Magnetic and thermomagnetic studies of the formation of the Rhometal powders by high energy mechanical milling

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Abstract. Nanocrystalline Rhometal (36Ni64Fe, wt. %) powders have been obtained by mechanical alloying under argon atmosphere. The initial mixture was milled up to 20 h. In order to eliminate internal stresses and to improve the solid state reaction annealing at 350 °C was performed for 4h. The alloy formation is obtained after 8 h of milling. A mean crystallite size of 10 ± 4 nm is obtained after 20 hours of milling. The magnetization values for the asmilled samples are between that of the starting sample and that of the as cast one. The evolution of the magnetization versus the milling time is discussed. The thermomagnetic analysis shows the Curie temperatures confirming the alloy formation by milling. As a result of the solid state reaction by milling means, a continuous decrease of the magnetization with increasing the temperature is recorded, similarly to the behaviour of the classical cast alloy.

1. Introduction

The nanocrystalline materials may exhibit superior properties compared with materials having polycrystalline structure. From the properties that could be amplified by the presence of the interfaces and by the large surface/volume ratio can be noted: superior hardness, amplified diffusion, superior ductility, reduced elastic module, higher electrical resistivity, higher specific heat, higher thermal dilatation coefficient, smaller thermal conductivity and higher soft magnetic properties [1].

In principle, the obtaining of the nanocrystalline materials can be performed using several techniques [1, 2, 4]. For the production of nanocrystalline/nanostructured materials in larges quantities only two techniques seem to be appropriates: the mechanical alloying and the re-crystallization of the amorphous ribbons.

Mechanical alloying (MA) is a technique for alloy obtaining in powder form, consisting from plastic deformation, mixing and plastic deformation repeatedly of the elemental or prealloyed powder [1, 2]. Many studies have been carried out in order to understand the process [4]. The final product of the MA technique depends on the energy involved. It was shown that for particular milling conditions a final product in nanocrystalline or amorphous state can be obtained. In order to predict the state of final milled product simulations have been made [5 - 7]. Also the effect of milled on the phase transition have been studied [8].
Soft magnetic materials from the Ni-Fe system were obtained by mechanical alloying in the whole composition range [9 - 16]. Our researches are focused on the obtaining of the commercial Ni-Fe soft magnetic alloys by mechanical alloying. In our previous studies we successfully obtained the Permalloy alloy (75Ni25Fe, wt. %) [13-16]. In this study, we focus our attention on an interesting alloy called Rhometal (36Ni64Fe, wt. %) which is known to present the highest resistivity among Ni-Fe alloys. In opposition with Permalloy, the Rhometal alloy is a biphasic alloy and this offers an interesting perspective on the structural and magnetic properties of the alloy obtained by mechanical alloying. In this study we discuss the alloy formation by mechanical alloying and some magnetic properties of the milled samples versus milling time.

2. Experimental
The Rhometal (36Ni64Fe, wt. %) alloy was obtained in a planetary ball mill Pulverisette 4 Fritch starting from a mixture of elemental iron and nickel powder weighed in the proper ratio. The powders used were commercial iron powder NC 100.24 and nickel powder 123 – carbonyl type. The mixture was first homogenized for 15 min in a Turbula type apparatus, and then milled in the planetary mill for time ranging from 1 to 20 hours. The starting powders mixture, unmilled, is called in papers “ss”. Argon gas was used as milling atmosphere. The powder/ball mass ratio was 8:1 at a filling factor of 40%. Several samples were sealed in silica tubes and annealed for 4h at 350 °C in order to improve the solid state reaction and to remove the internal stresses.

The alloy formation was investigated by X-ray diffraction in the angular range 2θ = 32 – 103 °. The X-ray patterns were recorded with a Bruker D8 powder diffractometer, operating with Cu – Kα radiation (λ = 1.54183 Å). The mean crystallite size was calculated using the Williamson & Hall method [17]. In order to confirm the alloy formation a mixture of iron and nickel powders having the same nominal composition was melted and used as reference (called in paper “cast ss” or “cast sample”) for the obtained phase by milling.

The magnetization curves were recorded at room temperature by extraction method technique in a continuous field of up to 8 T. The thermomagnetic analysis was performed by means of a LakeShore 7410 vibrating sample magnetometer in a field of 1 T.

3. Results and discussion
Rhometal alloy formation was studied by X-ray diffraction. Figure 1 presents the recorded patterns for the as-milled samples and for the starting sample mixture (“ss” refers to 0 h of milling) and for a cast alloy obtained from the starting mixture.

![Figure 1. X-ray diffraction patterns for the as-milled samples. For clarity the patterns are vertically shifted and for comparison the starting sample (ss) and the cast sample are also showed.](image-url)
The alloy formation is observed by disappearance of the Bragg peaks of Ni and Fe elements clearly observed in the 0 h milled sample and the shift of the remaining peaks toward the alloy position as compared with the cast sample. A close analysis of the diffraction patterns (figure 2) reveals the existence of an asymmetry of the Bragg peaks on the high angle side until 10 h of milling.

Figure 2. Detail of the diffraction patterns representing the (111) peak for the as-milled samples

The alloy formation by milling is accompanied by internal stress introduction by the milling process. First order internal stresses induced by milling leads to peak shifts toward lower angles. This evolution suggests the formation mechanism of the alloy: by high energy milling, stresses are induced at lattice level in the materials leading to enhanced atoms diffusion and favouring solid state reaction to form the alloy.

Figure 3. Annealing effect on the milled Rhometal samples exemplified for the (111) Bragg peak.

In order to eliminate the internal stresses induced by the milling process and to enhance the alloy formation, an annealing was performed at low temperature (for preventing the powders recrystallization) at 350 °C for 4 h. The effect of annealing is to release the internal stresses and to improve the solid state reaction. The improvement of the solid state reaction rate can be observed in
figure 3 by the peak asymmetry disappearance for samples milled more than 8h. After the X-ray studies can be concluded that for high milling times only one FCC phase is obtained and the Rhometal alloy is formed after 8h of milling followed by annealing at 350 °C for 4h.

A close analysis of the cast sample diffraction patterns reveals the existence of two phases: a fcc (Ni-Fe) phase and γ (Fe-Ni) phase. The existence of both phases is found also in practical Ni-Fe phase diagram [18]. Figure 2 presents the observed mixture of phases. For the 2h milled sample a very broad peak can be seen at a position corresponding to γ (Fe-Ni) phase. This peak cannot be seen for longer milling times, except for the 20h milled sample.

The mean crystallite size was calculated from the X-ray diffraction patterns using the Williamson – Hall plots. The obtained values are presented in figure 4.

Figure 4. Mean crystallite size versus the milling time for the Rhometal alloy.

The evolution of the mean crystallite size versus the milling time, illustrates a strong decrease for long milling times. After the phase obtaining in the whole sample volume, 8 h of milling, the mean crystallite size decrease toward a value of 10 ± 4 nm for 20h milled samples. The crystallite size reduction is seen by the broadening of the Bragg peaks for the milled sample. It is worth to note, that the broadening of the peaks is not entirely due to the crystallite size refinement but also to the introduction of the second order internal stress. Due to the Williamson Hall method procedure, the effects of stresses are eliminated from the crystallite size calculation.

Figure 5. Room temperature magnetization curves recorded for the as-milled samples. For comparison the cast and starting sample are also presented.

Figure 6. Spontaneous magnetization versus milling time. For comparison the magnetizations of the starting sample and of the cast sample are presented.
The obtained powders were magnetically characterized in fields up to 8 T. The measured curves are plotted in figures 5. The spontaneous magnetisation values have been derived from an extrapolation to zero field of the magnetisation obtained in magnetic fields between 4 and 8 T. The spontaneous magnetization versus milling time is shown in figure 6.

From figure 5 and 6, it can be concluded that the magnetization of the milled samples is ranging between the magnetization of the starting mixture (the "ss" sample) and that of the alloy obtained by melting (the as cast sample). For low milling times, interesting magnetic behaviour is observed. Due to the $\gamma$ (Fe-Ni) phase presence in the samples, after 2 h of milling, the magnetization decreases drastically to the value of the cast sample. Saturation magnetization increases versus milling time (for milling times longer than 2h) and is higher than the magnetization of the cast alloy, due to the elimination of the $\gamma$ (Fe-Ni) phase, which is antiferromagnetic, and to formation of the face centred cubic Rhometal alloy. The effect of the annealing is more pronounced for the short milling times (2h, where the phase $\gamma$ (Fe-Ni) is present and has limited effect at long milling times. Investigations of the structure effect on the magnetic behaviour of the milled powder are now in progress.

The thermomagnetic measurements are used to characterize the formation and magnetic behaviour of the Rhometal powders. The recorded curves are presented in figures 7 and 8.

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Figure 7. Thermomagnetic curves of the as-milled samples. For comparison the curves of the starting sample is also presented.

Figure 8. Comparison between the thermomagnetic curves of as-milled and annealed samples milled for 20h.

The thermal evolution of the magnetization for the starting sample presents two transitions corresponding to the elemental Ni and Fe. The beginning of milling (2h of milling), induces the alloy formation, thus leading to reduction of the first fall of magnetisation corresponding to the Curie temperature of the elemental Ni phase, followed by a change of slope (point A in figure 7). The slope change corresponds to the obtained Rhometal (36Ni64Fe). At higher temperature a large transition is observed, corresponding to the progressive formation of the alloy during heating (point B). The large transition expresses the existence of a large field of compositions. For higher milling times, a single Curie temperature is recorded (at 420 °C), the Curie temperature of Rhometal single phase. Similar thermomagnetic behaviour was found for the Ni-Fe-Mo alloys [19]. A supplementary analysis of the annealed samples was performed and the obtained curves for the as-milled and annealed samples are presented in figure 8. It is seen that in the curves are barely identical for the samples behaviour with or without annealing, suggesting that for this milling duration the Rhometal alloy is formed in the whole sample volume.

4. Summary
The Rhometal (36Ni64Fe, wt. %) powders were obtained by mechanical alloying and annealing. The X-ray and magnetic measurements indicate the complete alloy formation after 8 – 10 h of milling in
the whole sample volume. The obtained powders are nanocrystalline, with a mean crystallite size of 10 ± 4 nm after 20 h of milling.

The spontaneous magnetization of the milled samples is between the magnetization of the Ni-Fe starting sample and Rhometal alloy obtained by melting. After 2 h of milling, the spontaneous magnetization decreases toward a value close to the magnetization of the as cast sample, due to the presence of the γ (Fe-Ni) in the structure. Magnetization increases for further milling times higher than 2 h, as a result of the face centred cubic Rhometal structure formation by milling. The thermomagnetic measurements show the continuous formation of the alloy by heating for low milling times. The Curie temperature of the alloy obtained by mechanical alloying is 420 °C.

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