

# A novel metal–spinel ferrite composite $(\text{Ni}_{0.89}\text{Fe}_{0.11})_{0.59}\text{--}[\text{Fe}_{2.32}\text{Ni}_{0.68}\text{O}_{3.79}]$ : stability in air

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Composite materials have been the subject of intensive interest during the last four decades. Such materials have been developed to achieve a combination of properties not achievable by any of the elemental materials acting alone [1–3]. Recently we have developed an original method to obtain the composite  $(\text{Fe}_{0.2}\text{Co}_{0.8})_{0.8} [\text{Fe}_{2.38}\text{Co}_{0.62}\text{O}_4]$  in which  $\text{Fe}_{0.2}\text{Co}_{0.8}$  is an iron–cobalt alloy of b.c.c. structure and  $\text{Fe}_{2.38}\text{Co}_{0.62}\text{O}_4$  a cobalt-doped magnetite [4]. Cationic exchanges between metallic part and spinel phase are observed during thermal treatments highlighting the composite character of the material [5–7]. We present in this study another composite containing nickel and iron.

This composite has been obtained by adding nickel and ferrous chlorides  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  taken in a 1/2 ratio into a 20 N KOH solution heated in a stainless steel vessel on an electrical hot plate. The black powder has been filtered and washed with water. Chemical analysis has shown that  $[\text{Fe}^{\text{III}}]/[\text{Fe}^{\text{II}}] = 0.22$  and  $[\text{Ni}]/[\text{Fe}] = 0.5$ . The global formula is thus written  $\text{NiFe}_2\text{O}_{3.17}$ .

The X-ray diffraction pattern recorded at room temperature with a D500 Siemens diffractometer equipped with a primary beam quartz monochromator ( $\text{CoK}_{\alpha 1} = 0.178897 \text{ nm}$ ) exhibits the diffraction lines of a spinel phase with  $a = 0.8381 \text{ nm}$  and of f.c.c. cubic phase with  $a = 0.3534 \text{ nm}$  (Fig. 1) [3]. The spinel phase is close to magnetite while the f.c.c. phase corresponds to an iron–nickel alloy containing 10% Fe. The background is very low, ruling out the presence of amorphous phases. All the diffraction lines are symmetrical, ruling out crystallization of NiO, whose diffraction lines are slightly shifted towards large angles with respect to the magnetite ones.

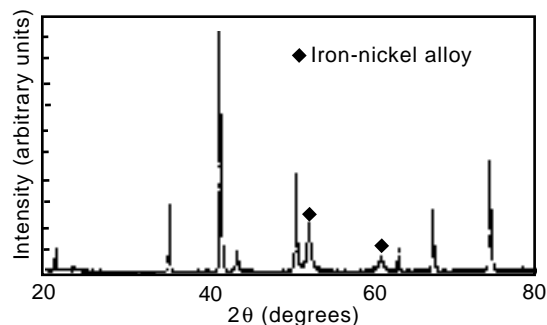


Figure 1 X-ray diffraction pattern of the composite.

The Mössbauer spectrum recorded at room temperature is shown in Fig. 2. The spectrum is characteristic of substituted magnetite including several sextuplets with various hyperfine fields corresponding to iron at the intermediate valence +2.5 in the octahedral site of the spinel structure. In addition a small metallic iron component is detected with a relative intensity near 3%, and a small paramagnetic component occurs, the relative intensity of which is smaller than 1% with parameters of a Fe oxide impurity. The typical parameter and the relative intensities are given in Table I. Taking into account the ratio  $[\text{Fe}]/[\text{Ni}] = 2$  and the respective concentration of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2.5+}$  on A and B sites, the chemical formula is written  $(\text{Ni}_{0.89}\text{Fe}_{11})_{0.59}\text{--}([\text{Ni}_{0.16}^{\text{II}}\text{Fe}_{0.84}^{\text{III}}]_{\text{A}} [\text{Fe}_{1.48}^{2.5}\text{Ni}_{0.52}^{\text{II}}]_{\text{B}}\text{O}_{3.79})$ . The respective concentrations of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2.5+}$  in A and B sites lead to oxygen vacancies and nickel in tetrahedral sites. That can be assigned to the low-temperature synthesis method which generates defaults.

The formula determined by Mössbauer spectroscopy is in agreement with the saturation magnetization of the composite  $\sigma_s = 69 \text{ Am}^2/\text{kg}$  measured at room temperature. The theoretical value for colinear structure is  $73 \text{ Am}^2/\text{kg}$  but this value can be slightly lowered by canted structure in octahedral site as seen in analogous compounds [6]. At room temperature,

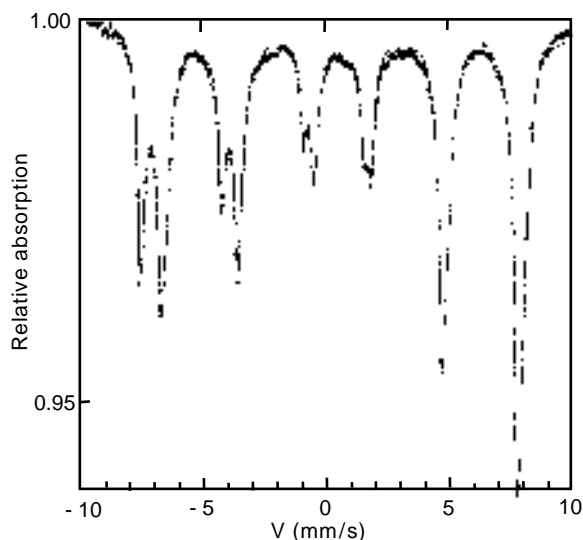


Figure 2 Mössbauer spectra at 300 K.

TABLE I Mössbauer parameters for the composite at 300 K: isomer shift values  $\delta$  with respect to the metallic iron (mm/s) ( $\pm 0.02$ ), hyperfine field values  $H_{\text{hyp}}$  (kA/m) ( $\pm 200$ ) relative intensities values (RI) for the various components ( $\pm 0.01$ )

	Spinel		Metal alloy
	Fe <sup>3+</sup> (A)	Fe <sup>2.5+</sup> (B)	Fe <sup>0</sup>
$\delta$	0.28	0.65	0.03
$H_{\text{hyp}}$	38300	35800	24900
RI	0.39	0.575	0.03

the hysteresis curve exhibits a coercive field of 12 000 A/m.

The oxidation of the composite in air has been studied by using a Setaram 92 apparatus and platinum crucibles. The heating rate was 1 K/min. The weight variation has been calculated after removing the signal of the empty crucible. No weight variation has been observed between 20 °C and 240 °C, showing the resistance to oxydation (Fig. 3). Between 240 °C and 500 °C, a large 6.0% weight increase occurs. This weight increase is in agreement with the oxidation of NiFe<sub>2</sub>O<sub>3,17</sub> into NiFe<sub>2</sub>O<sub>4</sub>.

On the X-ray diffraction patterns recorded at room temperature after 2 h annealing at temperatures between room temperature and 1000 °C, it can be observed that: at 200 °C, the crystallographic parameter of the spinel phase slightly decreases to  $a = 0.8375$  nm [5] and NiO crystallizes; at 300 °C, the crystallographic parameter of nickel metal does not change but the intensities of diffraction lines decrease. Nickel metal oxidizes into NiO and the crystallographic parameter of the spinel phase decreases up to 0.8362 nm [5]. This value is characteristic of a stabilized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>; the metal has disappeared at 400 °C and the spinel phase goes on oxidation; above 500 °C, the spinel phase changes into hematite which reacts with NiO in order to give NiFe<sub>2</sub>O<sub>4</sub>.

The variation of saturation magnetization follows these transformations: its value does not change below 240 °C, i.e. before the beginning of oxydation. Upon further annealing at higher temperatures, it decreases to 30 Am<sup>2</sup>/kg at 600 °C temperature for which  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is changed into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. At 1000 °C, the value of  $\sigma_s$ , measured at 300 K, is 44 Am<sup>2</sup>/kg, in agreement with NiFe<sub>2</sub>O<sub>4</sub> crystallization.

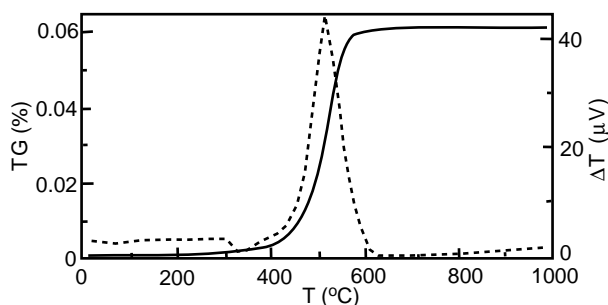


Figure 3 Thermogravimetric and thermal differential analysis of the precipitate in air (increasing rate 1 K/min).

In conclusion, the precipitation of nickel and ferrous chlorides in a strong basic solution allows one to synthesize a phase containing a nickel iron alloy and a spinel oxide. This is the result of the precipitation of a nickel ferrous hydroxide. Because of the high KOH concentration, this hydroxide dehydrates. Simultaneously, the disproportionation of Fe(II) into Fe<sup>0</sup> and Fe(III) occurs. Then Fe<sup>0</sup> reduces Ni(II) into Ni<sup>0</sup> in agreement with thermodynamic calculations. The disproportionation reaction which occurs in the basic solution is similar to that encountered for FeO at 400–500 °C following the reaction  $4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$  [9]. A Fe(II) disproportionation has also been reported in aqueous suspensions of Fe(OH)<sub>2</sub>. However, elemental iron reduces water and yields hydrogen [10–12]. In the present work, we have strongly increased the pH. Thus, the hydroxide dehydrates and the disproportionation occurs so rapidly that the metal is embedded within the oxide grains and cannot reduce water. This leads to crystallization of a metal–oxide composite, totally dehydrated. As a result of protection of the metal, the oxidation in air is not easy although the grains are 0.1–1 μm in size.

Moreover, the spinel phase contains oxygen vacancies, probably resulting from the low-temperature synthesis. These vacancies give it a strong instability: that is why NiO is rejected. Therefore the spinel phase is changed into a stabilized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Another point has to be noted: the presence of Ni<sup>II</sup> in tetrahedral sites, which is uncommon for NiFe<sub>2</sub>O<sub>4</sub> [13].

This method is easy to use for synthesizing metal–oxide composites. Studies have to be done to extend this method to other metal–oxide composites.

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