actually such a conversion is supported by observing that the DR/FT-IR spectrum of the NiO precursor shows a broad band between $1500\,cm^{-1}$ and $1200\,cm^{-1}$ with two maxima at $\approx1450\,cm^{-1}$ and $1390\,cm^{-1}$ that are characteristic, respectively of CO_3^{2-} and HCO_3^{-} (see Fig. 1). This fact has been taken into consideration in the preparation of the physical mixture of $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$–$FeC_2O_4\cdot2H_2O$ (molar ratio Fe/Ni = 2.0) were prepared by weighing the appropriate amounts of the reactants and by stirring them in acetone suspension for 3 h. Then the solvent was allowed to evaporate in an oven at 60 °C overnight.
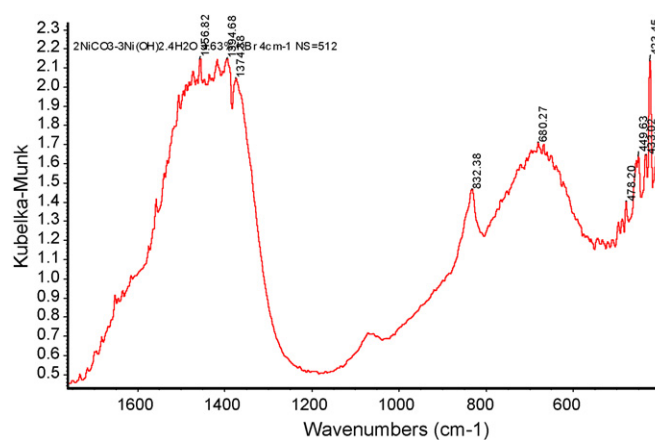

Fig. 1. DR/FT-IR spectrum of $2NiCO_3\cdot2Ni(OH)_2\cdot Ni(OH)HCO_3\cdot4H_2O$.

The mechanically activated mixtures were prepared by dry milling lots of 2 g of physical mixtures: the powders were put into zirconia jars (12.5 mL) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with five zirconia balls (12-mm diameter; the mass ratio between the milling balls and the sample powder was 7:1). The mill was operated at 450 rpm rotation speed for times up to 90 h.

2.2. Experimental techniques

The specific surface area of the starting reactants, of the mixtures and of the different samples of $NiFe_2O_4$ prepared was determined by N_2 adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 (Thermo Electron Corporation, operating with the static volumetric principle). The correction for the volume of the sample was introduced by measuring the He adsorption.

TG/DSC measurements were performed with a TG/DSC simultaneous thermogravimetric analyser (Q600, TA Instruments Inc., USA) connected to a computer (TA 3000) fitted with an appropriate software. Samples of $\approx$50 mg of the $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$–$FeC_2O_4\cdot2H_2O$ mixtures were placed in an alumina pan and heated at 10 K/min (under air flow of 100 mL/min) from 25 °C up to the temperature (600 °C) where a constant mass value is reached.

X-ray powder diffraction patterns were recorded in step scan mode (step 0.015°, 1 s/step, 40 kV, 30 mA, 2θ = 10–55°, Cu Kα) with an X-ray powder diffractometer (Bruker D5005) equipped with a position sensitive detector (PSD, Braun).

The specific heat capacity of the $NiFe_2O_4$ samples were determined by the Q2000 DSC (T_{zero} technology, TA Instruments Inc., USA) connected to a computer (TA 3000) fitted with an appropriate software. The samples ($\approx$10 mg) were placed in aluminium pans that were closed and heated at 20 K/min (under nitrogen flow of 50 mL/min) from 0 °C to 400 °C. The instrument, before the measurements, was calibrated, under the same experimental conditions, with a sapphire disk (mass 25.93 mg).
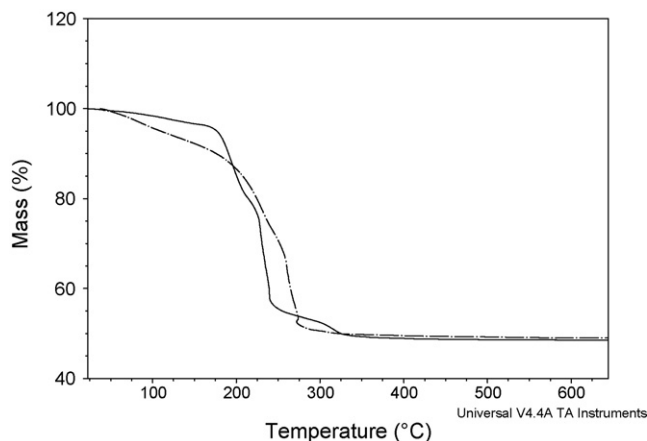
Fig. 2. TG curves for samples of physical (solid line) and milled (dashed line) mixture $2NiCO_3 \cdot 2Ni(OH)_2 \cdot Ni(OH)HCO_3 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$.
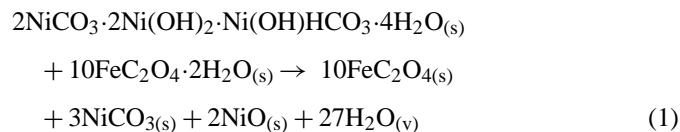
3. Results and discussion

3.1. TG/DSC measurements

TG measurements have been performed on samples of either physical and milled mixtures of $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$.

Fig. 2 compares TG run performed on samples of physical mixture and of milled mixture.

In the case of the sample of physical mixture, three mass loss processes can be individuated. The residual mass value obtained at the end of the first process ($T \approx 215\,°C$) is $80.06 \pm 0.18\%$ (mean of three runs). Such a mass value is in fair agreement with that expected (79.89%) for the reaction:

$$2NiCO_3 \cdot 2Ni(OH)_2 \cdot Ni(OH)HCO_3 \cdot 4H_2O_{(s)}$$
$$+ 10FeC_2O_4 \cdot 2H_2O_{(s)} \rightarrow 10FeC_2O_{4(s)}$$
$$+ 3NiCO_{3(s)} + 2NiO_{(s)} + 27H_2O_{(v)} \qquad (1)$$

The second stage ends at $T \approx 290\,°C$ and with a mass value of $53.61 \pm 0.28\%$ (mean of three runs) in good agreement with that expected (53.42%) if the following reaction would take place:

$$10FeC_2O_{4(s)} + (5/2)O_{2(g)}$$
$$\rightarrow 5Fe_2O_{3(s)} + 10CO_{(g)} + 10CO_{2(g)} \qquad (2)$$
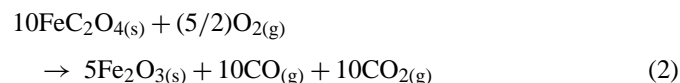
The last process ends with a mean mass value of $48.48 \pm 0.04\%$ that is in fair agreement with the value expected (47.96%) on the basis of the following reaction:

$$3NiCO_{3(s)} \rightarrow 3NiO_{(s)} + 3CO_{2(g)} \qquad (3)$$
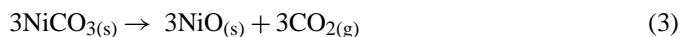
In the TG runs performed on the milled mixture reaction (1) cannot be individuated. The results show that a first stage of mass loss occurs whose final mass value decreases with increasing milling time: namely the mixture sample milled 90 h shows at $T \approx 300\,°C$ a mass value of 50.15% that corresponds to the % mass expected for the formation of a mixture of Fe_2O_3 (5 mol), NiO (4 mol) and $NiCO_3$ (1 mol). The second stage of mass loss occurs between $\approx 300\,°C$ and $\approx 400\,°C$ and shows a mean final mass of $48.16 \pm 0.20\%$ that very well agrees with the value

Table 1
Exothermic enthalpy values obtained in the DSC scans performed on samples of mixtures milled for increasing times

Milling time (h)	ΔH (J g^{-1})	T_{onset} (°C)	T_{max} (°C)
12	−32.0	464	505
30	−39.5	476	522
32	−44.4	474	522
48	−47.6	493	533
90	−49.6	519	554

expected (48.22%) for the formation of a mixture of Fe_2O_3 (5 mol) and NiO (5 mol). The importance of this second stage decreases with increasing milling time: it is no longer present in the TG curve of the mixture milled 90 h.

As concerns the calorimetric part of the thermal measurements, the DSC curve up to $\approx 400\,°C$ is constituted by the superimposition of endothermic peaks, due to the dehydration and decomposition processes, and of exothermic effects, due to the secondary oxidation $CO \rightarrow CO_2$. A broad exothermic peak is present between $\approx 470\,°C$ and $\approx 520\,°C$ in the DSC runs performed on milled mixture. The enthalpy values are reported in Table 1 and they show an increasing trend by increasing the milling time.

By considering that the standard free energy of the reaction $NiO + Fe_2O_3 \rightarrow NiFe_2O_4$ as a function of T (K) is expressed by the relationship [16]:

$$\Delta_{reac}G^\circ (J\,mol^{-1}) = -19,900 - 3.8T$$

the value $\Delta_{reac}H^\circ = -20\,kJ\,mol^{-1}$ is calculated at 800 K that corresponds to $-41.1\,J\,g^{-1}$. From the calorimetric data it can be seen that that a milling of ≈ 30 h is enough to trigger the complete reaction $NiO + Fe_2O_3 \rightarrow NiFe_2O_4$ to occur within 600 °C.

As a matter of fact XRPD patterns have been recorded on the residuals recovered after the TG/DSC runs: the reflexions of NiO and Fe_2O_3 only are present in the samples coming from the physical mixtures while the reflexions present in the residuals of the milled mixture are only those of $NiFe_2O_4$ (see Fig. 3).
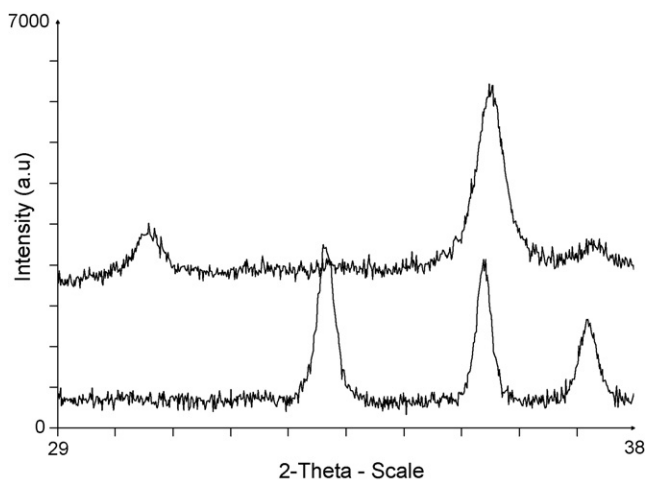

Fig. 3. Residuals recovered after TG run up to 650 °C in air on samples of physical mixtures (lower curve) and of milled mixtures (upper curve).

Table 2
Phases present in samples of physical mixtures after the annealing

T annealing (°C)	Time annealing (h)	Phases
600	12	NiO, Fe_2O_3
700	12	NiO, Fe_2O_3
800	12	NiO, Fe_2O_3
900	12	NiO, Fe_2O_3, $NiFe_2O_4$
1000	80	NiO, Fe_2O_3, $NiFe_2O_4$
1100	24	$NiFe_2O_4$

3.2. Annealing of mixtures and characterization of the products

The specific surface area of both precursors has been measured [$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$: 51.8735 $m^2 g^{-1}$; $FeC_2O_4 \cdot 2H_2O$: 1.8597 $m^2 g^{-1}$]. The specific surface area of the physical mixture is 14.9133 $m^2 g^{-1}$ that is in good agreement with the value calculated as the weighted mean of the specific surface areas of the two precursors (14.1124 $m^2 g^{-1}$). Milling of this mixture causes the surface area to increase from 14.9133 $m^2 g^{-1}$ to 18.4580 $m^2 g^{-1}$ ($\approx$31%).

About 500 mg of physical mixture were put into alumina boats and heated in air at 10 K/min up to different temperatures between 600 °C and 1100 °C where they have been annealed for different times. Table 2 reports the different phases found by XRPD after the annealing at each temperature and, from the data reported in Table 2, it can be concluded that $NiFe_2O_4$ can be prepared starting from a physical mixture only by a prolonged (24 h) thermal treatment in air at 1100 °C.

About 500 mg of the milled mixture were put into alumina boats and heated in air at 10 K/min up to different temperatures between 400 °C and 700 °C where they have been annealed for 12 h. Fig. 4 shows the patterns of the annealed samples: XRPD-pure $NiFe_2O_4$ is obtained after the annealing of 12 h annealing at 400 °C. Furthermore it can be seen that, by increasing the annealing temperature, the peaks of $NiFe_2O_4$ become increasingly narrow. The patterns of the mixture of the precursors annealed 36 h at 1100 °C is reported for sake of comparison.

The mean value of the Néel temperature (T_N determined by DSC) [17] of the samples of $NiFe_2O_4$ prepared from the milled mixture is $T_N = 589 \pm 2$ °C that does not significantly differ from that of the $NiFe_2O_4$ sample obtained from the physical mixture (590 °C).

Table 3 reports the surface area of the $NiFe_2O_4$ samples obtained from the milled mixture after 12 h annealing at 400 °C,
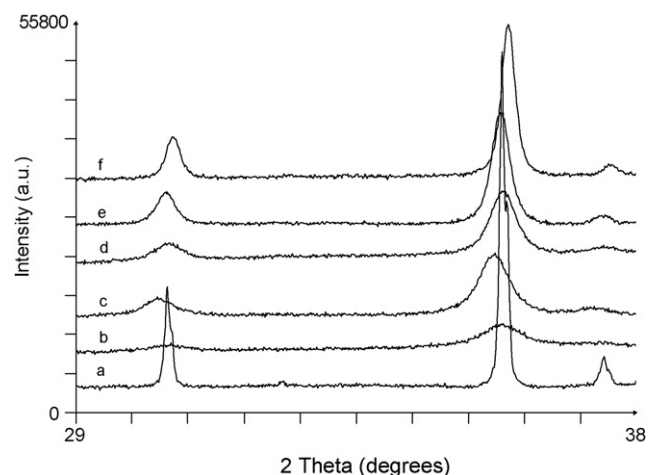

Fig. 4. XRPD patterns of sample of $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$ milled mixture annealed 12 h at temperatures of 400 °C (b); 450 °C (c); 500 °C (d); 600 °C (e) and 700 °C (f). The patterns (a) of the precursors mixture annealed 36 h at 1100 °C are reported for sake of comparison.

Table 3
Data of specific surface area of samples of mixtures $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$ subjected to different mechanical and/or thermal treatments

Mechanical/T (°C)/time (h)	A ($m^2 g^{-1}$)
Milled/–/–	18.4580
Milled/400/12	89.9488
Milled/450/12	47.7094
Milled/500/12	33.9285
Milled/600/24	14.1273
Milled/700/12	6.4454
–/1100/36	0.3032

450 °C, 500 °C, 600 °C and 700 °C. It can be seen that the annealing at 400 °C induces a very important increase of such a parameter that, then, decreases by annealing at higher temperatures. The surface area of $NiFe_2O_4$ obtained at 700 °C is $\approx$20 times that of $NiFe_2O_4$ obtained at the sample.

To try and discriminate between the different samples of nickel ferrite prepared at the different temperatures, the molar heat capacity of $NiFe_2O_4$ has been determined in the temperature range 0–400 °C. The C_p data of the $NiFe_2O_4$ sample obtained from the precursors subjected to different thermal and/or mechanical treatments have been fitted by the quadratic polynomial $C_p = A + BT + CT^2$. The values of the parameters A, B and C are reported in Table 4 for all the $NiFe_2O_4$ samples.

Table 4
C_p data (mean of three independent measurements) of the samples of $NiFe_2O_4$ obtained by different mechanical and thermal treatment of the mixture $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$–$FeC_2O_4 \cdot 2H_2O$

A	B	C	Sample
133.50 ± 11.25	0.1999 ± 0.0136	-3×10^{-4}	Milled + 12 h 400 °C
139.70 ± 6.48	0.2405 ± 0.0153	$-2.8 \times 10^{-4} \pm 0.4 \times 10^{-4}$	Milled + 12 h 450 °C
136.68 ± 7.75	0.2417 ± 0.0140	-3×10^{-4}	Milled + 12 h 500 °C
138.83 ± 2.26	0.2450 ± 0.0026	$-3.7 \times 10^{-4} \pm 0.5 \times 10^{-4}$	Milled + 12 h 600 °C
136.52 ± 5.08	0.2462 ± 0.0049	$-3.3 \times 10^{-4} \pm 0.4 \times 10^{-4}$	Milled + 12 h 700 °C
131.96 ± 7.27	0.2602 ± 0.0093	$-3.6 \times 10^{-4} \pm 0.5 \times 10^{-4}$	-/36 h 1100 °C

It can be observed that the values of the parameters of all the samples but that annealed at 400 °C coincide within the relevant standard deviation. The C_p results act as a confirmation that $NiFe_2O_4$ is obtained, provided high-energy milling of the mixture, by a thermal treatment of the mixture at temperatures as low as 450 °C while a thermal treatment at 1100 °C is needed to obtain the same compound when starting from a mixture not previously subject to mechanical activation.

4. Conclusions

The TG curves recorded on samples of physical mixture show that the reaction occurs in three steps in the case of the physical mixture: the dehydration of the mixture (stage 1) is followed from the decomposition of iron(II) oxalate to yield Fe_2O_3 (stage 2) and finally from the decomposition of $NiCO_3$ to NiO. Stage 1 cannot be individuated in the TG curves recorded on sample of mechanically activated mixture: the TG curves only show two stages. The first of them ends at a mass value that corresponds to a mixture constituted by 5 mol of Fe_2O_3, 4 mol of NiO and 1 mol of $NiCO_3$. The second stage, that nearly vanishes by increasing milling time, shows a final mass value in good agreement with that expected for the formation of a mixture $5NiO$–$5Fe_2O_3$.

Furthermore DSC data and XRPD of the residuals recovered after the TG measurements demonstrated that $NiFe_2O_4$ is produced within 600 °C only starting from the milled mixture.

XRPD patterns of samples of both physical and milled mixture annealed at temperatures between 400 °C and 1100 °C show that $NiFe_2O_4$ is obtained by 12 h annealing at temperatures as low as 400 °C while 24 h at 1100 °C are needed to yield $NiFe_2O_4$ when starting from the physical mixture. Actually C_p measurements indicated that $NiFe_2O_4$ is obtained from the mechanically activated mixture by 12 h annealing at 450 °C.

The surface area of $NiFe_2O_4$ obtained from the milled mixture is from ≈160 (450 °C) to ≈20 times (700 °C) higher than that of the physical one (1100 °C).

References

[1] M.H. Sousa, E. Hasmonay, J. Depeyrot, F.A. Tourinho, J.-C. Bacri, E. Dubois, R. Perzynski, Yu.L. Raikherb, J. Magn. Magn. Mater. 242 (2002) 572.
[2] G.G. Ramankutty, S. Suguman, Appl. Catal. A: Gen. 218 (39 51) (2001).
[3] V. Sepelak, D. Baabe, D. Mienert, D. Schulze, F. Krumeich, F.J. Litterst, K.D. Becker, J. Magn. Magn. Mater. 257 (377 86) (2003).
[4] C.H. Peng, C.-C. Hwang, C.K. Hong, S.Y. Chen, Mater. Sci. Eng. B 107 (2004) 295.
[5] J. Ding, X.Y. Liu, J. Wang, Y. Shi, Mater. Lett. 44 (2000) 19.
[6] J. Zhou, J. Ma, C. Sun, L. Xie, Z. Zhao, H. Tian, J. Am. Ceram. Soc. 88 (12) (2005) 3535.
[7] M.M. Bucko, K. Haberko, J. Eur. Ceram. Soc. 27 (2007) 723.
[8] J. Wang, Mater. Sci. Eng. B 127 (2006) 81.
[9] M.M. Rashad, O.A. Fouad, Mater. Chem. Phys. 94 (2005) 365.
[10] P.Y. Lee, K. Ishizaka, H. Suematsu, W. Jiang, K. Yatsui, J. Nanopart. Res. 8 (2006) 29.
[11] Z.X. Yue, J. Zhou, L.T. Li, H.G. Zhang, Z.L. Gui, J. Magn. Magn. Mater. 208 (2000) 50.
[12] V. Sepelak, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Mmenzel, F.J. Litterst, S.J. Campbell, K. Becker, J. Phys. Chem. C 111 (2007) 5026.
[13] S. Bid, P. Sahu, S.K. Pradhan, Physica E 39 (2007) 175.
[14] V. Berbenni, A. Marini, N.J. Welham, P. Galinetto, M.C. Mozzati, J. Eur. Ceram. Soc. 23 (2003) 179.
[15] V. Berbenni, C. Milanese, G. Bruni, A. Marini, I. Pallecchi, Thermochim. Acta 447 (2006) 184.
[16] O. Kubaschewski, High Temp. High Press. 4 (1972) 1.
[17] C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, R. Justin Joseyphus, B. Jeyadevan, K. Tohji, K. Chattopadhyay, J. Magn. Magn. Mater. 238 (2002) 281.