

STRUCTURE AND MAGNETIC PROPERTIES OF THE $Zr_{30}Fe_{35}Ni_{35}$ ALLOY FORMED BY MECHANICAL ALLOYING

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Abstract. The aim of this work was to study the structural transformations induced by mechanical alloying of the mixture of elemental powders with the composition of $Zr_{30}Fe_{35}Ni_{35}$. The structure of the powder samples was characterized by X-ray diffraction, Mössbauer spectroscopy and differential scanning calorimetry measurements as a function of the milling time up to 100 h. Mechanical alloying caused a partial amorphization in the samples milled for up to 50 h. Milling for longer time induced the formation of an inhomogeneous nanocrystalline structure. Magnetization measurements revealed the changes of magnetic properties related to the structure of the ball milled samples.

1. INTRODUCTION

It is well known that binary Zr-Fe and Zr-Ni systems can be obtained as amorphous alloys in a wide composition range by different preparation techniques [e.g. 1,2]. Ternary amorphous Zr-Fe-Ni alloys have been usually obtained by rapid solidification methods [3-6]. Recently, the mechanical alloying technique has been successfully applied in order to synthesize ternary Cu-Zr-Ni amorphous alloys [7]. The aim of this work was to study the structural transformations induced by mechanical alloying of the ternary $Zr_{30}Fe_{35}Ni_{35}$ alloy in which two potential amorphization processes could occur. The powder samples were characterized by X-ray diffraction (XRD), Mössbauer spectroscopy, differential scanning calorimetry (DSC) and magnetization measurements.

2. EXPERIMENTAL DETAILS

The $Zr_{30}Fe_{35}Ni_{35}$ alloy was prepared by high-energy ball milling of the mixture of pure elemental powders under Ar atmosphere. The Fritsch P5 planetary ball mill with steel vial and balls and 250 rpm was used. The samples structure was characterized by XRD (using CuK_{α} radiation) and Mössbauer spectroscopy measurements as a function of milling time up to 100 h. Mössbauer spectra were measured in transmission geometry at room temperature using a ^{57}Co -in-Rh source. Isomer shift data are given relative to α -Fe at room temperature. Thermal behaviour of the as-milled powders was studied using DSC technique with the scanning rate of 20 K min^{-1} . Faraday balance was used for magnetization measurements at elevated temperatures in the magnetic field up to 1.5 T that allowed us to calculate the magnetic moment per

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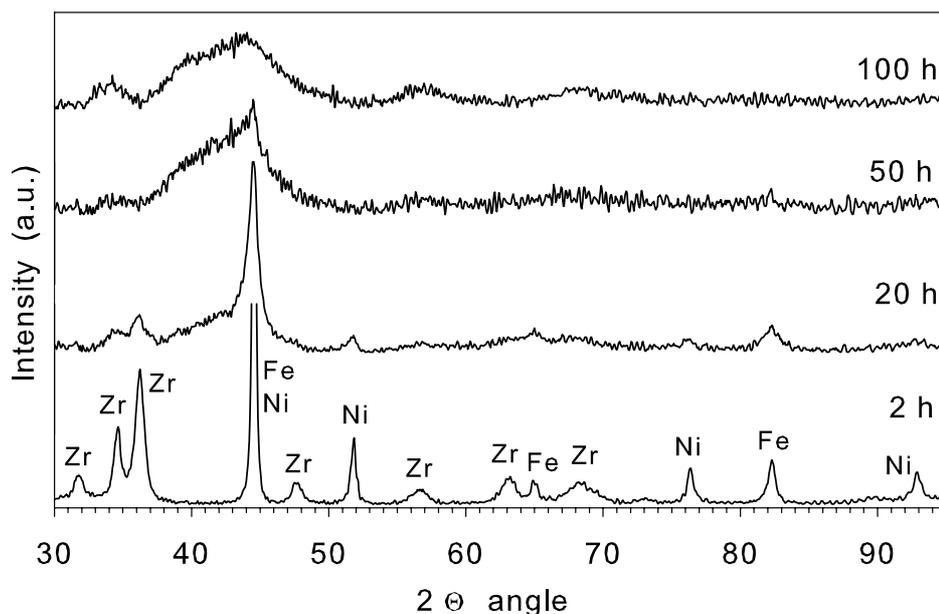


Fig. 1. XRD patterns of the $Zr_{30}Fe_{35}Ni_{35}$ powders recorded as a function of milling time.

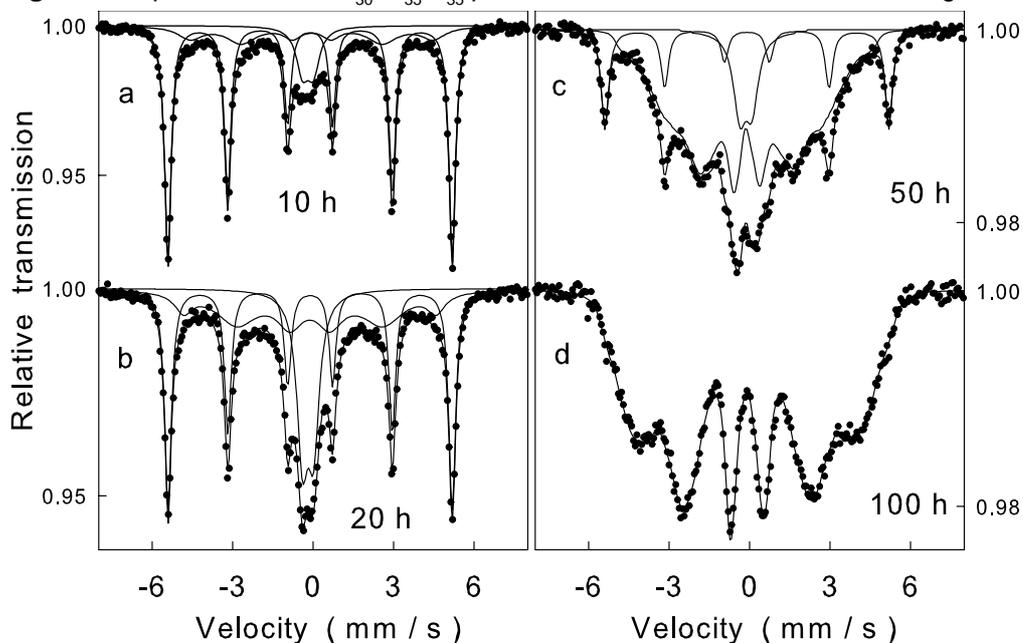


Fig. 2. Mössbauer spectra of the ball milled $Zr_{30}Fe_{35}Ni_{35}$ powders.

formula unit and Curie temperature of the alloys studied.

3. RESULTS

Structural transformations induced by ball milling of the mixture of elemental powders with the composition of $Zr_{30}Fe_{35}Ni_{35}$ can be followed in Fig. 1

presenting the XRD patterns recorded as a function of the milling time. A gradual refinement and alloying of the elements is observed with increasing the milling time as revealed by the appearance of broad peaks and by a decrease of intensity of the diffraction peaks related to the elemental powders. The alloying of Zr and Ni is more effective comparing to Fe up to about 50 h of milling. The

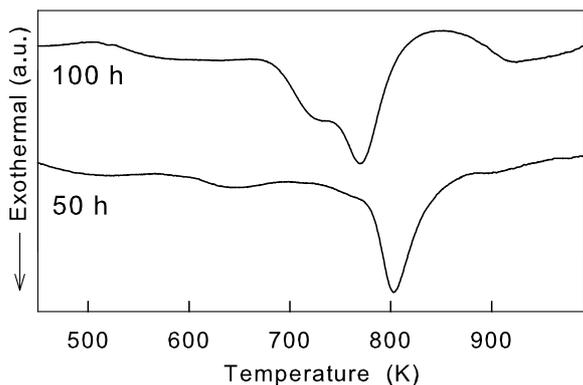


Fig. 3. DSC curves of the $Zr_{30}Fe_{35}Ni_{35}$ powder after 50 and 100 h of milling.

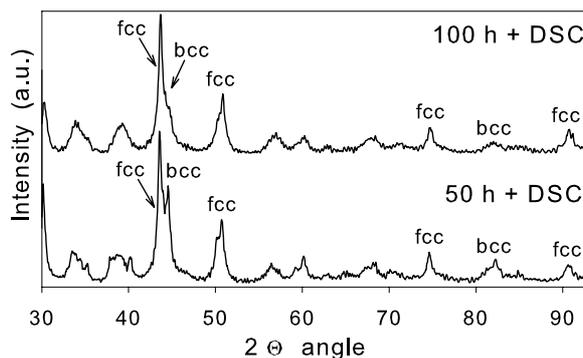


Fig. 4. XRD patterns of the powders milled for 50 and 100 h after DSC examination.

diffraction pattern obtained for the sample milled for 50 h resembles the ones characteristic for amorphous-like alloys, however, a small quantity of crystalline Fe is still evidenced. After milling for 100 h several broad peaks are observed in the XRD pattern suggesting a formation of nanocrystalline disordered solid solutions. The diffraction peaks at about 34° and 57° can be related to nanocrystalline Zr-rich regions [8], whereas peaks at about 40° and 44° are assigned to Ni- and Fe-rich regions. The average size of the Zr-rich clusters, estimated from broadening of the single diffraction peak at 57° using the Sherrer formula, was about 4 nm.

Mössbauer spectroscopy measurements provide structural information regarding the distribution of Fe atoms in the sample and their nearest atomic environment. The Mössbauer spectra shown in Fig. 2 reveal gradual mixing of the elemental powders. The relative intensity of the magnetic six-line component with sharp lines and hyperfine field of 32.95 T and isomer shift of 0.00 mm/s related to the elemental bcc Fe powder (Fig. 2a) decreases with increasing the milling time, indicating the alloying of Fe with other elements. In the case of the samples milled for up to 50 h a quadrupole doublet is observed in the central part of the spectra (Figs. 2a-2c). The hyperfine parameters of the doublet (the quadrupole splitting of 0.40 mm/s and isomer shift of -0.09 mm/s for the sample milled for 20 h) as well as its asymmetric shape indicate that this spectral component is related to a paramagnetic amorphous Fe-Zr phase (containing probably also some Ni atoms) with Zr content less than about 30 at.% [3,9]. Another evi-

dence of the alloying of Fe is the appearance of a sextet with broad lines and a reduced hyperfine field of about 29 T in the spectra of the samples milled for up to 20 h (Figs. 2a and 2b). This magnetic component can be assigned to the disordered Fe-Ni solid solution containing about 70% of Ni [10]. Upon further milling a significant reduction of the hyperfine field to about 16 T is observed for the broadened magnetically split component (Fig. 2c), suggesting a presence of a relatively large amount of Zr and Ni atoms in the vicinity of Fe.

A complete distribution of Fe atoms in the alloy is observed after about 100 h of the milling (Fig. 2d). The magnetic hyperfine structure observed in the Mössbauer spectrum of the sample milled for 100 h resembles the ones that are typical for ferromagnetic amorphous alloys. On the other hand, all known fully amorphous Fe-Zr alloys prepared by mechanical alloying are paramagnetic at room temperature [9]. As shown by the XRD results the majority of Zr seems to form Zr-rich clusters. Therefore, the presence of the broadened magnetic six-line component indicates the formation of a nanocrystalline disordered FeNi-based solid solution. The spectrum in Fig. 2d consists of six broad and overlapping lines due to the variety of local atomic arrangements around iron nuclei. The spectrum was fitted using the histogram hyperfine field distribution method that allowed us to calculate the average value of the hyperfine field of 22 T that is considerably lower than the hyperfine field of pure Fe.

Thermal behaviour of the as-milled samples was studied by DSC measurements up to 993K

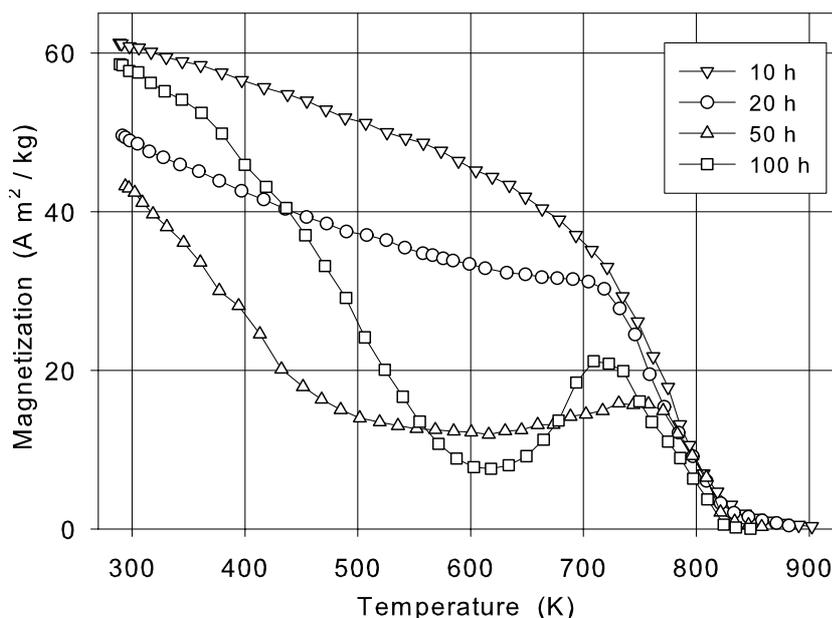


Fig. 5. Temperature variation of magnetization of the samples milled for 10-100 h.

(Fig. 3). For the sample milled for 50 h a single exothermic peak appears in the DSC curve, whereas for the sample milled for 100 h a double peak is observed. This may indicate more homogeneous structure of the 50 h sample as revealed also by the XRD results (Fig. 1). The XRD patterns of both samples after their DSC examination are shown in Fig. 4. The fcc Ni-based and the bcc Fe-based phases can be clearly identified for both samples. The relative intensity of the bcc peaks is larger for the sample milled for 50 h than for 100 h that can be related to the presence of unreacted Fe in the as-milled sample (50 h, Figs. 1 and 2c). The remained poorly resolved diffraction peaks in Fig. 4 (except for the one at about 30° related to Zr oxide) originate most probably from the regions with a $(\text{Fe,Ni})_{3\pm x}\text{Zr}$ -like structure.

The dependence between the structure and magnetic properties of the powder samples was studied by magnetization measurements at elevated temperatures. The temperature variations of magnetization shown in Fig. 5 are characteristic for ferromagnetically ordered solids for the whole range of the milling time studied. After the first 10 h of milling the magnetic moment per formula unit of the $\text{Zr}_{30}\text{Fe}_{35}\text{Ni}_{35}$ sample equals to $0.74 \mu_B$. Values of the Curie temperature, T_C , were determined

from a temperature derivative of magnetization. The calculated T_C of such an initially milled alloy ($T_C = 785\text{K}$) is more than 200K lower as compared to pure iron. However, the temperature variation of magnetization above 720K is surprisingly almost linear. When magnetization diminishes roughly proportionally to the temperature, even small deviations or noises may result in such a spurious T_C values. A more detailed inspection of magnetization data within a relatively broad temperature interval, where a derivative is strongly negative, shows that T_C exceeds 800K and is in the range of 820-830K. These values are close to T_C of the crystalline $\text{Ni}_{80}\text{Fe}_{20}$ alloy ($T_C = 833\text{K}$) that supports the assignment of the Mössbauer broadened six-line component to the Ni-rich phase (Figs. 2a and 2b). The fact that a distribution of T_C is observed rather than one value is characteristic for disordered alloys. The milling up to 20 h reduces the magnetic moment down to $0.6 \mu_B$ possibly due to the development of the amorphous paramagnetic phase (Fig. 2b). The magnetization versus temperature dependence for 50 and 100 h of milling is complex and typical for a multiphase material. A magnitude of magnetization between 600 and 700K allows us to conclude that the fraction of the bcc Fe-rich phase is suppressed more than twofold as com-

pared to the sample milled for 10 h. The room temperature value of the magnetic moment of the alloy milled for 100 h raises up to $0.71 \mu_B$. Magnetization of the Fe-rich phase (peaked at about 720K) becomes approximately 30% larger than after 50 h milling. This may demonstrate thermally induced structural changes related to the increase of the fraction of the bcc Fe-rich phase or additional diffusion of Fe atoms into this phase.

4. CONCLUSIONS

The high-energy ball milling of the mixture of elemental powders with the composition of $Zr_{30}Fe_{35}Ni_{35}$ caused partial amorphization of the powders for the milling time up to about 50 h. The paramagnetic amorphous FeZr-based phase was detected. Milling for longer time induced the formation of the inhomogeneous, nanocrystalline structure consisting of disordered solid solutions. After heating in the calorimeter the samples contained the fcc Ni-based and the bcc Fe-based phases along with the $(Fe,Ni)_3Zr$ -like clusters. Magnetization measurements revealed that all samples were ferromagnetic at room temperature. Changes in magnetic properties were related to the evolu-

tion of the samples structure during the mechanical or thermal treatment.

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