

ANALYSIS OF THE MECHANICALLY ALLOYED Fe₈₅Nb₅B₁₀ POWDER USING A NON UNIQUE LATTICE PARAMETER

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Abstract

X-ray diffraction patterns of mechanically alloyed Fe₈₅Nb₅B₁₀ powder were fitted using whole powder pattern decomposition procedure. A distribution of lattice parameters was proposed based on the asymmetry of the diffraction maxima and the broadening of the distribution of the powder particles composition. Analogously, a set of discrete sextets was used to represent the different local Fe environments.

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Nanocrystalline materials are defined by a crystal size below 100 nm. These materials have received much attention due to their physical (mechanical and magnetic) properties, which are clearly different from those exhibited by conventional microstructures and, in some cases, improve their technological applicability [1].

Mechanical alloying has become a very versatile technique used for direct production of metastable microstructures (amorphous, nanocrystalline, supersaturate solid solutions, etc) from elemental powders or alloys [1]. During milling process, the material is submitted to fracture and cold welding, as well as intensive plastic deformation, which define the powder morphology, microstructure and properties. The continuous storing of defects in crystalline phases during milling destabilizes them, leading to creation of nanocrystalline and/or amorphous structures.

In this work, the nanocrystalline microstructure of Fe₈₅Nb₅B₁₀ alloy developed through ball milling is studied. This composition was prepared in a shaker mill (Spex-8000) from elemental powders under argon atmosphere. The initial powder mass was 10 g and the ball-to-powder ratio was 12:1. After selected times, some powder was taken out from the vials to characterize the composition and microstructure by energy dispersive X-ray (EDX) spectrometry, X-ray diffraction (XRD), using Cu K α radiation, and Mössbauer spectrometry (MS) in a transmission geometry using a ⁵⁷Co(Rh) source. Values of the hyperfine parameters were obtained by fitting with NORMOS program [2].

1. Results

Before 15 h milling, the dispersion in the Fe content from EDX, Δ_{Fe} , continuously decreases down to 6 at.%, achieving a stationary value. XRD patterns show that diffraction peaks of bcc Nb phase gradually disappear with the milling time up to 10 h. Moreover, a strong displacement of the (110) diffraction peak of α -Fe towards lower 2θ values is evidenced, along with an increase of its full width at half maximum, FWHM, (from 0.50 to 0.96°) for milling times $t \leq 10$ h. For longer milling times (up to 40 h) FWHM increases.

The evolution of Δ_{Fe} is similar to that found in other milling studies [3], decreasing with t . Its final value can be ascribed to the presence of crystallites with a certain range of compositions. Based on this fact and on the asymmetry observed in the (110) diffraction peak of α -Fe phase, a distribution of lattice parameter, a , from $a = 2.866 \text{ \AA}$ (pure α -Fe) to 2.896 \AA , with a step of 0.01 \AA is proposed to fit the XRD patterns using the Pawley method [4] (Figure 1a). For $t = 3$ h only one contribution was necessary to fit the pattern, whereas, after 6 h milling, a second contribution is needed. The average lattice parameter, $\langle a \rangle$, matches that from the position of the (110) α -Fe, a_{exp} . For $t \geq 10$ h, the difference between the two lattice parameters used remains constant, in agreement with EDX results, where Δ_{Fe} remains constant after 10 h milling.

MS spectrum after 3 h milling was fitted using a single ferromagnetic site with hyperfine field, $HF = 33 \text{ T}$, of pure α -Fe (in agreement with the single pure α -Fe contribution found

from XRD), with absorption line width of 0.30 mm/s. For longer times, a broadening of the absorption lines is observed in the spectra and new sites with $HF < 33$ T appear. These new sites are related to the presence of Nb and B inside the crystals, in agreement with the distribution of lattice parameter proposed. In order to reduce the 1260 possible configurations (considering the first and second coordination shells), only Nb neighbors influence on hyperfine magnetic field of Fe were used. The Nb effect as nearest or next nearest neighbour has been assumed the same, taking the average over the reported values [5]. Consequently, the absorption lines of the used sextets become wider. Therefore, the values of HF used were 33, ~31, ~27 and ~13 T, from 0 to 3 Nb neighbors, respectively. These values agree with those for up to 2 Nb neighbors [5], but for 3 Nb neighbors linearity is lost. This also occurs for Si [6], Ga [7] and Ge [8].

2. Discussion

For each contribution used to fit the XRD patterns, the crystal size, D , and the microstrain, ε , were calculated (Fig. 1b and 1c, respectively). For the contribution with $a = 2.866$ Å (pure α -Fe), D decreases with t down to 13 nm. For larger a contributions, D is always lower than 15 nm. After $t = 40$ h, D is 7 nm for both contributions. On the other hand, ε increases for every a contribution with the milling time, being lower than 2 % after $t = 40$ h. It is worth mentioning that the values of D and ε from the fit are coherent with the approximation of a

minimum crystal size, D_{min} , and maximum microstrain, ε_{max} , considering every effect as the only responsible of the broad of diffraction peak [9].

From area fraction of the site within 33 T (pure α -Fe environments), A_{33} , it is possible to estimate the Nb content into the Fe crystals, C_{Nb} . The probability of 0 Nb neighbors is:

$$P_0 = (1 - C_{Nb})^{14}, \text{ where } C_{Nb} \text{ is the Nb concentration in the set of 14 atoms surrounding a Fe}$$

atom. The relationship between P_0 and A_{33} is: $P_0 = A_{33} \left[1 + \frac{2\delta}{D} \right]^3$, where $\delta \sim 0.5$ nm [10] is

the interface thickness.

Figure 2a shows C_{Nb} as a function of milling time. C_{Nb} increases with t up to ~ 3 at.% for $t = 10$ h and for longer t , it remains constant (in agreement with the stability of Δ_{Fe} and $\langle a \rangle$). This amount of Nb into bcc Fe agrees with those reported in other Fe-Nb ball milled compositions [5,11].

Figure 2b shows the average hyperfine magnetic field, $\langle HF \rangle$, obtained after fitting using the sextets described above, along with the value obtained using a distribution of hyperfine fields from 0 to 36 T. Both curves show the same behaviour, which supports the previous description of the Fe environment. Contributions with more than 3 Nb as neighbors were not found, in agreement with their low probability for the calculated C_{Nb} (< 0.001).

In conclusion, no significant changes between the microstrain of the different bcc Fe contributions and ε_{max} were found. D_{min} is slightly below D values of the individual

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contributions and those of non pure Fe contributions are always below 15 nm. The maximum amount of Nb inside the nanocrystals has been estimated ~3 at.%.

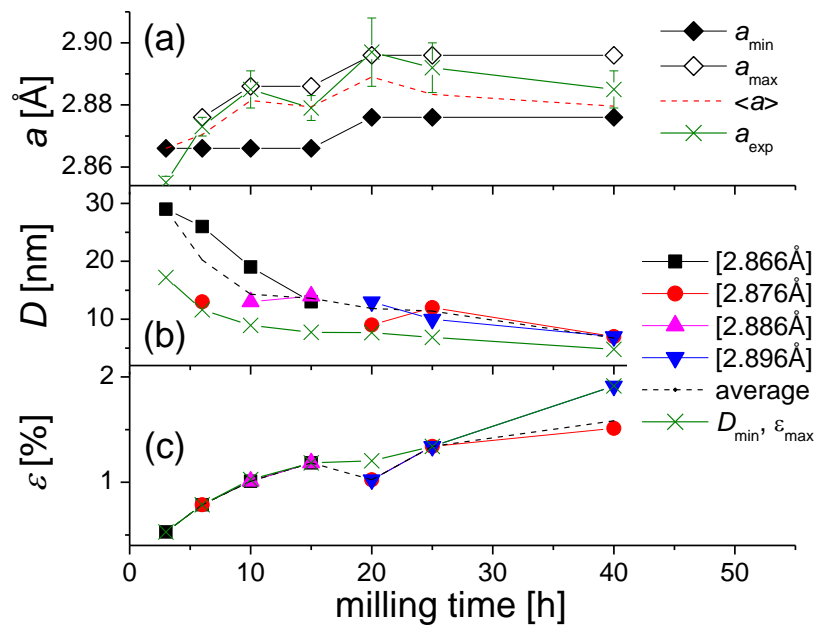
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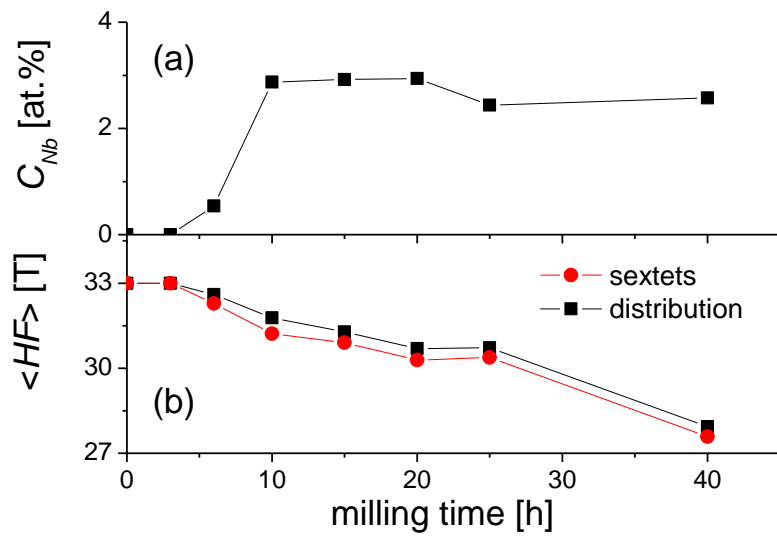
Figure captions

Figure 1. (a) Lattice parameter, (b) crystal size and (c) microstrain vs. milling time.

Figure 2. (a) Nb content in the Fe crystallites and (b) average hyperfine field vs. milling time.

Figure 1





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