NANO QUANTITATIVE METALLOGRAPHY INVESTIGATION ON THE MECHANICAL ALLOYED Fe5Co95 COMPOSITION

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Abstract

Nanoparticles of Fe5Co95 wt. % solid solution were obtained after 12 hours of milling. This state was established by Williamson – Hall technique from an X-ray diffraction spectrum. The quantitative metallography was done by investigation of the powder sample by AFM tapping mode, acquiring topography and phase image. The AFM images were analyzed by AFM Image Processing Soft and classical quantitative metallography resulting in an average diameter of 21 nm. The resulting mean diameter is in accordance to the resulting value from X-ray data, respectively 20 nm. Based on the obtained results we could affirm that the nanocrystalline state of Fe5Co95 wt.% solid solution mechanical alloyed powder presents equiaxial nanograins with an irregular border, caused by cracking phenomena during milling.

Keywords: Fe5Co95, mechanical alloying, nanostrutures, metallographic analysis

INTRODUCTION

Nanostructural alloys are achieved usually by mechanical alloying [1]. It is a difficult matter to calculate an appropriate value for the size of nanoparticles or nanograins. The X-ray analysis is usually used for determination of nanocrystal dimension [2,3], resulting in an estimative value which depends on the applied method. The classical Scherer formula seems to give only qualitative information about nanostructure [4], and for a better quantitative analysis for the mechanical alloyed powder there must be used some analytical methods, such as the Williamson-Hall method [5], to take into account the residual stress accumulated in powders. On the other hand, there could be determined the exact average diameter of grains [6,7] in classical quantitative metallography. If we could apply the quantitative metallographic analysis at the nano level, we could directly characterize the nanostructure. The level of investigation technique nowadays is so advanced that the nanostructure were successfully visualized on biological or alloys thin films [8,9] by Atomic Force Microscopy (AFM). The AFM investigation could be difficult to apply on mechanical alloyed powders due to their morphology. In the literature, there was reported successful AFM imaging of $Mg_{2-x}M_xNi$ mechanical alloyed composition [10], this is an important step for the direct investigation of mechanical alloyed powders. The aim of this article is to give a quantitative analysis of the nanostructure of Fe5Co95 mechanical alloyed powder by X-ray diffraction and by AFM.

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EXPERIMENTAL PROCEDURE

Elemental iron and cobalt powders were used for the mechanical alloying experiment. The mixture dosed for Fe5Co95 wt.% percentage was milled for 12 hours in a planetary ball mill (featuring a 20 g acceleration field in milling vials and 12 mm diameter steel balls as milling bodies). The samples from this powder were investigated by X-ray diffraction with a DRON 3 diffractometer equipped with a data acquisition module, using Cu k_α radiation. Also we prepare AFM samples by sticking a thin layer of powder on double stick tape. These samples were investigated with a Jeol JSPM 4210 AFM microscope in tapping mode using the NSC 11 cantilever type, Micromasch Estonia, 330 kHz resonance frequency and a 50 N/m spring constant.

RESULTS AND DISCUSSION

The resulting powder by milling was investigated by X-ray diffraction, giving an X-ray spectrum, Fig.1.

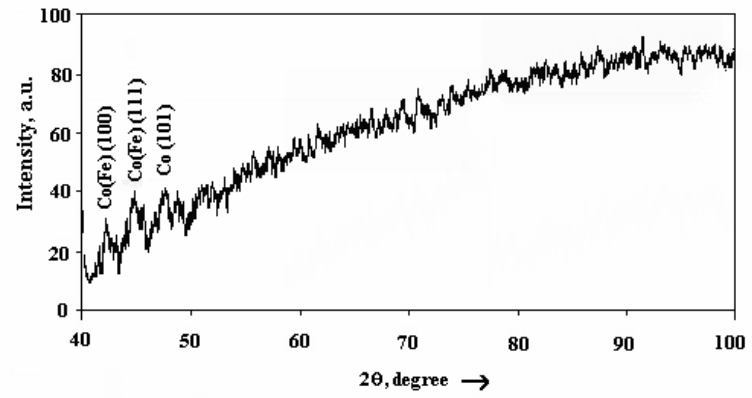

Fig.1. X-ray spectrum for Fe5Co95 composition milled for 12 hours.

Indexing of the X–ray spectrum was done in Fig.1, revealing peaks for Co only, the iron peaks were missing. The X – ray diffraction data are presented in Table 1. The calculation of c/a ratio, using the HCP model, gave a value of 1.46, comparing to 1.41 c/a ratio reported after the first hour of milling [11].

Tab.1. The X-ray data for Fe5Co95.

Miller indices	d/n, pm	β, deg
Co (100)	214.6	0.46
Co (111), Fe	202.5	0.75
Co (101)	191.1	0.63

The Fe missing peaks show that Fe disappears as distinct phase in the Fe5Co95 mixture milled for 12 hours. The iron atomic radius is 126 pm and, respectively, 125 pm for cobalt.

We observe that the c/a ratio is increased after 12 hours of milling and the Fe diffraction peaks disappear. This is due to Fe atoms solved into the Co crystal lattice resulting a substitution solid solution.

Usually after several milling hours the resulting powder is in a nanocrystalline state. The most common method for nanocrystalline state identification is the grain size calculation from the X-ray spectra. There are several methods for this calculation. In our case we apply the Scherrer formula and the Williamson – Hall method.

Calculating the grain size according to the Scherrer formula results 13.64 nm. This value could be affected by residual stress caused by the milling effect. There are some mathematical methods to eliminate residual stress influence on the grain size as resulted by X-ray calculation. In this paper we used the Williamson – Hall method [5], see equation

$$\beta \cos\theta = (k \lambda) / d + \eta \sin\theta, \quad (1)$$

where: d – grain size; k – coefficient (between 0.9 – 1); λ – wave length of used X-ray; β - full width at half height FWHM (Table 1); θ – Bragg diffraction angle. η – the slope of sinθ vs. d cosθ graph.

Applying Williamson – Hall method results in a 19.42 nm grain size for Fe5Co95 solid solution. Comparing to the value obtained using the Scherrer formula this value is sensibly increased. Based on those results we could state a 20 nm grain size as reference value obtained by the X–ray diffraction calculation. Of course to give a more adequate characterization of nanostructure we need some special investigations which allow for imaging the nanograins.

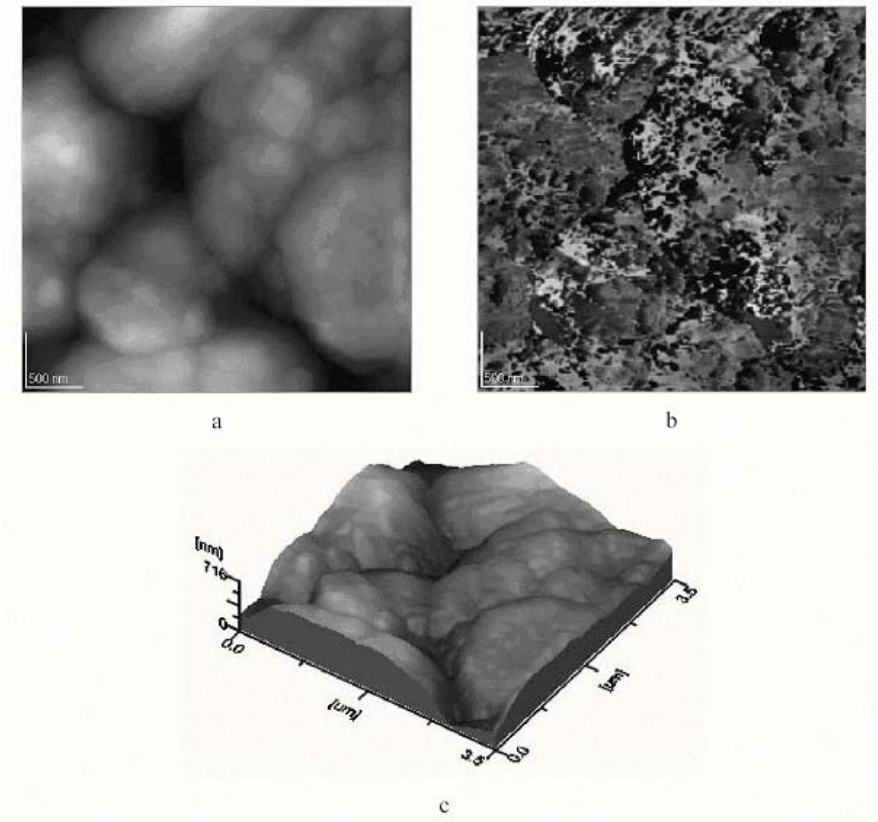

Fig.2. AFM images of the Fe5Co95 solid solution obtained by mechanical alloying: a) topography image, b) phase image and c) 3D view of topography image. Scanned area 3.5 X 3.5 μm^2.

The Atomic Force Microscopy (AFM) is the most sensitive surface investigation method which could reveal images at nano level. It is a great challenge to use this sensitive method for mechanical alloyed powders. In tapping mode, AFM features two basic imaging modes: topography which reveals the surface topography and phase imaging which is related to the sample properties.

Figure 2a presents the surface topography of the powder sample. We could observe several particles having irregular - rounded shape. The topography imaging represents the height of the sample on the scannedarea, which allows special investigation such as profile detail and particle analysis performed by WinSPM processing soft, JEOL accesories to the AFM microscope. Figure 2b presents phase image and Fig.2c a 3D view of the topography image.

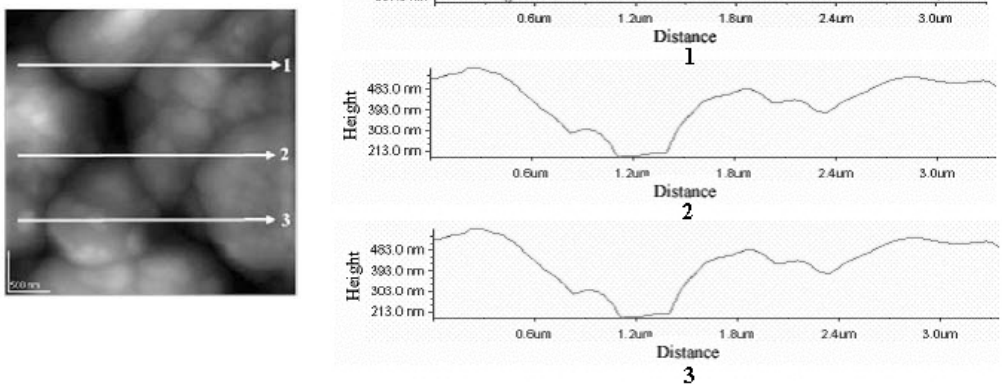

Fig.3. Profile detail of the topography image, the direction on the white arrows.

We calculated the image height of 716 nm, corresponding to 128 nm mean surface roughness, with the processing soft, on the topography profile details, Fig.3, the average particle size resulting in 1.2 μm diameter, formed by visible nanograins on the height vs. distance plots. A more sensitive analysis is given by the particle analysis performed with processing soft, obtaining the histogram in Fig.4.

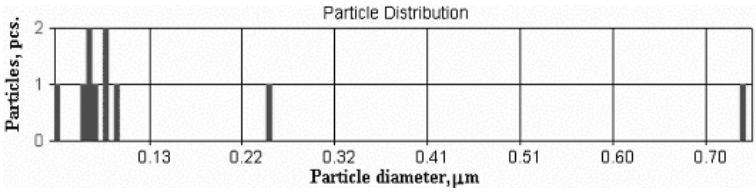

Fig.4. Particle distribution histogram on the topography image.

Particle size analysis performed on the topography image shows that we have 10 particles with an average area of 536 nm^2. It means that those 10 particles obviously seen in Fig.2a are formed by smaller particles. Those smaller particles are detected by particle analysis function and also appear distinct in the profile detail. There is no match comparing to the value of grain size obtained by X-ray diffraction. Obviously the nanograins represent

a more refined structure in the greater particles. To detect them among the particles we need a more sophisticated technique. This technique is the phase imaging, Fig.2b.

It is easy to understand the formation of the topography image in tapping mode. The cantilever is oscillated near the resonance frequency and taps the sample. The topography details cause cantilever deflection proportionally with their dimensions. On the cantilever there is focused a laser beam which is also deflected on a photodiode resulting in a signal for topography image [12]. The piezo-material of the cantilever holder is used to oscillate the cantilever but also to sense this oscillation by an electronic extended module [13] which could detect the signal phase shift. This signal phase shift is used to achieve the phase image. The signal phase is affected by the changing of material properties rather than topography that is why the phase image is flat [13].

In our case the nanograin boundaries act differently than the material inside of them, and we obtain distinct nanograins against borders. If we look to the phase image, Fig.2b, acquired simultaneously with the topography image we could observe as distinct parts the nanograins and the boundaries between those 8 great particles reported in the topography image. We perform particle analysis on the phase image to measure the nanostructure elements of the Fe5Co95 solid solution, see histogram in Fig.5.

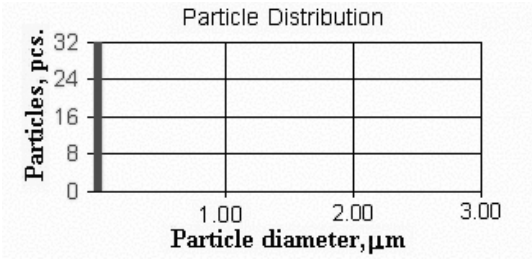

Fig.5. Particle distribution histogram on the phase image.

On the particle analysis performed on the phase image we obtain: 32 particles having an average area of 317 nm^2. Considering nanograins having a circular shape results in an average diameter of 20 nm, similar with value obtained with the Williamson – Hall method.

For a more accurate result we perform a quantitative metallographic analysis on the phase image. The classic quantitative metallography is based on measuring the diameter of the grains revealed on the metallographic image (optical microscope), along to several lines displaced at equal distances. In our case we could perform profile detail on the phase image similar to the lines on classic quantitative metallography. For that purpose we took 10 profile details on the phase image as it is shown in Fig.6a. The nanograins are distinctly revealed by profile details, being able for quantitative metallography. Figure 6b presents only 3 profile details, but in the metallographic calculation there were counted all 10 profiles.

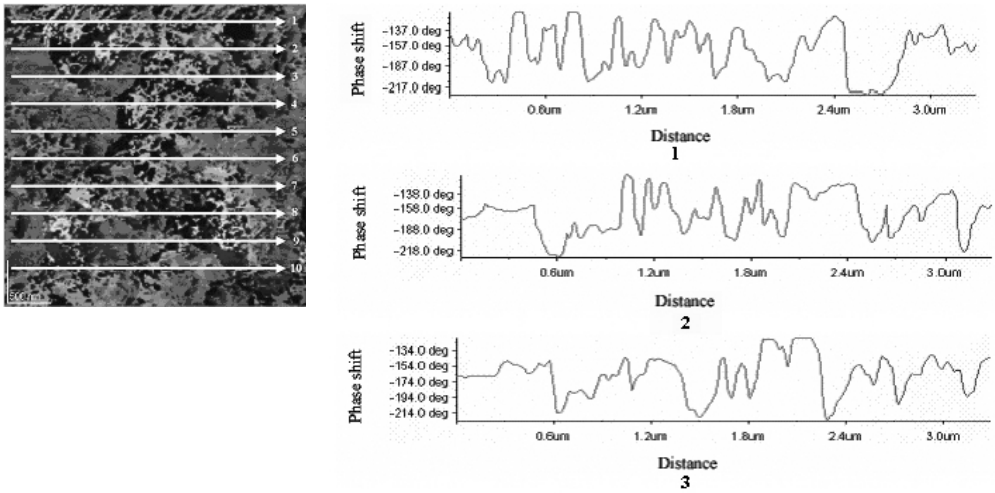

Fig.6. Profile details on phase image: a) direction of profiles and b) detail plots.

In the profile details, Fig.6, we find 153 particles along 33 μm, calculating we obtain an 21.56 nm average diameter. This analytical method is based on the full phase image being an independent method to processing soft. We could observe a great difference between the number of particles obtained by particle analysis procedure, 32, and the number of particles obtained by classic quantitative metalography, 153 respectively. That difference could result because of the connectivity between pixels in particle analysis procedure, where due to less contrast some parts of images could miss analysis, compared to the classic method where all particles are counted.

However, the results obtained by both methods are very close, 20 nm and respectively 21.56 nm diameter of each nanograin. Considering that classic quantitative metalography provides more accurate results and counting that the value obtained by particle analysis procedure we could affirms that we have 153 nanograins with an average diameter of 21 nm. The value of average diameter obtained by nano – quantitative metallography is very close to the value of 20 nm obtained by the Williamson – Hall method from an X-ray spectrum.

CONCLUSIONS

Applying the Williamson – Hall method on the Fe5Co95 solid solution obtained by mechanical alloying, resulted in a bigger value for the nanocrystal diameter than the Scherrer formula (13.64 nm) 19.42 nm respectively. This value was corroborated with nano – quantitative analysis based on AFM – phase imaging, resulting in a 21 nm diameter which is a very close value compared to XRD grain size. Finally, results that the Williamson – Hall method provides better results and AFM – phase imaging is a fruitful method for the nanostructure investigation of mechanical alloyed powders, providing direct imaging and more accurate quantitative values.

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