SYNTHESIS AND MICROSTRUCTURAL OBSERVATIONS DURING BALL MILLING IN $Fe_{88}Zr_7B_4Cu_1$ NANOSTRUCTURED ALLOYS

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Scopul lucrării este acela de a studia sinteza prin aliere mecanică şi evoluția morfologică a particulelor de material în timpul sintezei. Pulberea de aliaj NANOPERM a fost preparată prin aliere mecanică. Evoluția cristalinității şi a dimensiunii de grăunte în timpul sintezei a fost investigată cu ajutorul difracției de raze , experimentele au fost efectuate la linia de difracție de înaltă rezoluție B2 de la synchrotronul DESY/HASYLAB, Hamburg, Germania. Observațiile privind evoluția morfologică a particulelor în timpul sintezei au fost efectuate cu ajutorul unui microscop SEM Tescan VEGA II – XMU.

The aim of the present work is to study the ball milling synthesis and microstructural changes in particles morphology during ball-milling. NANOPERM alloy powders were prepared by high-energy ball-milling. The as-milled alloys consist of an iron-based nanocrystalline solid solution. The evolution of crystallinity and grain-size during the ball-milling process was evaluated using synchrotron radiation X-ray diffraction. The experiments were performed at the B2 beamline at DESY/HASYLAB, Hamburg, Germany. The microstructural observations concerning particles morphology during ball milling were made using a Tescan VEGA II – XMU SEM.

Keywords: magnetic materials, nanostructured materials, mechanical alloying

1. Introduction

Amorphous and more recently nanocrystalline materials were investigated for applications in magnetic devices such as transformers, inductive devices, etc, which use soft-magnetic materials. The interest in developing nanocrystalline soft-magnetic alloys has dramatically increased during the past few years.

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Bulk soft-magnetic materials need to have both high induction and permeability, as well as many non-magnetic issues such as mechanical properties, corrosion resistance, etc. Key issues include alloy chemistry, structure and the ability to tailor microstructural features. Nanocrystalline magnets used in soft magnetic applications must therefore be optimised in terms of intrinsic and extrinsic magnetic properties as well as their morphology [1].

The key intrinsic magnetic properties, the saturation magnetic induction (Bs), the Curie temperature (T_C), are determined by the alloy composition and crystal structure. The extrinsic property of interest are the magnetic permeability (μ) and the magnetic response function in an applied field, which usually is inverse related to the coercivity (H_C) of the magnetic material. In particular, alloys with small magnetocrystalline anisotropy and magnetostrictive coefficients give rise to improved soft magnetic materials [2].

2. Experimental procedure

Nanocrystalline powder precursors for the soft magnetic alloy $Fe_{88}Zr_7B_4Cu_1$ (NANOPERM) were obtained by high-energy ball-milling (RETSCH 400 PM planetary ball-mill) from high-purity elemental powders with an average particle-size close to 100 μm.

The elemental powders were immersed in hexane and mechanically milled in stainless steel vials (250 ml) with stainless steel balls (20 mm diameter) at 250 rotations per minute (rpm). The ball-to-powder mass ratio was 20:1 and the total milling time was 90 hours. The resulting milling parameters were as follows: impact energy E = 0.1378 Joule and milling intensity I = 2.4806 Watt. During milling, small quantities of powder were taken out for further investigations. The grain-size evolution during milling was investigated at the high-resolution powder diffractometer instrument B2 beamline from DESY/HASYLAB (Hamburg, Germany). Morphological observation upon ball-milled powder was made using a scanning electron microscope TESCAN VEGA II – XMU.

3. Results

3.1. Grain-size evolution during milling

The grain-size evolution during the ball-milling process was obtained from synchrotron radiation X-ray diffraction experiments.

The evolution of X-ray diffraction patterns is presented in figure 1, where the bcc-α(110), bcc-α(200) and bcc-α(211) peaks of Fe are shown. The diffraction patterns were fitted using the PeakFit v4.11 software package (SYSTAT Software Inc.). The Fe diffraction peaks suffer changes during milling, i.e., the peaks intensities decrease and the full-width-at-half-maximum (FWHM)

parameter increases, during milling, meaning that the average dimensions of crystalline domains become smaller [3-5].

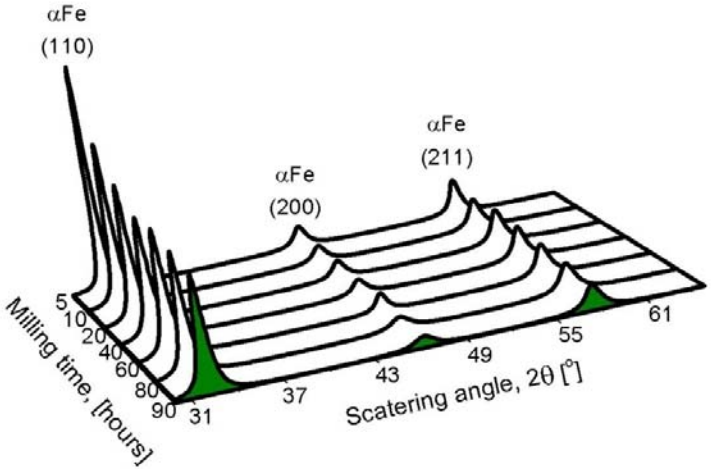


Fig. 1. Powder diffraction spectra evolution during milling

The calculated values for the grain-size evolution are presented in figure 2 and figure 3. Figure 2 illustrates the evolution of dimensions of crystalline domains as obtained from the FWHM of the bcc-αFe (110) peak, using the Scherrer equation (equation 1) [6]:

$$\beta \cdot \cos\theta = \frac{k \cdot \lambda}{D} \quad \text{(Scherrer)} \tag{1}$$

where β is the pure broadening of the diffraction peak measured at half the maximum intensity (FWHM parameter), θ the Bragg angle, k the shape factor (k = 0.9), λ = 0.1135 nm is the wavelength of the X-ray radiation, and *D* the average dimension of crystallites (grain-size).

Figure 3 illustrates the evolution of grain-size and the average internal microstrain. If the internal microstrain is considered then equation 1 can be rewritten as [6]:

$$\beta \cdot \cos\theta = 2 \cdot \varepsilon \cdot \sin\theta + 0{,}9 \cdot \frac{\lambda}{D} \quad \text{(Williamson-Hall)} \tag{2}$$

where ε is the average microstrain.

The grain-size evolution during milling is as follows: after 5 hours milling time the value of grain-size is equal to 21 nm if internal microstrains are ignored and 27 nm if the influence of internal microstrains is taken into account. At the end of the milling process the grain-size equals 9 nm (Scherrer) or 13 nm if the Williamson-Hall procedure (equation 2) is used.

The internal strain shows a small increase in the initial part of the milling process (up to 2 % after 20 hours of milling). The microstrain decreases to approx.

1 % towards the end of the milling process. It was also observed that the grain-size decreases with milling time up a critical grain-size of about 15 nm. For milling times beyond 40 hours the grain-size reduction process stops.

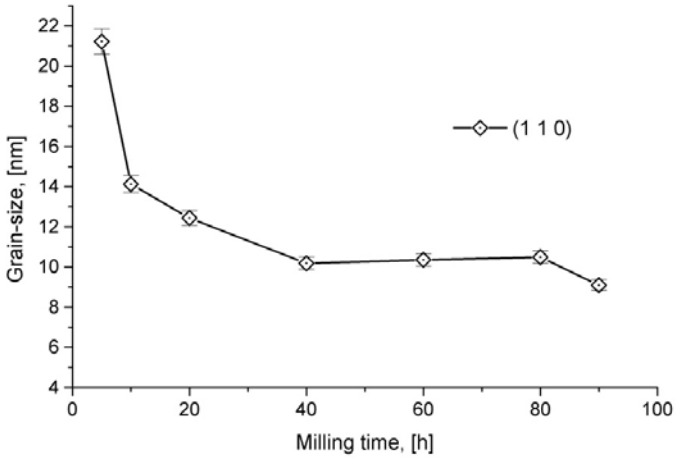


Fig. 2. Grain-size evolution during milling using Scherrer equation
(the line is a guide to the eye)

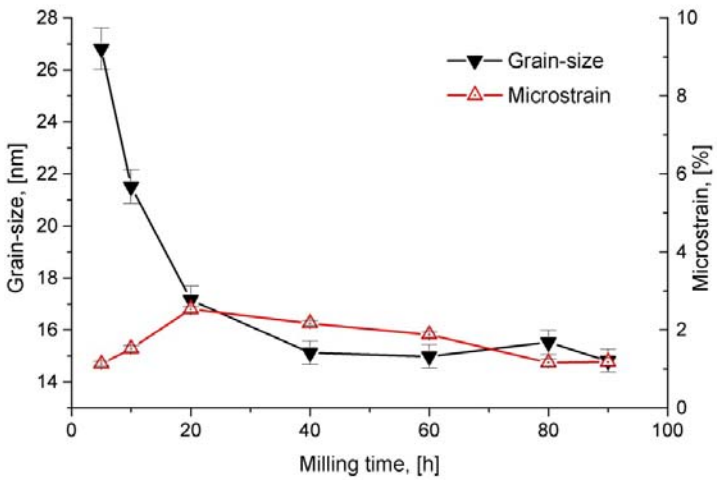
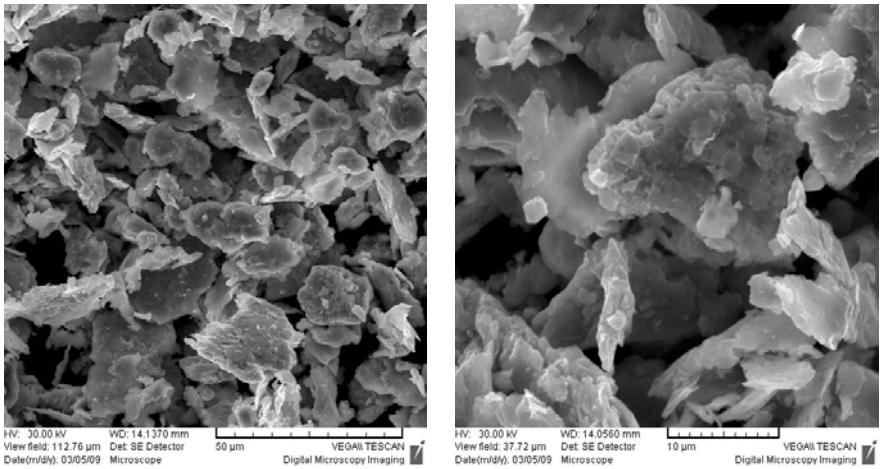


Fig. 3. Grain-size and internal strain evolution during milling.
(the lines are guides to the eye)

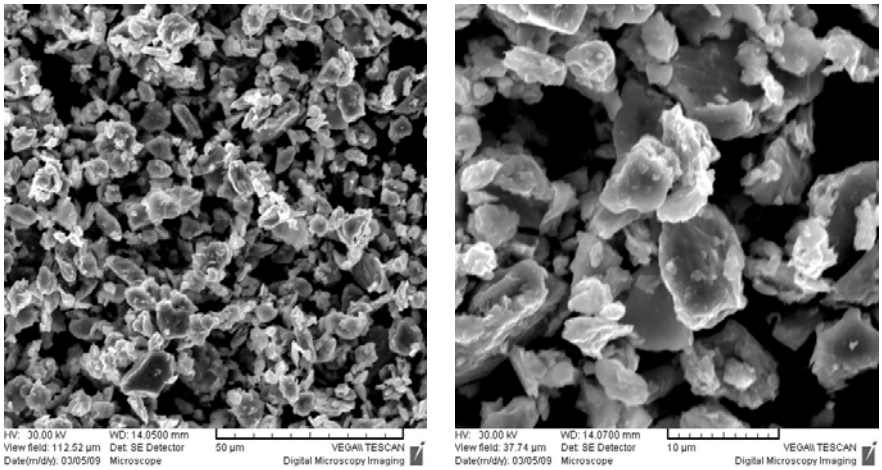
3.2. Particle-size evolution during milling

As observed in figure 4 – 8 one can see that for short milling time, see fig. 4, flake-like layered particles are formed. For 5 hours milling time (fig. 4a, 4b), average particle size is situated to approx. 25 μm. A small fraction of particles with small dimensions are present.



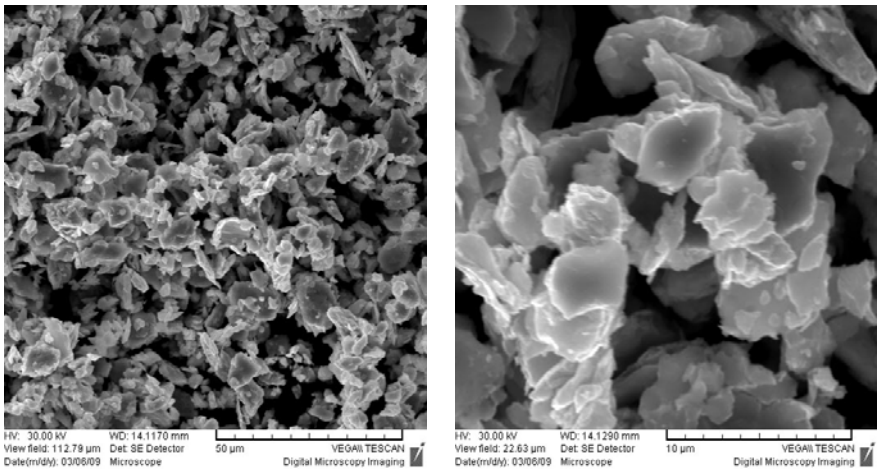
(a) (b)

Fig. 4. SEM images for 5 hours milled powder



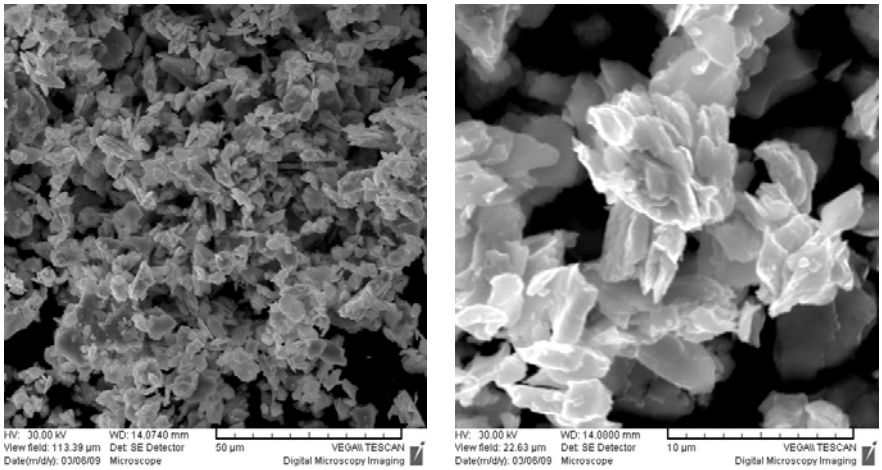
(a) (b)

Fig. 5. SEM images for 10 hours milled powder



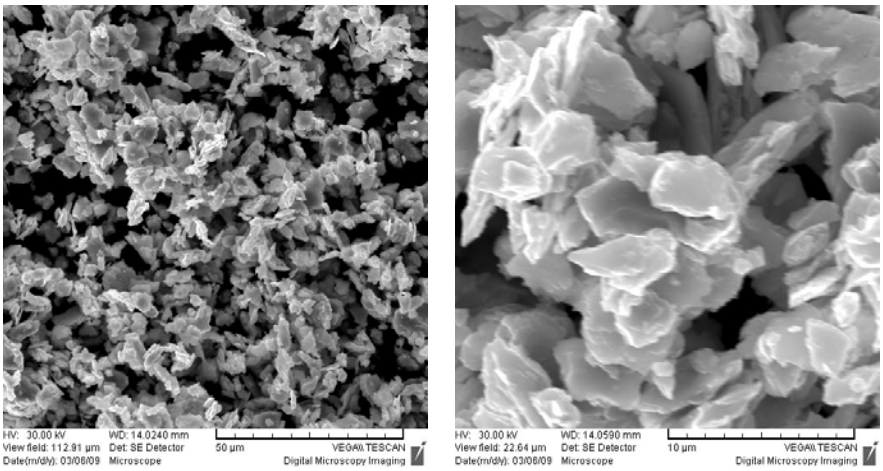
(a) (b)

Fig. 6. SEM images for 20 hours milled powder



(a) (b)

Fig. 7. SEM images for 40 hours milled powder



(a) (b)

Fig. 8. SEM images for 60 hours milled powder

Increasing the milling time to 10 hours (see fig. 5a, 5b), general flakes-like layered particle shape is maintained, a large decreasing in average particle size is observed. Average particle size is situated to approx. 12 μm. The fraction of smaller size particles, presented on particle surfaces, is increasing.

For 20 hours milling time (fig. 6a, 6b), a decreasing in average particle size is observed. Average particle size is situated to approx. 7 μm. The fraction of smaller size particles, presented on large particle surfaces, is increasing also.

For 40 hours milling time (see fig. 7a, 7b), also a decreasing in average particle size is present. Average particle size is situated to approx. 5 μm. Aglomerated particles are observed.

For 60 hours milling time (fig. 8a, 8b), an uniformisation in particles distribution is observed, due to the high intensity particle fragmentation during higher milling times. Average particle size is situated to approx. 5 μm.

4. Discussion

As observed in fig. 2 and 3 the grain-size evolution during ball-milling is situated in nanometer scale after few hours of milling, at 5 hours milling time a maximum 28 nm size is observed, final grain-size being situated to 15 nm for 90 hours milling time, if microstrain is taken into account. Also, it can be observed that the milling process is effective up to 40 - 60 hours of milling when the grain-size evolution reaches a minimum, after that a small increase in grain-size can be observed. The resulted average internal microstrain (calculated with eq. 3) did not exceed 2.2% during milling.

A flake-like shape for milled particles is observed, due to the milling mechanisms. The plackets have a layered structure consisting in many initial particles stacked and flatted together during milling. During milling, a small fraction of smaller size particles is present, this fraction increases during milling due to the particles fragmentation process. For larger milling times the particles manifest an uniformisation process.

5. Conclusions

High-energy ball-milling synthesis was demonstrated to be a reliable preparation technique for nanostructured NANOPERM alloys. A milling time up to 40 – 60 hours was shown to be sufficient to obtain a nanostructured powder. Flake-like particle were obtained in first stages of milling, after longer milling time a particles fragmentation was observed. After longer milling times (more then 60 hours) an uniformisation in particle shape was present.

R E F E R E N C E S

[1] *M.E. McHenry, M.A. Willard, D.E. Laughlin*, Amorphous and nanocrystalline materials for applications as soft magnets, Progress in Material Science, **44**, 1999, 291-433

[2] *M. E. McHenry, M. A. Willard, H. Iwanabe, R. A. Sutton, Z. Turgut, A. Hsiao, D. E. Laughlin*, Nanocrystalline materials for high temperature soft magnetic applications: A current prospectus, Bulletin of Material Science, **22**, 1999, 495-501

[3] *V.D. Cojocaru*, Ball-milling synthesis of nanostructured NANOPERM alloys, Metalurgia International, 10/2, 2005, 11-13

[4] *S.R. Cojocaru, R. Saban, V.D. Cojocaru*, Compression behaviour of NANOPERM-type Fe86Nb7B4Cu1Ag1 nanostructured alloy at 500°C, University POLITEHNICA of Bucharest Scientific Bulletin, Series B, **67**, 4/2005, 77-82

[5] *S.R. Cojocaru, R. Şaban, V.D. Cojocaru*, Synthesis of NANOPERM-type Fe86Nb7B4Cu1Ag1 nanostructured alloy by mechanical alloying, University POLITEHNICA of Bucharest Scientific Bulletin, Series B, **67**, 2/2005, 83-88

[6] *J. He, F. Zhou, G. Chang, E.J. Lavernia*, Influence of mechanical milling on microstructure of 49Fe-49Co-2V soft magnetic alloy, Journal of Materials Science, 36, 2001, 2955-2964.