SYNTHESIS OF THE NiFeCuMo SOFT MAGNETIC POWDERS BY MECHANICAL ALLOYING

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Abstract: Soft magnetic nanocrystalline Ni-Fe-Cu-Mo powders were obtained by mechanical alloying in a planetary mill under Ar atmosphere. Several milling times have been used ranging from 2 to 8 hours. A heat treatment of 30 min, 1, 2 and 4 hours at temperature of 350 °C has been performed in vacuum in order to improve the alloying process and remove the internal stresses. The formation of the Ni-Fe-Cu-Mo alloys by mechanical alloying and annealing was evidenced by X-ray diffraction. A typical grain size of 16 ± 2 nm has been obtained after 8 h milling. The chemical homogeneity composition and the morphology of the powder particles have been studied by X-ray microanalysis and scanning electron microscopy respectively.

Keyword: mechanical alloying, nanocrystalline materials, soft magnetic powders

1. INTRODUCTION

The Ni-Fe alloys present interesting magnetic properties; consequently these materials are widely studied for both fundamental and application point of view. Most ~~k~~new alloy from this class are Permalloy and Supermalloy. Useful practical properties can be obtained by adding to this material small amount of copper and/or molybdenum, in this manner we can grow the range of compositions with high permeability and we can improve the annealing treatment [1]. A high permeability is obtained if two conditions are fulfilled, first the magneto crystalline anisotropy is as small possible (zero in the ideal case), and second a zero magnetostriction constant. The alloys Ni-Fe-Cu-Mo have a zero line of magnetostriction constant in their phase diagram; this can be combined with a small anisotropy constant of Ni-Fe alloys to obtain materials with special properties [2].

Mechanical alloying is nowadays a widely used technique to obtain extended solution, non equilibrium structure/microstructure including amorphous alloys, nanocrystalline materials and quasi crystals [3-8]. Also the studies of parameter and process variables are currently in progress [9-14]. Mechanical alloying involves the synthesis of materials by high-energy ball milling, in which elemental blends (or pre-alloyed powders, oxides, nitrides, etc) are milled to achieve alloys or composite materials.

In the last years some researches about powders of Ni-rich Ni-Fe alloys produced by mechanical alloying were reported [15-18]. Other alloys Ni-Fe (from Fe-rich region of Ni-Fe phase diagram) were obtained by mechanical alloying also [14, 19-22].

In our previous study we focussed our attention on the development of a method to obtain the nanocrystalline Ni_3Fe intermetallic compound [23-26] and nanocrystalline Supermalloy (79Ni16Fe5Mo, wt %) powders [27, 28] by mechanical alloying and subsequent annealing. We have shown that a milling time of about 8 to 10 hours is sufficient for the formation of the Ni_3Fe phase. The Supermalloy phase is mainly formed after 16h of alloying. In order to discuss the influence of the synthesis conditions on the Ni_3Fe phase formation in the whole sample, a *Milling - Annealing - Transformation* (MAT) diagram was proposed [26]. Magnetic properties of the soft magnetic composites based on the mechanically alloyed nanocrystalline Ni_3Fe intermetallic compound was reported also [29].

In addition to our previous study [23-28], this study is aimed to obtain the alloy 77Ni14Fe5Cu4Mo (wt. %) with a nanocrystalline grain size by mechanical milling and annealing. At this nanometer scale when the grain size decreases the coercive field also decreases and for a critical grain size zero anisotropy constant can be reached.

2. EXPERIMENTAL

For the mechanical milling, 123-carbonil nickel, NC 100.24 iron, Mo powder produced by chemical reduction and copper powder were used starting materials. A mixture of elemental powders heaving the following composition 77Ni14Fe5Cu4Mo wt. % was homogenized for 15 min with a Turbula type apparatus. After that the mixture was milled in a planetary mill under argon atmosphere for times ranging from 2 to 8 h. In order to remove the internal stresses and to observe the influence of annealing, samples of milled powder was sealed in evacuated silica tubes and heated at 350°C for 30 min, 1, 2, 4 h.

X-ray patterns were recorded on a Siemens D500 diffractometer, operating with $Cu_{K\alpha 1}$ radiation. The angular range chosen was $2\theta = 32\text{-}103°$. The mean size of nanocrystallites was calculated from diffraction pattern with Sherrer's formula [30]. In order to do so, the resolution of the diffractometer has been determined from the diffraction pattern of a reference sample. Details of this procedure can be found in reference [23].

Scanning electron microscopy and X-ray microanalysis studies were performed on a JEOL - JSM 5600 LV microscope equipped with an EDX spectrometer (Oxford Instruments, INCA 200 soft).

3. RESULTS AND DISCUSSION

X-ray diffraction patterns are presented in Fig.1 for the samples obtained by mechanical milling for times ranging from 2 to 8 h. For comparison is represented the starting mixture having the composition 77Ni14Fe5Cu4Mo wt. % (this sample is denoted starting sample (ss), which has been only homogenised. In general the diffraction peaks observed after long milling time exhibit both a large broadening and a displacement to smaller angles. After 4 h of milling we can see a peak shift to smaller angles (Fig. 2). This displacement and the broadening are due to internal stress accumulation, but also to the solid state reaction which starts to form an alloy. The presence of the first order internal stresses acts at a macroscopic level and modifies the lattice parameters consequently producing an angular shift of the X-ray diffraction peaks. The second-order internal stresses act at a microscopic level of the crystallites and produce a broadening of the X-ray diffraction peaks [25, 31].

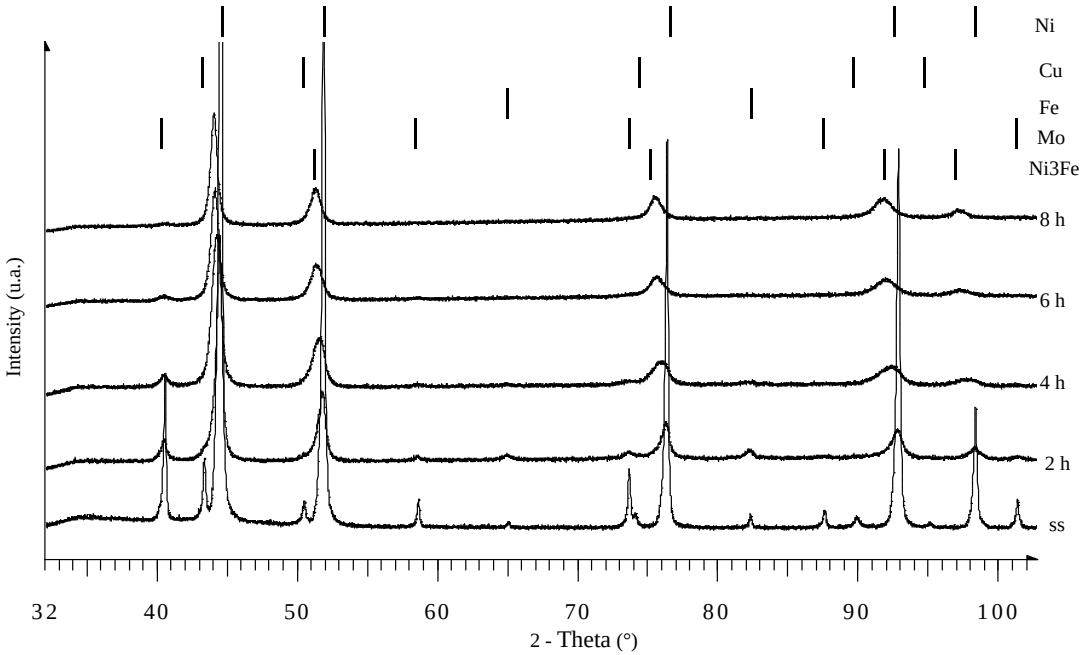


Fig. 1. The X – ray diffraction patterns of as-milled samples (2, 4, 6, 8 h) and of the as-mixed sample (ss – 0 h milled). For clarity, the spectra have been vertically shifted. Peak position for Ni, Fe, Mo, Cu and Ni_3Fe are marked.

One can observe that the intensity of copper Bragg peaks already vanish from pattern starting with 2 h of milling. After 6 h of milling the intensity of the copper peaks is zero. So it is possible that Cu goes in a solid solution or in a compound with the other elements. Regarding the molybdenum peaks, their intensity continuously reduces intensity, after 6 h of milling (110) is the only peak that remains in diffraction pattern. After 8 h of milling the molybdenum peaks are almost completely eliminated from the X-ray diffraction pattern. In the case of the iron, we can not see any peaks after 6 h of milling. It is worth to note that after 8 h of milling the new position of Ni picks are corresponding with a good estimate to that of Ni_3Fe. It can presume that the alloy formed by mechanical milling has the same structure than Ni_3Fe. A solid solution of this compound could be already formed with other elemental powder mixed at the beginning of the process. Concerning the stage of the mechanical alloying process, it can conclude that NiFeCuMo alloy is mainly formed after 8 h of milling, but it is not yet formed in the whole volume of the sample.

By annealing the milled samples it is possible to induce solid-state reactions, but only for the proportion of the sample composed of very intimately mixed Ni, Fe, Cu and Mo elements, but not yet reacted during the milling. The heat treatment also relaxes the second order internal stresses and consequently induces a slight sharpening of the diffraction peaks [25-27]. The diffraction patterns of the samples milled for different duration, and subsequently annealed at 350 °C for 30 min and 1, 2 and 4 hours, show the cumulative effect of the Mo, Cu and Fe

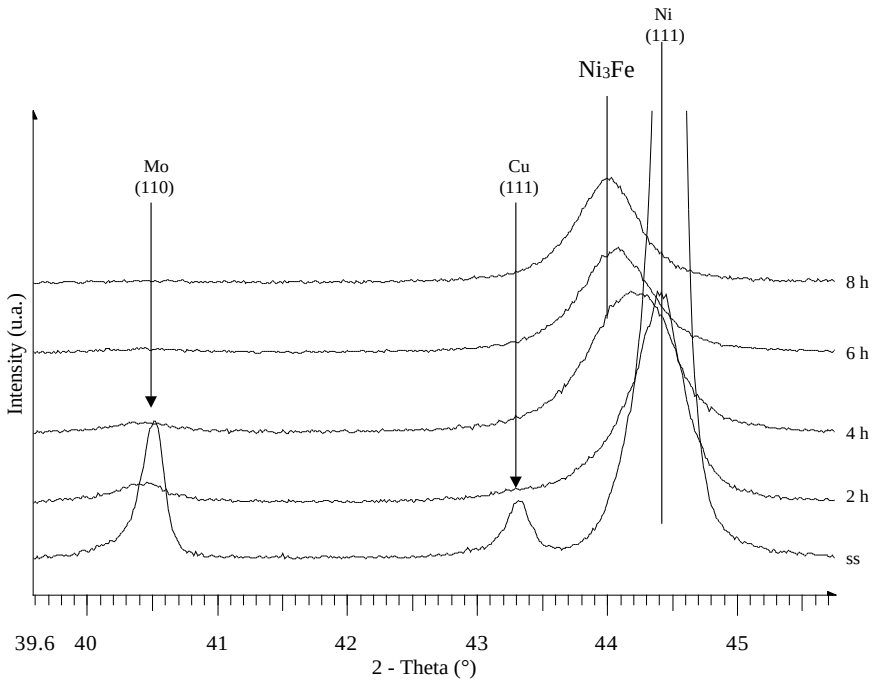


Fig.2 Detailed analysis of the (111) Ni peak of samples milled 2, 4, 6, 8 h and mixed samples (0 h milled). The Cu peaks disappear after only 2 h of milling and the nickel peak position after 8 h of milling.

atoms dissolution in the Ni lattice and of the internal stresses removal by annealing. For short milling time, the annealing has no significant effect on the position, intensity of the diffraction pattern, the effect is only a widening of the observed peaks. For long milling time (6 – 8 h) a change of the Mo peak intensity is observed. With longer annealing time, the intensity of this peak decreases, Fig. 3. In the case of the 8 hours milled sample, after 2- 4 hours of annealing the (110) Mo peak disappears and it can be concluded that, in limit of this method, Mo is dissolved in the Ni_3Fe lattice. For the same milling time it is observed that annealing increases the peak definition, due to the elimination of the second order internal stresses. The last two observations may drive the idea that an alloy or a solid solution of Ni_3Fe – (Mo, Cu) is previously formed and their formation is finished by annealing. In other words this peak width reduction could be the effect of an ordered and stabilised structure in the formation process by annealing.

The calculated size of the crystallites shows that the structure of the NiFeCuMo powders obtained by mechanical alloying is nanocrystalline. After 8 hours of milling and 4 hours of annealing at 350 °C, in order to remove the internal stresses, the mean size of the crystallites is 16 ± 2 nanometers.

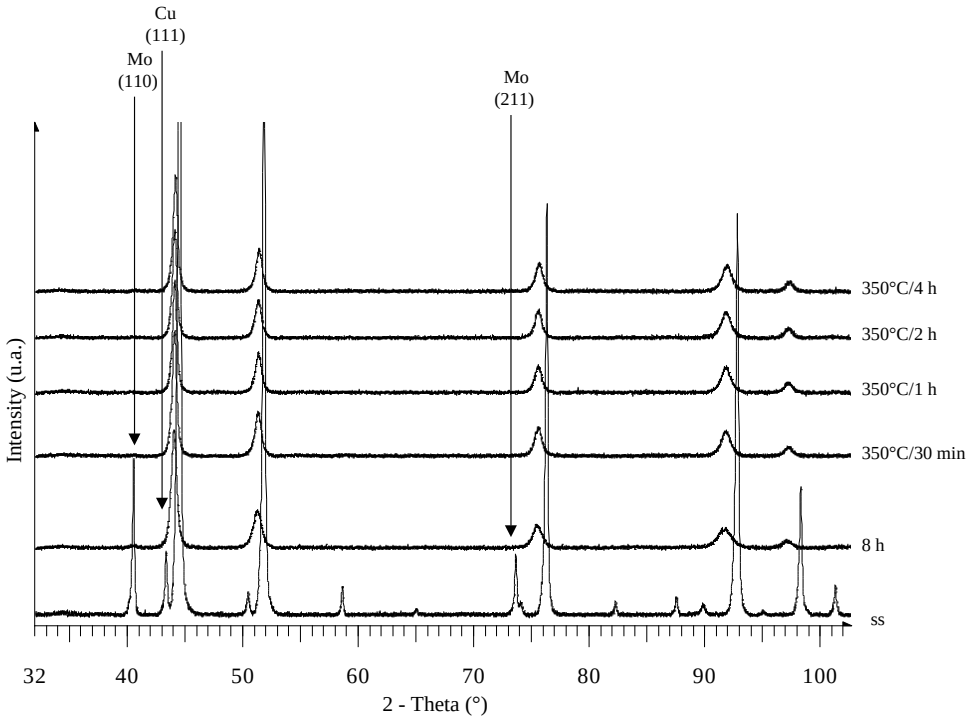


Fig. 3. The influence of annealing on the solid state reaction of 77Ni14Fe5Cu4Mo (wt. %) formation on the 8 h milled sample. The annealing temperature and time used for the annealing process are indicated. For clarity, the spectra have been shifted vertically.

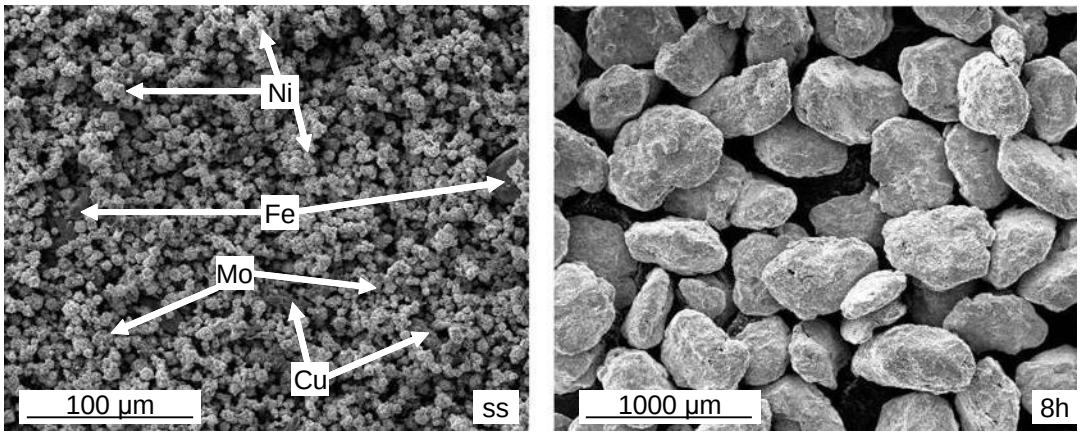


Fig. 4. Scanning electron microscope (SEM) image of the starting mixture of Ni, Fe, Cu and Mo powders (left) and of the powder obtained after 8 hours of mechanical milling (right).

The particle morphology for the starting sample and for the 8 h milled sample are shown in Fig. 4. For the starting material it is clearly evidenced that there are Ni, Fe, Cu and Mo particles (they are marked on the picture on the X-ray analysis base). For the 8 h milled sample only one kind of particles, corresponding to the alloy composition are present. It can be see that the NiFeCuMo particles obtained after 8 hours of milling are of polyhedral shape

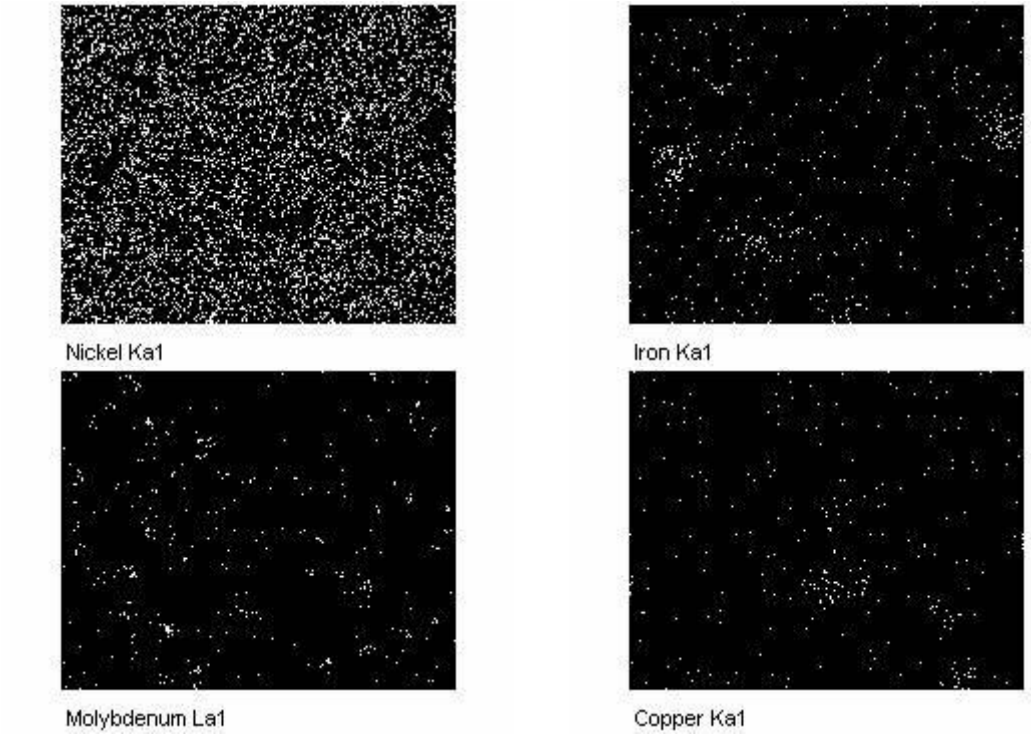
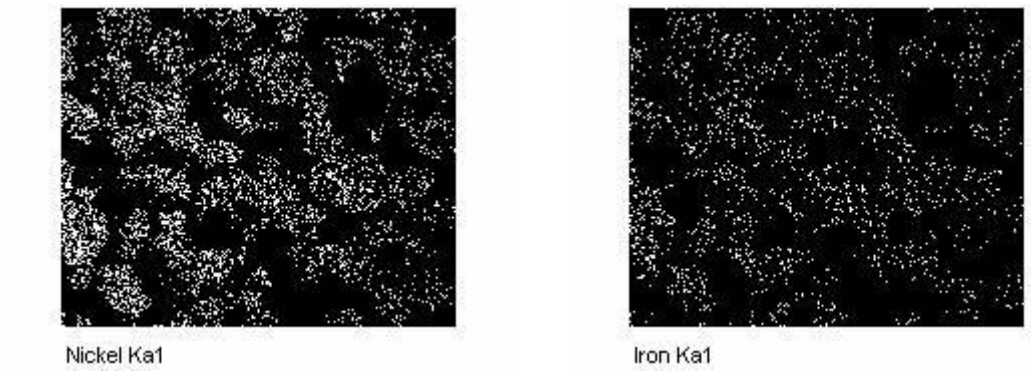


Fig. 5. The maps of Ni, Fe, Mo and Cu distributions for the starting sample (ss) The X-ray microanalysis (EDX) was performed on the selected area presented in Fig 4.



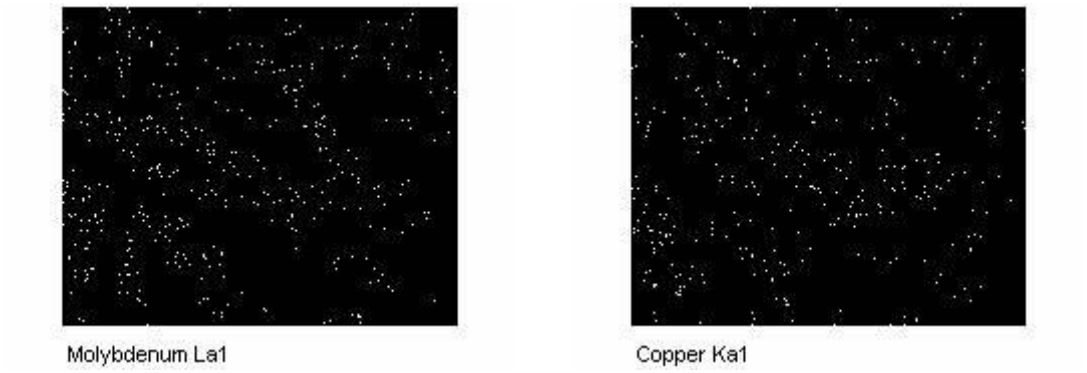


Fig. 6. The maps of Ni, Fe, Mo and Cu distributions for the 8 h milled sample. The X-ray microanalysis (EDX) was performed on the selected area presented in Fig 4.

and their particle size distribution is strongly shifted to the higher values. The X-ray microanalysis (EDX), performed on the selected areas presented in Fig 4, is shown in Fig. 5 and 6. It can be observed that the maps of Ni, Fe, Cu and Mo distributions are very different for the starting mixed powders (ss), Fig. 5, but are identical, in the error limits of this method, after 8 h of milling, Fig. 6. This shows a very good homogenisation of the starting powders mixture and that all particles exhibit chemical homogeneity after 8 hours of milling. It is worth to note that the chemical homogeneity of the particles determined by EDX is not a proof of the new phase formation, without X-ray diffraction studies.

4. CONCLUSIONS

The evolution of the formation of the 77Ni14Fe5Cu4Mo (wt %) powders by mechanical alloying and subsequent annealing has been studied by using X-ray diffraction, SEM and X-ray microanalysis. The NiFeCuMo alloy was mainly obtained after 8 hours of milling, but not in the whole volume of the sample. This fact suggests that new experiments of mechanical alloying for longer milling times are necessary. A mean crystallite size of 16 ± 2 nm was obtained after 8 hours of milling and 4 hours of annealing at 350 °C in order to remove the internal stresses. On the other hand, the NiFeCuMo phase formation has been found to be improved by annealing. Annealing has a significant effect especially for long milling time (notably for 8 h of milling). Thus, it seems that the NiFeCuMo powders were obtained after 8 h milling and 4 hours annealing at 350 °C.

The SEM studies show that the NiFeCuMo particles obtained after 8 hours of milling are of polyhedral shape and their particle size distribution is strongly shifted to larger particle size values. The chemical homogeneity and composition of the powder particles are in good agreement with the results of the X-ray diffraction studies.

A complete analysis of the magnetic and crystallographic properties of the nanocrystalline NiFeCuMo powders produced by mechanical alloying is in progress

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