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Synthesis of the supermalloy powders by mechanical alloying

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The mixture of the Ni, Fe and Mo elemental powders with the nominal composition of the Supermalloy was milled in a planetary mill under Ar atmosphere. Several milling times have been used ranging from 4 to 16 h. A heat treatment of 30 min, 1, 2 and 4 h 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 Fe-Ni-Mo alloys by mechanical alloying was evidenced by X-ray diffraction. The nanocrystalline Supermalloy powders have been obtained after 16 h milling and after 8 h milling followed by 4 h annealing. A typical grain size of 11 ± 2 nm have been obtained after 16 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.

1. Introduction

Besides the incipient crystallization of amorphous solids, mechanical alloying is one of the widely used preparation techniques to obtain nanocrystalline structures. Mechanical alloying involves the synthesis of materials by high-energy ball milling of powders [1–3]. This technique allows producing nonequilibrium structure/microstructure including amorphous alloys, extended solid solutions, metastable crystalline phases, nanocrystalline solids and quasicrystalline materials [3–6].

Fe-Ni alloys around the Permalloy composition and Fe-Ni-Mo alloys, namely Supermalloy, are well known for their high performances as soft magnetic materials. In the last years some researches about powders from Ni-Fe system produced by mechanical alloying were reported [7–10]. In our previous study we focused our attention on the development of a method to obtain the nanocrystalline Ni_3Fe intermetallic compound by mechanical alloying and annealing. We have shown [11–13] that a milling time of about 8 to 10 h is sufficient for the formation of the Ni_3Fe phase. 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 [14].

In addition to our previous study [11–14] we develop a new research concerning the preparation of the nanocrystalline Supermalloy (79Ni-16Fe-5Mo) powders by mechanical alloying.

2. Experimental

For the mechanical milling the starting materials 123-carbonyl nickel, NC 100.24 iron powder and Mo powder produced by chemical reduction were used. The mixture with a composition corresponding to Supermalloy (79Ni-16Fe-5Mo, wt%) was homogenized for 15 min in a Turbula type apparatus, and then mechanically alloyed in argon atmosphere in a planetary mill. Several milling times were used ranging from 4 up to 16 h. In order to remove internal stresses induced by milling and to investigate the influence of the annealing on the evolution of the Supermalloy formation by mechanical milling, samples of milled powder were sealed in evacuated silica tubes and heated at 350°C for 30 min and 1, 2 and 4 h. It is worth to remark that the chosen annealing temperature is smaller than the Ni_3Fe composition recrystallization temperature of 475°C.

X-ray diffraction patterns were recorded in the angular range $2\theta = 35–110°$. For these experiments

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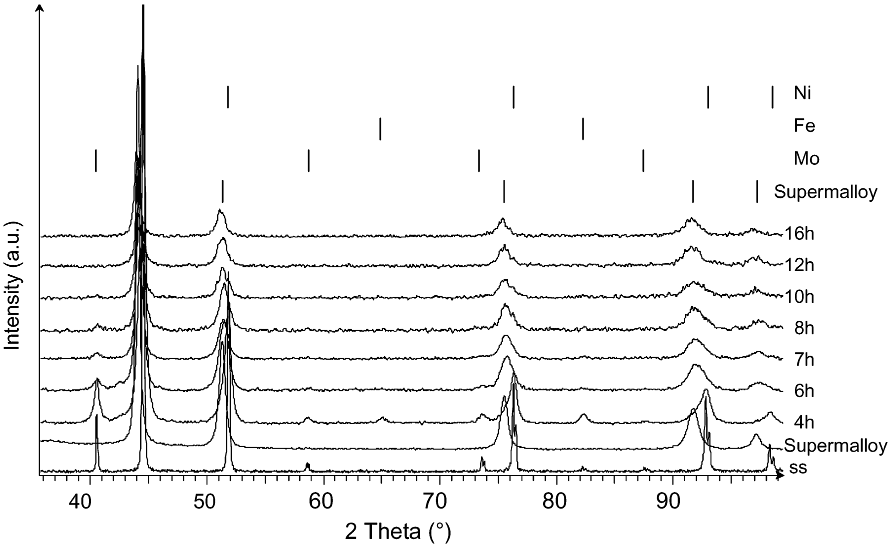


Figure 1 The X-ray diffraction patterns of the as milled samples (4, 6, 7, 8, 10, 12, 16 h), of the as cast Supermalloy sample and of the starting sample (ss–0 h milled). For clarity, the spectra have been shifted vertically.

a BRUCKER D8 diffractometer, operating with Cu K$_\alpha$ radiation, was used. The mean size of the nanocrystallites was calculated from Full-Width-at-Half-Maximum of the diffraction peaks according to Scherrer's formula [15]. 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 Ref. [11].

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 discussions

In Fig. 1, the X-ray diffraction pattern of the starting sample is compared with those of the samples obtained after different milling times. By ss (starting sample) we note the starting mixed Ni, Fe and Mo powder (79 wt%Ni + 16 wt%Fe + 5 wt%Mo, zero milling time) given for reference. For a best understanding, in Fig. 1 the X-ray diffraction pattern of the as cast Supermalloy is also given and Ni, Fe and Mo peaks position are marked. For milling time up to 6 h a broadening of the Ni diffraction peaks due to second-order internal stresses is evidenced. A little angular shift, attributed to incipient formation of alloy and to the first order internal stresses induced by milling, can also be observed. As can be seen from Fig. 2, this shift is very well defined for 6 h of milling and increases continuously with milling time. Thus, for milling time higher than 16 h the peaks positions are at angles lower than those of the Supermalloy peaks. At higher 2θ values the $k_{\alpha 1}$ and $k_{\alpha 2}$ doublet separation disappears, due to the peaks broadening produced by the second order internal stresses. This effect could explain the small angular shift to higher angles for 4 h milled sample, when mechanical alloying process is incipient.

Concerning Mo peaks, after 4 h of milling time, their intensity decreases continuously during the mechanical alloying process and after 6 h of milling only the principal peak (110) is observed. The (110) Mo peak

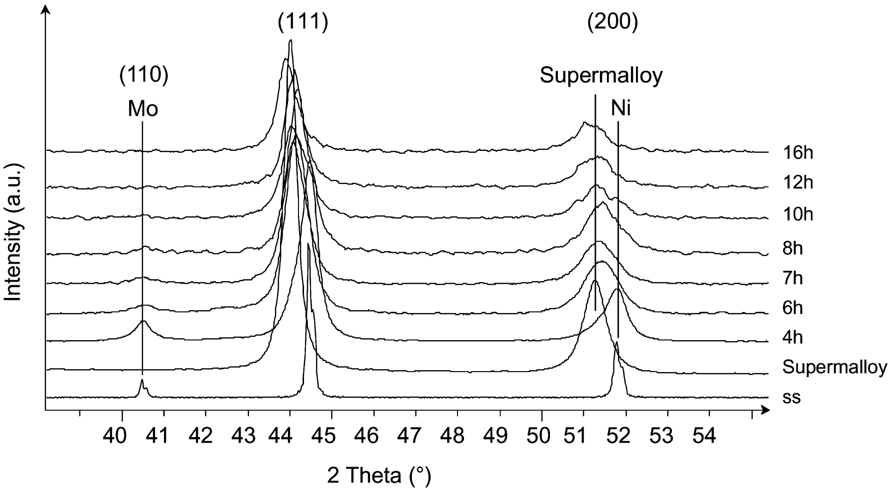


Figure 2 A detailed analysis of the (110) Mo peak and (111) and (200) Ni peaks of the as milled samples (4, 6, 7, 8, 10, 12, 16 h), of the as cast Supermalloy sample and of the starting sample (ss–0 h milled). For clarity, the spectra have been shifted vertically.

decreases with milling and disappears completely after 12 h of milling. In correlation with the evolution of the (200) peak, it can be concluded that Supermalloy powders were mainly obtained after 16 h of milling.

The diffraction patterns of the samples milled for different times, and subsequently annealed at 350°C for 30 min and 1, 2 and 4 h, show the cumulative effect of the Mo and Fe atoms dissolution in the Ni lattice and of the removal of the internal stresses. For milling time up to 10 h the effect of the heat treatment of 30 min and 1–2 h consists in a shift of the peaks to lower angles, whereas for annealing of 4 h the effect is opposite, the shift of the peaks after annealing is to higher angles. This effect is shown in Figs 3 and 4 for 6 and 8 h milled samples. This behavior is connected with the fact that the first order internal stresses and the formation of the alloy shift the peaks to lower angles. A similar behavior was observed at producing Ni_3Fe compound by mechanical alloying and annealing [13, 14].

A very interesting effect of the annealing was observed on the Mo peaks. Reaction of Mo atoms dissolution in Ni was evidenced in the case of the 4 h milled sample even for short annealing of 30 min. This is characterized by a reduction of the intensity followed by a disappearance of the Mo peaks, except the (110) one. For 6 h milled sample an annealing of 1 h produces almost the disappearance of the (110) peak, but this peak again is slowly evidenced after 2 and 4 h of annealing, see Fig. 3. This behavior is due to the cumulative effect of the induction of the solid-state reaction and the

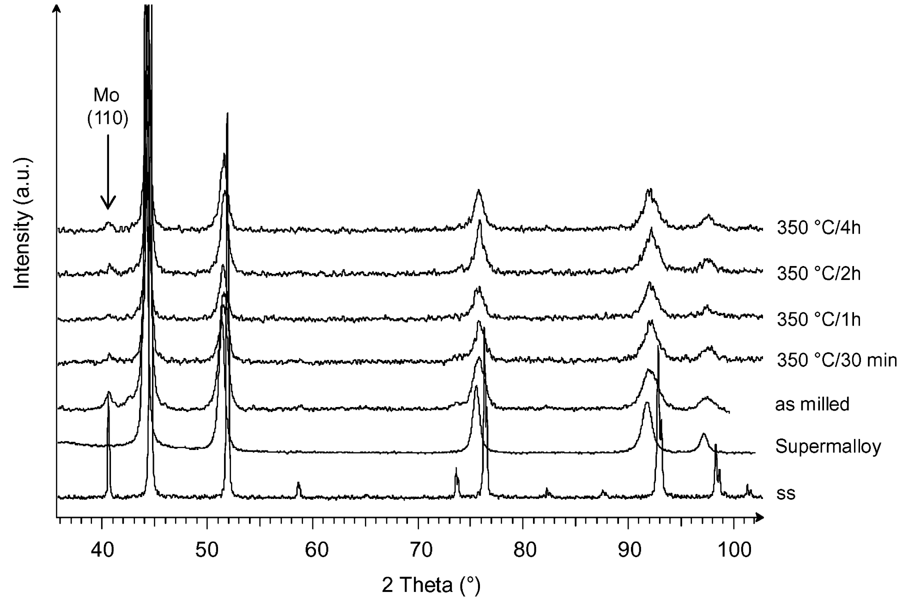


Figure 3 The influence of the annealing conditions on the solid-state reaction of Supermalloy formation on 6 h milled sample. The indicated annealing conditions are temperature/time. Supermalloy and ss refer to the as cast Supermalloy and the starting sample respectively. For clarity, the spectra have been shifted vertically.

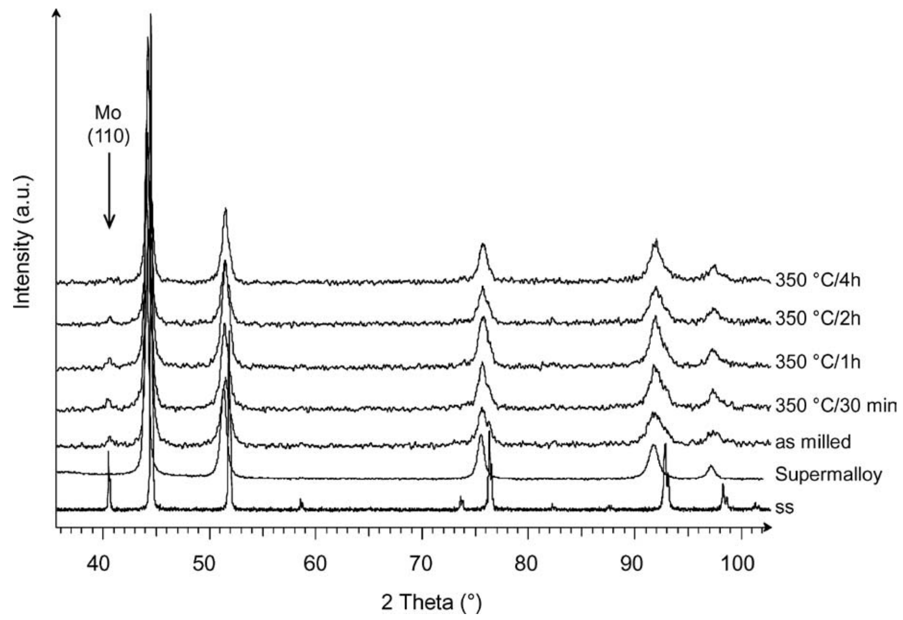
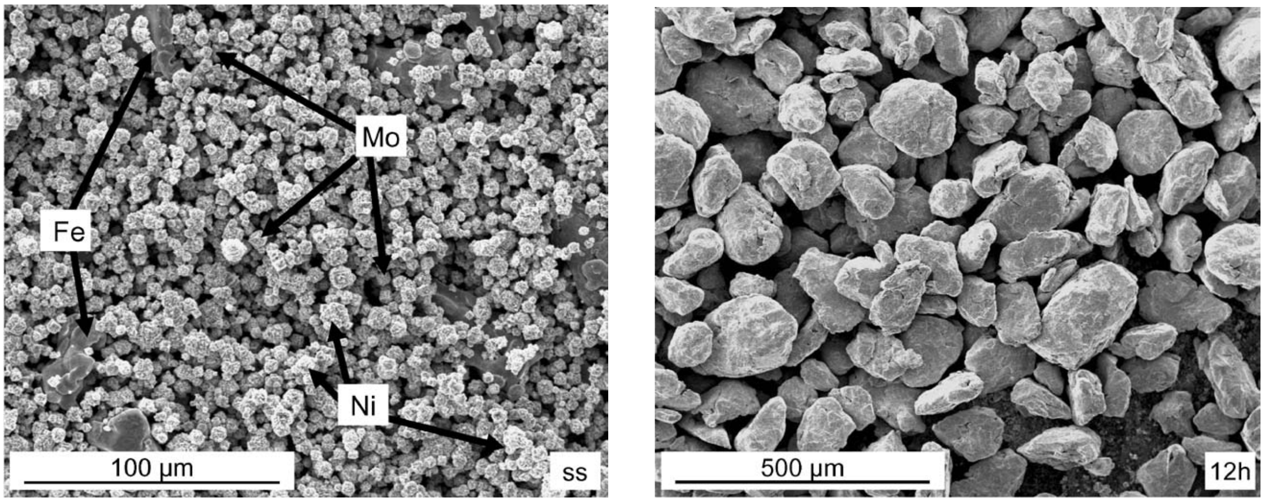


Figure 4 The influence of the annealing conditions on the solid-state reaction of Supermalloy formation on 8 h milled sample. The indicated annealing conditions are temperature/time. Supermalloy and ss refer to the as cast Supermalloy and the starting sample respectively. For clarity, the spectra have been shifted vertically.

removal of the second order internal stresses. Thus, by annealing for 1 h it is possible to induce solid-state reaction only for that proportion of the sample composed of very intimately mixed Ni and Mo particles, but that had not reacted during the milling. By removing the second order internal stresses upon 2 and 4 h annealing a sharpening of the diffraction peak is produced and the (110) Mo peak appears again. In the case of the 8 h milled sample, after 4 h of annealing the (110) Mo peak disappears and it can be concluded that synthesis of the Supermalloy is achieved, see Fig. 4.

The lattice parameters determined on the sample obtained after 8 h of milling followed by 4 h of annealing is 0.3551 nm, in a good agreement with the Supermalloy lattice parameters, $a = 0.3553$ nm. The calculated size of the crystallites shows that the structure of the Supermalloy powders obtained by mechanical alloying is nanocrystalline. Thus, the mean dimension of the nanocrystallites of the 16 h milled sample and annealed at 350°C for 2 h is 11 ± 2nm.

The particle morphology for the starting sample and for the 12 h milled sample are shown in Fig. 5. For the starting material it is clearly evidenced that there are Ni, Fe and Mo particles (they are marked on the picture on the basis of the X-ray microanalysis). For the 12 h milled sample, only one kind of particles,



(a) (b)

Figure 5 The SEM image of the starting mixture of Ni, Fe and Mo powders (ss) and of Supermalloy powders obtained after 12 h of mechanical milling (12 h).

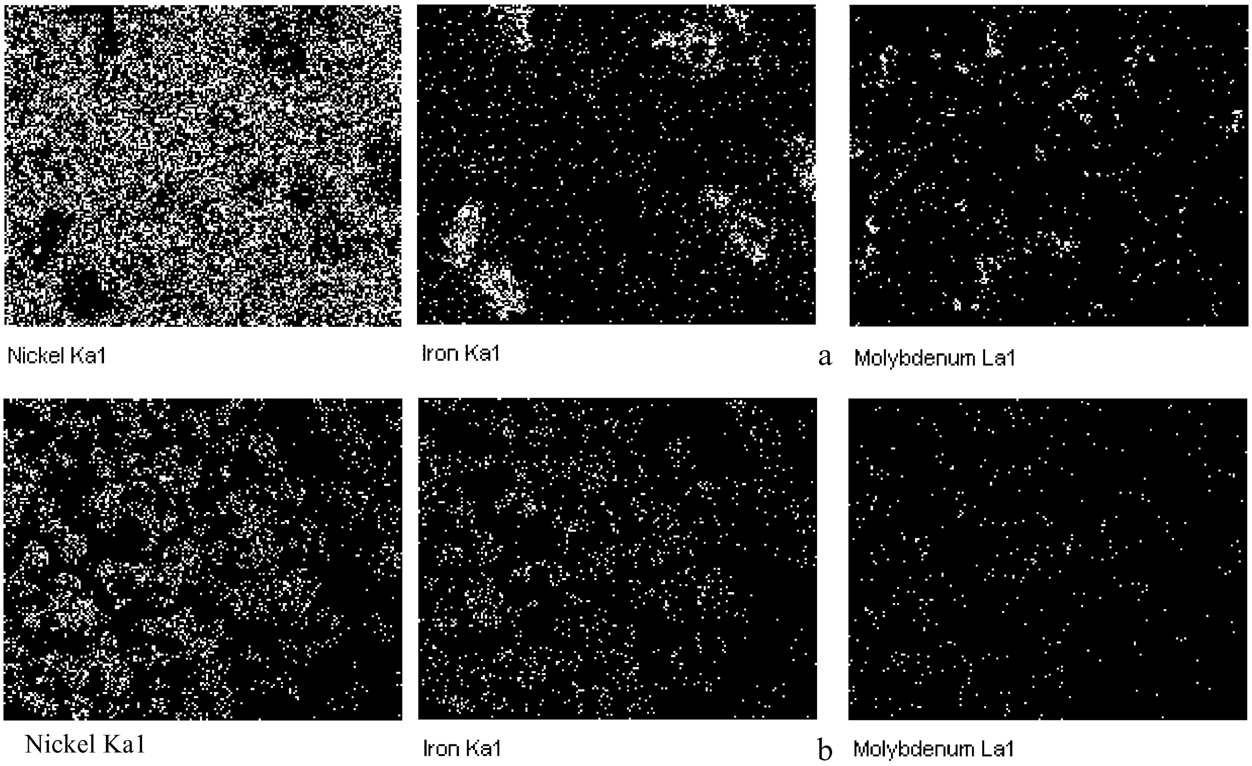


Figure 6 The maps of Ni, Fe and Mo distributions for starting samples (a) and for 12 h milled sample (b). The X-ray microanalysis performed on the selected areas presented in Fig. 5.

corresponding to the Supermalloy composition is present. The X-ray microanalysis, performed on the selected areas presented in Fig. 5, is shown in Fig. 6. It can be observed that the maps of Ni, Fe and Mo distributions are very different for the starting mixed powders (ss), see Fig. 6a, but are identical, in the error limits of this method, after 12 h of milling, see Fig. 6b. In addition to the X-ray diffraction studies, the X-ray microanalysis performed on the particles surface shows that all particles exhibit chemical homogeneity.

4. Conclusions

The evolution of the formation of the Supermalloy powders by mechanical alloying and subsequent heat treatment has been studied by using X-ray diffraction, SEM and X-ray microanalysis. The Supermalloy powders were obtained after 16 h of milling. A mean crystallite size of 11 ± 2 nanometers was obtained after 16 h of milling and 2 h of annealing at 350°C in order to remove the internal stresses. On the other hand, the Supermalloy formation has been found to be improved by annealing. Thus, the Supermalloy powders were obtained after 8 h milling and 4 h annealing at 350°C too. The SEM and X-ray microanalysis show that the chemical homogeneity and composition of the powder particles are in good agreement with the results of the X-ray diffraction studies.

The magnetic properties of these nanocrystalline Supermalloy powders are expected to be very good for applications as soft magnetic materials. A complete analysis of the magnetic and crystallographic properties of the nanocrystalline Supermalloy powders produced by mechanical alloying is in progress and will be published in a forthcoming article [16].

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