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Effect of pre-alloying FeNi on Ag diffusion on the ternary system

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Abstract

Mechanical alloying (MA) is a process that has proven to be a versatile tool to produce nanostructured composites and alloys from normally immiscible materials. The process parameters can be varied to control the degree of alloying and the microstructure characteristics, so it is possible to produce magnetic materials with novel properties. The phase diagrams of Ni–Ag and Fe–Ag show that mutual solubility is very low in both solid and liquid states. However, partial solid solution has been found in these systems prepared by sputtering [N. Kataoka, K. Sumiyama, Y. Nakamura, J. Phys. F: Metal. Phys. 15 (1985) 1405–1411] and also by mechanical alloying [S. Nasu, S. Morimoto, H. Tanimoto, B. Huang, T. Tanaka, J. Kuyama, K.N. Ishihara, P.H. Shingu, Hyperfine Interact. 67 (1991) 681–686]. The ball milling process as a non-equilibrium technique can force the mixing of immiscible systems. We report a study on the Fe–Ni–Ag system by mechanically alloying the individual powders in different compositions Fe_x–Ni_x–Ag_{100-2x} ($x = 20$, 40, 60) and also by preparing the solid solution (Fe, Ni) compound by mechanical alloying the powders for 50 h and then this pre-alloyed powder is further mechanically alloyed with Ag in different proportion to obtain the alloy $(FeNi)_xAg_{100-x}$. The system prepared by the alloying of the three elements show inmiscibility with Ag, but in the pre-alloyed FeNi further addition of silver seems to diffuse into the FeNi lattice indicating a partial solubility of Ag into the FeNi.

Keywords: Fe–Ni–Ag system; Mechanical alloying; Ternary systems

1. Introduction

In the past years, mechanical alloying has been used to produce metastable alloys of normally immiscible elements characterized by a high positive heat of mixing. These alloys are interesting because of potential applications. In this work we study the ternary system Fe–Ni–Ag. Under equilibrium conditions Ag is immiscible, even in liquid state, in iron and in nickel. However, solid solutions up to 50 at.% Ag in Fe have been reported in sputtering experiments [1], and a small fraction of solid solution was reported in mechanical alloying [2,3]. On the other hand, the formation of solid solution of Ni and Ag by mechanical alloying has been reported [4,5]. In the case of the ternary system, Bennett et al. [6] have reported alloying in the system Fe–Ni–Ag which consists FeNi particles separated by Ag.

Our interest in this system comes from the fact that granular binary alloys of FeAg exhibit giant magnetoresistance (GMR), so the electric resistance of the alloy can change highly by applying of magnetic field. This kind of materials has potential application in magnetic sensors. Furthermore, we want to know if the addition of Ni to the system Fe–Ag can be a way to control its microstructure in such a way that it improves magnetoresistance properties because of the magnetic properties of the FeNi system.

In this work, we prepared samples by mechanical alloying in two different ways. In one way, we proceed with milling of three elements with a certain composition. In the other way, we mechanically pre-alloy of Fe and Ni, and then we proceed to the milling of FeNi and Ag.

2. Experimental method

First, commercial elemental powders of silver, iron and nickel (99.9% purity and initial particle size less than 50 μm) were blended in compositions $Fe_xNi_xAg_{100-2x}$ ($x = 20$, 30, 40), in a WAV turbula for 2 h. The milling was carried out using a SPEX 8000 mixer/mill with hardened steel balls and vial. The ball-to-powder weight ratio was 8:1. In the milling procedure 1 g of sample was

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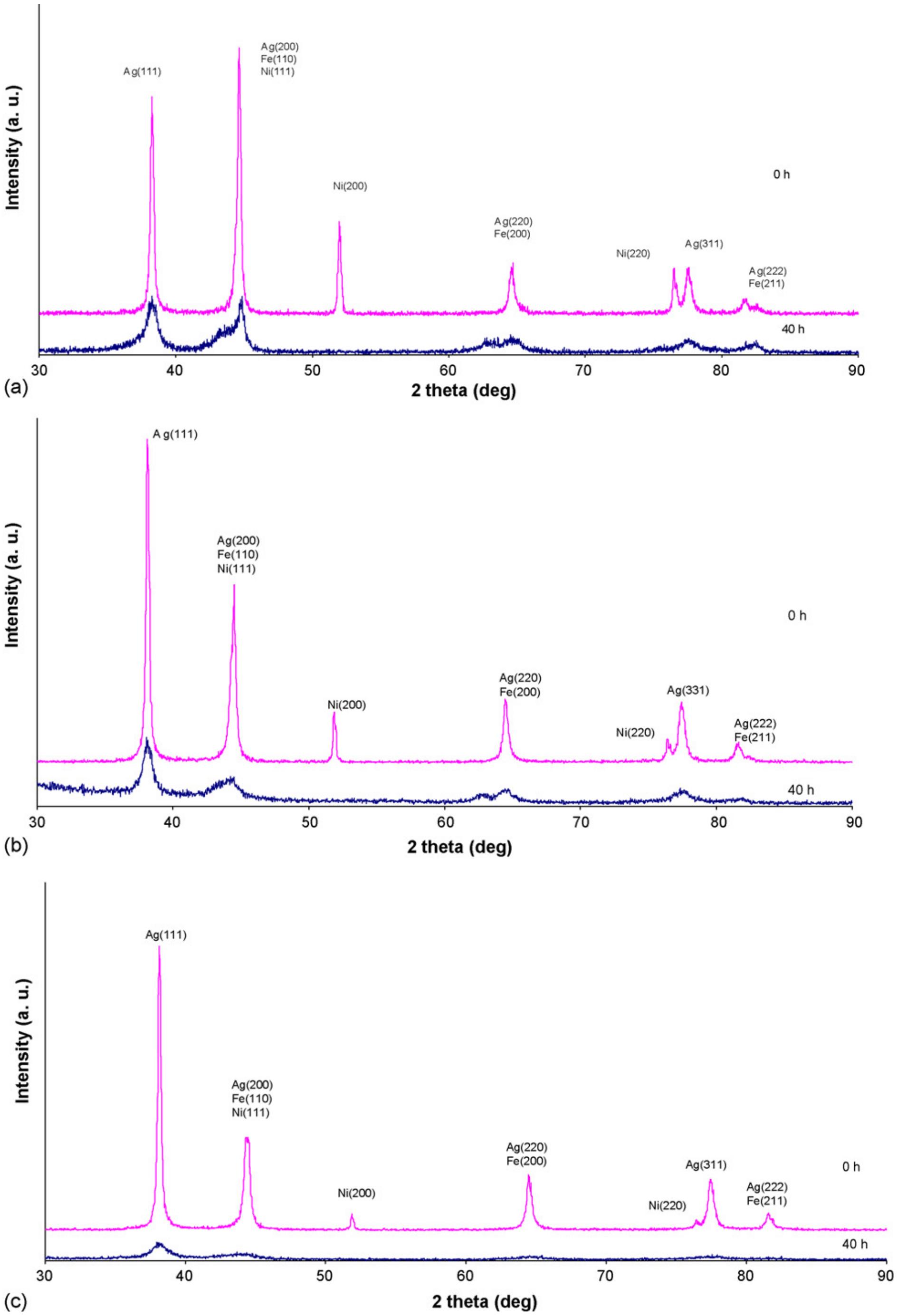

Fig. 1. XRD patterns for (a) $Fe_{40}Ni_{40}Ag_{20}$, (b) $Fe_{30}Ni_{30}Ag_{40}$, and (c) $Fe_{20}Ni_{20}Ag_{60}$.

used in every case and the vial was sealed in nitrogen atmosphere and tightly clamped to prevent oxidation. The vial was processed for times of 10, 20 and 40 h, and the milling was performed by repeated cycles of half hour period, then interrupted half an hour to cool down the vials. Equiatomic mixture of Fe and Ni was milled for 50 h in order to obtain a solid solution compound, as verified by X-ray diffraction. Then we blended this compound with Ag at the compositions $(FeNi)_xAg_{100-x}$ ($x = 40$, 60, and 80), and milled 25 h. X-ray diffraction experiments were carried out using Cu Kα radiation ($\lambda = 0.1542$ nm) (Ni filter) on a Siemens D5000 X-ray diffractometer. Transmission electron microscopy (TEM) was carried out in a Phillips CM10 operating at 120 kV. TEM specimens were ultrasonically dispersed in a water-ethanol solution and few drops placed on a carbon coated grid. Thin sections were obtained by ultramicrotomy. Mössbauer spectra were obtained at room temperature (RT) using a constant-acceleration transducer arranged in a transmission geometry, with a ^{57}Co source of 50 mCi in Rh matrix. A triangular drive waveform was used and the data were collected in 512 channels, with ∼10^6 counts per channel, and were folded to remove any base-line curvature. The velocity scale for Mössbauer spectra was calibrated related to α-Fe at RT.

3. Results and discussion

The microstructural characterization of the ball milled powders was followed by XRD, TEM and Mössbauer spectroscopy. Fig. 1a–c, show the XRD patterns for compositions

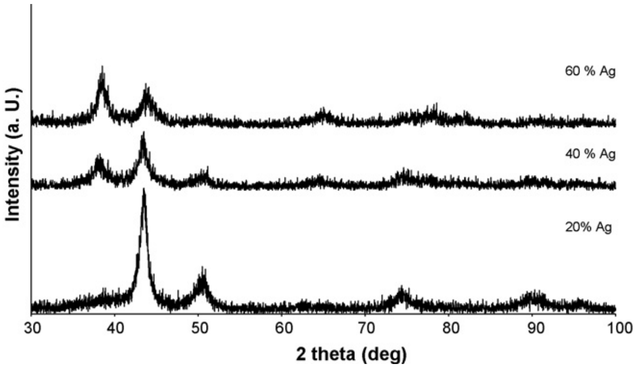

Fig. 2. XRD patterns for $(FeNi)_xAg_{100-x}$ ($x = 40$, 60, and 80).

Fe_x–Ni_x–Ag_{100-2x} ($x = 20$, 40, and 60), after 0 and 40 h of milling time. Due the overlap of Ag(2 0 0) with Fe(1 1 0) and Ag(2 2 0) with Fe(2 0 0) Bragg peaks after 40 h of milling, only the Ag(1 1 1), Ag(3 1 1) and Ag(2 2 2) peaks can be observed separately. Furthermore, we can see that after 40 h of milling the Ni peaks disappear completely, indicating the formation of the bcc solid solution α-Fe(Ni). With prolonged milling time diffraction peaks broaden significantly, indicating the refinement of the grain size and the introduction of internal strain. Using the Scherrer formula, we found that average particle size after 40 h milling time is in the range of 9–11 nm for the different compositions.

Fig. 2 shows the diffraction patterns of $(FeNi)_xAg_{100-x}$ ($x = 40$, 60, and 80), milled for 25 h. For $x = 80$, the formation of the solid solution γ-(Fe, Ni) is observed, also there are no peaks of Ag present in the pattern. This observation suggest that Ag could diffuse into the γ-(FeNi) lattice. However, for $x = 40$ and 60, there are peaks of Ag and γ-(FeNi), so it seems that there are mixtures of γ-(FeNi)-rich and Ag-rich phases. The average particle size is in the range of 8 and 9 nm.

TEM images are shown in Fig. 3. We can see that nanograins of Ag and (Fe, Ni) coexisting separately and electron diffraction patterns show that those grains are randomly oriented when the

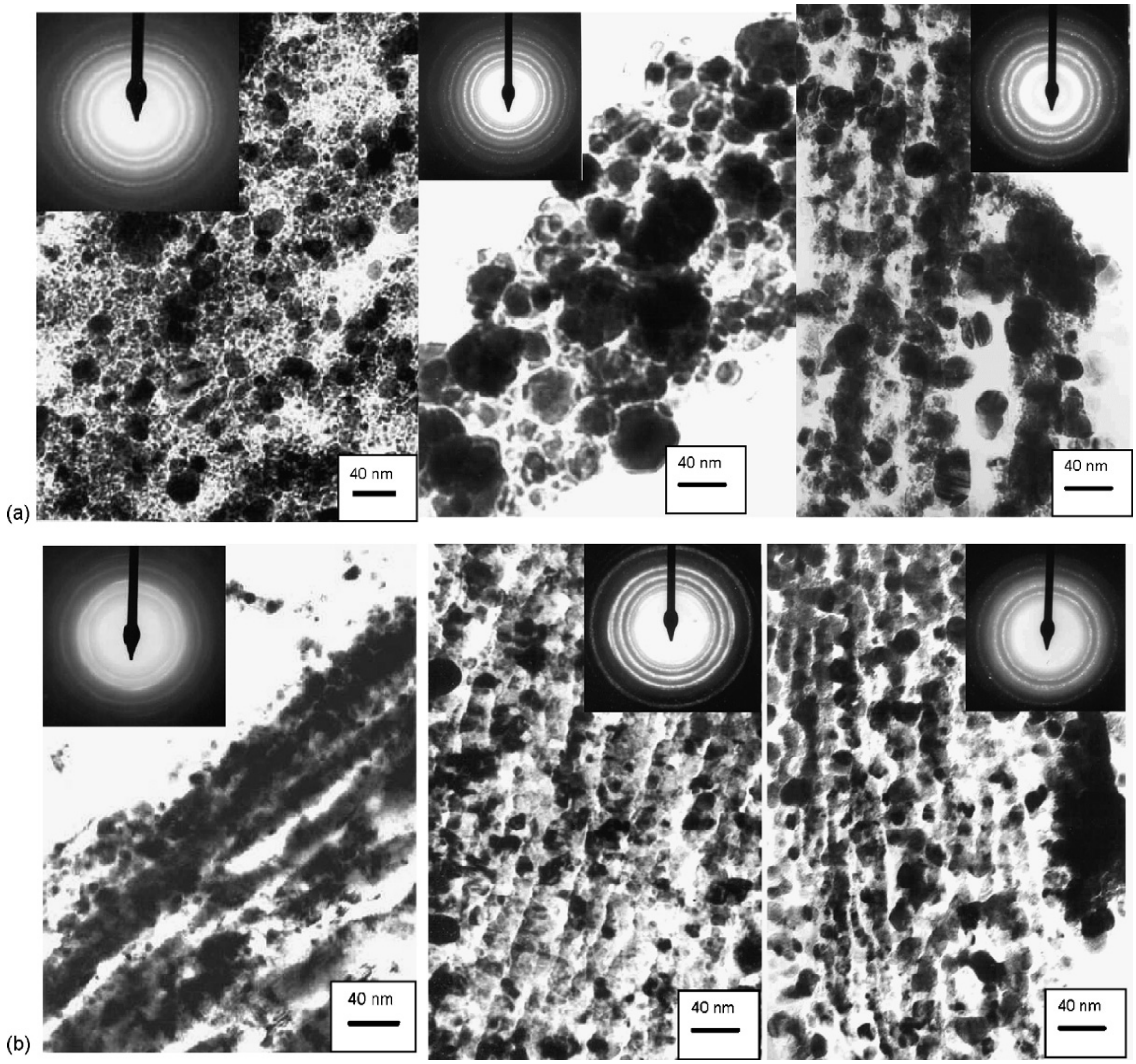

Fig. 3. (a) TEM bright field images for $Fe_{40}Ni_{40}Ag_{20}$, $Fe_{30}Ni_{30}Ag_{40}$, $Fe_{20}Ni_{20}Ag_{60}$ 40 h milling time; (b) TEM bright field image for $(FeNi)_{80}Ag_{20}$, $(FeNi)_{60}Ag_{40}$, $(FeNi)_{40}Ag_{60}$, 25 h milling time.

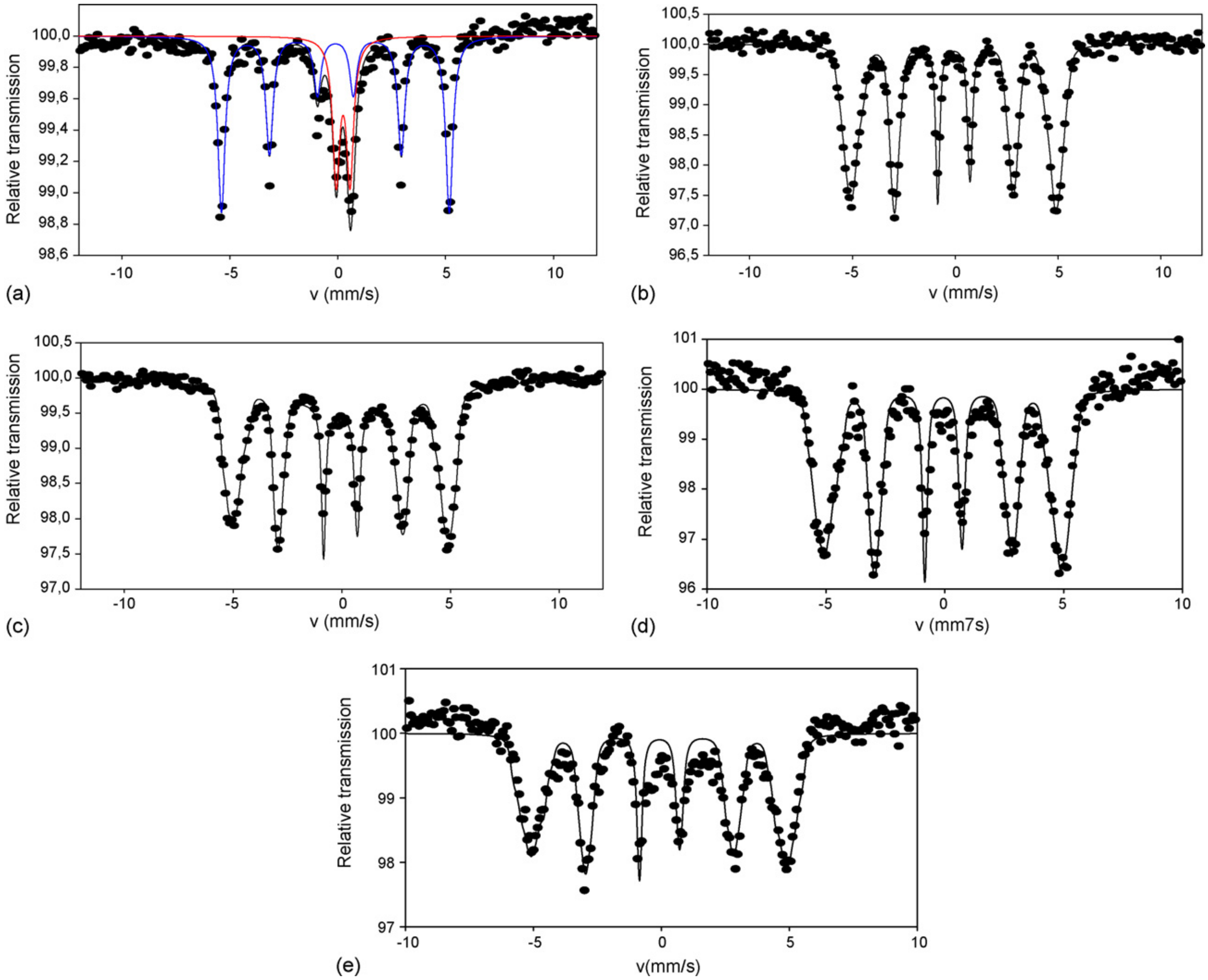

Fig. 4. (a) Mössbauer spectrum at RT for $Fe_{40}Ni_{40}Ag_{20}$, 40 h milling time. (b) Mössbauer spectrum at RT for $Fe_{50}Ni_{50}$, 50 h milling time. (c) Mössbauer spectrum at RT for $(FeNi)_{80}Ag_{20}$, 25 h milling time. (d) Mössbauer spectrum at RT for $(FeNi)_{60}Ag_{40}$, 25 h milling time. (e) Mössbauer spectrum at RT for $(FeNi)_{40}Ag_{60}$, 25 h milling time.

powders were blended. Fig. 3a shows bright field image and electron diffraction pattern for $Fe_{40}Ni_{40}Ag_{20}$, $Fe_{30}Ni_{30}Ag_{40}$ and $Fe_{20}Ni_{20}Ag_{60}$ after 40 h milling time. The particle size is very uniform and the grains of larger size correspond to the Ag. As the Ag content increases the darker Ag particle size also increases. In the diffraction pattern we can observe Ag and FeNi reflections. Fig. 3b shows bright field image and electron diffraction patterns for $(FeNi)_{80}Ag_{20}$, $(FeNi)_{60}Ag_{40}$. $(FeNi)_{40}Ag_{60}$. The electron diffraction pattern shows fcc γ(Fe, Ni) solid solution and Ag reflections. The Ag dark grain size is much smaller than in the previous case and in smaller amount indicating some diffusion of Ag into the (Fe, Ni). Bright field image shows the formation of quite uniform particles size.

Mössbauer spectra were fitted with a least square program, taking as hyperfine parameters: the isomer shift (IS), the quadrupolar splitting (QS), the full width at half maximum (FWHM) and the hyperfine field (HF). The correlation usually observed in FeNi [7] between QS and the HF in the distribution of the hyperfine parameters was taken into account. Fig. 4a shows the Mössbauer spectrum for $Fe_{40}Ni_{40}Ag_{20}$ after 40 h milling time. The spectrum has two components; one is a six-line component, with hyperfine field of 328 kG, which is basically due to ferromagnetic α-Fe. The other one is a doublet, probably due to small particles effect or to iron oxide. In order to resolve this, is necessary to perform a detailed study at low temperatures. If there is any mutual interdiffusion, it should be very small. Fig. 4b shows the Mössbauer spectrum for $Fe_{50}Ni_{50}$ after 50 h of milling. The line asymmetry is quite notorious which indicates mutual interdiffusion. The hyperfine field is 310 kG, which is characteristic of a disordered phase of FeNi. This also has been reported by Xia et al. [8]. Fig. 4c–e, show the Mössbauer spectra for $(FeNi)_{80}Ag_{20}$, $(FeNi)_{60}Ag_{40}$ and $(FeNi)_{40}Ag_{60}$ after 25 h milling time. The hyperfine fields are 305, 310 and 310 kG, respectively. They are similar to the Mössbauer spectrum for $Fe_{50}Ni_{50}$. However, we can see a broadening of the hyperfine parameters, which indicates the diffusion of Ag in FeNi.

4. Conclusions

We have found that pre-alloying of Fe and Ni to form the solid solution compound γ-(Fe, Ni) and then further mechanical alloying with Ag results in a more homogeneous structure. This procedure seems to promote some diffusion of Ag into γ-(Fe, Ni) and might be due to the similarity of both crystal structures. The results are completely different when we start with elemental pure Fe, Ni and Ag powders, where the Ag does not seem to diffuse into α-Fe(Ni) after milling. This effect is similar to that of the Fe–Co–Ag system as reported by González et al. [9].

References

[1] N. Kataoka, K. Sumiyama, Y. Nakamura, J. Phys. F: Metal. Phys. 15 (1985) 1405–1411.

[2] S. Nasu, S. Morimoto, H. Tanimoto, B. Huang, T. Tanaka, J. Kuyama, K.N. Ishihara, P.H. Shingu, Hyperfine Interact. 67 (1991) 681–686.

[3] D. Bonyuet, G. González, J. Ochoa, F. González-Jiménez, L. D'Onofrio, Latin Am. J. Met. Mat. 22 (2002) 8–11.

[4] J. Xu, U. Herr, T. Klassen, R.S. Averback, J. Appl. Phys. 79 (1996) 3935–3945.

[5] S. Zghal, P. Bhattacharya, R. Twesten, F. Wu, P. Bellon, Mater. Sci. Forum 386–388 (2002) 165–174.

[6] L.H. Bennett, L. Takacs, L.J. Swartzendruber, J. Weissmüler, L.A. Bendersky, A.J. Shapiro, Scripta Metallur. Mater. 33 (1995) 1717–1724.

[7] H.P. Chocrón, R. Iraldi, F. González-Jiménez, Acta Científica Venezolana 40 (1989) 74–78.

[8] S.K. Xia, R.B. Scorzelli, I. Souza Azevedo, E. Baggio-Saitovich, A.Y. Takeuchi, Mater. Sci. Forum 225–227 (1996) 453–458.

[9] G. González, A. Sagarzazu, R. Villalba, J. Ochoa, Metastable, Mech. Alloy. Nanocrystal. Mater. 20–21 (2004) 219–224.