ELSEVIER

Journal of Alloys and Compounds 434–435 (2007) 437–441

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Mechanical alloying of the FeNi–Ag system

G. González [a,b,*], D. Ibarra [a], J. Ochoa [a], R. Villalba [a], A. Sagarzazu [a]

[a] *Laboratorio de Ciencias e Ingeniería de Materiales, Departamento de Ingeniería, Instituto Venezolano de Investigaciones Científicas, Apdo. 21827, Caracas 1020A, Venezuela*

[b] *Departamento de Física, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*

Available online 12 October 2006

Abstract

The Fe–Ni–Ag system is of particular interest for its potential applications as soft magnetic granular material with small magnetic grains embedded in a non-magnetic metal matrix. Under equilibrium conditions: Fe–Ag and Ni–Ag are immiscible and Fe–Ni shows complete solubility. These materials are particularly important for magnetoresistivity properties. The properties of these alloys are closely related to their microstructure; therefore, a detailed study of the transformations occurring during milling was undertaken using pre-alloyed Fe_xNi_{100-x} ($x = 30$, 50 and 70) further milled with different Ag content to give the following alloys compositions $(Fe_x–Ni_{100-x})_{100-y}Ag_y$ ($y = 5$, 20, 60). Consolidation of the mechanically alloyed powders by sintering at 950 °C was performed. Morphological and structural characterization of the sintered powders was carried out by scanning and transmission electron microscopy and X-ray diffraction.

$Fe_{30}Ni_{70}$ and $Fe_{50}Ni_{50}$ formed ordered $FeNi_3$ compound. $Fe_{70}Ni_{30}$ showed the formation of a mixture of γ-(Fe,Ni) and α-Fe(Ni) solid solutions. The mixture of these systems with Ag showed the metal solid solutions surrounded by Ag islands of Fe_xNi_y–Ag, There was also evidence of Ag diffusing into the γ-(Fe,Ni). High Ag content (60%) shows formation of islands of FeNi surrounded by Ag. Sintering is always improved with the Ag content.

Keywords: Intermetallics; Nanostructures; Mechanical alloying; X-ray diffraction

1. Introduction

Nanophase materials have a great potential to improve both magnetic and mechanical properties due to characteristic length scale of the same order for both properties. Mechanical alloying (MA) has been used to produce immiscible nanogranular alloys. Therefore, the possibility of obtaining a granular structure of Fe–Ni magnetic nanoparticles separated by non-magnetic Ag particles by mechanical alloying seems attractive.

There are some reports on Fe–Ni mechanically alloyed [1–9] system and very limited literature on the Fe–Ni–Ag system [10]. Fe–Ag and Ni–Ag are immiscible at equilibrium and Fe–Ni shows complete solubility. However, by mechanical alloying it is possible to produce metastable materials with extended solubility. Neither the process of alloying nor the consolidation of $(Fe_xNi_{100-x})_{100-y}$–Ag_y system prepared by mechanical alloying has been extensively studied. Therefore, in the present work a detailed study of the transformations occurring during milling was undertaken for the system Fe_xNi_{100-x} ($x = 30$, 50 and 70) and then further milled with different Ag content to give the following alloys compositions $(Fe_x–Ni_{100-x})_{100-y}Ag_y$ ($y = 5$, 20, 60). Consolidation by sintering was also carried out.

2. Experimental

Elemental high purity (99.99%) Fe and Ni powders with an average particle size of 4.5 and 2.2 μm, respectively, were blended in a WAV turbule for 2 h, in proportions of 30, 50 and 70 at.%, and then mechanically alloyed under nitrogen atmosphere, using a SPEX 8000, for different milling periods: 1, 3, 5, 10 and 25 h using vial and balls of stainless steel, and a ball-to-powder weight ratio (BPR) of 8:1. The pre-alloyed powders were then MA 10 h with high purity Ag powders with a particle size of 1.3 μm, in proportions of 5, 20 and 60 at.% to obtain alloy compositions $(Fe_xNi_{100-x})_{100-y}$–Ag_y ($y = 5$, 20, 60). The powders from the different milling periods and compositions were pressed at 350 MPa and sintered in a graphite crucible at 900 °C for 40 min in argon atmosphere. The characterization of powders and sintered material was carried out by X-ray diffraction (XRD) using a Siemens 5005 diffractometer with Cu Kα radiation ($\lambda = 0.1542$ nm) (Ni filter) operating at 40 keV and 20 mA. The mean grain size was calculated from full-width-at-half-maximum (FWHM) of the diffraction peaks applying the Scherrer equation. Scanning electron microscopy (SEM) was performed in a Phillips XL30 equipped with an EDX DX4. Transmission electron microscopy (TEM) was carried out in a Phillips CM10.

* Corresponding author. Tel.: +58 2125041430; fax: +58 2125041418.
E-mail address: gemagonz@ivic.ve (G. González).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.293

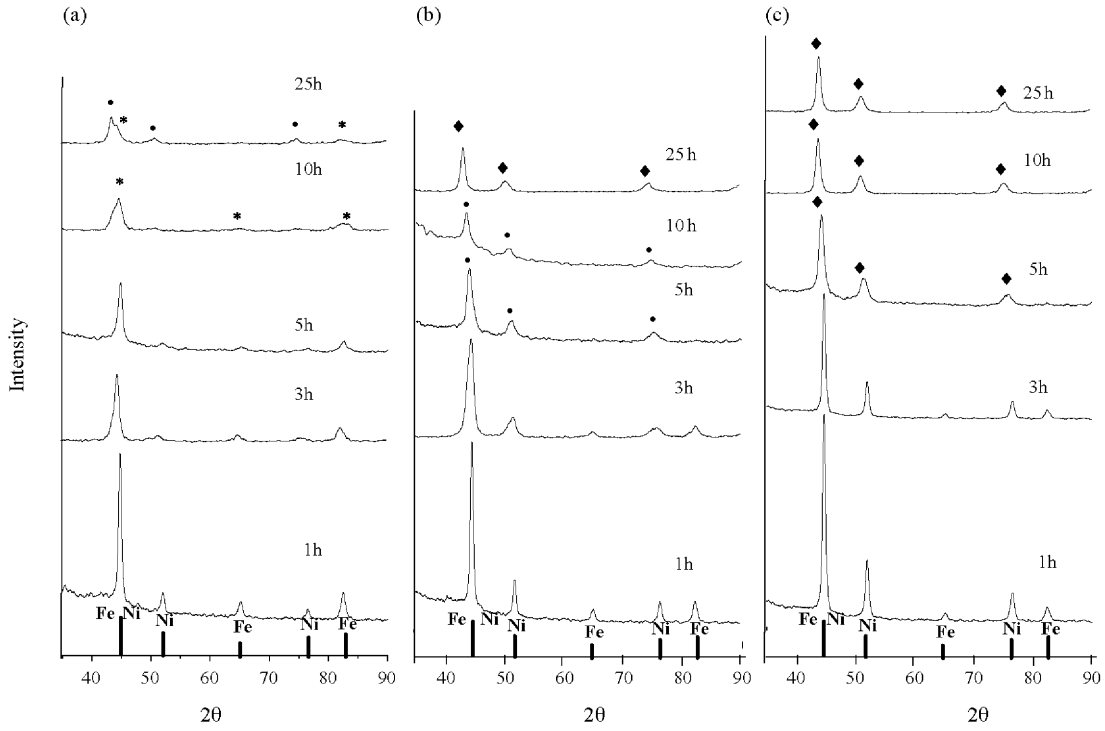

Fig. 1. XRD patterns of mechanically alloyed 1–25 h: (a) $Fe_{70}Ni_{30}$; (b) $Fe_{50}Ni_{50}$; (c) $Fe_{30}Ni_{70}$. (*) α-Fe; (●) γ-(Fe,Ni); (♦) $FeNi_3$.

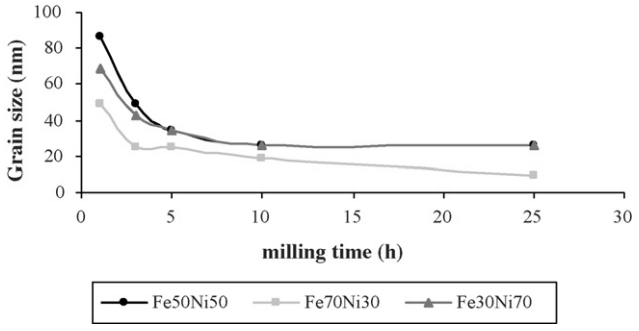

Fig. 2. Variation of grain size with milling time.

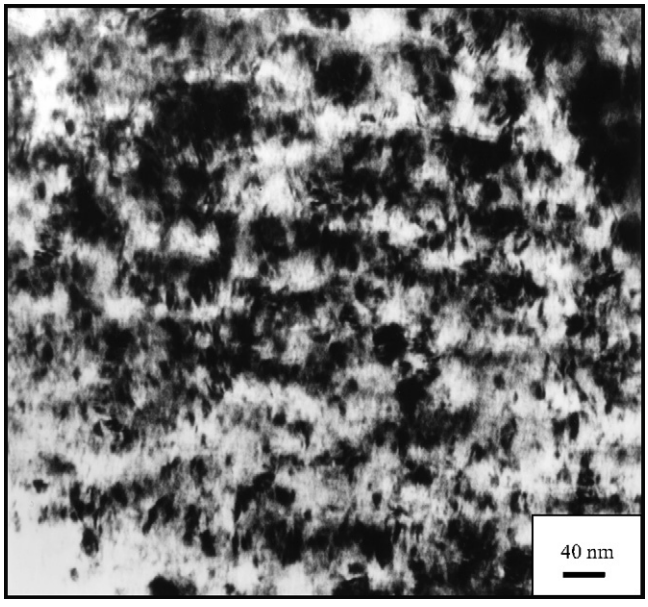

Fig. 3. TEM bright field image of $Fe_{50}Ni_{50}$ milled 25 h.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for $Fe_{70}Ni_{30}$, $Fe_{50}Ni_{50}$, and $Fe_{30}Ni_{70}$ alloys mechanically alloyed from 1 to 25 h. The formation of a fcc γ-(Fe,Ni) solid solution was observed for Fe–50 at.% Ni after 5 h, this phase is present up to 10 h of milling and then prolonged milling for 25 h resulted in the formation Ni_3Fe, significant peak broadening and decrease in intensity with milling time due to refinement of grain size down

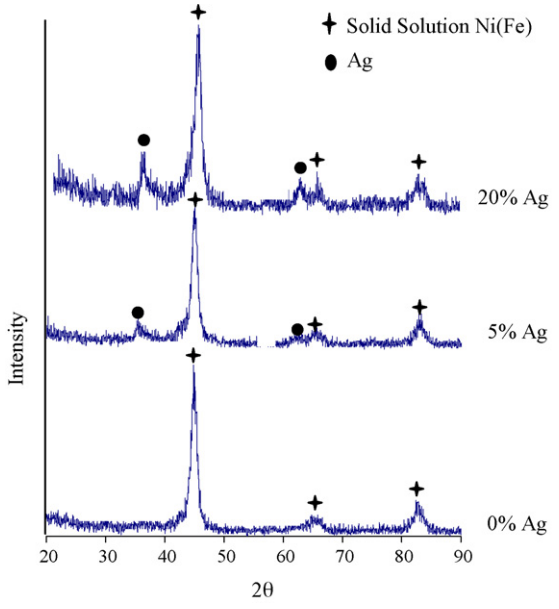

Fig. 4. XRD of $(Fe_{50}Ni_{50})_{1-x}$–Ag_x mechanically alloyed.

to 26 nm for the $Fe_{50}Ni_{50}$. For the $Fe_{70}Ni_{30}$ alloy, formation of γ-(Fe,Ni) and bcc solid solution α-Fe(Ni) was observed after 10 h of milling. $Fe_{30}Ni_{70}$ shows formation of the $FeNi_3$ intermetallic compound after 5 h of milling, this phase is maintained up to 25 h and it reaches a final grain size of 26 nm. Shifting of Bragg peaks towards lower angles with milling time was observed for all the alloys as milling proceeded due to interdiffusion of iron and Ni. The variation of grain size with milling time is shown in Fig. 2 for the three alloys, the behavior in general is very similar, only the $Fe_{70}Ni_{30}$ reaches a finer grain size of 9 nm after 25 h of milling. Fig. 3 shows a TEM bright field image of the $Fe_{50}Ni_{50}$ after 25 h of milling, a narrow grain size distribution is observed.

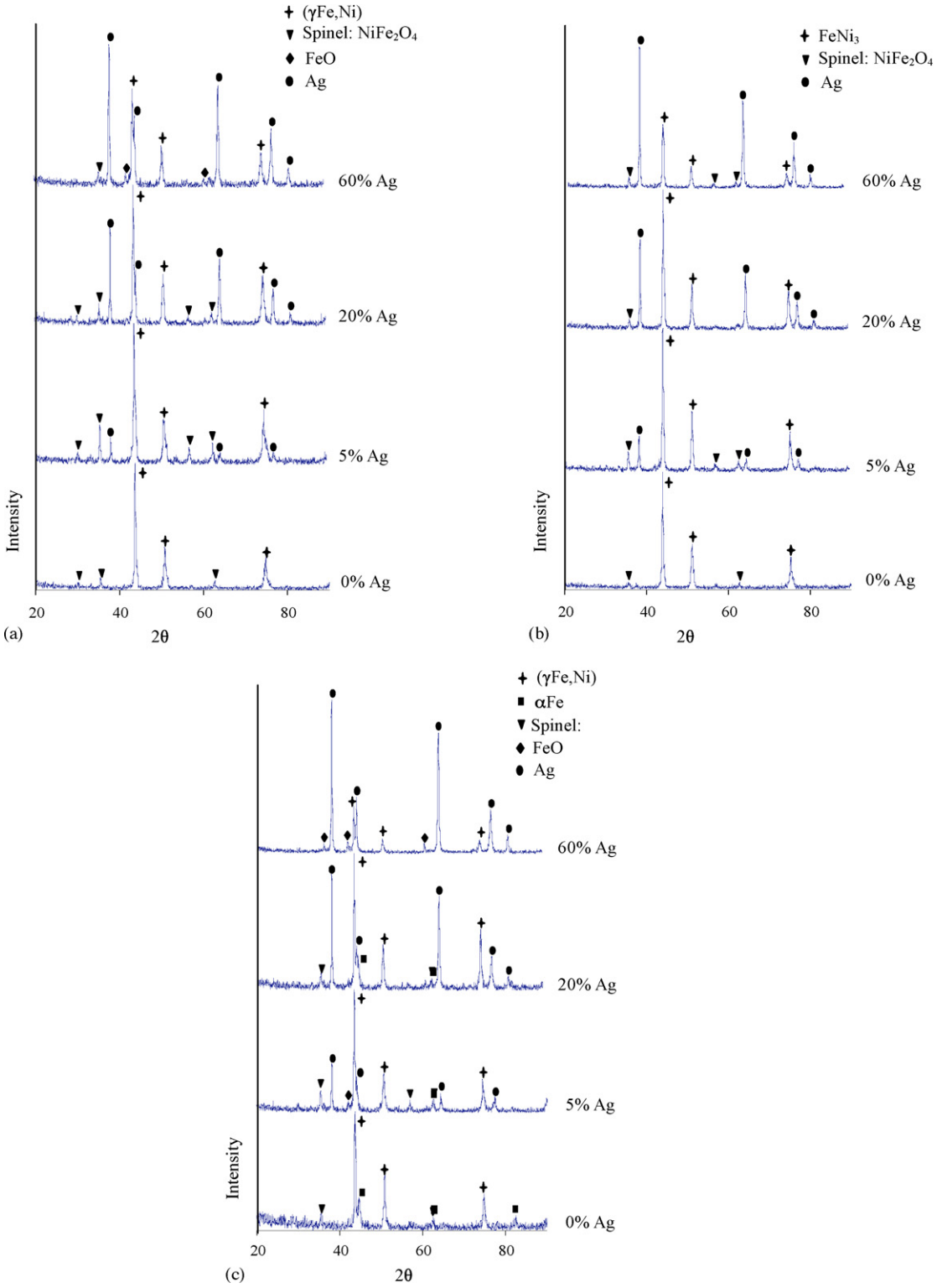

Fig. 5. XRD patterns: (a) $(Fe_{50}Ni_{50})_{1-x}$–Ag_x; (b) $(Fe_{30}Ni_{70})_{1-x}$–Ag_x; (c) $(Fe_{70}Ni_{30})_{1-x}$–Ag_x sintered alloys.

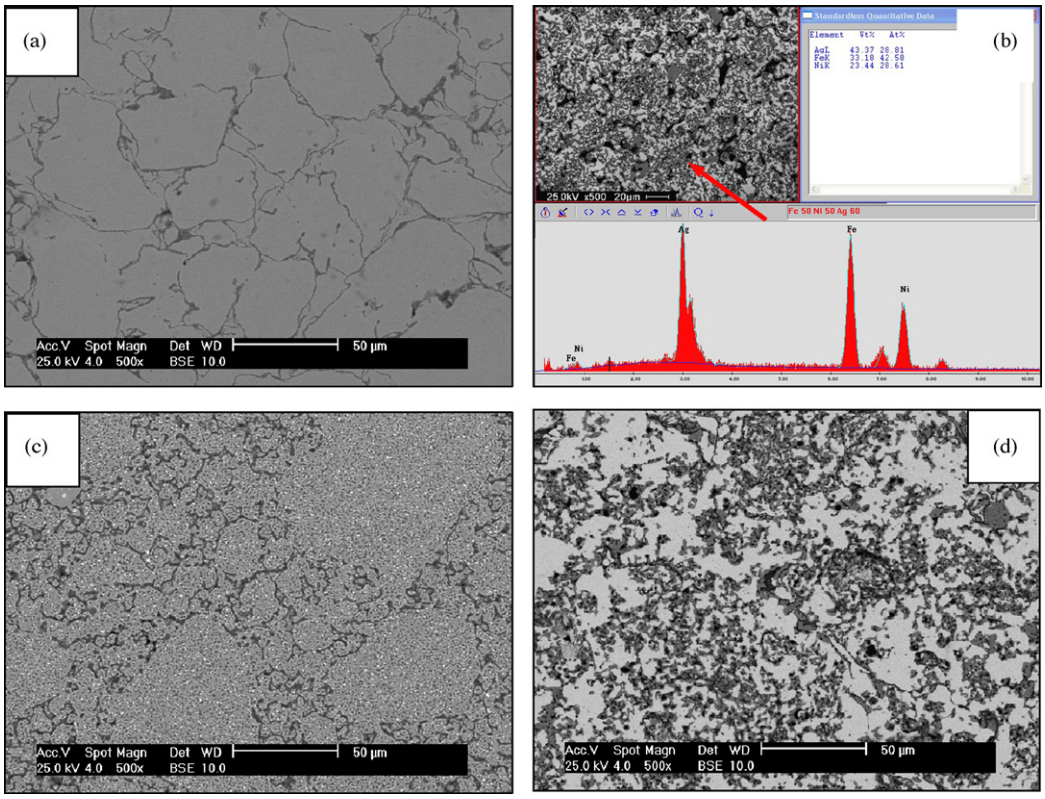

Fig. 6. Scanning electron microscopy images and EDX analysis of mechanically alloyed and sintered (a) $Fe_{50}Ni_{50}$; (b) $(Fe_{50}Ni_{50})_{40}Ag_{60}$; (c) $(Fe_{70}Ni_{30})_{95}$–Ag_5; (d) $(Fe_{70}Ni_{30})_{40}$–Ag_{60}.

Different contents of Ag additions were incorporated by mechanical alloying to these Fe_xNi_{100-x} pre-alloyed powders. The XRD patterns show presence of Ag peaks and a small shift of the (1 1 1) reflection towards lower angles, suggesting some diffusion of Ag into the FeNi lattice. Fig. 4 shows the XRD patterns for $(Fe_{50}Ni_{50})_{100-x}$–Ag_x.

The different alloys with Ag were sintered at 950 °C for 40 min, the XRD patterns are shown in Fig. 5. For $Fe_{50}Ni_{50}$ the formation of the fcc solid solution γ-(Fe,Ni) was observed, also the formation of a small amount of the spinel $NiFe_2O_4$ and FeO. Ag additions did not have any significant effect on the FeNi reflections, suggesting that Ag comes out of the solid solution formed during the milling process, due to heat treatment at high temperature that activates diffusion and phase separation as expected from the phase diagram. High Ag content surrounds the FeNi particles and seems to protect against oxidation.

The sintered $Fe_{70}Ni_{30}$ alloy shows also the formation of γ-(Fe,Ni) and bcc α-Fe phases. The consolidated sample with Ag addition also shows these phases and well-defined Ag reflections. Shift in the XRD diffraction peaks were not observed indicating immiscibility of Ag. Presence of small amounts of $NiFeO_4$ and FeO were also observed. For high Ag concentrations protection against oxidation was observed. The $Fe_{30}Ni_{70}$ remains in the $FeNi_3$ state after sintering; a very small amount of $NiFe_2O_4$ was detected. Ag additions follow the same behavior as the other alloys described above.

SEM image of Fig. 6a shows the sintered $Fe_{50}Ni_{50,}$ indicating good consolidation without porosity. Fig. 6b corresponds $(Fe_{50}Ni_{50})_{40}Ag_{60}$, particles of FeNi surrounded by Ag creating islands of magnetic FeNi into shells of non-magnetic Ag. This microstructure could potentially have interesting magnetic properties. This effect is only observed for high Ag contents, for low Ag contents, this element is found distributed in small particles into the matrix. The SEM micrographs of the sintered $(Fe_{70}Ni_{30})_{95}Ag_5$ and $(Fe_{70}Ni_{30})_{40}Ag_{60}$ are shown in Fig. 6c and d, respectively. For low concentration, Ag particles are well distributed into the FeNi matrix, as Ag concentration increases it locates around the FeNi particles. Ag always diffuses out to the surface with heat treatment, if there was a little diffusion of silver into the matrix around the interface area, with the process of thermal treatment it comes out of the matrix and surrounds the grains and particles, keeping its immiscible character.

4. Conclusions

The formation of fcc γ-(Fe,Ni) solid solution was observed for Fe–50 at.% Ni after 5 h, this phase is present up to 10 h of milling and then prolonged milling for 25 h resulted in the formation Ni_3Fe.

For the $Fe_{70}Ni_{30}$ alloy, γ-(Fe,Ni) and bcc solid solution α-Fe(Ni) were present after 10 h of milling. $Fe_{30}Ni_{70}$ showed formation of the $FeNi_3$ intermetallic compound after 5 h of milling and maintained up to 25 h.

Nanometric grain size was obtained for all the alloys after 25 h of milling.

Some diffusion of Ag into the FeNi lattice was observed for all compositions of the milled alloys.

The sintered alloys maintain the phases formed by prolonged milling; however, the grain size increased with heat treatment. Ag always diffuses out to the surface with heat treatment.

References

[1] C. Kuhrt, Schultz, J. Appl. Phys. 73 (1993) 6588.
[2] Yu.V. Baldokhin, V.V. Tcherdyntsev, S.D. Kaloshkin, G.A. Kochetov, Yu.A. Postov, J. Magn. Magn. Mater. 203 (1999) 313.
[3] E. Jartych, J.K. Zurawicz, P. Oleszak, M. Pekala, J. Magn. Magn. Mater. 208 (2000) 221.
[4] L.-H. Zhu, X.-M. Ma, L. Zhao, J. Mater. Sci. 36 (2001) 5571–5574.
[5] S.D. Kaloshkin, V.V. Tcherdyntsev, I.A. Tomilin, Yu.A. Baldokhin, E.V. Shelekhov, Physica B 299 (2001) 236–241.
[6] A. Djekoun, B. Bouzabata, A. Otmani, J.M. Greneche, Catal. Today 89 (2004) 319–323.
[7] I. Chicinas, V. Pop, O. Isnard, J. Magn. Magn. Mater. 242–245 (2002) 885–887.
[8] I. Chicinas, V. Pop, O. Isnard, J.M. Le Breton, J. Juraszek, J. Alloys Compd. 352 (2003) 34–40.
[9] V. Pop, O. Isnard, I. Chicinas, J. Alloys Compd. 361 (2003) 144–152.
[10] L.H. Bennett, L. Tackacs, L.J. Swartzendruber, J. Weissmuller, L.A. Bendersky, A.J. Shapiro, Scripta Metall. Mater. 33 (10–11) (1995) 1717–1724.