Magnetic study of Fe$_{65}$Ni$_{20}$Nb$_6$B$_9$ nanocomposite alloys

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Abstract

The alloy Fe$_{65}$Ni$_{20}$Nb$_6$B$_9$ was obtained from the elemental constituents in a high-energy planetary ball mill and subsequently thermally treated at 873 and 900 K in order to obtain the equilibrium phases. The as-prepared nanocrystalline alloy consists primarily of metastable BCC $\gamma$-Fe(Ni) nanocrystals while the treated ones consist of a mixture of BCC (ferromagnetic) and FCC (paramagnetic at room temperature) phases. Hysteresis loops at 5 and 300 K present low remanence and coercivity. As-prepared sample exhibits the best soft magnetic properties. In all samples, the susceptibility curves suggest magnetic collective (long-range order) behavior with a maximum between 70 and 90 K. This feature is caused by nanometric-sized magnetic particles. The huge difference between blocking and irreversibility temperatures in the field cooling and zero-field cooling scans indicates a wide grain-size distribution.

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Keywords: Mechanical alloying; $\gamma\rightarrow\gamma$ FeNi transition; Mössbauer spectroscopy

1. Introduction

The procedure of quenching and subsequent annealing is a basic approach to control the microstructure of materials and thereby to achieve the optimum physical properties for the final product. Mechanical alloying is a suitable solid-state technique by which novel materials may be synthesized from elemental or prealloyed powders. Both methods enable the preparation of systems consisting of magnetic nanocrystals embedded in a magnetic or non-magnetic amorphous matrix. Based on the well-known ductility and soft magnetic properties of Ni–Fe alloys [1], this work investigates the thermally induced transformation of Fe$_{65}$Ni$_{20}$Nb$_6$B$_9$ disordered materials obtained from the elemental powders in a high-energy planetary ball mill. The aim of this article is to present the magnetic characterization of the as-prepared and thermal treated (873 and 900 K)
samples and discuss it on the basis of their composition, structure and microstructure.

2. Experimental

The sample preparation was described elsewhere [2]. Mössbauer effect (ME) spectra were recorded in transmission geometry using a conventional constant acceleration spectrometer with a 30 mCi $^{57}$Co(Rh) source at room temperature (RT). The magnetic measurements were performed using a superconducting quantum interference device (SQUID), zero-field cooling (ZFC) and field cooling (FC) scans with a maximum applied field of 5 T and hysteresis loops at 5 and 300 K with a maximum applied field of 20 Oe, at UNICAMP, Brazil. AC susceptibility measurements were carried out in a LakeShore 7130 susceptometer at temperatures from 13 to 325 K and frequencies from 5 to 9920 Hz at UNLP, Argentina. To avoid nonlinear magnetization effects a low enough field $H_{AC} = 1$ Oe was used.

3. Results and discussion

Fig. 1 plots the RT Mössbauer spectra corresponding to as-prepared and thermally treated (TT) at 873 and 900 K samples. The Mössbauer spectrum of the as-prepared alloy shows a magnetically split pattern with six broad lines. It was fitted with three magnetic distributions each one described with a Voigtian function (a Gaussian distribution of Lorentzian absorption line). Each contribution was related to Fe in different environments, the two components with higher hyperfine magnetic field ($B \sim 34$ T) are mainly associated with iron in a BCC-Fe(Ni) [3]. The other one ($B \sim 28$ T) is tentatively ascribed to atoms probe in a probably BCC disorder matrix containing B and Nb [4] and/or to a FCC-Fe$_{65}$Ni$_{35}$ phase [3]. Diffractograms are consistent with about 80% of the material in the BCC structure and 20% in the FCC one, both showing signs of structural and chemical disorder. A spectrum taken at 673 K [2] displays an important paramagnetic contribution which disappears when the sample returns to room temperature. It was ascribed to the FCC phase which must have a Ni concentration above 33% [5] to account for its ordering temperature well above RT. A small fraction of a paramagnetic contribution (approximately 3%) is required to improve the theoretical fits, this contribution could be associated with atoms probes in a Fe-rich FCC-Fe(Ni) phase. The spectra obtained after the thermal treatments at 873 and 900 K are similar. An important contribution (~40%) appears in the central part of them, consistent with the development and Fe enrichment of the FCC phase resulting in a composition with less than 32 at% of Ni [2]. The relative fraction of this phase may be underestimated because of ME saturation effects, expected for optimal thickness absorbers when spectra concentrate in a narrow velocity range. This Fe-rich FCC phase orders antiferromagnetically with a Néel temperature of approximately 20–25 K [6]. Two magnetic contributions, with BCC structure and composition different from the precursor one, remain (60%).

The ZFC and FC magnetization curves are shown in Fig. 2. A noticeable feature is the huge difference between blocking temperature and irreversibility temperatures indicating a wide grain size distribution. The decrease of this difference with the annealing temperature and the shift of the irreversible temperature to lower values indicate a
reduction of the grain size distribution \[7\]. Evidence of the grain growth appears from comparison of the maximum of FC magnetization for the 873 and 900 K treated samples. The difference \(D_M(4 K) = M_{FC}(4 K) - M_{ZFC}(4 K)\) is larger for the treated samples (especially for the treated at 873 K) than for the as-prepared one. This fact may be associated to the development of antiferromagnetic FCC-Fe(Ni) and to its coupling to the ferromagnetic BCC phase. Then the antiferromagnetic clusters would pin the ferromagnetic ones causing them to have lower magnetization values for the same applied field. Within this frame, the sudden diminution of the ZFC magnetization signal around 25 K may be ascribed to the antiferromagnetic transition temperature of FCC-phase.

The hysteresis loops (Fig. 3) were reproduced using an empirical-fitting function \[8\] usually employed for ferromagnetic phases. The samples present hysteretic behavior indicating the presence of ferromagnetic particles. The coercivity values at 5 K were 35.4, 143.6 and 161.8 (10^{-4} T) for as-prepared, 873 and 900 K treated samples, respectively. At 300 K, lower values were obtained than those recorded at 5 K, as expected due to thermal agitation. Saturation magnetization fitted values at 5 K were 174.6, 108.7 and 105.7 emu/g, respectively. The values obtained at 300 K for as-prepared and annealed samples were 11% and 27% lower than the 5 K ones, respectively. The much larger decrease of \(M_{sat}\) (for the treated samples) with \(T\) suggests that a fraction of these samples undergoes a ferro to paramagnetic (or superparamagnetic) transition in this temperature interval. The as-prepared sample shows the best soft magnetic properties.

AC-susceptibility curves corresponding to 873 and 900 K treated samples show broad maximum with low-frequency sensitivity. This indicates the existence of strong interactions between magnetic particles suggesting a magnetic collective (long-range order) behavior at mean temperatures below approximately 80 K. Curves of the sample treated at 873 K, measured between 25 and 300 K using different frequencies, are presented in Fig. 4.

4. Conclusions

Fe_{65}Ni_{20}Nb_{6}B_{9} mechanically alloyed consists mainly of BCC and FCC-(Fe,Ni) phases, both showing chemical disorder. The ZFC and FC magnetization curves reveal a wide grain-size distribution that narrows with thermal annealing. Antiferromagnetic FCC phase, with less than 32 at% of Ni, was obtained after thermal treatments, this phase pins the ferromagnetic one, preventing it to reach the maximum magnetization value for 20 Oe applied field. The FCC-(Fe,Ni)
phase (Ni at% less than 32) displays a Neel temperature of about 25 K. The presence of this antiferromagnetic phase lowers the saturation magnetization at RT. The existence of strong interactions between magnetic particles was observed for temperatures below 80 K.

**Acknowledgements**

Partial support from CONICET, UNLP, FA-PESP and CAPES are acknowledged. The authors like to thanks Dr. Suñol for preparing the samples.

**References**