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Synthesis, characterization and thermal behaviour of Fe$_{0.65}$Co$_{0.35}$-MgAl$_2$O$_4$ and Fe$_{0.65}$Ni$_{0.35}$-MgAl$_2$O$_4$ nanocomposite powders

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Fe$_{1-x}$Co$_x$$_2$MgAl$_2$O$_4$ and Fe$_{1-x}$Ni$_x$$_2$MgAl$_2$O$_4$ nanocomposite powders are prepared by selective hydrogen reduction of monophasic oxide solid solutions synthesized by combustion in urea. The alloy particles, which are dispersed in the spinel matrix, are about 10 nm in size. An increase in reduction temperature from 700 to 1000 °C produces a narrowing of the particles’ composition range and an average composition closer to the target one. The magnetic nature of the alloy nanoparticles is discussed. The nanoparticles dispersed inside the oxide grains, which account for more than two thirds of the total metallic phase, are stable in air up to ca. 800 °C.

Experimental

The appropriate amounts of the desired metal nitrates (Mg, Al, Fe, Co, Ni) were mixed in stoichiometric proportions with urea and dissolved in the minimum amount of water in a Pyrex vessel. It should be noted that the transition-metal nitrates were added in substitution for Mg nitrate. The stoichiometric composition of the redox mixtures was calculated using the total oxidizing and reducing valency of the metal nitrates (oxidizer) and urea (fuel), which serve as numerical coefficients for the stoichiometric balance, so that the equivalence ratio is equal to unity. The vessel containing the solution was inserted into a furnace pre-heated at 600 °C. The solution immediately started to boil and undergo dehydration. The decomposition of the metal nitrates was accompanied by a large release of gases (oxides of nitrogen and ammonia). The obtained paste frothed and formed a foam which swelled and then blazed up. A white flame occurred with the production of a material which swelled to the capacity of the Pyrex vessel. The total combustion process takes place in less than 5 min. One combustion batch yields about 6 g of powder. The combustion products were mechanically ground using zirconia balls and vessel, giving rise to the hereafter designated ‘as-prepared’ oxide powders. The as-prepared oxides were reduced for 1 h in dry hydrogen at different temperatures (T) as required for the study. A total reduction of the transition metal ions would yield 4 mass% of metallic phase in the thus-obtained metal-oxide composite powders.

Elemental analysis was performed by atomic absorption spectroscopy. Phase detection and identification was carried out by X-ray diffraction (XRD) analysis. Transmission electron microscopy (SEM) and electron microdiffraction (EMD) analysis. The composition of the metal nanoparticles was evaluated by TEM energy-dispersive X-ray spectroscopy (EDX) from the results of about 20 analyses per composite powder (spot diameter equal to 2 or 7 nm according to the size of the particle under investigation). SEM specimens were prepared by ultrasonic dispersion in ethanol, deposited onto an aluminum sample holder and coated with Ag to prevent charge accumulation.
The powders for TEM examination were sonicated in ethanol and a drop of the dispersion was deposited onto a copper grid coated with a collodion film. The oxidation of the composite powders was investigated by thermogravimetry (TG) in flowing air (heating rate 3 °C min⁻¹).

The Mössbauer spectra of the as-prepared powders were recorded with a ⁵⁷Co (Rh) source in a conventional time-mode spectrometer with constant-acceleration drive and a triangular reference signal. The spectra for the oxides and nanocomposite powders were collected with the absorbers at 9 K and also at 298 K for some specimens. One spectrum was run at 273 K in an external field of 6 T applied parallel to the γ-ray beam. Accumulation of the data was performed in 2048 channels until a background of at least 10⁷ counts per channel was reached. The spectrometer was calibrated by collecting at room temperature the spectrum of a standard Fe foil and the centre shift (δ values quoted hereafter) are with reference to this standard (centre shift=- intrinsic isomer shift+ second order Doppler shift). The Mössbauer spectra of the Fe₃O₄·MgAl₂O₄ samples were analysed assuming symmetrical components with a Lorentzian line shape, while those of the oxides and those of the Fe₂Ni₄·MgAl₂O₄ composites fitted with a hyperfine field distribution (each sub-spectrum of the distribution is composed of Lorentzian lines). This latter procedure was chosen because the corresponding Mössbauer patterns were strongly asymmetrical.

Results and Discussion

Oxides

Elemental analysis (Table 1) shows that the as-prepared oxides contain the desired proportions of Mg, Al, Fe and Co or Ni. As expected, the Co-containing powder is dark blue and the Ni-containing powder is green-grey. The only phase detected on both XRD patterns is the desired spinel (Fig. 1). The lattice parameter measured for both oxides (a=0.8085 nm) is in good agreement with that calculated using Vegard’s law (0.806 nm and 0.8084 nm for Mg₂Fe₂₋₃Ni₀₋₃Al₄O₁₄ and Mg₂Fe₂₋₃Co₀₋₃Al₄O₁₄, respectively). The results show that the presence of iron promotes the formation of monophasic products.

Table 1 Elemental analysis (±2 mass%) and some characteristics of the as-prepared oxides, a= lattice parameter (nm), Sₚ specific surface area (m² g⁻¹).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>phase (XRD)</th>
<th>a</th>
<th>color</th>
<th>Sₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>14.7</td>
<td>36.5</td>
<td>2.5</td>
<td>1.4</td>
<td>spinel</td>
<td>0.8085</td>
<td>dark blue</td>
</tr>
<tr>
<td>Al</td>
<td>14.8</td>
<td>36.5</td>
<td>2.6</td>
<td>1.4</td>
<td>spinel</td>
<td>0.8085</td>
<td>grey</td>
</tr>
<tr>
<td>Fe</td>
<td>21.8</td>
<td>36.5</td>
<td>2.6</td>
<td>1.4</td>
<td>spinel</td>
<td>0.8085</td>
<td>grey</td>
</tr>
</tbody>
</table>

Fig. 1 XRD patterns of the as-prepared (a) Co- and (b) Ni-containing oxides (sp. spinel phase)

Indeed, it has been shown in a previous work that similar Fe-free compounds (Mg₆₋₇M₄₋₅Al₁₀O₁₄, M=Co, Ni) consist in fact of a mixture of MgO (in very small amount) and a spinel phase, which thus contains an excess of trivalent cations. This finding is consistent with the MgO-Al₂O₃ phase diagram which indeed indicates that the spinel phase may be non-stoichiometric at temperatures similar to the one reached in the combustion process (ca. 1200 °C). Moreover, Navrotsky and Kleppa proposed that a considerable solid-solution range exists on the Al₂O₃-rich side of the stoichiometric NiAl₂O₄ (Ni=Mg, Mn, Fe, Co, Ni, Cu) spinels.

Mössbauer spectra of the as-prepared oxides at 9 K are shown in Fig. 2. At this temperature, the electron hopping that may occur between iron(II) and iron(III) ions located in the octahedral sites is suppressed. The best fit was obtained assuming a superposition of two quadrupole-splitting distributions (accounting for the Fe²⁺ and Fe³⁺ ions), their values being linearly correlated with the centre shifts. The corresponding Mössbauer parameters are given in Table 2. The quadrupole splitting distribution profiles of the two components both show two peaks, that one is tempted to relate to tetrahedral Fe²⁺ and Fe³⁺ ions, respectively. The agreement between the XRD patterns is the desired spinel (Fig. 1). The lattice parameter measured for both oxides (a=0.8085 nm) is in good agreement with that calculated using Vegard’s law (0.806 nm and 0.8084 nm for Mg₂Fe₂₋₃Ni₀₋₃Al₄O₁₄ and Mg₂Fe₂₋₃Co₀₋₃Al₄O₁₄, respectively). These results show that the Ni-containing powder is dark blue and the Co-containing powder is green-grey. The only phase detected on both XRD patterns is the desired spinel (Fig. 1). The lattice parameter measured for both oxides (a=0.8085 nm) is in good agreement with that calculated using Vegard’s law (0.806 nm and 0.8084 nm for Mg₂Fe₂₋₃Ni₀₋₃Al₄O₁₄ and Mg₂Fe₂₋₃Co₀₋₃Al₄O₁₄, respectively). The results show that the presence of iron promotes the formation of monophasic products.
Fig. 2 Mössbauer spectra (9 K) of the as-prepared (a) Co- and (b) Ni-containing oxides and the corresponding quadrupole-splitting distributions for the Fe$^{2+}$ and Fe$^{3+}$ components

Table 2 Mössbauer parameters measured at 9 K of the as-prepared oxides

<table>
<thead>
<tr>
<th>specimen</th>
<th>$\delta$</th>
<th>$\Delta E_q$</th>
<th>$\Gamma$</th>
<th>$P$</th>
<th>$\delta$</th>
<th>$\Delta E_q$</th>
<th>$\Gamma$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-containing</td>
<td>(1)</td>
<td>1.07</td>
<td>2.45</td>
<td>0.42</td>
<td>0.37</td>
<td>0.40</td>
<td>0.95</td>
<td>55</td>
</tr>
<tr>
<td>oxide</td>
<td>(2)</td>
<td>1.05</td>
<td>3.05</td>
<td>0.35</td>
<td>0.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-containing</td>
<td>(1)</td>
<td>1.08</td>
<td>2.45</td>
<td>0.31</td>
<td>0.35</td>
<td>0.35</td>
<td>0.75</td>
<td>67</td>
</tr>
<tr>
<td>oxide</td>
<td>(2)</td>
<td>1.05</td>
<td>3.10</td>
<td>0.41</td>
<td>0.75</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\delta$ = centre shift (mm s$^{-1}$); $\Delta E_q$ = quadrupole splitting (mm s$^{-1}$); $\Gamma$ = half width at half height (mm s$^{-1}$); $P$ = proportion (%). The $\delta$ and $\Delta E_q$ values are those of the two peaks detected in the quadrupole-splitting distribution profiles: notations (1) and (2) refer to the lower and higher quadrupole-splitting components, respectively.

Nanocomposite powders

The as-prepared oxide powders have been reduced in hydrogen at $T_r = 700$, 750, 800, 950 and 1000 °C. For the sake of brevity, the resulting composite powders will be denoted as FeCoR700, FeCoR750, …, FeNiR1000 in the following section. Analysis of the XRD patterns of the composite powders (Fig. 5) reveals the presence of bcc Fe/Co (110) peak. Since the bcc Fe/Co (110) peak can not be resolved because of its superposition with the (400) spinel peak (measured interplanar distance 0.202 nm), we have calculated the ratio

$$R_1 = \frac{I_{(400)\text{spinel}} + I_{(311)\text{FeCo}}}{I_{(400)\text{spinel}}}$$

in which $I_{(400)\text{spinel}}$ and $I_{(311)\text{FeCo}}$ represent the relative intensities of the spinel (400) and (311) peaks respectively. $R_1$ is found to increase with increasing $T_r$ up to 900 °C and then remains constant (Fig. 6(a)), which demonstrates the evolving formation of bcc Fe/Co alloy(s) and suggests that the reduction of the transition-metal ions is completed at 900 °C. The γ-FeNi (311) and (200) peaks (measured inter-reticular distances 0.207 and 0.180 nm respectively) are clearly detected in the XRD patterns (Fig. 5(b)). Their intensities increase with increasing $T_r$. Using
Fig. 4 TEM micrograph (a) and EMD pattern (b) of the as-prepared Co-containing oxide

The evolution of the ratio

$$R_2 = \frac{I_{111}(\text{Fe/Ni})}{I_{311}(\text{spinel})}$$

with $I_{111}$ and $I_{311}$ the relative intensities of the spinel (311) and the Fe/Ni (111) peaks respectively, one can approximately follow the reduction of the oxide with the increase in $T_r$ [Fig. 6(b)]. $R_2$ keeps increasing in the entire temperature range (700–1000 °C), indicating that the reduction of the transition metal ions is not complete below 1000 °C. These findings are in good agreement with an earlier work showing that the reduction of the transition metal ions to the metallic state in the oxide matrix (Fig. 8). The metal particles are pictured as small, dark areas on the micrographs as can be seen by comparing the images of the oxide [Fig. 4(a)] and of the composites [Fig. 8(b) and (c)]. The number of particles is higher in the R900 and R1000 composites than in R700 and R800 specimens. It is interesting to note the presence of a shell, about 2 nm thick, surrounding the metal particles in the FeCoR800 composite [Fig. 8(a)]. Such a core–shell nanostructure has been observed earlier in Fe/Ru-Al$_2$O$_3$ and Fe-Al$_2$O$_3$ nanocomposite powders: in the former case, it points to a bimetallic nature of the nanoparticles (Ru-rich core and Fe-rich shell) and in the latter case at Fe particles (core) separated from the Al$_2$O$_3$ matrix by a thin FeAl$_2$O$_4$ layer (shell) which is formed because the reduction temperature was sufficiently low (800 °C) in order not to totally reduce the Fe ionic species to metallic iron. The explanation given for the Fe/Ru-Al$_2$O$_3$ nanocomposite can probably be ruled out in the present case since Fe and Co cannot be distinguished from one another at the TEM magnification used in this study ($\times$ 100 000). High-resolution electron microscopy would be helpful to clarify this point.

The metal-particles size distributions (in number) were derived from the measurement of the size of about 200 particles.
Fig. 6 Evolution of $R_1$ (a) and $R_2$ (b) with the reduction temperature ($T_r$). See text for the definitions of $R_1$ and $R_2$.

Fig. 7 Evolution of the specific surface area ($S_w$) of Fe/Co-MgAl$_2$O$_4$ (●) and Fe/Ni-MgAl$_2$O$_4$ (□) composite powders with the reduction temperature ($T_r$).

Fig. 8 TEM micrographs of the Fe/Co-MgAl$_2$O$_4$ powder prepared by reduction at 800 °C (a) and 1000 °C (b) and of the Fe/Ni-MgAl$_2$O$_4$ the size distributions are unimodal and rather narrow. Previous works have shown that this feature mainly results from the monophase nature of the starting oxide solid solutions and also from their relatively low specific surface area. The average size of the metal particles increases with increasing $T_r$ from 6.3 to 12.5 nm for FeCoR700 and FeCoR1000 respectively, and from 6.5 to 10.1 nm for FeNiR700 and FeNiR1000 respectively. The position of the peak in the distribution follows a similar evolution. The rather high average size (11.4 nm) obtained for the FeCoR800 specimen is due to the presence of the above discussed shell around the particles. One can also observe that the increase in $T_r$ from 900 to 1000 °C gives rise to a marked broadening of the Fe/Co particle-size distribution. This could indicate that the reduction of the transition metal ions is completed at 900 °C, in line with the XRD observations, and that a higher reduction temperature only results in a coalescence of the metal particles. In contrast, such a phenomenon is not observed in the case of the Fe/Ni-MgAl$_2$O$_4$ composites.

The metal nanoparticles were further examined by EDX analysis. In contrast to previous results on Fe/Cr-Al$_2$O$_3$ powders, no correlation has been found between the composition and the size of the particles. However, the EDX results (Table 3) show that an increase in $T_r$ leads to a more narrow composition range on the one hand and to an average composition closer to the desired one (Fe$_{0.65}$M$_{0.35}$, M=Co or Ni) on the other.
Table 3 Composition range and average composition of the metal nanoparticles in the Fe–Co–MgAlO₄ and Fe–Ni–MgAlO₄ composite powders. \( \Delta \% \) represents the difference between the maximum and minimum measured Co or Ni content in the metal particles of a given nanocomposite powder.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition range (( \pm 2 ) atom%)</th>
<th>Average composition (( \pm 2 ) atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCoR1000</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
<tr>
<td>FeCoR800</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
<tr>
<td>FeCoR700</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
<tr>
<td>FeNiR1000</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
<tr>
<td>FeNiR800</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
<tr>
<td>FeNiR700</td>
<td>Fe₂₉Co₃₃Ni₂₈Co₂₅₆₇O₄</td>
<td>Fe₂₉Co₃₃Ni₂₆₅₈Co₂₅₆₇O₄</td>
</tr>
</tbody>
</table>

MgAlO₄ composites, obtained after reduction at 700, 800, 900 and 1000 °C, have been recorded at 9 K. They have been fitted with a doublet representing the Fe⁺ ions and a sextet accounting for the ferromagnetic Fe/Co or Fe/Ni alloys. Fe⁺ ions were not detected, meaning that the reduction to the iron(0) state is complete at temperatures below 700 °C. As mentioned earlier, this observation suggests that the Fe⁺ ions are located at or near the surface of the oxide crystals and, indeed, the corresponding reduction temperature (\( \leq 700 \) °C) is considerably lower than those reported for Fe⁺ ions substituting in the lattices of Al₂O₃ (1300 °C)18 MgO (1200 °C)23 and Cr₂O₃ (1200 °C).24 The evolution of the Fe⁺/Fe²⁺ proportions, calculated from the relative spectral area of the doublet with respect to the sextet, allows one to quantify the reduction of the Fe⁺ ions with the increase in \( T_r \).

First, the Mössbauer spectrum of the Fe-Co-MgAlO₄ composites (Fig. 10 and Table 4) will be discussed. The proportion of Fe⁺⁺ ions sharply decreases from 84 to 9% on increasing \( T_r \) from 700 to 800 °C, eventually reaching 0% for \( T_r \geq 900 \) °C. This confirms that the reduction of this system is complete at 900 °C. The Fe/Co particles, the proportion of which accordingly increases, exhibit the same value for the hyperfine field \( (H = 367 \text{ kG}) \) although their composition is different from one composite to the other as discussed above. This finding is in agreement with the room-temperature Mössbauer-spectroscopy study of Johnson et al.19 which revealed a nearly constant \( H \) value \( (H = 365 \text{ kG}) \) in the Fe₉Co₃₃O₄-Fe₉Co₃₃O₄ composition range.

For the Fe/Co-MgAlO₄ composites (Fig. 11 and Table 5), the Mössbauer results confirm that the reduction is complete only at 1000 °C. It may thus be inferred that the reduction of Co³⁺ ions promotes the Fe⁺⁺ reduction more efficiently than the reduction of Ni³⁺ ions. Moreover, it should be noted that Fe/Co-MgAlO₄ composites are much more easily prepared than Fe-Ni-MgO composites (total reduction at 1300 °C only).15 It is further worth mentioning that no ferromagnetic n-Fe/Ni has been detected (neither by Mössbauer spectroscopy at 9 K, nor in the XRD patterns), showing that the martensitic \( \gamma \rightarrow \alpha \) transformation upon cooling is suppressed in fine alloy particles containing > 20 atom% Ni, as indicated on the Fe-Ni phase diagram proposed by Hansen.24 Since the \( \gamma \rightarrow \alpha \) transformation temperature dramatically increases with decreasing Ni content, this also confirms the present EDX results detecting no alloy particles with <35 atom% Ni.

The hyperfine field distribution \( P(H) \) of the sextets (Fig. 11) is broad, ranging between 250 and 400 kG. It has not been necessary to consider lower hyperfine field values to obtain acceptable fits, in contrast to what has been claimed by Gonser et al.25 who reported a field distribution with two broad maxima centred around 80 and 300 kG at 22 K under an external field of 5 T. These authors assigned the high-field component to a ferromagnetic ordering of the alloy and the...
23 field distribution line shapes in the present Fe results. In the case of FeNiR700, one can assume that the netic contributions to the room-temperature Mo¨ssbauer spec-

Fig. 10 Mo¨ssbauer spectra (9 K) of the Fe-Co–NiAl–Ga alloys prepared by reduction at (a) 700, (b) 800, (c) 900 and (d) 1000 °C.
trum of a synthetic bulk Fe32Ni68 alloy. They proposed that these contributions respectively arise from metastable precipitates of a low-spin \( \gamma \)-FeNi phase \( (\gamma_{2s}) \) embedded in a matrix of high-spin \( \gamma \)-FeNi phase \( (\gamma_{1s}) \), the ordinary quenched FeNi phase of the same controlled composition. They point out that this model is not to be confused with that of Weiss because \( \gamma_{1s} \) could occur as a distinct phase. It is also worth mentioning that this model was successfully applied to specimens of the Santa Catalina meteorite, which contains several FeNi phases. However, detailed low-temperature, in-field Mössbauer spectroscopy studies on several slices of the same meteorite have led to the conclusion that the unsplit line probably arises from a \( \gamma \)-FeNi matrix, the magnetic nature of which may be described as a mixture of paramagnetic and ferromagnetic parts owing to slight composition fluctuations. The singlet observed in the present Mössbauer spectrum of the nanocomposite powders could a priori account for either a superparamagnetic, a paramagnetic or an antiferromagnetic phase. Indeed, superparamagnetic behaviour has been reported for FeNi alloys in the forms of thin foils and fine particles. A paramagnetic \( \gamma \)-phase has been detected by Widatallah et al. on FeC1000, and FeNi1000 fine particles, a composition which is quite far from that of the present particles. Baldokhin et al. observed coexistence of paramagnetism and ferromagnetism on FeNi1000; fine particles (between 5 and 15 nm in diameter) and proposed explanations according to Weiss's model.

In order to get more information on the origin of the room-temperature single line and to determine the magnetic nature of the corresponding phase, which seems to be ferromagnetic at 9 K, a spectrum of the FeNiR1000 powder was measured at \( T = 9 \) K. A low external field applied parallel to the \( \gamma \)-ray beam. The resulting Mössbauer spectrum consists of two subspectra (Fig. 1), showing that the phase giving rise to the singlet in the in-field Mössbauer spectrum is not superparamagnetic. A fit has been attempted assuming that one subspectrum was the quadruplet of the ferromagnetic phase, the second one being a sextet (fixed area ratio 3:2:1) representing an antiferromagnetic alloy. The result was a poor description of the central part of the spectrum. The best fit has been obtained assuming that two quadruplets (fixed area ratio 3:0:1) composed the total spectrum. The first quadruplet \( (\delta = 0.01 \text{ mm s }^{-1}, 2\Delta = 0.01 \text{ mm s }^{-1}, H = -45 \text{ kG}) \) is consistent with a paramagnetic \( \gamma \)-FeNi phase and its proportion (20%) corresponds to that of the singlet in the spectrum recorded without applied field.

One can consider several mechanisms to explain the paramagnetic behaviour observed for the FeNiR1000 composite. Existence of two states of the iron atoms as proposed by different authors can be ruled out because the Mössbauer spectrum of FeNiR1000 recorded at 9 K shows only one sextet representative of a ferromagnetic alloy. According to Kachi and Asano, paramagnetism could also appear due to fluctuations of the Ni content. In the present case, one has to consider the fluctuations that most probably exist from one alloy particle to the other (as indicated by the EDA results) on the one hand and concentration inhomogeneities within a given alloy particle on the other hand. In the latter case, one may assume that the surface alloy particles, which are formed first, are more homogeneous than the intragranular ones, for which the slight differences in Ni\(^{+2}\) and Fe\(^{+2}\) ions reduction temperatures could have provoked a composition gradient. Thus, the intragranular particles would have a Ni-rich internal part and a Fe-rich external part, leading to the ferromagnetic and paramagnetic behaviours respectively. The observed proportion of paramagnetic phase (20%) would correspond to an Fe-rich zone extending over the two external atomic layers of a metallic particle 10 nm in diameter (and thus containing about 25 atomic layers). Such an explanation is not unrealistic. Another possibility is that the room-temperature paramagnetic behaviour is due to some very small FeNi particles, the Curie temperature of which is known to strongly decrease with decreasing particle size. The data obtained so far do not allow one to discriminate between these assumptions, but other results, presented hereafter, seem to point out that particular concentration fluctuations are most likely involved in the observed room-temperature paramagnetism.

### Oxidation of the nanocomposite powders

The oxidation behaviour of the FeCoR1000 and FeNiR1000 powders was investigated by heating them in air up to 1100 °C in a thermobalance. XRD analysis showed that the oxidation products consist of spinel phases similar to the as-prepared oxides. Fe- and Co- or Ni-based oxides were not detected. The mass gain measured after the oxidation run (1.50% corresponds to that of fully reduced 4 mass% Fe\(_{2}Co\)) was small. The mass gain for FeCoR1000 and FeNiR1000, respectively, was determined by thermal gravimetry (DTG) curves (Fig. 14) show that the oxidation of the composites occurs in several steps, some of them at relatively low temperatures, which is quite far from that of the intragranular metal particles. This has been evidenced by the DTG curves of powders which had been treated in HCl (boiling, 1 mol l\(^{-1}\)) prior to the thermal analysis, showing the low-temperature oxidation phenomena to be absent as the corresponding metal particles located at the surface and in the open porosity of the oxide matrix and the latter one is that of the intragranular metal particles. On the contrary, the high-temperature oxidation phenomena remain unchanged because the oxide grains, which were not affected by the acid treatment, protected the metal particles dispersed within their matrix. It thus can roughly be estimated that more than two-thirds of the metallic phase (ca. 68% and 87% for FeCoR1000 and FeNiR1000, respectively) is dispersed as intragranular particles. A major difference with the oxidation behaviour of the Co- and Ni-MgAl\(_{2}O_{4}\) nanocomposites is the position of the high-temperature oxidation peak, which is about 160 °C lower in the present powders (780 and 800 °C in the Fe-Co and Fe-Ni-MgAl\(_{2}O_{4}\) composites respectively) and 940 and 970 °C in the Co- and Ni-MgAl\(_{2}O_{4}\) composites respectively.

### Table 4: Mössbauer parameters (9 K) of the Fe-Co-MgAl\(_{2}O_{4}\) composites prepared by reduction at different temperatures

<table>
<thead>
<tr>
<th>Composite</th>
<th>Fe(^{3+})</th>
<th>Fe(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCoR700</td>
<td>1.05</td>
<td>2.66</td>
</tr>
<tr>
<td>FeCoR800</td>
<td>1.04</td>
<td>2.78</td>
</tr>
<tr>
<td>FeNiR1000</td>
<td>0.93</td>
<td>2.80</td>
</tr>
</tbody>
</table>

\[ H = \text{hyperfine field, } \delta = \text{centre shift, } \Gamma = \text{mm s }^{-1}, \Delta = \text{quadrupole splitting, } P = \text{proportion (\%) of ferromagnetic phase.} \]
Fig. 11 Mössbauer spectra (9 K) of the FeNi-MgAl\(_2\)O\(_4\) powders prepared by reduction at (a) 700, (b) 800, (c) 900, (d) 1000 °C and the corresponding calculated field probability distributions (e, f, g, h respectively).

This obviously is related to the presence of iron, the Fe/Co and Fe/Ni alloy particles appearing to be more sensitive to air oxidation than pure Co and Ni particles. The Mössbauer spectrum of the HCl-treated FeNiR1000 powder was recorded at room temperature. Assuming that all the surface Fe/Ni particles have been removed by the acid etching, we may consider that this spectrum is representative for the intragranular Fe/Ni alloy particles only. The best fit has been obtained assuming that the Mössbauer spectrum is composed of a sextet and a singlet. The sextet (\(\delta = 0.03 \text{ mm s}^{-1}\), \(2\gamma_0 = 0 \text{ mm s}^{-1}\)) has an average hyperfine field (\(H = 300 \text{ kG}\)) characteristic of ferromagnetic Fe\(_{0.65}\)Ni\(_{0.35}\) and Fe/Ni alloy particles appearing to be more sensitive to air oxidation than pure Co and Ni particles. The singlet (\(\delta = 0.80 \text{ mm s}^{-1}\)) accounts for paramagnetic FeNi. The proportions of the sextet and singlet are 89 and 11% of the total spectrum, respectively. Considering these figures and those derived from the Mössbauer spectrum of the untreated powder (ferromagnetic and paramagnetic Fe in the proportions 80:20) on the one hand and the fact that the intragranular Fe represents about 87% of the total Fe content on the other hand (we derive this latter figure from the TG...
Table 1
Mössbauer parameters (9 K) of the FeNi/MgAl$_2$O$_4$ composites prepared by reduction at different temperatures

<table>
<thead>
<tr>
<th>composite</th>
<th>Fe$^{2+}$</th>
<th>ferro-Fe/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\Delta E_Q$</td>
</tr>
<tr>
<td>FeNiR700</td>
<td>1.22</td>
<td>2.62</td>
</tr>
<tr>
<td>FeNiR800</td>
<td>1.22</td>
<td>2.50</td>
</tr>
<tr>
<td>FeNiR900</td>
<td>1.15</td>
<td>2.61</td>
</tr>
<tr>
<td>FeNiR1000</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$H$ = average hyperfine field/kG; $\delta$ = isomer shift/mm s$^{-1}$; $\Delta E_Q$ = quadrupole splitting/mm s$^{-1}$; $\Gamma$ = half width at half height/mm s$^{-1}$; $P$ = proportion (%); ferro = ferromagnetic.

Table 2
Mössbauer parameters measured at room temperature of the FeCo/MgAl$_2$O$_4$ and FeNi/MgAl$_2$O$_4$ composites obtained after reduction at 1000°C

<table>
<thead>
<tr>
<th>specimen</th>
<th>ferro-Fe/M (M = Co or Ni)</th>
<th>non-ferro-Fe/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H$</td>
<td>$\delta$</td>
</tr>
<tr>
<td>FeCoR1000</td>
<td>365</td>
<td>0.04</td>
</tr>
<tr>
<td>FeNiR1000</td>
<td>300</td>
<td>0.04</td>
</tr>
</tbody>
</table>

$H$ = hyperfine field/kG; $\delta$ = isomer shift/mm s$^{-1}$; $\Delta E_Q$ = quadrupole shift/mm s$^{-1}$; $\Gamma$ = half width at half height/mm s$^{-1}$; $P$ = proportion (%); ferro = ferromagnetic.

measurements, assuming that there is no composition difference between the surface metal particles and the intragranular ones, so that the observed proportion of intragranular Fe/Ni alloy can be equated to the proportion of intragranular Fe, one may obtain a rough estimation of the proportions of the different Fe species with respect to the total metal content. Indeed, we find that the ferromagnetic and paramagnetic surface Fe account for 3 and 10%, respectively, whereas the ferromagnetic and paramagnetic intragranular Fe account for 77 and 10%, respectively. It appears that the paramagnetic particles are evenly distributed at the surface of the matrix grains and inside them. A striking feature is the very high proportion found for the ferromagnetic intragranular Fe. Since the intragranular particles are generally smaller than the surface ones, it seems that these results rule out the above mentioned proposition that the room-temperature paramagnetism is based on a size effect, because one would then have observed a majority of paramagnetic intragranular metal particles. Furthermore, the large amount of ferromagnetic intragranular Fe is in opposition to the hypothesis of concentration fluctuations within individual particles being the main cause of room-temperature paramagnetism. Thus, we tentatively attribute this phenomenon to composition fluctuations from one alloy particle to the other. It is interesting to note that the critical composition below which our Fe/Ni alloy nanoparticles are paramagnetic (between 35 and 40 Ni atom%) in FeNiR1000 is of the order of, but slightly higher than the highest one (32 Ni atom%) reported by Kachi and Asano.$^{32}$ This difference in critical concentration could reflect a difference in size between the present alloy particles (ca. 10 nm) and those of Kachi and Asano.$^{33}$
Thermogravimetry indicates that the nanometric metal par-

Fig. 14 DTG curves measured in flowing air of the Fe/Co-MgAl₂O₄
(a) and Fe/ Ni-MgAl₂O₄ (b) powders prepared by reduction at 1000°C

Conclusions

Fe₈₆Co₁₈Mg₄Al₆O₁₆ and Fe₇₆Ni₃Co₄Mg₃Al₄O₁₈ nanocomposite powders have been prepared by selective hydrogen reduction of oxide solid solutions of spinel structure synthesized by combustion in air. Owing to the monophasic nature of the as-prepared oxides, the metallic alloy particles formed upon reduction are homogeneously dispersed in the spinel matrix. They are about 10 nm in diameter. The increase in reduction temperature from 700 to 1000°C produces a narrowing of the particles composition range and an average composition closer and closer to the target one (Fe₅₀Co₅₀)ₐₒₓ₋ₚₐₓ₋₇ and (Fe₇₀Ni₃₀)ₐₒₓ₋₅₋₇. It has been found that the Co²⁺ ions promote the reduction of the Fe³⁺ ions more efficiently than the Ni²⁺ ions; indeed, the reduction is 29% faster than in Fe/Co and Fe/ Ni particles in the a (bcc) and γ (fcc) phases respectively. Mössbauer spectroscopy studies revealed that the Fe/Co particles are ferromagnetic at 9 K but a significant fraction (20%) of Fe was found to be engaged in a paramagnetic phase at room temperature. This may be explained by composition fluctuations from one alloy particle to the other. Thermogravimetry indicates that the nanometric metal particles located at the surface and in the open porosity of the matrix are totally oxidized at temperatures lower than 600°C, whereas those intragranularly dispersed are stable up to 800°C. These latter particles account for more than two thirds of the total metal content.

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