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Mechanical alloying of Ni_3Fe in the presence of Ni_3Fe nanocrystalline germs

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Abstract

The influence of nanocrystalline germs on the production of the Ni_3Fe intermetallic compound by mechanical alloying is reported. These germs consist in Ni_3Fe nanocrystalline particles previously obtained by mechanical alloying which have been added to the Ni–Fe mixture: $0.8(3Ni + Fe) + 0.2Ni_3Fe = Ni_3Fe$. The powder mixture was milled in a planetary mill in argon atmosphere. Several milling times have been used ranging from 2 to 8 h. A Ni–Fe mixture at nominal composition of Ni_3Fe compound was milled in the same conditions, as blind samples. A heat treatment at 350 °C for 0.5, 1, 2 and 4 h has been performed in order to remove the internal stresses induced by milling and to improve the solid-state reaction. The formation of the Ni_3Fe phase was checked by X-ray diffraction and magnetic measurements. The germs inoculation improves the synthesis of the Ni_3Fe phase by combined mechanical alloying and annealing technique. This influence is more effective for short milling times (typically lower than 4 h). For samples milled more than 4 h the influence of the germs inoculation is more reduced, due to the Ni_3Fe germs self-formation by milling.

Keywords: Intermetallics; Mechanical alloying; X-ray diffraction; Magnetic measurements

1. Introduction

A huge development has occurred in the research of nanocrystalline materials in the last years. Besides the incipient crystallisation of amorphous solids [1], mechanical alloying is a well-established technique to obtain nanocrystalline structures. Mechanical alloying is basically a dry high-energy milling process, in which elemental blends (or prealloyed powders, oxides, nitrides, etc.) are milled to achieve alloys or composite materials [2–4]. This technique allows to produce nonequilibrium structures/microstructures including amorphous alloys, extended solid solutions, metastable crystalline phases, nanocrystalline materials and quasi crystals [4–10]. Mechanical alloying involves a lot of parameters and process variables that influence the kinetic and mechanism of alloying process and the quality of the alloying products [11–14]. An analysis of the parameters that influence the powder contamination during mechanical alloying/milling was performed by an exhaustive selection of the factors that influence contamination, followed by their classification [15]. Also an exhaustive analysis of the parameters that influence the mechanical alloying/milling processes is made and will be published [16].

The milling time necessary to obtain intermetallic compound depends on both mill type and milling conditions. This is due to the fact that the solid-state reaction of intermetallic compound synthesis by mechanical alloying is a reaction that needs an initiation time, which is a relatively long one. In this paper, our research is focused on the mechanical alloying process in the presence of the inoculated nanocrystalline germs of the same reaction product. Our study is devoted to the Ni_3Fe intermetallic compound synthesis by mechanical alloying.

2. Theoretical base of the method

The solid-state reaction of A_mB_n intermetallic compound or α-solid solution synthesis by mechanical alloying is a metallurgical process, which is developed in heterogeneous phase (at interface). The kinetic of the A_mB_n intermetallic compound synthesis consist in the following stages: (i) initiation stage, (ii)

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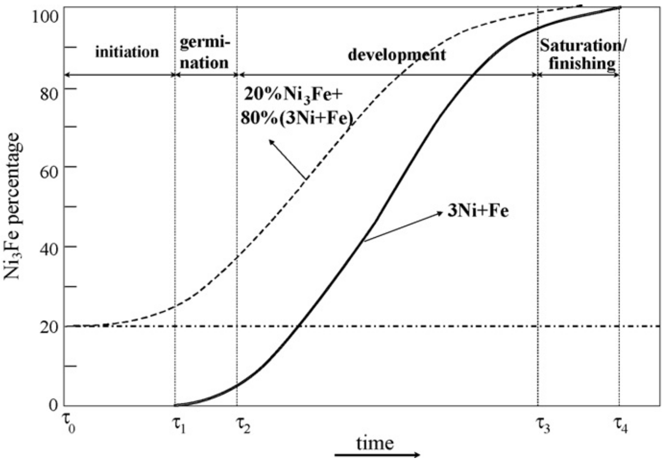

Fig. 1. The influence of milling time on the Ni$_3$Fe fraction synthesized from Ni–Fe mixture and from 80% (3Ni + Fe) + 20% Ni$_3$Fe germs mixture (dashed curve).

germination of the A_mB_n new phase, (iii) stage of accelerating (development), due to the increase of the inter-phase surface and (iv) stage of saturation (finishing), due to the decrease of the inter-phase surface and to the exhaustion of the reactants. The mechanism of the A_mB_n intermetallic compound synthesis involves the following stages: (i) reciprocal diffusion of the component A and B, (ii) adsorption process at interface and (iii) crystallo-chemical reaction.

The use of exogenous germs of the same product added in the mechanical alloying process is justified by experimental data which prove that the necessary milling time for first endogen germs formation is relatively large one (few hours).

Basically, the idea of the method consists in changing the solid-state reaction of A_mB_n intermetallic compound synthesis from the classical form:

$$mA + nB = A_m B_n \tag{1}$$

to the form:

$$(1 - x)(mA + nB) + xA_m B_n = A_m B_n \tag{2}$$

By this method, we suppose that it is possible to reduce the milling time necessary for obtaining A_mB_n intermetallic compound in the whole volume of the powders mixture subjected to the mechanical alloying.

The kinetic of the processes described by the (1) and (2) relations is shown in Fig. 1. The milling times τ_1, τ_2, τ_3 and τ_4 are the times that mark the stages of the solid-state reaction for intermetallic compound synthesis in the case of relation (1). By adding the germs of the same product, process described by relation (2), it is possible to reduce the milling time τ_1 and consequently the time τ_4.

3. Experimental

In order to study the mechanical alloying process in the presence of the germs of the same reaction product the intermetallic compound Ni$_3$Fe has been chosen. The used Ni$_3$Fe germs were Ni$_3$Fe powder obtained after 21 h of mechanical milling, as it is reported in our previously papers [17–19]. The particle size of the Ni$_3$Fe germs was below 80 μm and their crystallite size was 20 ± 2 nm. As Ni and Fe elemental powders, NC 100.24 iron powder and 123-carbonyl nickel powder were used. For milling experiments a charge of 80% (3Ni + Fe) + 20% Ni$_3$Fe germs was used. This powders mixture was homogenised for 15 min in a Turbula type blender, and then mechanically milled in argon atmosphere in a high-energy planetary mill. A Ni–Fe mixture at nominal composition of Ni$_3$Fe compound was milled in the same conditions, as blind samples. Several milling times have been used ranging from 2 to 8 h.

A heat treatment at 350 °C for 0.5, 1, 2 and 4 h have been performed in order to remove the internal stresses induced by milling and also to improve the solid-state reaction [19].

X-ray diffraction patterns were recorded in the angular range $2\theta = 30–100°$. For these experiments a Siemens D5000 powder diffractometer with the Kα_1 radiation of copper ($\lambda = 1.5406$ Å), was used. Scanning electron microscopy (SEM) and X-ray microanalysis studies were performed on a JEOL-JSM 5600 LV microscope equipped with an EDX spectrometer (Oxford Instruments, INCA 200 soft).

The magnetisation curves were recorded at 4 K and room temperature by the extraction method [20] in a continuous field of up to 8 T. The saturation magnetisation values have been derived from an extrapolation to zero field of the magnetisation obtained in fields higher than 4 T.

4. Results and discussions

X-ray diffraction studies were performed on as-milled powder samples and also on annealed samples at 350 °C for 0.5, 1, 2 and 4 h. In Fig. 2, the (1 1 1) Bragg peak of the samples with Ni$_3$Fe germs obtained after 2 h of milling in as-milled state and subsequently annealed at 350 °C for 0.5, 1, 2 and 4 h is compared with those of the blind samples (only Ni–Fe mixtures, without inoculated germs). For a better understanding the (1 1 1) peaks of the starting samples (0 h of milling) with and without germs in as-milled state and in annealing state are shown too in Fig. 2. The (1 1 1) peaks of the Ni$_3$Fe germs in as-milled state (21 h of milling) and of the Ni$_3$Fe obtained after 39 h of milling and

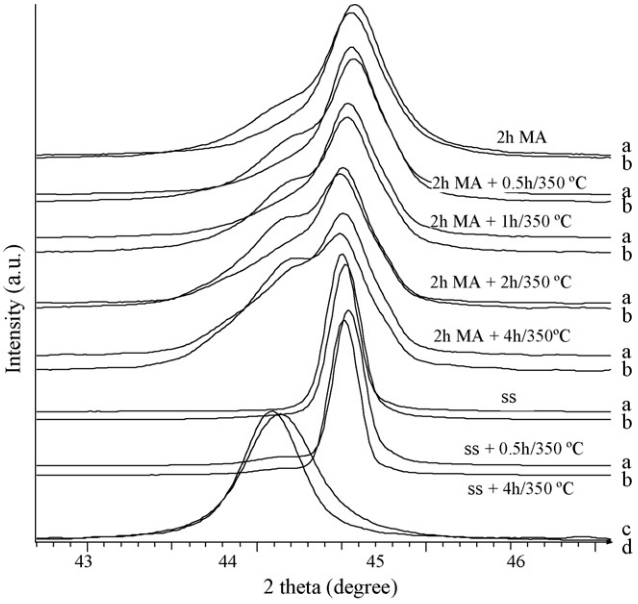

Fig. 2. The Ni$_3$Fe (1 1 1) Bragg peak evolution of the 2 h as-milled samples with and without inoculated Ni$_3$Fe germs and of the samples milled for 2 h and subsequently annealed at 350 °C for 0.5, 1, 2 and 4 h; ss: the starting sample (0 h milled); a, Ni–Fe (3:1) mixture; b, Ni–Fe (3:1) + 20% Ni$_3$Fe mixture; c, Ni$_3$Fe after 21 h mechanical alloying; d, Ni$_3$Fe after 39 h mechanical alloying and annealing at 350 °C for 4 h. For clarity, the spectra have been shifted vertically.

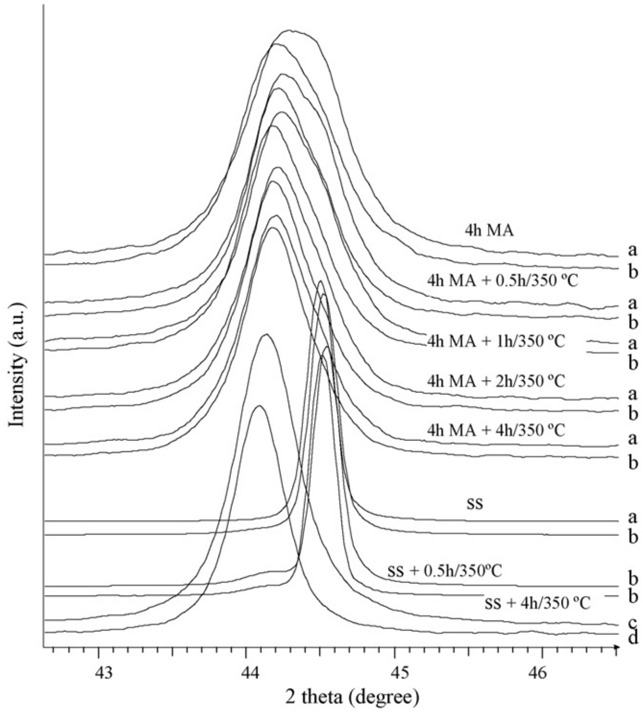

Fig. 3. The Ni_3Fe (1 1 1) Bragg peak evolution of the 4 h as-milled samples with and without inoculated Ni_3Fe germs and of the samples 4 h milled and subsequently annealed at 350 °C for 0.5, 1, 2 and 4 h; ss: the starting sample (0 h milled); a, Ni–Fe (3:1) mixture; b, Ni–Fe (3:1) + 20% Ni_3Fe mixture; c, Ni_3Fe after 21 h mechanical alloying; d, Ni_3Fe after 39 h mechanical alloying and annealing at 350 °C for 4 h. For clarity, the spectra have been shifted vertically.

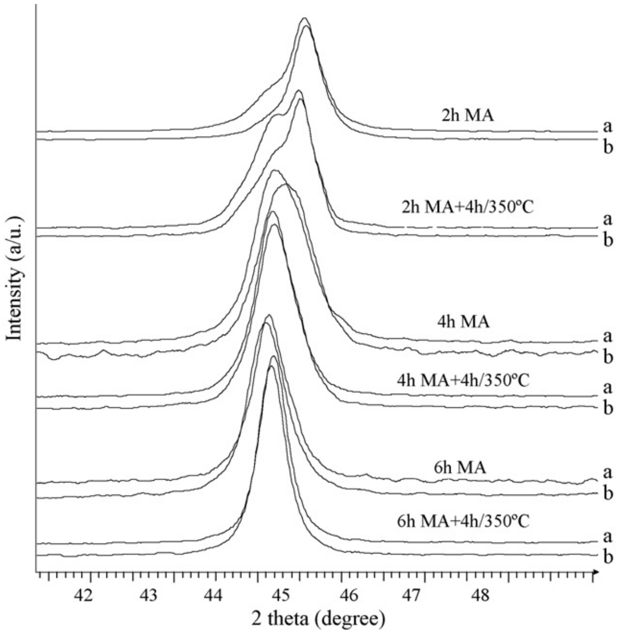

Fig. 4. The Ni_3Fe (1 1 1) Bragg peak evolution of the 2, 4 and 6 h as-milled samples with and without inoculated Ni_3Fe germs and of the same samples milled and subsequently annealed at 350 °C for 4 h; a, Ni–Fe (3:1) mixture; b, Ni–Fe (3:1) + 20% Ni_3Fe mixture. For clarity, the spectra have been shifted vertically.

annealed 4 h at 350 °C is given for comparison. It can be seen from Fig. 2 that the Ni_3Fe (1 1 1) peak in as-milled state is more pronounced for the samples with germs as compared with the mixture Ni–Fe, without inoculated germs. Taking in account that in the starting sample with germs, the (1 1 1) Ni_3Fe peak is very weak even after 4 h at 350 °C, it can be concluded that the Ni_3Fe germs presence significantly enhances the solid-state reaction of Ni_3Fe phase formation. The progressive formation of the Ni_3Fe phase by annealing for 2 h-milled sample can be well observed too in Fig. 2. Thus, the Ni_3Fe (1 1 1) peak increases with increase of the annealing time and this effect is more pronounced in presence of the Ni_3Fe germs.

The (1 1 1) peaks of the same combination of the X-ray diffraction patterns for 4 h of milling are shown in Fig. 3. It can be seen that the influence of the germs inoculation is more reduced as compared with the samples obtained after 2 h of milling. This behaviour can be explained by the fact that for samples milled 4 h and more the quantity of Ni_3Fe germs, self-formed by milling, become significant. This effect is even better shown in Fig. 4, where it can see that after 6 h of milling the effect of germs inoculation is strongly reduced.

In addition to the X-ray studies, magnetic measurements can give additional information about the effect of Ni_3Fe germs on the solid-state reaction of Ni_3Fe formation by mechanical alloying. The spontaneous magnetisation, M_s, at 300 K, computed from magnetisation isotherms, are presented versus milling time for different annealing conditions for the samples with and without germs in Fig. 5. Magnetic data do not present a saturation tendency up to 5 h of milling, but the magnetisation values for 5 h of milling, in the presence of germs, are comparable with those obtained after 10 h of milling in the case of the synthesis without germs.

The particles morphology and chemical homogeneity studied by SEM and EDX show that for 6–8 h milled samples only one kind of particles, with polyhedral shape, corresponding to the alloy composition are present.

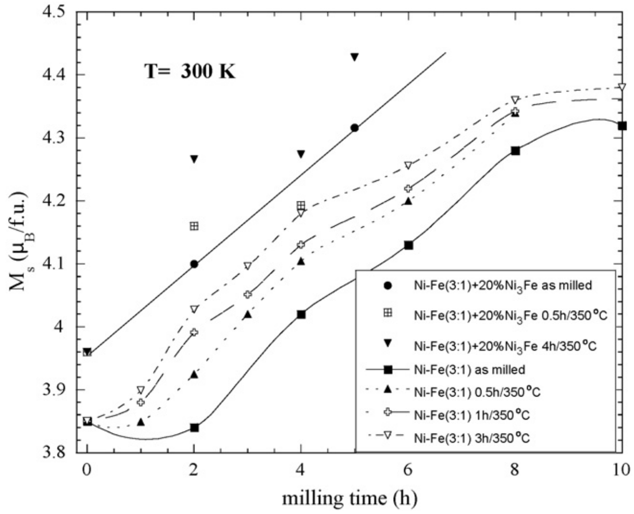

Fig. 5. Evolution of the spontaneous magnetisation at 300 K vs. milling time for different annealing conditions for the samples with and without inoculated Ni_3Fe germs. The lines are a guide for the eyes.

5. Conclusions

The evolution of the X-ray patterns and of the magnetisation shows that the presence of Ni_3Fe germs favours the process of synthesis of Ni_3Fe compound by mechanical alloying. This effect is most important for the short milling times. Magnetic data do not present a saturation tendency up to 5 h of milling, but the magnetisation values for 5 h of milling, in the presence of germs, are comparable with those obtained after 10 h of milling in the case of synthesis without germs.

For a better quantification of the influence of initial germs of Ni_3Fe on the Ni–Fe solid-state reaction, new researches are in progress. The following directions of study are considered: (i) the influence of the fraction and quality of the germs (particle size, crystallite size, structural state, etc.), (ii) a quantitative analysis of the influence of the germs on the Ni_3Fe fraction evolution and (iii) the influence of Ni_3Fe germs inoculation on the efficiency of the mechanical alloying process.

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