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Nanostructure formation in mechanically alloyed Fe_5Co_{95} revealed by X - ray diffraction and atomic force microscopy

I. PETEAN[a,b], G. ARGHIR[a], M. TOMOAIA-COTISEL[b*], O. HOROVITZ[b], D. A. POP[a]
[a]*Technical University of Cluj – Napoca, Faculty of Material Science and Engineering, 103 – 105 Muncii Ave., 400641 Cluj-Napoca, Romania*
[b]*Babes-Bolyai University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, 11 Arany J. Str., 400028 Cluj – Napoca, Romania*

This work is focused on the formation of Fe_5Co_{95} nanostructure by mechanical alloying. Elemental Fe and Co powder mixture, weight dosed to Fe_5Co_{95}, was used. This mixture was milled in a planetary ball mill for 1, 2, 4, 8, and 12 hours and samples for analysis were taken out at each milling time. The powder mixture samples were investigated by X – ray diffraction (i.e., full width at half maximum of diffraction peaks: FWHM) and atomic force microscopy (AFM) tapping mode. Grain size obtained by Williamson–Hall technique matches with values obtained by AFM. Three stages for the nanostructure formation of Fe_5Co_{95} mechanically alloyed solid solution were found. In the first stage, after 1 hour of milling, powder particles form a two phase micro scale composite having about 100 nm grain size. After 2 hours of milling, the second stage begins and is characterized by crack initiation due to cold hardening. In this stage a solid solution is formed and grain size decreases to reach the nanoscale level of about 60 nm. After 4 hours of milling a solid solution is formed with grain size of about 40 nm. Further, the third stage (after 8 hours up to 12 hours of milling) leads to the complete formation of nanostructure with grain size of around 20 nm.

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1. Introduction

Mechanical alloying represents an unconventional technology for making solid solutions or intermetallic compounds [1, 2]. This method uses elemental powders, which are milled in high energy mills such as planetary mill [3, 4]. During the milling process, the powder mixture is subjected to severe structure and morphology changes according to the mixture specifications.

The Fe – Co system acts as a ductile brittle system where Fe is the ductile component and Co is the brittle one [1, 5]. This means that Fe particles in the first stage of milling get into a smooth shape, embedding the Co particles which are brittle. Thereby, a micro scale granulated sandwich mixture results in a two phase composition. By continuing the milling, the second stage begins where cold hardening is the driving phenomenon. The micro scale particles are cracked, reducing considerably their size. Thus, Fe and Co are mixed at nanoscale level. Since cold hardening effect involves crystal lattice defects, which promote the diffusion of Fe and Co, a solid solution results. Finally, the component in excess will build the resident crystal structure and the alloying element will replace some atoms in this crystal lattice. In the case of Fe-Co mixtures, with high Co content, we expect the Co crystal lattice to be the host for the Fe atoms, forming a mechanical alloyed solid solution. The strong reduction of particles size causes also the formation of the nanostructure.

This behavior concerning the nanostructure formation was reported for Fe50Co50 composition subjected to mechanical alloying [6, 7, 8]. For different compositions, in the range of 40 – 70 wt. % Fe, the 10 nm grain size was detected after 30 hours of milling [9].

The Co rich region of the Fe-Co equilibrium diagram presents the eutectoid phase transformation [10]. Thus, it is interesting to subject such compositions to mechanical alloying in order to achieve a nanocrystalline solid solution.

On the other hand, since magnetic cell separation is currently developed with success for medical applications, magnetic nanostructures are in the attention of researchers [11, 12].

In the present work, we focus our study on a Fe - Co mixture with very high Co content, namely Fe_5Co_{95} mechanically alloyed powder. This Fe_5Co_{95} powder could be a very useful material for designing and developing some magnetic procedures for cell selection.

This Fe_5Co_{95} composition is situated in the hipoeutectoid domain of Fe-Co phase diagram [10]. Therefore, it is interesting to subject this composition to mechanical alloying in order to achieve a nanocrystalline solid solution.

The formation of the nanostructure in the mechanically alloyed powder can be revealed by X-ray diffraction (XRD), based on the Scherrer formula [13] and on the Williamson – Hall method. We note that the Williamson – Hall method allows the elimination of the

micro stress influence from the X – ray data calculation [14]. This method is mainly based on the influence of the grain size on the full width at half maximum of X – ray diffraction peaks (FWHM). However, a direct technique is necessary to reveal the nanostructure of this type of material.

The powerful technique for the nanostructure determination is atomic force microscopy (AFM), which allows the observation of the nanoscale features [15, 16]. In this regard, we have a suitable experience in visualization of various nanoparticles, biological structures and nanocomposite materials [17, 18, 19]. However, it is a challenge in samples preparation, since they have to be thin layers of powder, perfectly bonded to a substrate, in order to meet AFM demands.

2. Experimental procedure

For mechanical alloying, we used elementary Fe and Co powders (producer Ductile Powder – Buzau). Milling was executed in planetary ball mills (acceleration field 20 g at the center of containers). The initial powder mixture was dosed for a Fe 5 wt.% and Co 95 wt.% composition.

A container's charge included the powders mixture and the balls for bearings of 12.5 mm diameter in the ratio balls / powder of about 3.2. As such, the composition Fe_5Co_{95} was milled for 1, 2, 4, 8, and respectively 12 hours. Samples were taken out at each milling time for investigation by X-ray diffraction and AFM.

For X-ray diffraction measurements, DRON 3 diffractometer with data acquisition module was used. Measurements and primary calculations of the diffractograms were performed using MATMEC IV.0 software.

The AFM investigation was performed on a JEOL Scanning Probe Microscope JSPM 4210 in tapping mode. Standard cantilevers, with noncontact conical shaped tips of silicon nitride coated with aluminium, were used. The tip was on a cantilever with a resonant frequency in the range of 200 - 300 kHz a spring constant of 17.5 N/m. All images were scanned at $2.5 \times 2.5\ \mu m^2$ and were processed using the standard procedures for AFM. The proper AFM observation on the Fe_5Co_{95} mechanical alloyed powder mixture requires special samples preparation which uses adhesive tape for immobilization of granular material into a thin layer. Such sample-tapes were prepared for each milling time. Each sample-tape was mounted on the sample stab and investigated in tapping mode. The topography and phase images were scanned and acquired.

3. Results and discussion

The X-ray diffraction analysis allows the phase identification in the Fe_5Co_{95} mixture during the mechanical alloying experiment. To this purpose the diffractograms were registered in the 2θ range from 40-160 degrees. Since diffraction maxima were observed only in the medium angles range, in Fig. 1 and Table 1 only the relevant data for 2θ range, between 40 and 54 degrees, are given.

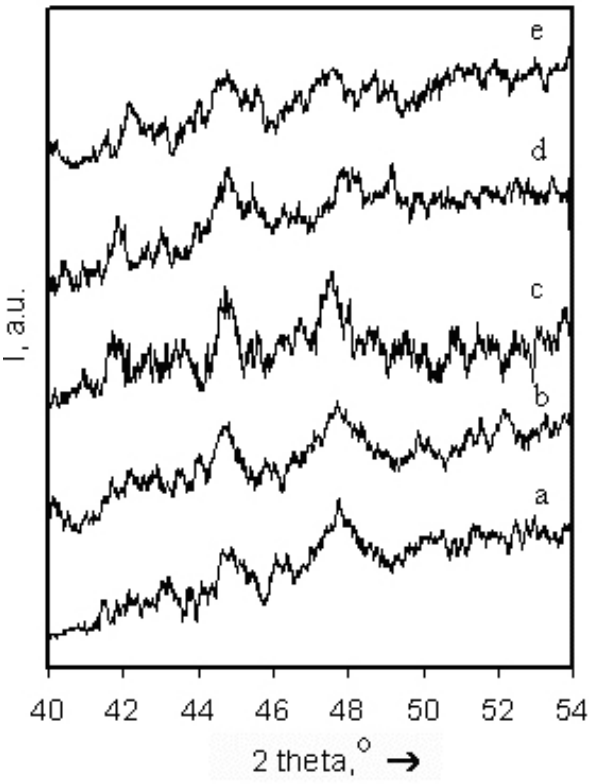

Fig. 1. X-ray spectra, 2θ: 40÷54°, for Fe5Co95 composition milled for different milling times: (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, and (e) 12 h.

After the first milling hour the specific diffraction maxima for Fe are still observed, Fig.1a, implying a two phase mixture, with Fe and Co as distinct phases. After the second milling hour the specific Fe maxima in the diffraction spectrum disappear, only the Co maxima being observed. This denotes a single phase being present for the Fe_5Co_{95} mixture, retaining the cobalt hexagonal close packing (HCP) crystalline structure [10]. Therefore, the Fe atoms were dissolved by the Co crystal lattice, as an important step towards the formation of the substitutional solid solution. This means mechanical alloying has been initiated, with Fe atoms substitutionally incorporated. Fe and Co atomic radii having close values (Fe: 126 pm and Co: 125 pm), this arrangement is possible. Nevertheless, Fe atoms are slightly larger than Co atoms, leading to distortions of the Co crystal lattice. So the C-axis of the Co unit cell is susceptible for higher deformations than the A-axis, thus the ratio of the lattice parameter *c* – corresponding to the C-axis and the *a*-parameter – corresponding to the A-axis should increase. This increase is actually observed in Fig. 2, representing the evolution of the *c/a* ratio against the milling time, pointing at the formation of the substitutional solid solution of Fe in Co HCP. This Fe_5Co_{95} solid solution constitutes a metastable

phase, an extension of the solubility zone beyond that existing in the equilibrium diagram, where there is a system of hypoeutectoid nature.

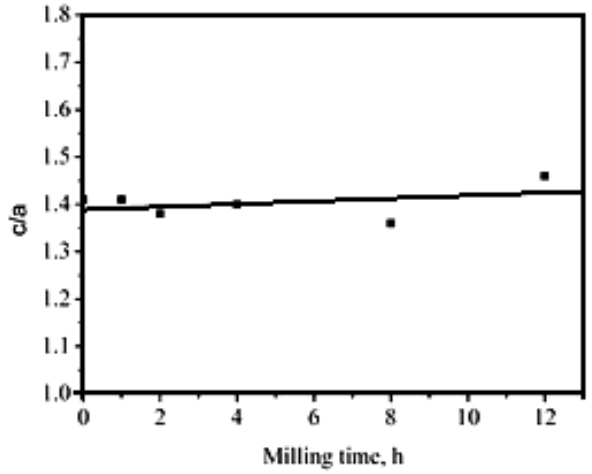

Fig. 2. Variation of c/a ratio versus milling time.

X ray diffraction in metallic and alloys systems allows, beside phase identification, also the calculation of the average size of crystallites, by several methods.

Scherrer formula [13] allows the calculation of grain size from FWHM determined on the XRD spectra mainly for bulk materials without strains at crystal lattice level. The strong deformation of particles during mechanical alloying process induces stress at the crystal lattice level. Those strains also affect the FWHM value. The Williamson – Hall method allows the elimination of stress effect on the FWHM value [14]. We calculated the grain size from FWHM using both methods, and the results are presented in Table 1 (t_m – milling time, d_1 – grain size calculated with Scherrer formula and d_2 – grain size calculated by Williamson - Hall method).

Table 1. Grain size calculated from FWHM.

t_m, h	1	2	4	8	12
d_1, nm	16.72	9.88	6.60	4.23	3.30
d_2, nm	103.24	61.40	33.09	24.86	19.42

Comparing the values, given in Tab. 1, obtained by both methods, it results that Scherrer formula provides too small values to be considered as an appropriate one.

Further, Fig. 3 presents the variation of d_1 vs. milling time. Eliminating the stress influence, by using the Williamson – Hall method, we obtain larger values which are probably closer to the actual structure. Fig. 4 presents the plot of d_2 with milling time. The curve in Fig. 3 is similar with the one given in Fig. 4, representing the same processes, but at different scale.

In this case we could conclude that Scherrer formula is not suitable for calculating the grain sizes of particulate matter and especially for mechanical alloyed powders.

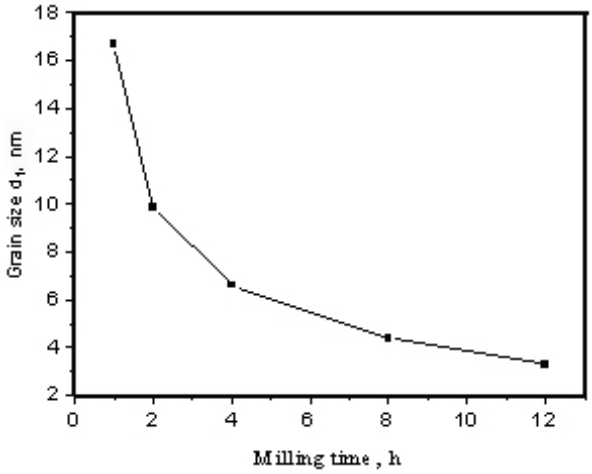

Fig. 3. Grain size obtained by Scherrer formula, d_1, versus milling time.

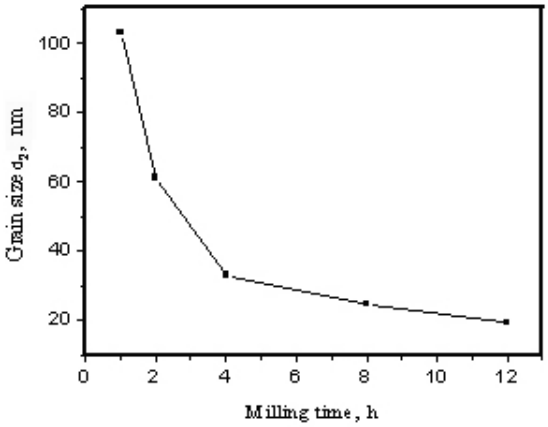

Fig. 4. Grain size obtained by Williamson – Hall method, d_2, versus milling time.

In the following we will refer only to the values obtained by Williamson – Hall method and to the data presented in Fig. 4.

After the first hour of milling the value of grain size is about 103.24 nm, considered as an average value. The literature states the upper limit of nanocrystalline domain at 100 nm [20]. It means that the Fe_5Co_{95} powder mixture milled 1 hour is at the upper level of nanocrystalline state being a polycristal particulate material.

After 2 and respectively 4 hours of milling the grain size values are 61.40 and 33.09 nm, i.e. nanocrystaline state appears in the milled composition. In this range of milling time, in Fig. 2 an increase of c/a ratio is evidenced indicating that a solid solution is formed.

After 4 to 12 hours of milling, the plot in Fig. 4 shows a slow decreasing of grain size. It results that nanocrystalline state has been achieved. The grain size variation is asymptotic, resulting in an average value of 20 nm. The grain size will not decrease under this value. This

variation of grain size, resulted from FWHM of Fe5Co95 indicates that the mechanical alloying process acts in ductile- brittle behavior.

FWHM calculation of grain size provides a theoretical value, which is quite exact for a quantitative characterization of the grain size for Fe_5Co_{95} mechanically alloyed mixture, but it is not sufficient for the characterization of the nanostructure formation. For this purpose we need a direct observation of the nanostructure as atomic force microscopy (AFM) can provide.

Fig. 5 presents AFM images for the Fe_5Co_{95} powder after one hour milling time. Smooth particles are observed, of micrometric size, as shown in the topography image Fig. 5a. These are the specific kind of particles for the first stage of the mechanical alloying ductile brittle system in agreement with published data [1].

The surface roughness, Rq, is given as root mean square on the profile (Fig. 5 (c)) and it is about 169 nm. The Rq value is caused by the presence of crystallite boundaries, evidenced also in the phase image, Fig. 5b.

The general aspect of Fig. 5 represents with great accuracy the first stage of mechanical alloying as mentioned above. In this case of particulate materials, the phase image (Fig. 5 (b)) presents a higher contrast than topography image (Fig. 5 (a)).

The second stage begins after the second hour of milling time. The aspect of the Fe_5Co_{95} powder mixture is given in Fig. 6. After 2 hours of milling the topography image, Fig. 6 (a), reveals groups of particles of about 500 nm stacked one to another with several crack lines.

From the cross section, Fig. 6 (c), we find the Rq value of about 89 nm. Again, the value of Rq is also related to the nanoscale features revealed by phase image, Fig. 6 (b). It is evident that the second stage begins at 2 hours of milling for Fe_5Co_{95} mixture in the milling conditions described in the experimental section.

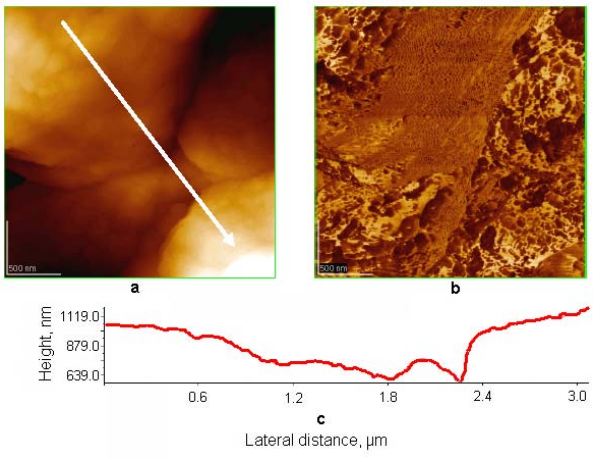

Fig. 5. AFM images of Fe_5Co_{95} mixture milled 1 hour: (a) topography image, (b) phase image, and (c) cross section profile along the arrow marked on (a) image; Rq is about 169 nm.

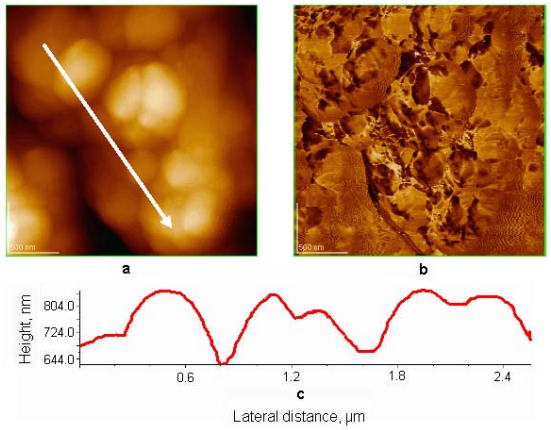

Fig. 6. AFM images of Fe_5Co_{95} mixture milled 2 hours: (a) topography image, (b) phase image, and (c) cross section profile along the arrow marked on (a) image; Rq is about 89 nm.

After 4 hours milling time, the powder presents a significantly modified aspect, as seen in Fig. 7. The powder particles present traces of consecutive rupture and cold welding, resulting in polyhedral groups of agglomerate particles, with average diameters in the 400 – 500 nm range.

A presentation of the crystallites structure is observed in the phase image, Fig. 7 (b). The surface roughness, Rq value is about 72 nm for these nano crystallites.

At 8 hours of milling the powder mixture is even more advanced processed, as observed in topography image (Fig. 8 (a)). The phase image shows distinct boundaries for nanostructured grains, Fig. 8 (b). The Fig. 8 (c) presents the cross section giving Rq value of about 48 nm.

Taking into account the above, we suggest that the nanocrystalline state of Fe_5Co_{95} powder mixture is extended in the whole composition.

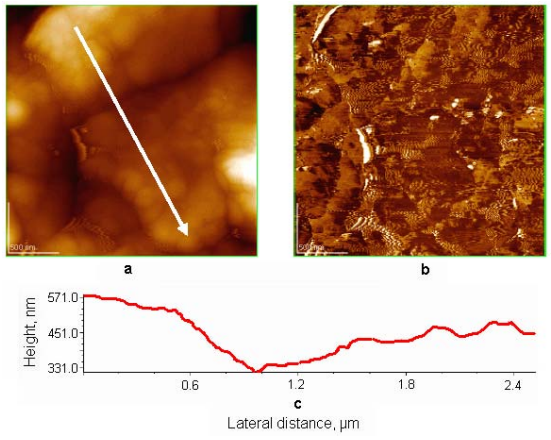

Fig. 7. AFM images of Fe_5Co_95 mixture milled 4 hours: (a) topography image, (b) phase image, and (c) cross section profile along the arrow marked on (a) image; Rq is about 72 nm.

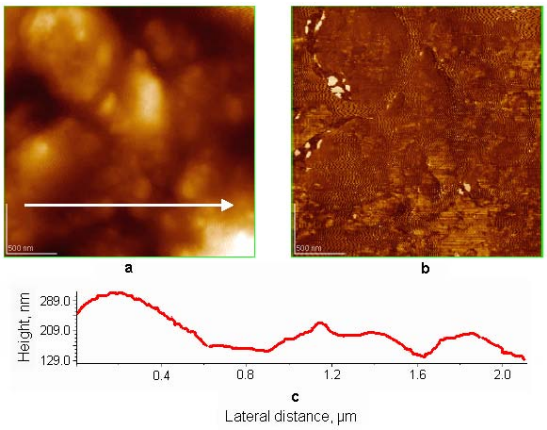

Fig. 8. AFM images of Fe_5Co_{95} mixture milled 8 hours: (a) topography image, (b) phase image, and (c) cross section profile along the arrow marked on (a) image; Rq is about 48 nm.

After 12 hours of milling, Fig. 9, we observe more clearly the shape of particles featured on the topography of the sample surface.

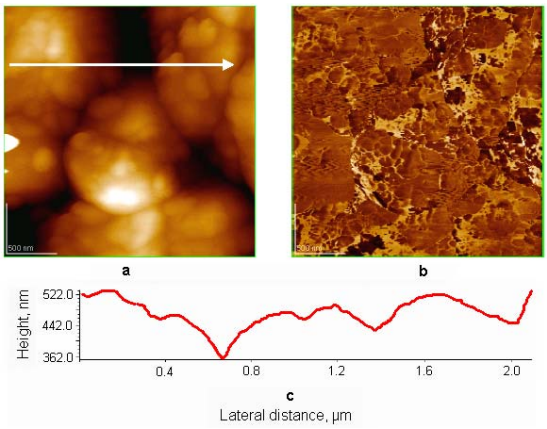

Fig. 9. AFM images of Fe_5Co_{95} mixture milled 12 hours: (a) topography image, (b) phase image, and (c) cross section profile along the arrow marked on (a) image; Rq is about 38 nm.

The observed particles contain inside the nanograins which could be observed especially in the phase image (Fig. 9 (b)). The cross section, in Fig 9 (c), leads to the value of Rq of about 38 nm.

It is important to notice that the phase image is scanned simultaneously with topography image and it is based on phase shift of the signal collected by extended electronics module (EEM) of the AFM [21].

The cantilever deflection due to sample features causes the phase shift, recorded by EEM and transformed in electric signal, which is the source of phase image. This particular source of signal allows imaging of sample details, without the influence of image height [22], in our case evidencing the grain borders.

Thus, phase image represents a contrast image which gives complementary information related to the features revealed in the topography image. This allows us to perform quantitative measurements on the nanograins revealed in phase image.

We performed the quantitative analysis of nanograins and the results are given in Table 2 and Fig. 10.

Table 2. Grain size (d_3) and Rq values determined from AFM images.

t_m, h	1	2	4	8	12
d_3, nm	109.09	60.00	39.28	36.93	33.00
R_q, nm	169.00	89.00	72.00	48.00	38.00

The plot in Fig. 10 shows the same shape variation of the grains size also observed in Figure 4.

It is to be observed that the resulted data from metallographic quantitative analysis (Fig. 10) follow rather well the values obtained by calculations with Williamson - Hall method (Fig. 4) proving support for the validity of this method against Scherrer formula (Fig. 3).

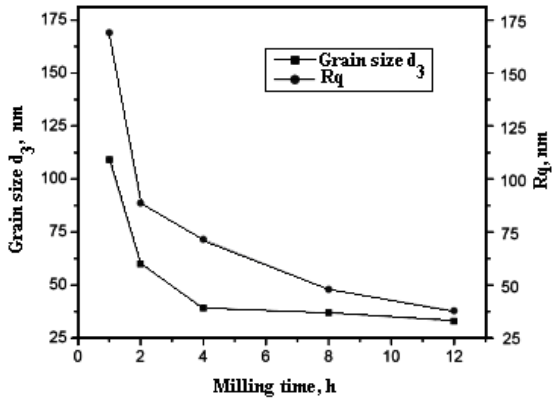

Fig. 10. Grain size resulted from phase images quantitative metallographic analysis and Rq values versus milling time.

This variation of d_3 is that expected for a ductile brittle system and indicates the complete nanocrystaline state formation at 8 hours of milling. In this particular case we could state that the nanocrystalline state formation represents a third stage of mechanical alloying.

The presence of nanograins borders revealed in phase images is also observed on the cross section profile. The roughness Rq on profiles provides values in concordance with values obtained from phase images analysis (Fig. 10).

We determined on each AFM image the roughness Rq on the given profile at each milling time. At nanolevel in the case of alloys, in general, and particularly for Fe_5Co_{95} mechanically alloyed powders, that roughness is also given by the influence of grains boundaries, which appear to be relevant for image height analysis on the sample.

However, the little higher value of Rq roughness on profile comparing to the grain size d_3 (Fig. 10) is due to the

effect of sample height combined with grain border influence.

Analyzing the data given in Fig. 10 we observe that it is a great similitude with the variation for grain size versus milling time obtained by William – Hall method. The values resulted for each milling time are very close in both the William – Hall FWHM method and AFM.

All experimental results are in accordance revealing the nanostructure formation in Fe_5Co_{95} wt. % composition subjected to mechanical alloying which is developed in the three stages according to the ductile-brittle system.

The first stage represents the cold welding between particles conducting to a smooth two phase mixture, specific after 1 hour of milling. In this stage the particles become smooth and present grain size of about 100 nm as confirmed by Williamson – Hall FWHM method and AFM direct observation.

The second stage represents the cracking initiation and the development due to cold hardening effect. In this stage grain size decreases from values of about 60 nm for 2 hours of milling to about 40 nm for 4 hours of milling. The second stage was analyzed, resulting that the most important factor in formation of nanostructure is cold hardening effect.

Finally, the third stage represents the complete formation of nanostructure by samples milled for 8 and 12 hours featuring the grain size of about 20 nm.

The behavior of Fe_5Co_{95} mixture during all three stages indicates that nanostructure formation is a complex phenomenon due to the milling conditions. In the used experimental conditions the mechanical alloying process and the nanostructure formation could not be separated, being two aspects of the same complex process.

This investigation also proves that AFM is able to reveal in tapping mode the nanostructure of mechanically alloyed powders in a straight forward manner.

4. Conclusions

The Fe5Co95 wt. % composition was subjected to mechanical alloying by milling in a planetary ball mill for 12 hours of milling, taking samples at 1, 2, 4, 8, and 12 hours. Those powder mixture samples were investigated by X-ray diffraction and AFM.

The X-ray diffraction analysis confirms the formation of Co (HCP) solid solution after 2 hours of milling, being a solubility extension against the hypo eutectoid mixture reported at in the equilibrium phase diagram.

The X-ray calculations of grain size using Williamson – Hall method based on FWHM are in agreement with AFM results, while Scherrer formula gives improper values.

On the base of the above mentioned we could state that the nanostructure in the Fe_5Co_{95} wt. % composition is formed in three stages.

The first stage, initiation of alloying featuring flat sandwich particles with two phase structure, took place after 1 hour of milling.

The second stage, representing the initiation and developing of cracking phenomenon, which leads to particles refinement and respectively to the formation of nano – grains, is found between 2 and 4 hours of milling.

The third stage represents the complete nanostructure formation, between 8 and 12 hours of milling.

The grain sizes approximate values for the nanostructure formation in the first stage are about 100 nm, for the second stage around 40 nm and for the last stage about 20 nm.

Thus, the AFM investigation represents a useful tool for direct investigation of mechanically alloyed samples to give a complete characterization of nanostructure formation.

References

[1] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).
[2] H. Bakker, L. M. Di, Mater. Sci. Forum **88–90**, 27 (1992).
[3] P. P.Chattopadhyay, I. Manna, S. Talapatra, S. K. Pabi, Mater. Chem. Phys. **68**, 85 (2001).
[4] J. Zbiral, G. Jangg, G. Korb, Mater. Sci. Forum **88–90**, 19 (1992).
[5] I. Petean, G. Arghir, In: Third International Conference on Powder Metallurgy ROPM Sinaia, Edit.R.L. Orban 857 (2005).
[6] L. Baek–Hee, B. S. Ahn, D. G. Kim, S. T. Oh, H. Jeon, J. Ahn, Y. D. Kim, Mater. Lett. **57**, 1103 (2003).
[7] M. Sorescu, A. Grabias, Intermetallics **10**, 317 (2002).
[8] H. Moumeni, S. Alleg, J. M. Greneche, J. Alloy. Compd. **386**, 12 (2005).
[9] A. Zelenakova, D. Oleksakova, J. Degmova, J. Kovak, P. Kollar, M. Kusy, P. Sovak, J. Magn. Magn. Mater. **316**, e519 (2007).
[10] T. Nishizawa, in ASM Handbook **3**, 2141 (1997).
[11] M. Zborowski, L. Sun, L. R. Moore, P. S. Williams, J. J. Chalmers, J. Magn. Magn. Mater. **194**, 224 (1999).
[12] L. R. Moore, A. R. Rodriguez, P. S. Williams, K. McCloskey, B. J. Bolwell, M. Nakamura, J. J. Chalmers, M. Zborowski, J. Magn. Magn. Mater. **225**, 277 (2001).
[13] G. Arghir, Crystal Characterization of metals and alloys by X-ray diffraction, UTC – N Press, Cluj-Napoca 1993.
[14] M. Meier, Measuring crystallite size using X-ray diffraction, the Williamson-Hall technique, University of California, Davis, 2005.
[15] M. Stark, C. Moller, D. J. Muller, R. Guckenberger, Biophys. J. **80**, 3009 (2001).
[16] M. Tomoaia-Cotisel, in Convergence of Micro-Nano-Biotechnologies, Series in Micro and Nanoengineering **9**, Editors: M. Zaharescu, E. Burzo, L. Dumitru, I. Kleps, D. Dascalu, Rom. Acad. Press, Bucharest, 147 (2006).

[17] I. Petean, Gh. Tomoaia, O. Horovitz, A. Mocanu, M. Tomoaia-Cotisel, J. Optoelectron. Adv. Mater. **10**(9), 2289 (2008).
[18] Gh. Tomoaia, M. Tomoaia-Cotisel, A. Mocanu, O. Horovitz, L. D. Bobos, M. Crisan, I. Petean, J. Optoelectron. And Adv. Mater. **10**(4), 961 (2008).
[19] C. Prejmerean, Gh. Tomoaia, M. Tomoaia-Cotisel, A. Mocanu, O.Horovitz, M. Moldovan, D. Dudea, G. Voicu, I. Petean, J. Optoelectron. and Adv. Mater. **10**(3), 597 (2008).
[20] N. Jumate, V. Pop, I. Chicinas, Nanocrystalline and amorphous materials, U.T. Press, Cluj – Napoca 2002.
[21] X. Chen, S. L. McGurk, M. C. Davies, C. J. Roberts, K. M. Shakesheff, S. J. B. Tendler, P. M. Williams, J. Davies, A. C. Dawkes, A. Domb, Macromolecules **31**, 2278 (1998).
[22] D. Verma, K. S. Katti, D. R. Katti, B. Mohanty, Mater. Sci. Eng. C **28**, 399 (2008).

*Corresponding author: mcotisel.chem.ubbcluj.ro@gmail.com