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CURIE TEMPERATURE IN Fe(Ni)Nb BASED MECHANICALLY ALLOYED MATERIALS

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A conventional thermogravimeter has been adapted with a small magnet to detect the Curie temperature, T_C. The measurements were performed in several Fe(Ni)NbB alloys developed in a nanocrystalline form by mechanical alloying. The B addition favors a slight diminution (10–20ºC), and the Ni addition the existence of three transitions related with bccFe, fcc(Fe–Ni) abd fccNi-rich environments. Furthermore, complementary analysis were performed by means of differential thermal analysis, scanning electron microscopy with energy dispersive X-ray microanalysis and by induced coupled plasma. Small contamination was found. A mass increase (about 1 mass%) was detected by thermogravimetry related to oxidation. Analysis allows us to state the inhomogeneity of the alloys obtained after 80 h of milling.

Keywords: *Curie temperature, Fe–Nb based alloys, mechanical alloying, TG*

Introduction

Developed by Benjamin, mechanical alloying (MA) is an alternative technique for the fabrication of powder particles [1]. MA is a solid-state powder process that represents a non-expensive versatile route able to produce equilibrium as well as non-equilibrium materials including amorphous, nanostructured and extended solid solution systems [2–4]. During mechanical alloying, powder particles are subjected to severe mechanical deformation and are repeatedly deformed, cold-welded and fractured. The resulting fresh surfaces help reaggregation of the powdered components with the formation of new particles, where the elements become stacked in layers, then allowing diffusion of one into the others.

Over the last decades, amorphous and more recently nanocrystalline materials have been investigated for applications in magnetic devices requiring magnetically soft materials [5]. Amorphous Fe–Zr–B and Fe–Nb–B alloys containing α-Fe nanocrystallites with the bcc structure are of interest as a superior soft magnetic materials [6–8].

Furthermore, it is important to measure the Curie temperature that determines the transition from the ferromagnetic to the paramagnetic state. Thermal analysis is an alternative route to detect this characteristic temperature [9–11]. In this paper we describe the thermal behavior of several Fe(Ni)NbB nanocrystalline alloys produced by MA.

Experimental

Mechanical alloying was carried out in a planetary high-energy ball mill (Fritsch Pulverisette P7) starting from pure element and compound powders (Fe of 99.7% purity, with a particle size under 10 μm; Nb of 99.85% purity, with a particle size under 74 μm; B of 99.6% purity, with a particle size 50 μm and Ni of 99.8% purity, with a particle size under 7 μm). The compositions analyzed in this article were $Fe_{85}Nb_6B_9$, $Fe_{80}Nb_6B_{14}$ and $Fe_{65}Ni_{20}Nb_6B_9$, labeled as A, B and C, respectively. Each of the powder samples was loaded into a cylindrical Cr–Ni stainless-steel vial together with balls of the same material in an argon atmosphere. The balls to powder ratio was 5:1. The milling process was performed at a speed of 600 rpm for 10, 20, 40 and 80 h.

The sample thermal characterization was carried out by thermogravimetry (TG) and differential thermal analysis (DTA) under an argon atmosphere in a TGA851-SDTA Mettler Toledo equipment. The evolution of the magnetic interaction with the milling time was evaluated by means the Curie temperature, T_C. The thermogravimeter equipped with a small permanent magnet was used for the thermomagnetometry measurements. The morphology and composition study was performed by scanning electron microscopy (SEM) in a DSM960 A Zeiss equipment with energy dispersive X-ray microanalysis (EDX) and by induced coupled plasma (ICP) in a Liberty-RL ICP Varian equipment. Furthermore, wavelength dispersive spectroscopy (WDS) analysis was used to check the homogeneity of the alloy.

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Results and discussion

By means of apparent mass thermomagnetic curves, TM, the ferromagnetic to paramagnetic transition can be observed as an apparent mass increase. The magnet was kept in the same position as much as possible, in order to the magnetic field gradient affecting the samples becomes the same in the standard TG apparatus. The first experiments were performed with Fe, Co and Ni. It is known that temperature for a TG apparatus can be calibrated by means of the Curie temperatures of known ferromagnetic materials [12].

Figure 1 shows the TM curve, of alloy A milled for 80 h. To determine the Curie temperature the first derivative, DTM curve, was used, and its maximum was used as T_C value. In this case, the magnetic transition associate to the iron magnetic transformation was found at 759.9ºC. Furthermore, the asymmetry of the shape in the DTM curve indicates inhomogeneity in the alloy. A general view of a thermogravimetry curve is given in Fig. 2, corresponding to alloy B milled for 10 h. The main process, at 757.8ºC, is associated with the iron rich environments. The minor effect detected at about 580ºC is related with the iron oxide, Fe_2O_3, magnetic transition. The contamination was measured by EDX and ICP and increases with the milling time. Nevertheless, the results show only slight (<1.0 at%) contamination from the milling tools (Fe, Ni and Cr) after 80 h MA. Furthermore, several microanalysis were performed and the oxygen presence detected was <2 at% and related with surface oxidation favored by the high specific surface of powdered alloys [13]. Similar results were found in Fe based alloys with similar composition [14].

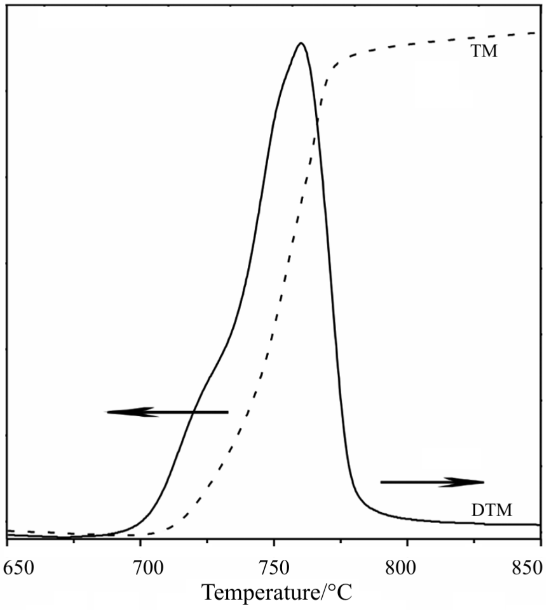

Fig. 1 Thermomagnetic apparent mass, TM, and their derivate, DTM, curves of alloy $Fe_{85}Nb_6B_9$ milled for 80 h

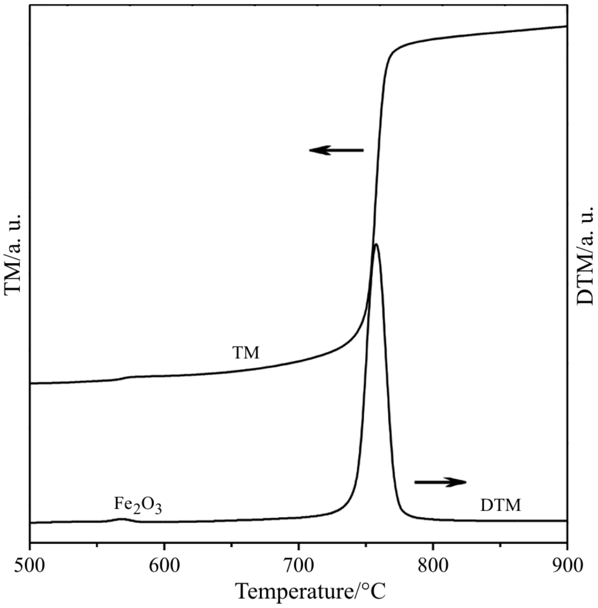

Fig. 2 Thermomagnetic apparent mass, TM, and their derivate, DTM, curves of alloy $Fe_{80}Nb_6B_{14}$ milled for 10 h

In alloy with Ni the recorded experiments are more complex. As an example, Fig. 3 shows the curves associated with alloy C after 10 h of milling. The main process presents a maximum in the DTM curve at 749.9ºC and corresponds to iron rich environments. The asymmetric shape as well as the diminution of T_C it is associated to the introduction of Ni by solid solution in the bcc iron. The intermediate temperature process, at about 570ºC, corresponds to the magnetic transition of fcc(Ni,Fe) and the low temperature process, at about 354ºC to the fccNi-rich phase [15]. The thermal evolution of samples has been followed with simultaneous DTA. The thermal event beginning around 200ºC is related to structural relaxation or recovery of stresses induced in the milling process. Also, several exothermic processes appear in the DTA curve in between 400 and 750ºC. These processes are overlapped in temperature and can correspond to the crystalline growth, as detected in alloys with similar composition by X-ray diffraction [16]. Complementary structural analysis of the as annealed milled powders performed by X-ray diffraction is needed to confirm it. The broadening of both exothermic processes suggests a broader grain size distribution of nanocrystals. The peak over 800ºC probably corresponds to a secondary crystallization. This behavior was also found in Fe–M–B (*M*=Zr, Hf or Nb) alloys [17].

Figure 4 shows the evolution of T_C as a function of milling time. In alloys without Ni, as increasing the milling time the Curie temperature decreases between

10 and 20ºC. As increasing/decreasing the Nb/Fe content the T_C value is lower, probably due to the disorder favored by B addition in this kind of alloys. The alloy C presents a T_C value around 670ºC associated with Ni in solid solution (about 20 at%) [15]. The Curie transition of fccNi cannot be clearly measured at 40 h of milling.

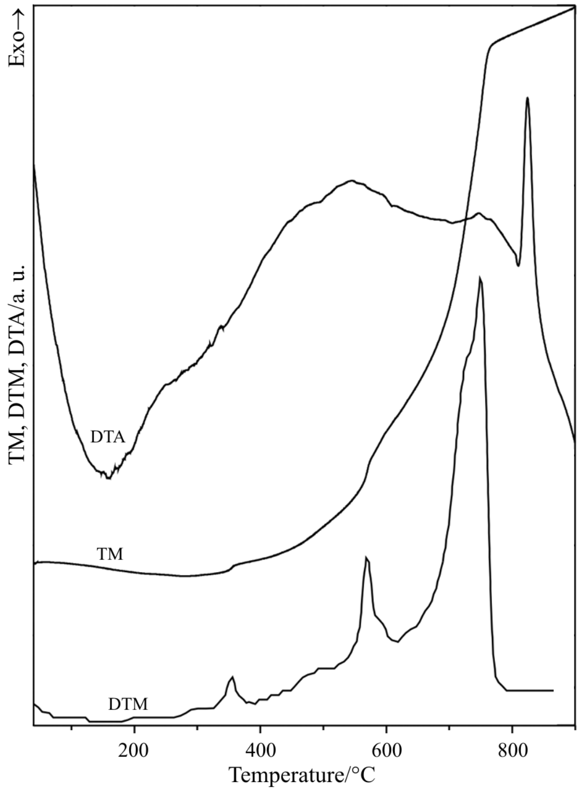

Fig. 3 Thermomagnetic apparent mass, TM, their derivate, DTM, and DTA curves of alloy $Fe_{65}Ni_{20}Nb_9B_6$ milled for 10 h

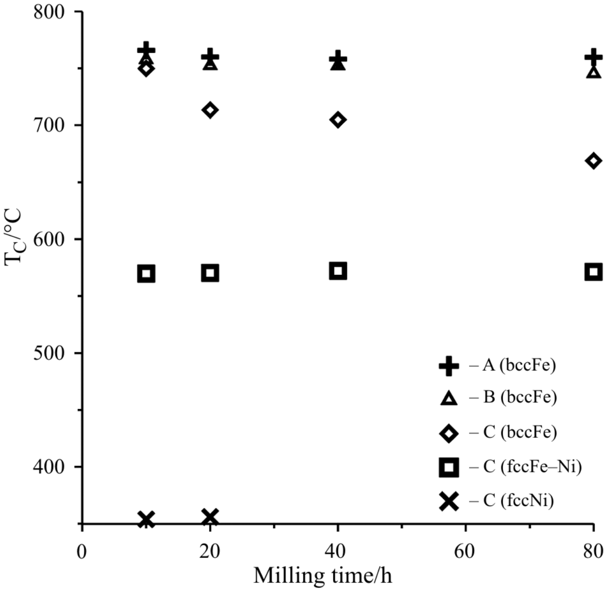

Fig. 4 Curie temperature as a function of the milling time

Furthermore, usual thermogravimetry analysis was performed on the samples without the magnet. Data were collected during heating at 20 K min^{-1} under flowing Ar. TG shows a slight increase (<1.0 at%) of the mass when the samples were heated. The mass gain is associated with a small oxidation of the alloy. It was found that the superficial oxidation occurs gradually through most of the temperature range. This minor effect can be substracted from the thermomagnetic analysis performed on the samples. Similar behavior was found in Fe–Cu alloys obtained by mechanical alloying [18].

The morphology of the powders was followed by scanning electron microscopy. As an example, Fig. 5

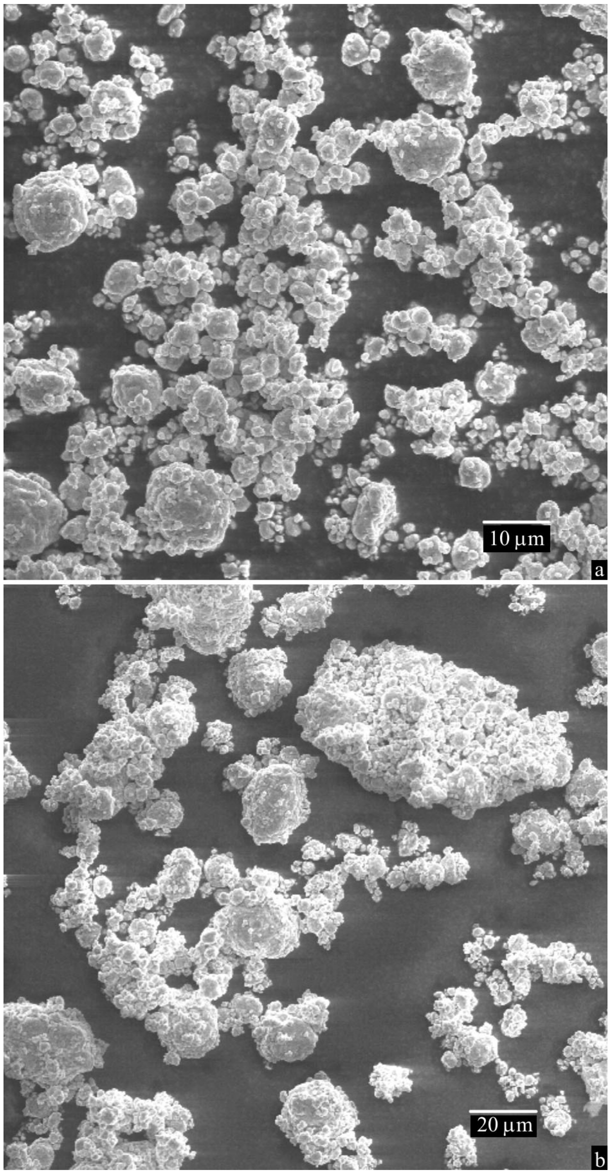

Fig. 5 SEM micrographs of alloys a – $Fe_{85}Nb_6B_9$ and b – $Fe_{80}Nb_6B_{14}$ milled for 80 h

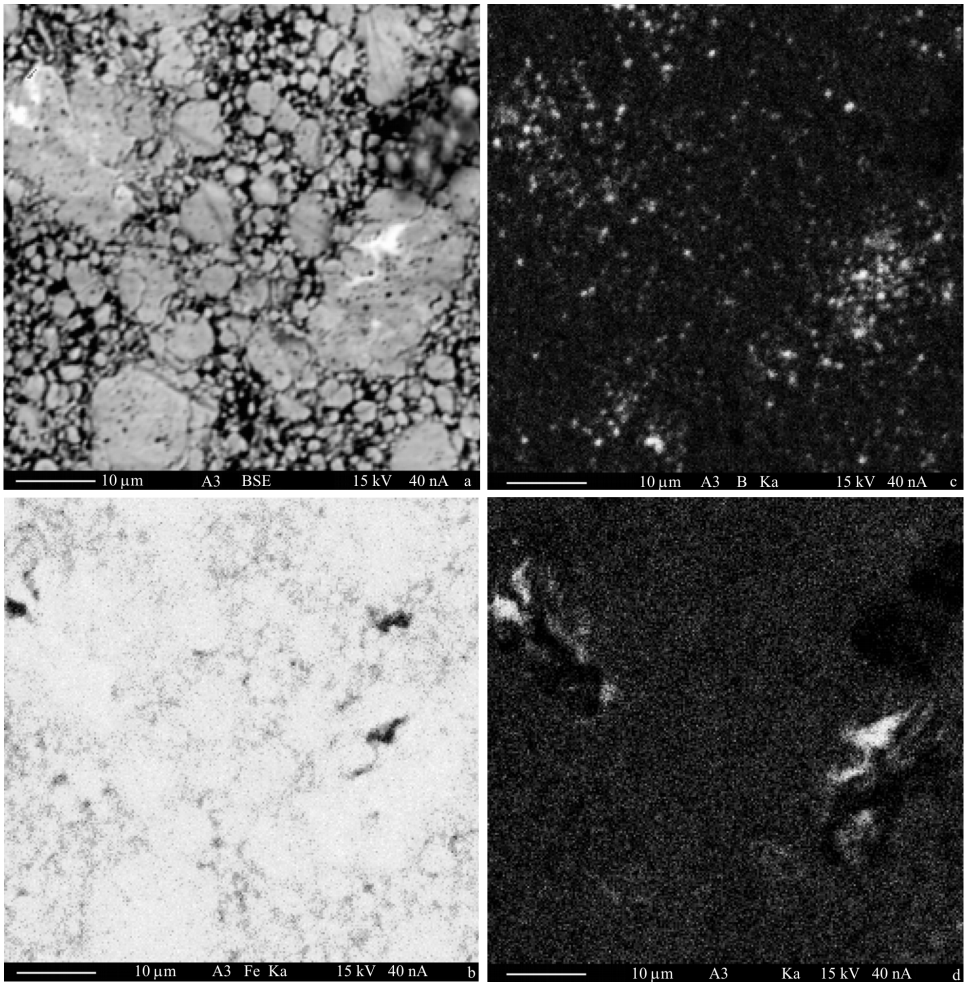

Fig. 6 Wavelength dispersive spectroscopy images of a – alloy A milled for 80 h, and b – the corresponding Fe, c – B and d – Nb zones

shows the micrographs that corresponds to alloys A and B after 80 h of milling. Furthermore, powders were prepared in a metallographic way to be observed by wavelength dispersive spectroscopy. The WDS images of Fe, B and Nb are given in Fig. 6 for alloy A milled for 80 h. The result allows us to state the inhomogeneity of the alloys, as confirmed by TM measurements. In mechanically alloyed samples, to obtain a more homogeneous alloy sometimes is needed to increase the milling time [19].

Conclusions

Three alloys: $Fe_{85}Nb_6B_9$, $Fe_{80}Nb_6B_{14}$ and $Fe_{65}Ni_{20}Nb_6B_9$ were produced in a nanocrystalline form by mechanical alloying. The thermogravimeter was adapted to measure the Curie temperature. Their correct determination is important in ferromagnetic iron based alloys because determines the transition from the ferromagnetic behavior to the paramagnetic state. As increasing the B content the T_C value of bccFe-rich phase decreases (10–20ºC), probably due to the disorder favored by B addition. The alloy with Ni presents a T_C value around 670ºC at 80 h milling associated with Ni in solid solution (about 20 at%) in the bccFe-rich phase. The processes at about 570 and 354ºC corresponds to the magnetic transition of fcc(Ni,Fe) and the fccNi-rich phase respectively the last one clearly measured only at low milling times. The Curie transition of fccNi cannot be clearly measured after 40 h of milling.

The wavelength dispersive spectroscopy images and the thermomagnetic measurements confirm the inhomogeneity of the alloys.

Furthermore, a thermally induced oxidation was detected by thermogravimetry and slight contamination was found by microanalysis and by ICP. Thermal measurements show several exothermic processes related to structural relaxation and crystalline grain growth.

Acknowledgements

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