

# Influence of process control agents in the development of a metastable Fe–Zr based alloy

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## Abstract

In this work, a Fe–Zr based alloy prepared by mechanical alloying (MA) was investigated. The balance between cold welding and fracturing is controlled by the addition of a surface additive, a process control agent (PCA). Several PCAs such as hexane, polyethylene glycol, cyclopentane, naphthalene and hexanone were used. The results indicate that PCAs produce considerable effects on the particle size as well as on the structural behavior and thermal stability of the as milled powders, if compared with material synthesized without surfactant. We develop materials with higher thermal stability and disordered structure. Nevertheless, in other samples high crystallite size (>100 nm) was found. Thermal analysis confirms the higher thermal stability of the disordered phase in the sample with hexane and naphthalene as PCA, probably due to C solid solution.

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## 1. Introduction

Mechanical alloying (MA) of multi-component powders is a solid state process capable to obtain metastable structures as amorphous and nanocrystalline materials with high thermal stability [1]. Powder particles in the ball mill are subjected to high-energy collision, which causes the powder particles to be cold-welded together and fractured [2].

A process control agent (PCA) is a surface additive normally used in the milling processes to control the balance between the fracture and welding in order to modify the grain refinement and/or the final structure of the material [3]. In this work we report on the effect and the role of different PCAs on the structural, compositional and thermal evolution of the alloy structure of a FeNiZrB alloy developed by MA. We essay to obtain a more disordered and

thermally stable alloy because FeZr alloys with controlled nanostructure presents higher soft magnetic properties [4].

## 2. Materials and methods

The composition of the alloy is  $\text{Fe}_{70}(\text{Ni}_7\text{Zr}_3)_{15}\text{B}_{15}$  obtained by mixing powder particles of elemental Fe and B with a  $\text{Ni}_7\text{Zr}_3$  compound. The material was milled in a planetary ball mill (Fritsch P7) with Ar atmosphere. Samples are (a) non-PCA, (b) naphthalene, (c) hexane, (d) cyclopentane, (e) hexanone and (f) polyethylene glycol. As much as 3 ml of PCA was added to the powders. The ball to powder weight ratio was 5:1 and the milling was performed at 600 r.p.m.

Morphology evolution was followed by scanning electron spectroscopy (SEM). Contamination analysis from milling tools and PCAs, elemental and chemical analysis was performed by energy dispersive X-ray spectroscopy (EDX), induction coupled plasma spectroscopy (ICP) and chemical analysis. Thermal analysis was performed under Ar atmosphere using a differential scanning calorimeter.

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X-ray diffraction (XRD) patterns were carried out in a D-500 Siemens equipment using Cu  $K_{\alpha}$  radiation.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns obtained for the alloys milled for 80 h. The X-ray diffraction peaks corresponds to the bcc Fe phase. The crystallite size and the lattice strain,  $\epsilon$ , were determined by using the Williamson–Hall analysis. The sample with polyethylene glycol and hexanone presents the larger crystalline size ( $>100$  nm). Only samples milled with hexane and naphthalene presents broader peaks related to a more disordered structure that sample milled without PCA. Their patterns seem to indicate the formation of an amorphous-like or highly disordered structure

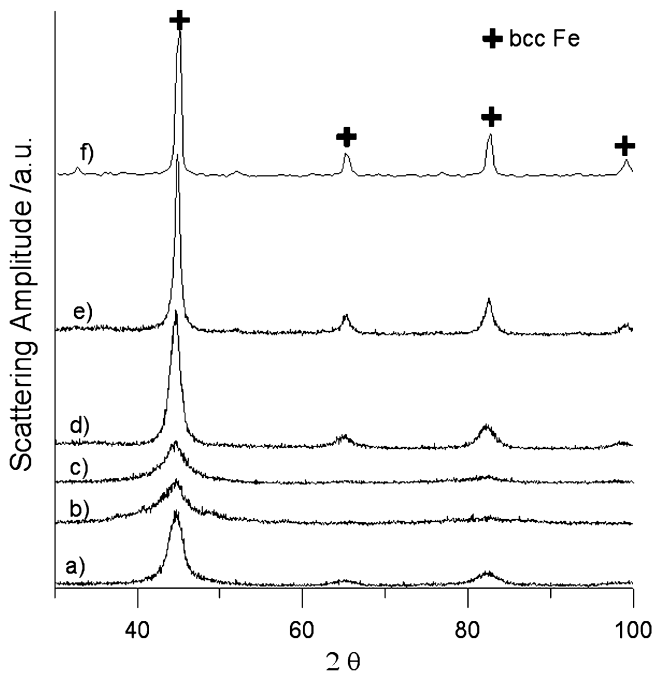


Fig. 1. XRD patterns of samples milled for 80 h.

( $\sim 4$  nm). From XRD analysis we can state that hexanone, cyclopentane and polyethylene glycol are not the most indicated PCA, at least, in the concentration and milling conditions chosen. To analyze if the structure differences can be promoted by the modification of main particle size electronic microscopy was performed. Lower size,  $\sim 2$   $\mu\text{m}$ , corresponds to alloys milled with hexane or naphthalene, see Fig. 2. We can state that samples with lower average particle size have the lower crystallite size. This behavior was found in CoFeZr alloys milled with  $\text{CCl}_4$  [5].

A serious problem in MA process is the potential for significant contamination from the milling media (balls and vial) or atmosphere as well as the formation of non-desired phases as oxides, hydrides, nitrides or carbides [6]. Nevertheless, the EDX and ICP results show only slight ( $<1.5$  at.%) contamination from the solid milling tools (Fe, Ni and Cr) after 40–80 h MA. The hexane and naphthalene samples present lower oxygen (0.8 at.%) contamination if compared with samples milled with other PCA, but significant C content ( $>1.8$  at.%).

As shown in Fig. 3, hexane and non-PCA samples have similar thermal crystallization behavior, two peaks, one at low temperature (near  $380$   $^{\circ}\text{C}$ ) and a main process. This main process is about  $43$   $^{\circ}\text{C}$  displaced to higher temperature in the case of hexane. The sample milled with naphthalene has only one exothermic process beginning at about  $480$   $^{\circ}\text{C}$ . Combination of higher activation energy and crystallization temperature indicates high thermal stability of the metastable structure obtained after milling. The apparent activation energy,  $E$ , for the main crystallization processes of alloy milled 80 h was evaluated using the Kissinger method. The lower values  $2.1 \pm 0.2$  and  $2.5 \pm 0.2$  eV corresponds to alloys with hexanone and PEG, respectively. A high defect of the lattice, the immense magnification of the boundary surface and high diffusion rate leads to low activation energies for the transformation of the structure [7]. The higher value,  $3.7 \pm 0.3$  eV, corresponds to cyclopentane sample. Naphthalene and hexane samples have similar activation energies,  $3.2 \pm 0.2$  eV and  $3.1 \pm 0.2$  eV, close to  $3.1 \pm 0.2$  eV value of sample milled

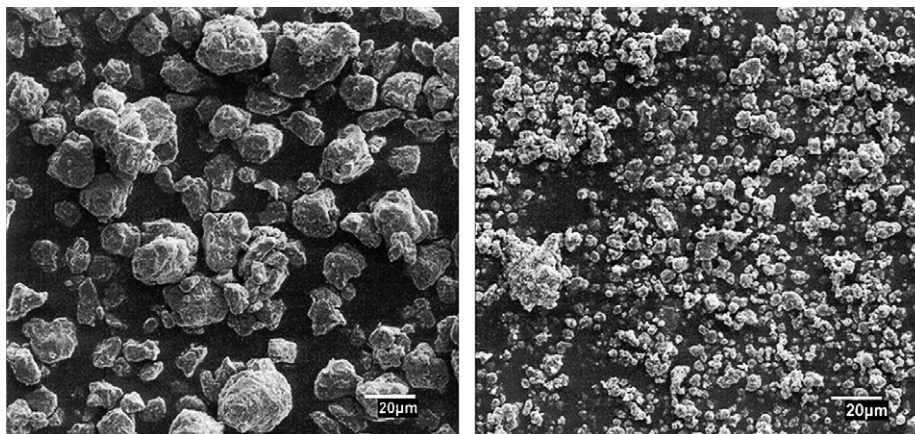


Fig. 2. SEM micrographs of sample milled for 80 h: (left) without PCA, (right) with hexane. Bar:  $20$   $\mu\text{m}$ .

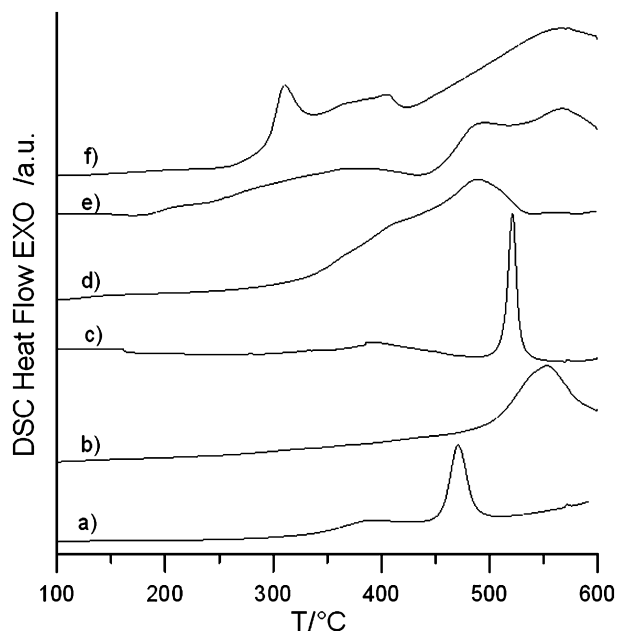


Fig. 3. DSC scans of samples milled for 80 h.

without PCA. From DSC and XRD results, it is clear that better candidates to be compared to sample without PCA are the hexane, naphthalene and cyclopentane. The results after annealing at 450 °C confirm the higher thermal stability of the disordered phase ( $\sim 4.5$  nm) in the samples with hexane and naphthalene.

It is known that the carbon from the decomposition of an organic PCA as hexane increases the formation of a disordered phase in the Fe–B system by C dissolution in this phase without the formation of crystalline carbide [8].

#### 4. Conclusions

The results indicate that PCAs produce considerable effects on the particle size as well as on the structural behavior of the as milled powders. Furthermore, the thermal stability was modified. The activation energy values range between 2.1 and 3.7 eV. Materials with higher thermal stability of the metastable structure were developed with hexane, cyclopentane or naphthalene, probably due to C solution. Lower crystalline size, at about 4 nm, was found in samples milled with hexane or naphthalene.

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