Structural evolution and magnetic aspects in nanostructured (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ alloys

D Garzón$^1$, J M Marín-Ramírez$^1$, F H Sánchez$^2$, C Ostos$^3$, F J Bolívar$^1$, and O Arnache$^1$

$^1$Universidad de Antioquia, Medellín, Colombia
$^2$Universidad Nacional de La Plata, La Plata, Argentina

E-mail: diego.garzon@udea.edu.co

Abstract. Magnetic powder alloys (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ were produced by using a combination of two synthesis techniques, casting and ball milling. Bulk samples were reached from casting while milling yield to powders to induce a homogenized structural phase. The structural analysis confirmed that initially an α-Fe phase (bcc) was formed with space group Im-3m. As the milling time goes from 0 to 36 h, small changes in the lattice parameter were noticed, going from 0.285 nm to 0.287 nm. Magnetic hysteresis loops measurements revealed that the samples are ferromagnetic at room temperature, with a maximum saturation magnetization ~ 161 emu/g for 0 h and ~ 150 emu/g for 36 h. Likewise, the powder samples are magnetically soft at room temperature, with coercive field values below 50 Oe.

1. Introduction

FeMB alloys, where M represents a transition metal (M = Zr, Cu, Ni), have stimulated recent interest given their excellent magnetic properties, with a high saturation magnetization (Ms), low coercive field (Hc), and small magnetic hysteresis area. Specially, these soft magnetic materials are in high demand for applications in microdevices, such as magnetic and electromagnetic sensors. Furthermore, these FeMB alloys present interesting magnetocaloric properties, due to their high relative cooling power (RCP) and high magnetic entropy change (ΔSM) around the critical temperature (Tc), can be considered for potential candidates in magnetic refrigeration applications [1-4].

FeZrB alloys, commonly named nanoperm (Fe$_{91}$Zr$_7$B$_2$, Fe$_{88}$Zr$_8$B$_4$, Fe$_{87}$Zr$_8$B$_6$Cu, and Fe$_{80}$Zr$_{10}$B$_{10}$) [5-7], are amorphous materials. Additionally, their Tc can be tuned (in a range of 295 K-380 K) either by using heat treatments and/or increasing/decreasing the concentration of Zr or B, which is appropriate for room-temperature magnetic refrigeration applications [8], especially seen in magnetic tape-like systems, that have shown high values for both ΔSM and RCP [5,6,9].

In this work, the structural and magnetic properties of (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ alloys (FZB) were studied. Using a casting method and subsequently employing mechanical alloying the gradual incorporation of Zr and B into the bcc-Fe matrix, that is, the homogenization of the bcc-(Fe$_{92}$Zr$_8$)$_{96}$B$_4$ phase was obtained. Likewise, an initial exploration of the magnetic nanoparticles powder samples led to interesting properties such as high Ms and low Hc values, which are relevant for potential technological applications of these types of alloys.
2. Methodology

By using a casting and ball milling pulverizing process, (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ (FZB) alloys in the powder were obtained varying the milling times from 0 h, 12 h, 24 h, and 36 h. A planetary ball mill (Fritsch Pulverisette 5) with a constant rotation speed of 250 rpm at room temperature was employed. Additionally, the mechanical alloying was carried out in an argon atmosphere at a pressure of $\sim 4.0 \times 10^{-3}$ Torr to avoid oxidation [10]. According to the different milling times the (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ samples were labeled as follows, FZB-0, FZB-12, FZB-24, and FZB-36.

A Panalytical Empyrean series 2 (CuKα 1.5405 Å) was used to determine the crystalline structure using X-ray diffraction (XRD) analysis. Employing a scanning electron microscope (SEM-EDX) JEOL-JSM 6490LV and a wavelength-dispersive X-ray fluorescence spectrometer (WDXRF) the grain morphology and elemental composition were determinate. Finally, magnetic measurements of the FZB alloys were performed employing a vibrating-sample magnetometer (VSM) module in a physical properties measurement system (PPMS by Quantum Design). Finally, Mössbauer spectroscopy in transmission geometry, using a $^{57}$Co(Rh) radioactive source at room temperature, was used to analyze the samples [11].

3. Results and discussion

The results obtained throughout the research are shown in the following sections.

3.1. Structural analysis of (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ powder alloys

Figure 1(a) to Figure 1(d), shows the XRD for the (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ mechanically alloyed samples using different milling times (MT). XRD refinement indicates that the alloys present the bcc desired phase without any impurities, as confirmed by the positions of the different diffraction peaks. The black circles are the experimental data, the solid line in red corresponds to the Rietveld adjustment, while the blue line is associated with the residual value.

![Figure 1](image-url)

**Figure 1.** XRD diffractograms for the mechanically alloyed (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ systems at different milling times, (a) 0 h; (b) 12 h; (c) 24 h; (d) 36 h.

The inset in Figure 1(a) correspond to the (Fe$_{92}$Zr$_{8}$)$_{96}$B$_4$ structure; in Figure 1(b) zoom of the diffraction peak evolution at 65° is shown. The lattice parameter obtained for this phase (bcc) is close to 0.2861 (nm), slightly smaller than that reported for a pure α-Fe phase (0.2868 nm) [12-14]. However,
the solid solution of α-Fe (B) is unstable and can change, this is noticeable after 12 h, where reflections belonging to an intermetallic phase (ZrB) are observed below 2θ = 38° [15]. A comparison of the evolution in the intensities for the main reflections in the (200) directions is shown in the inset in Figure 1(b). As the MT increases there is a significant broadening of the reflections, which is more noticeable for FZB-36. This broadening is related to the gradual refinement of the α-Fe grains and the increase in the deformation of the crystalline structure [16,17]. This phenomenon is corroborated by the displacement of the main peak (110) towards lower angles and slightly higher lattice parameters [18].

Furthermore, the peak-width for the (110) and (200) reflections were analyzed through the Williamson-Hall (WH) method [19], to estimate the mean grain size corresponding to the bcc-Fe phase. Both lattice parameter (a = 0.203 nm) and the interatomic distances (d~0.202 nm) remain nearly constant independent of the MT; thus, the atomic volume (Ω~5.896 nm³) is not affected by the milling conditions. The expressions involved in the calculation of d and Ω are given by authors in [20]. The Rietveld refinement combined with WH analysis showed that the mechanical alloying conditions generate only a 1% increase in the micro-strain and a considerable reduction in the crystallite size of the powder nanoparticles from ~100 nm to ~20nm.

### 3.2. Morphological and compositional analysis

SEM analysis for (Fe₉₂Zr₈)₉₆B₄ powder alloys is presented in Figure 2(a) to Figure 2(d) as a function of the milling time. Figure 2(a) (FZB-0 sample) shows grains with spherical morphology and an average size of ~10 μm. Similarly, after 12 h Figure 2(b) the powder’s morphology changes to a flat circular shape (corn flake-like form). This behavior remains after 24 h of MT Figure 2(c). Finally, for the FZB-36 system Figure 2(d), the morphology switches both in size and shape, going from the circular laminar shape to small particles with rocky morphology [21,22].

![Figure 2](image-url)

**Figure 2.** SEM micrographs for (Fe₉₂Zr₈)₉₆B₄ alloys shows the morphological evolution of the powders after each milling cycle, (a) FZB-0; (b) FZB-12; (c) FZB-24; (d) FZB-36.

The compositional characterization by EDX is shown in Figure 3. Only the peaks corresponding to the presence of Fe and Zr in the alloys can be observed, due to the rather small emission energy of B is rather small, which cannot be detected using this method. The relative positions of the emission peaks agree with the standard values for Fe and Zr, independent of the MT, as seen in Figure 3(a) to Figure 3(d). Additionally, EDX showed that the Fe: Zr ratio is ~ 81.6 for Fe and ~ 7.2 for Zr, which is in line with the initial stoichiometric composition for the sample, namely (Fe₉₂Zr₈)₉₆B₄. Complementary
to the elemental composition (Fe: Zr ratio) using the EDX method, WDXRF measurements were performed. WDXRF analysis showed that there was no impurities present independent of the milling process. These morphological results indicate that there is a homogenization of the Fe and Zr precursors in agreement with the XRD analysis.

![EDX spectra](image)

**Figure 3.** EDX spectra of $(\text{Fe}_{92}\text{Zr}_{8})_{96}\text{B}_{4}$ alloys for different milling time (a) 0 h; (b) 12 h; (c) 24 h; (d) 36 h.

3.3. Magnetic properties

Mössbauer spectra (MS) for each milling time are shown in Figure 4. Typical $\alpha$-Fe sextets with well-defined lines are evidenced independent of the MT, this magnetic site exhibits a hyperfine field close to 33 T which is associated with Fe-rich regions [16,23]. Furthermore, two independent sites (dashed line in green and solid in blue) were considered for the FZB-0 alloy corresponding to sextets (Figure 4(a)). For the other nanoparticle systems (FZB-12, FZB-24, and FZB-36) an additional doublet magnetic site (continuous violet line) was used (see Figure 4(b) to Figure 4(d)).

![Mössbauer spectra](image)

**Figure 4.** Mössbauer spectra measured at room temperature for the $(\text{Fe}_{92}\text{Zr}_{8})_{96}\text{B}_{4}$ powder alloy systems with different milling times (a) 0 h, (b) 12 h, (c) 24 h, and (d) 36 h.
The spectra indicate that the same crystalline phase was formed from 12 h to 36 h, in agreement with the results reported in references [23]. The hyperfine parameters obtained from the MS fit are shown in Table 1. The initial magnetic components (sexets) correspond to two different magnetic environments: one related to precipitated grains and the other (overlapping broad lines with a continuous distribution of hyperfine fields $B_{hf}$) attributed to the crystalline matrix of the material [23–25]. On the other hand, the emergence of the doublet after 12 h of MT, might be the effect of Fe environments surrounded by Zr as a product of the continuous mechanical alloying, which can generate losses in the magnetic momentum of Fe as typically depicted by $\alpha$-Fe$_x$Zr$_{100-x}$ alloys [26].

### Table 1. Hyperfine parameters of Mössbauer analysis on (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ at each milling stage.

| Component | $B_{hf}$ (T) | QS (mm/s) | IS (mm/s) |
|-----------|--------------|-----------|-----------|
| Sextet-1  | 33           | 0.0       | 0.001     |
| Sextet-2  | 24           | 0.11      | 0.02      |
| Sextet-1  | 32.8         | 0.004     | 0.001     |
| Sextet-2  | 25           | -0.7      | -0.5      |
| Sextet-1  | 32.92        | -0.0001   | 0.001     |
| Sextet-2  | 20.23        | 0.16      | -0.5      |
| Sextet-1  | 33           | 0.9       | 1.5       |
| Sextet-2  | 24           | 0.11      | 0.11      |

Finally, the ferromagnetic behavior for the (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ alloys was verified using magnetization (M) as a function of the external field (H) curves at room temperature Figure 5(a). The samples are ferromagnetic and magnetically soft as expected independent of the milling time. In addition, the saturation magnetization (Ms) and the coercive field (Hc) were determined using the Langevin distribution fitting function see inset in Figure 5(a). The changes in magnitude for Hc and Ms as a function of the milling time are presented in Figure 5(b).

**Figure 5.** (a) Room temperature magnetic hysteresis loops for all (Fe$_{92}$Zr$_8$)$_{96}$B$_4$ powder alloys. The inset show $M(H)$ curve fitted by Langevin function; (b) evolution of magnetization saturation (Ms) and coercive field (Hc) as a function of the milling time.
The highest Ms values were reached for FZB-0 (~ 162 emu/g) and FZB-36 (~ 151 emu/g), which can be related to the fact that, for these samples, a unit crystalline α-Fe phase was reached, thus leading to higher magnetization values due to lower disorder and enhanced Fe-Fe interactions. However, for FZB-12 and FZB-24, the Ms decreased substantially ~31 and ~43 emu/g, respectively, due to the increase in the fractions of particles with reduced sizes [16] and to the presence of a paramagnetic site (doublets) as observed in the MS results. A significant improvement in coercivity can be attributed to the disappearance of the intermetallic phases, together with the improvement of the nanocrystalline phase of magnetic α-Fe [15,16,25].

4. Conclusions
The structural and magnetic evolution of (Fe$_{80}$Zr$_{8}$)$_{86}$B$_{4}$ nanoparticles obtained by mechanical milling means was studied. Independent of the milling time the microstructural analysis confirmed the existence of the bcc-(Fe$_{80}$Zr$_{8}$)$_{86}$B$_{4}$ crystal structure. X-ray diffraction measurements revealed that the incorporation of the ZrB phase into the bcc α-Fe structure, led to an increase in the widths for the (110) and (200) reflections, alongside their decrease in intensity. Furthermore, elemental analysis by employing a scanning electron microscope and X-ray fluorescence spectrometer confirm the homogeneity and stoichiometric composition of the (Fe$_{80}$Zr$_{8}$)$_{86}$B$_{4}$ alloys. Mössbauer’s spectra analysis indicated that the magnetic environments of the samples are affected by the milling time and thus the Fe-Fe interactions are inhibited by the presence of Zr-rich zones. This effect was also present in the evolution of the magnetization saturation values reached using the magnetic hysteresis loops, attributed as well to a decrease of the particles size as per the Rietveld analysis. We hope that our initial assessment of the magnetic properties of (Fe$_{80}$Zr$_{8}$)$_{86}$B$_{4}$ nanoparticles can be used to review their magnetocaloric properties as a potential material for applications in magnetic refrigeration.

Acknowledgments
D. G. and J.M.M.R. acknowledge “Ministerio de Ciencia, Tecnología e Innovación (MinCiencias)”, Colombia, for their Ph.D. fellowship. O.A thanks the financial support within the framework of the Solid-State Research group sustainability strategy 2020-2021.

References
[1] Du S W, Ramanujan R V 2005 Mechanical alloying of Fe–Ni based nanostructured magnetic materials Journal of magnetism and magnetic materials 292 286
[2] Ucar H, Ipus J J, Laughlin D E, McHenry M E 2013 Tuning the Curie temperature in γ-FeNi nanoparticles for magnetocaloric applications by controlling the oxidation kinetics Journal of Applied Physics 113(17A918) 1
[3] Kiyonori S, et al. 1991 Soft magnetic properties of nanocrystalline bcc Fe-Zr-B and Fe-M-B-Cu (M=transition metal) alloys with high saturation magnetization Journal of Applied Physics 70(10) 6232
[4] Fadaie A, Akdeniz M V, Mekhabrov A O 2014 Synthesis and characterization of Fe80B20 nanoalloys produced by surfactant assisted ball milling Acta Physica Polonica Series A 125 597
[5] Chaudhary V, et al. 2017 Tuning the phase stability and magnetic properties of laser additively processed Fe-30at% Ni soft magnetic alloys J. Appl. Phys 192 88
[6] Kiss L F, Kemeny T, Franco V, Conde A 2015 Enhancement of magnetocaloric effect in B-rich FeZrBCu amorphous alloys Journal of Alloys and Compound 622 756-760
[7] Carrillo A, Escoda L, Saurina J, Sunol J J 2018 AIP Advances 8(047704) 1
[8] Maheswar Repaka D V, Sharma V, Ramanujan R V 2017 Near room temperature magnetocaloric properties and critical behavior of binary Fe$_{100}$x-X nanoparticles Journal of Alloys and Compounds 690 575
[9] Guo D Q, Chan K C, Xia L, Yu P 2017 Magneto-caloric effect of Fe$_{100-x}$Zr$_{x}$ metallic ribbons for room temperature magnetic refrigeration Journal of Magnetism and Magnetic Materials 423 379
[10] Garzón D, Arnache O, Aristizabal R, Santacruz A, Ostos C, Echavarria A 2019 Parameters optimization in the casting processes of Fe$_{32}$Cu$_{6}$4B$_{4}$ magnetic alloys J. Phys. Conf. Ser 1247(1) 012012:1
[11] Rancourt D G, Ping J Y 1991 Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 58(1) 85
Álvarez P, Gorria P, Sánchez Marcos J 2010 The role of boron on the magneto-caloric effect of FeZrB metallic glasses Intermetallics 18 2464

Alvarez Alonso P 2011 Magnetocaloric and Magnetovolume Effect in Fe-Based Alloys (España: Universidad de Oviedo)

Khlifa H B, M'nassrib R, Cheikhrouhou Koubaa W, Schmerberc G, Cheikhrouhoua A 2018 Critical properties and field dependence of the magnetic entropy change in Pr0. 8K0. 2MnO3 ceramic: a comparison between solid-solid state and sol-gel process Journal of Magnetism and Magnetic Materials 466 7

Kong L H, Gao Y L, Song T T, Zhai Q J 2011 Journal of Magnetism and Magnetic Materials 323 2165

Hua Z, Sun Y M, Yu W Q, Wei M B, Li L H 2009 Structure and magnetic properties of Fe88− xZrxB12 (x= 5, 10, 20) alloys prepared by mechanical alloying Journal of Alloys and Compounds 477 529

Hellstern E, Fecht H J, Fu Z, Johnson W L 1989 Structural and thermodynamic properties of heavily mechanically deformed Ru and AlRu Journal of Applied Physics 65 7

Grabias A, Kopcewicz M 1999 Transmission and conversion electron Mössbauer study of crystallization of amorphous FeZrB alloy Acta Physica Polonica A 96 123

Williamson G K, et al. 1953 X-ray line broadening from filed aluminium and wolfram Acta Metall 1 23

Huang J, et al. 1997 Microstructure and nanoscale composition analysis of the mechanical alloying of FexCu100− x (X= 16, 60) alloys Mater. Sci. Forum 725 269

Juárez R, Suñol J J, Berlanga R, Bonastre J, Escoda L 2007 The effects of process control agents on mechanical alloying behavior of a Fe–Zr based alloy Journal of Alloys and Compounds 434 472

Brzózk K, Ślawska Wniewska A, Jezuita K 1996 Mössbauer studies of FeZrB (Cu) amorphous alloys Journal of Magnetism and Magnetic Materials 160 255

Brzózk K, Ślawska-Waniewska A, Nowicki P, Jezuita K 1997 Hyperfine magnetic fields in FeZrB (Cu) alloys Materials Science and Engineering A 228 654

Grabias A, Kopcewicz M 1998 Crystallization of the amorphous Fe81Zr7B12 alloy induced by short time annealing Mater. Sci. Forum 725 269

Unruh K M, Chien C L 1984 Magnetic properties and hyperfine interactions in amorphous Fe-Zr alloys Physical Review B 30(9) 4968