Heat-treatment influence on Ni–Fe–Cu–Mo nanocrystalline alloy obtained by mechanical alloying

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Abstract The 77Ni14Fe5Cu4Mo (wt%) powders have been obtained by dry mechanical alloying of elemental powders in a planetary mill under argon atmosphere for milling durations ranging from 2 to 28 h. The alloy formation is obtained after 12–16 h of milling, as shown by the X-ray diffraction and magnetic studies. The crystallite mean size is 13 ± 2 nm after 28 h of milling. An optimal heat-treatment temperature was chosen after the analysis of the DSC signals. and the samples were heated at 350 °C for different durations ranging from 0.5 to 4 h. The heat treatment was continued to enhance the alloy formation and to eliminate the internal stresses induced during the milling process. The evolution of the phases amount during the heat treatment was calculated from the X-ray patterns using the Rietveld procedure.

Introduction

The binary Ni–Fe alloys have very good magnetic properties, but they also have low electrical resistivity, an

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important parameter for high-frequency applications. One way to improve the electrical properties and to obtain higher machinability can be achieved by adding small amounts of copper and/or molybdenum to Ni–Fe alloys. By doing thus, one can obtain composition's range exhibiting high permeability which can be improved by annealing treatment. Such approach has led to the development of the quaternary 77Ni14Fe5Cu4Mo (wt%) alloy with face-centred cubic (fcc) structure. This ferromagnetic alloy has an important initial permeability (70,000 G/Oe) and a Curie temperature of 400 °C. Also, the presence of molybdenum especially, favours reduction of the eddy current losses [1–3].

For superior soft magnetic properties of the Ni–Fe alloys, it is important to have low coercivity and high permeability. According to the random anisotropy model at nanocrystalline state, it is possible to obtain these two requirements simultaneously for the same composition by a proper choice of nanoparticle's sizes distribution [4].

Among the techniques used to obtain nanocrystalline alloys is also included the mechanical alloying (MA). It seems to be the most promising technique for the obtainment of a large amount of nanocrystalline materials. It has also the advantage of obtaining materials in the powder form, more easily for the industrial application using the well-known process of powder metallurgy [5–9].

The MA technique imply the obtaining of alloys by solid-state reaction of elemental powders or simple compounds, reaction driven by the collision processes between the milling media (ball-to-ball and ball-to-vial) and particles [10]. Using the MA technique, a large number of alloys have been obtained, including the Ni–Fe alloy. The Ni–Fe alloys have been obtained in the whole composition range [11–20]. Our previous studies have considered the obtainment of the Ni₃Fe intermetallic compound [13–15]

and also Supermalloy [21–23] and Ni–Fe–Cu–Mo alloy [24] having nanocrystalline grain size.

The aim of this article is to study the thermal behaviour of the milled samples for a proper choice of the heat-treatment temperature and time to keep the powder's grain size at nanometric level, but stress free. Indeed, it has been reported that the thermal stability of the nanocrystalline materials depend on the particle size [25].

The thermal evolution of the Ni–Fe–Cu–Mo powder obtained by mechanical alloying is analysed by differential scanning calorimetry (DSC). Based on the DSC data, the annealing influence on the alloy formation was investigated by X-ray diffraction. Also after heat treatment, the evolution of the phase concentration in the Ni–Fe–Cu–Mo alloy is analysed for the short milling durations.

Experimental

The starting materials for sample preparation were commercial nickel powder (123–carbonyl type), iron powder (NC 100.24 type), molybdenum powder produced by chemical reduction, and copper powder. A mixture of elemental powders having the following composition 77Ni14Fe5Cu4Mo–wt% (77.98Ni14.88Fe4.76Cu2.38Mo–at%) has been homogenized for 15 min in a Turbula blender. Then, the mixture was milled, under argon atmosphere, in a planetary ball mill for durations ranging from 2 to 28 h.

The ball/powder mass ration was 8:1, and the filling factor of the vial was 60%. After each chosen milling time, the milling process was stopped and for the superior milling time, the process was started from the beginning with new initial mixture. The planetary ball mill used here is a homemade high-energy apparatus with $\Omega = 290$ rpm as main disc speed, and $\omega = 240$ rpm as vial speed.

A cast alloy sample has been prepared by arc melting of the starting mixture under purified argon atmosphere and was used as reference bulk sample.

X-ray diffraction (XRD) patterns were recorded in the 2θ range from 35 to 103° using a Siemens D 5000 diffractometer, operating with $CuK_{\alpha 1}$ radiation. The mean crystallite size was calculated using the Scherrer formula [26]. The resolution of the diffractometer has been determined from a well-crystallized reference Ni–Fe–Cu–Mo sample at higher temperature. The diffraction patterns were analysed with Fullprof software, and the phase concentrations were calculated using a Rietveld refinement program incorporated in the software [27].

The DSC curves were recorded using a NETZSCH–DSC 404S apparatus in the temperature range of 30–700 °C in argon atmosphere to avoid oxidation of the powders upon heating. The DSC curves were recorded at a heating rate of 10 °C/min.

Results and discussion

The Ni–Fe–Cu–Mo powders milled for different durations were analysed by DSC measurements. On the DSC curves, two exothermic peaks can be observed, as shown in Fig. 1, for a sample milled 24 h. The first broad DSC signal is recorded at 210 °C and is associated with the internal stresses removal in the milled samples. The appearance of this signal is expected considering the large amount of internal stresses induced during milling. On further heating of the sample, a second exothermic peak emerges with an onset at 485 °C. This second peak is attributed to the sample re-crystallization, as expected for the nanometric powders obtained by milling. The difference between these two temperatures (internal stress removal peak and re-crystallization peak) allows using a reasonably wide temperature range for performing different heat treatments to obtain stress-free samples and to enhance the alloy formation.

Although the powders are ferromagnetic, the Ni–Fe–Cu–Mo Curie temperature is difficult to determine in the DSC experiment, being overtaken by the large re-crystallization peak that starts to develop at the same temperature range.

A comparison of the DSC curves recorded for different milling duration with a cast and a starting sample (0-h milled, denoted "SS") is shown in Fig. 2.

For the as-cast sample, only a small change in the signal is recorded at the Ni–Fe–Cu–Mo alloy Curie temperature. Such endothermic signal is occurring around 400 °C, a value in reasonable agreement with earlier reported data
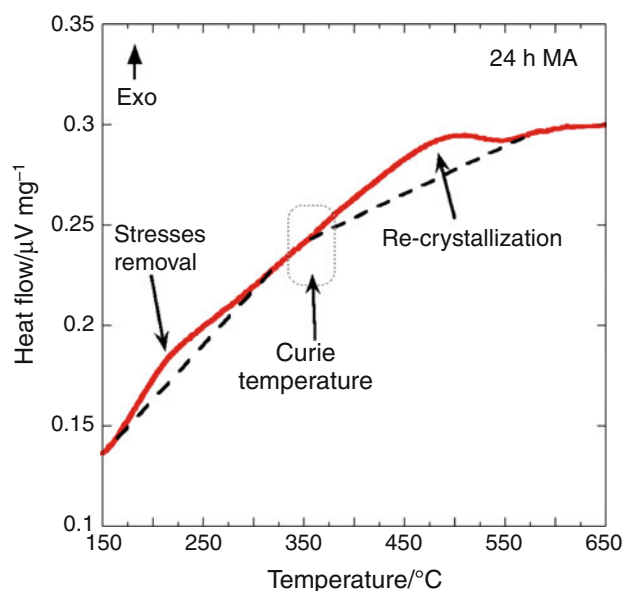

Fig. 1 DSC curves for a Ni–Fe–Cu–Mo nanocrystalline sample obtained by mechanical milling for 24 h
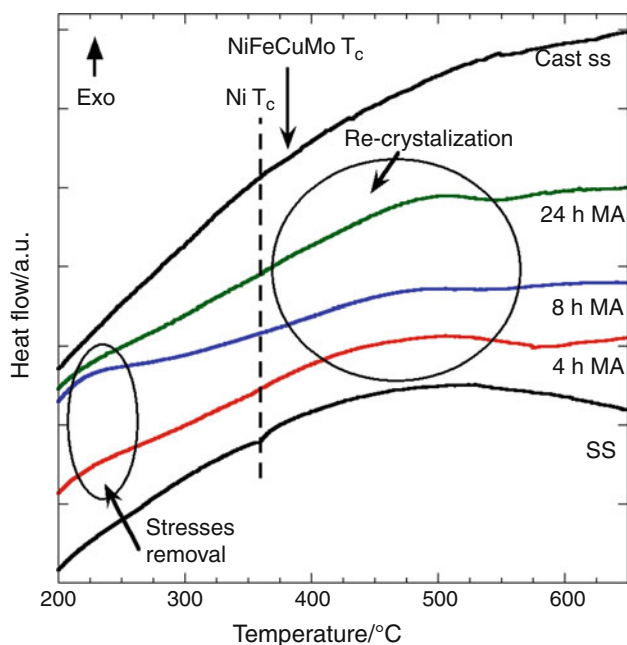
Fig. 2 Comparison of DSC curves recorded for Ni–Fe–Cu–Mo samples obtained for different milling durations with the one recorded for the starting sample SS (elemental powder mixture) and the as-cast sample

Fig. 3 Evolution of the diffraction maxima versus the heat treatment time for the Ni–Fe–Cu–Mo alloy samples milled for 2–4 h. For comparison, the diffraction patterns recorded for the starting sample (*ss*) and after DSC measurement of the as-milled sample (for 4 h) are also shown

obtained from thermomagnetic measurements [24]. A DSC measurement has also been performed for the starting sample (a mixture of the elemental powders). In this case, only the Curie temperature of the elemental Ni is observed at 350 °C.

None of the DSC curves, recorded for the samples milled for more than 4 h, presents the endothermic peak corresponding to the Curie temperature of elemental Ni. Such absence of elemental Ni in the DSC experiments is indicative of the alloying of the elements under successive effect of milling and heating processes. All the milled samples exhibit an exothermic signal at low temperature and another exothermic peak at high temperature assigned, respectively, to the internal stress removal and re-crystallization. The onset of the re-crystallization peak is recorded at almost the same temperature for all the samples. For shorter milling durations (<12 h), the peaks are larger due to the incomplete formation of the alloy by mechanical alloying. Consequently, the effect of the heat treatment during the DSC measurement to promote the alloy formation is larger.

Based on the above discussed DSC results, a temperature of 350 °C was chosen for the heat treatment, and the duration of the treatment ranged from 0.5 to 4 h. The above temperature was chosen to continue the heat treatment further for short milling durations in order to enhance the alloy formation and to obtain a stress-free sample. In Fig. 3, the changes induced by the heat treatment are exemplified for samples milled for 2–4 h, respectively.
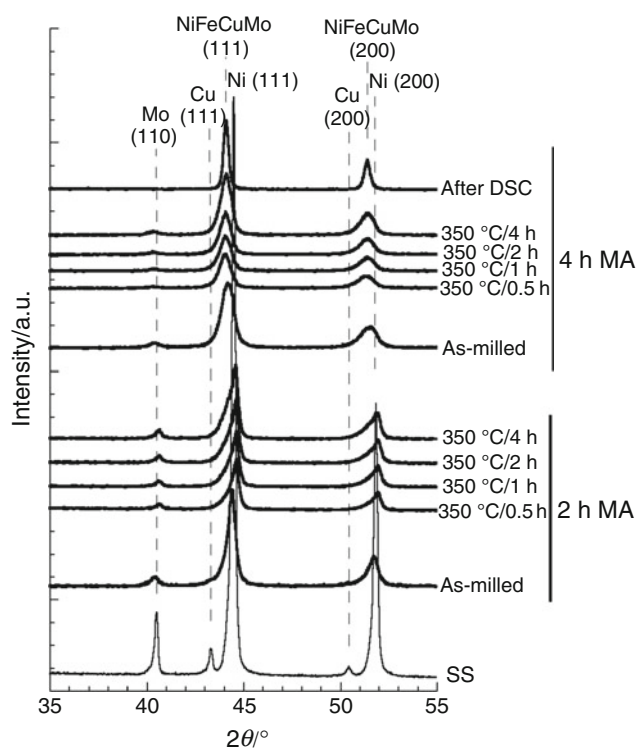
After 2 h of milling, the as-milled sample exhibits a diminution in the Mo (110) and Cu (111) peak intensity and the appearance of a large asymmetry on the Ni peaks. The elemental peak intensity reduction and the asymmetry apparition suggest the start of a reaction process between the elements upon milling. A short heat treatment, for only 30 min leads to an even more pronounced asymmetry on the Ni peaks, asymmetry that clearly indicates the presence of a second peak. This second peak represents the emergence of a new phase, the fcc Ni–Fe–Cu–Mo alloy that was partly formed after the milling and is enhanced by the heat treatment. The peaks of the Ni–Fe–Cu–Mo alloy are located at smaller Bragg angles than those corresponding to the elemental Ni. The continuation of the heat treatment does not change much the position of the peaks, but the intensity of the Ni–Fe–Cu–Mo phase increases for longer annealing durations. This increase of the Ni–Fe–Cu–Mo phase concentration is possible, if after the milling, a large number of regions of Ni–Fe–Cu–Mo exist, which are well mixed but unreacted. In these regions, the temperature drives an alloying reaction during the heating of the sample.

For the 4-h milling duration, Fig. 3, the effect of the temperature is more clearly visible. For the as-milled

sample, the ratio of (111) peak intensity of Ni to Ni–Fe–Cu–Mo indicates that nickel is the main phase. After heating at 350 °C for 2 or 4 h, the relative intensity ratio changes in the favour of the (111) peak characteristic for Ni–Fe–Cu–Mo structure, indicating a progress in alloy formation by subsequent annealing of the as-milled powders. This change evidences that after 2–4 h of heat treatment at 350 °C, the Ni–Fe–Cu–Mo phase is the dominant phase in the samples milled for 4 h. For longer milling durations of 6–8 h, the peaks of the fcc Ni–Fe–Cu–Mo phase become the most intense in the diffraction patterns. The peaks of Cu, Fe and Mo disappear progressively after 4 and 6 h of milling and subsequent annealing, as seen from Fig. 4.

The increase of the new phase quantity is illustrated in Fig. 5, where the relative quantities of Ni–Fe–Cu–Mo phase versus the annealing time are plotted. In order to obtain the data plotted in Fig. 5, a deconvolution of the peaks for Ni and Ni–Fe–Cu–Mo phases was performed.

In Fig. 5, it is seen that for low milling durations (2–6 h), the temperature has a major influence, leading to an increase of the concentration of Ni–Fe–Cu–Mo phase by increasing the overall homogeneity degree of the powder composition, as expected from the peak intensity evolution. As the milling time increases, the effect of low temperature annealing is reduced and at 8 h, the effect on phase modification is negligible.

Annealing up to 4 h leads to further Ni–Fe–Cu–Mo alloy formation of about 20–25 wt% of well-mixed
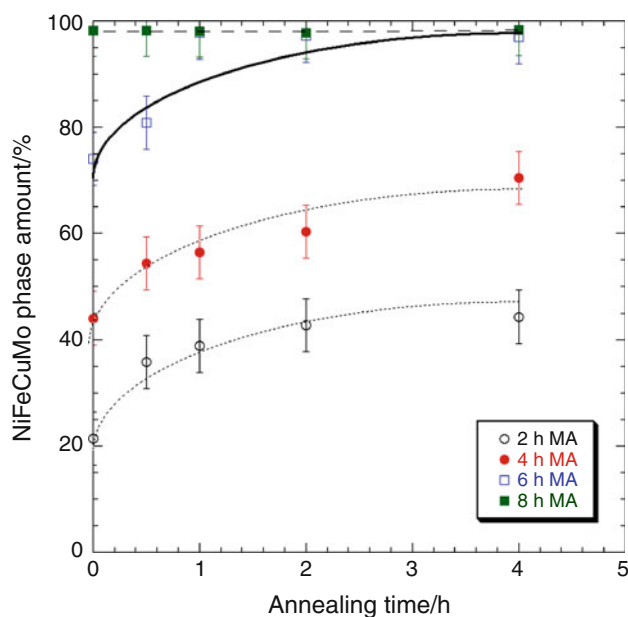
Fig. 5 Ni–Fe–Cu–Mo phase evolution with the annealing time at 350 °C: as derived from X-ray diffraction

elemental blend, but not of alloyed powder. A clear tendency to saturation is observed for 4 h.

As the milling time increases to 8 h, in the diffraction pattern, only the peaks of the fcc Ni–Fe–Cu–Mo phase and a very low intensity (110) Mo peak are recorded. For this milling duration, the heat treatment leads to complete disappearance of (110) Mo peak after 2 h of annealing at 350 °C. The elemental Mo is more difficult to be alloyed with Ni–Fe mixture and consequently longer milling durations are necessary to achieve a full chemical homogeneity of the powders. It is worth to observe that for 6 h milling duration, a subsequent annealing at 350 °C for 4 h increases the amount of 77Ni14Fe5Cu4Mo alloy up to almost 100%. A little iron contamination can occur in the milled powders, but for the milling durations shorter than 8 h, where the alloy starts to form, this contamination can be neglected.

In order to obtain the fcc 77Ni14Fe5Cu4Mo single phase in the milled powders without subsequent annealing, a milling time of 12–16 h is needed [24].

It is seen from Figs. 3 and 4 that the Bragg peaks are broadened, suggesting that the powders have a mean crystalline size in the nanometric range. Using a deconvolution of the peaks for both Ni and Ni–Fe–Cu–Mo phases, it was possible to estimate the mean crystallite size for the samples.

After an annealing at low temperature, the crystallite size of the powders remains low and at nanometric scale (8–17 nm), the temperature chosen for the heat treatment is just above the stress release temperature as recorded by DSC measurements. However, after the DSC measurement, the crystallite size increases dramatically (up to
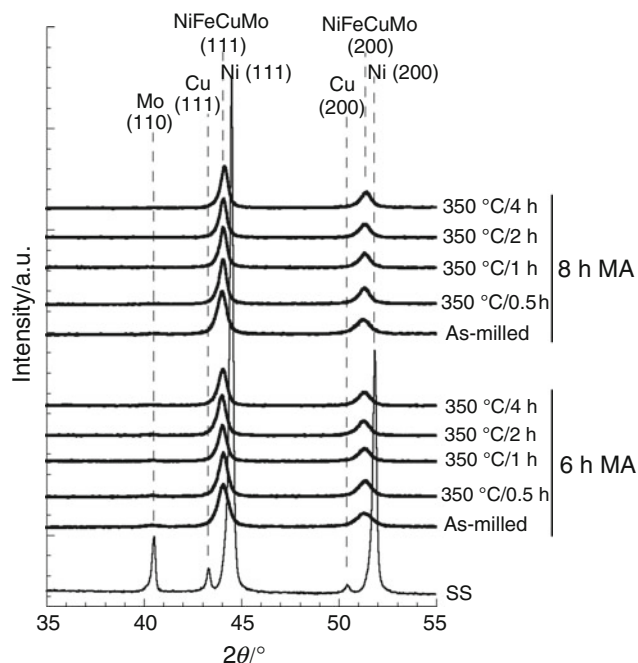

Fig. 4 Evolution of the diffraction maxima versus the heat treatment time for the Ni–Fe–Cu–Mo alloy samples milled for 6 h and 8 h. For comparison, the diffraction patterns recorded for the starting sample (ss) is also shown

64 nm) since the re-crystallization temperature was reached. For the short milling time, increase of the mean crystallite size is hindered by the relatively small amount of Ni–Fe–Cu–Mo phase. The effect of grain size increase after the DSC measurement can be deduced in Fig. 4 from the sharpening of the diffraction peak for the samples subjected to DSC investigation.

The evolution of the mean crystallite size versus the annealing time for different milling durations has shown that at the chosen annealing temperature the mean crystallite size remains constant within the error bars of the Scherrer method.

Conclusions

In the case of the milled samples, the DSC curves present an exothermic signal around 250 °C, representing the removal of internal stresses induced by milling. A second exothermic signal recorded around 480 °C was attributed to the re-crystallization of the nanometric powders. According to the DSC data, a temperature of 350 °C was chosen for optimum heating treatment. For short milling duration, the heat treatment enhances the alloy formation. The amount of fcc Ni–Fe–Cu–Mo phase increases with the increasing annealing duration, as derived from Rietveld analysis of the X-ray diffraction data. After the heat treatment performed at temperature of 350 °C, lower than the re-crystallization temperature, the crystallite size of the powders remains in nanoscale range.

We conclude that the heat treatment is mainly efficient during the first 30 min and has a more pronounced influence for short milling durations (2–6 h). For the 6-h-milled samples, an annealing done at at 350 °C for 4 h increases up to almost 100% the 77Ni14Fe5Cu4Mo phase. Also, the fcc 77Ni14Fe5Cu4Mo phase is completely obtained after 12–16 h of milling without annealing.

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