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Structure and soft magnetic properties of FINEMET type alloys: $Fe_{73.5}Si_{13.5}Nb_{3-x}Mo_xB_9Cu_1$ ($x = 1.5, 2$)

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Abstract FINEMET type ribbons ($Fe_{73.5}Si_{13.5}Nb_{3-x}Mo_xB_9Cu_1$, x = 1.5, 2 at.%) were produced by the planar flow casting technique and subsequently heat treated at 823 K to induce nanocrystallization and to optimize its soft magnetic properties. The coercivity, measured by conventional fluxmetric method, resulted in $H_C = 0.53 \pm 0.10$ and 0.41 ± 0.05 A/m for $x = 1.5$ and 2 respectively. A correlation between magnetic properties and the amorphous and nanocrystalline phases when Nb was partially substituted with Mo was studied by means of Mössbauer spectroscopy and X-ray diffraction.

Keywords Nanocrystalline alloys · Substitution · Structure · Magnetic properties

1 Introduction

There has been a great effort in the past decades on the development of new soft magnetic materials for their technological application such as transformer cores, inductive devices, magnetic shielding, sensors, etc. [1]. In 1988 Yoshizawa et al. [2] reported FINEMET ($Fe_{73.5}Si_{13.5}Nb_3B_9Cu_1$), a nanocrystalline ferromagnetic material, i.e. FeSi nanocrystals (grain size d = 10–20 nm) embedded in a ferromagnetic

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amorphous matrix. Since then, numerous works on this type of alloys have been published in order to improve and understand their magnetic properties. The amorphous structure is achieved through a rapid solidification technique. Then, the alloy is annealed and the nanocrystallization takes place: Cu acts as nucleation centres and Nb controls grain growth.

Good soft magnetic properties can also be obtained by replacing Nb by another refractory metal such as Mo, Ta and W [2]. However, it was said [3] that Nb is the most preferable element to improve the soft magnetic properties and it seems to be related to the fact that it is the most effective element for decreasing d: for small grains ($d < 40$ nm) coercivity, H_C, is proportional to d^6 [4].

Numerous researchers have investigated the effects on the magnetic properties and structure of the total [3] or partial [4–8] substitution of Nb and/or Fe by other refractory metals on FINEMET-like alloys. These are some of the achieved conclusions from the latter:

1. When 2% of the Nb content was replaced by another refractory element:
   - Crystalline volume fraction: Nb = Ta < Mo < V [5, 6].
   - Nanocrystals Si content: V < Nb < Mo [6].
   - Crystallization temperature: Nb = Ta < W < Mo < V [5].
   - d: Nb = Ta < W < Mo < V [5, 6].
   - H_C: the results depended not only on the refractory metal substitution, but also on Fe/Si/B ratios and annealing temperatures [5, 6].
2. When Nb was gradually replaced by Mo:
   - Nanocrystals Si content: There was an increase of Si content while partially replacing Nb with Mo [7].
   - Crystallization temperature: decreased when increasing Mo content [8].
   - d: with the exception of the 3 at.% Mo alloy, which exhibited a ∼30% larger d, the partial substitution of Mo by Nb slightly increased d [7, 8].
   - H_C: alloys containing Nb generally exhibited much lower coercivities than the 3 at.% Mo alloy. The lowest H_C was developed in the alloy with mixed refractory metals [7]. On the other hand, a different result was obtained in a FINEMET-like composition [8] where H_C increased with Mo concentration.

In sum, the former statement that the best magnetic properties are achieved in FINEMETs using Nb as refractory element is not so straight forward: for some still unknown reason and although there are some discrepancies in the results, better properties can be attained with a partial substitution of Nb, i.e. mixed refractory elements. In this work, we looked for a further comprehension of the influence of Nb partial substitution by Mo, complementing X-ray diffraction (XRD) and magnetic measurements with Mössbauer spectroscopy (MS). Results were compared to typical FINEMET ($Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$, called from now on Mo0) previously reported [9].

2 Experimental

FINEMET type ribbons 10 mm wide and 20 μm thick of compositions $x = 1.5$ and 2 (Mo1.5 and Mo2 respectively) were produced by the planar flow casting technique in

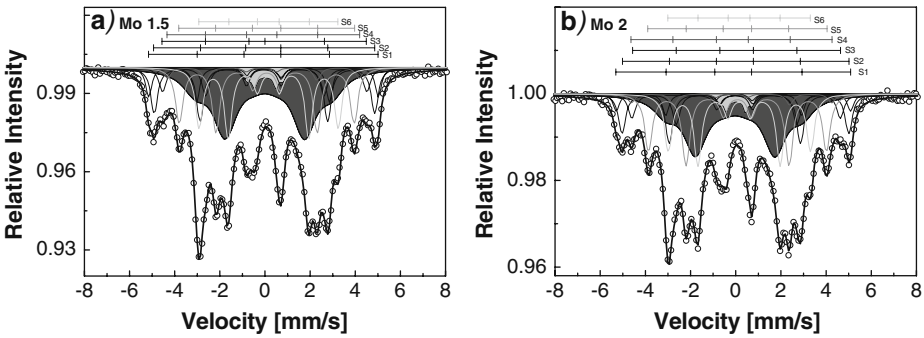

Fig. 1 Mössbauer spectra and fitting for annealed samples: **a** Mo1.5 and **b** Mo2. *Shaded* subspectra represent amorphous phases (*dark grey* Am1, *light grey* Am2), while the *lines* (S1–S6) correspond to crystalline sites

air. The amorphous structure was checked on both sides by XRD and the chemical composition by inductively coupled plasma spectroscopy. Nanocrystallization was induced through annealing in vacuum at 823 K for 1 h.

The structure of the annealed samples was analysed by XRD and MS at room temperature. XRD was performed using a Rigaku Geiger Flex D-Max II TC diffractometer. All scans were run at 40 kV/20 mA with monochromatic radiation Cu K_α (1.5418 Å) and Ni filter. MS was carried out in transmission geometry using a constant acceleration drive and a ^{57}Co in Rh source. The calibration was done with an α-Fe foil and isomer shifts (IS) are given relative to α-Fe. The spectra were fitted using the NORMOS programme [10] considering six sextets for the different crystalline sites of Fe atoms in a Fe_3Si non-stoichiometric DO_3 structure (S1 to S6) and two wide sextets for fitting the subspectra corresponding to the amorphous phase (Am1 and Am2) [9].

Hysteresis loops were obtained using a quasistatic fluxmetric method by applying a longitudinal magnetic field on the sample ($H_{max} = 740$ A/m).

3 Results and discussion

Mo1.5 and Mo2 Mössbauer spectra were very similar to each other (Fig. 1) and even to that of Mo0 alloy. As an example, some hyperfine parameters obtained from the fitting of Mo2 sample spectrum are shown in Table 1. The greatest difference found was between the areas corresponding to crystalline and amorphous sites: the resonant area relative to the amorphous phase decreased with increasing Mo content. Another difference was related to the chemical composition of the nanocrystals when compared Mo1.5 and Mo2 to the Mo0 alloy: the Si content of the crystalline phase was obtained from the probability of occurrence of each kind of Fe environment (S1 to S4, S5 and S6) using a binomial distribution [11]. Our results indicated a Si % of about 20.5 ± 0.3 for Mo1.5 and Mo2 (see Table 2), showing a higher Si concentration than Mo0 (∼19%). This trend was in agreement with the decrease in the lattice parameter on Mo containing alloys obtained in [7]. Likewise, we also obtained from XRD a nanograins lattice parameter of 2.834 ± 0.001 Å for both

Table 1 Parameters obtained from the Mössbauer spectrum fitting for annealed Mo2

Subspectrum	IS (mm/s)	BHF (T)	Area (%)
S1	0.01 (1)	32.14 (9)	4.8 (2)
S2	0.081 (5)	31.09 (4)	12.4 (2)
S3	0.137 (9)	28.74 (8)	7.4 (2)
S4	−0.01 (2)	27.4 (2)	3.7 (2)
S5	0.187 (4)	24.39 (3)	19.5 (2)
S6	0.264 (4)	19.51 (3)	19.0 (2)
Am1	0.05 (1)	18.7 (1)	30.6 (3)
Am2	0.11 (1)	4.5 (1)	2.6 (1)

The numbers in parentheses are the statistical errors in the last digit
IS isomer shift, *BHF* hyperfine magnetic field, *Area* relative resonant Fe area

Table 2 Chemical composition of the crystallites and of the amorphous matrix of Mo0, Mo1.5 and Mo2 (in at.%)

	Mo 0	Mo 1.5	Mo 2
Crystalline fraction	61 (1)	64 (1)	67 (1)
Grains composition			
Fe	81.0 (3)	79.7 (3)	79.5 (3)
Si	19.0 (3)	20.3 (3)	20.5 (3)
Amorphous fraction	39 (2)	36 (2)	33 (2)
Matrix composition			
Fe	62 (2)	63 (2)	62 (2)
Si	5 (2)	2 (1)	0 (1)
Cu	2.4 (1)	2.6 (1)	2.8 (1)
Nb	7.3 (3)	4.0 (1)	2.8 (1)
Mo	–	4.0 (1)	5.7 (2)
B	22.1 (8)	24.0 (9)	26.0 (9)

The numbers in parentheses are the statistical errors in the last digit. Percentages may not add up to 100% because of rounding

alloys, which was in accordance with the Si % values obtained by Mössbauer [12]. By fitting FeSi 110 peak with a Voigt distribution and applying Scherrer formula [13], a mean grain size of 18 ± 1 nm for Mo1.5 and Mo2 was estimated, in agreement with [8].

Knowing the relative fraction of ^{57}Fe in the amorphous and crystalline phases (which could be considered approximately proportional to the resonant area of each phase), the chemical composition of the crystalline phase and the nominal chemical composition of the as-quenched sample, it was possible to estimate the chemical composition of the matrix. These results are enlisted in Table 2 and compared with Mo0. Although there was an increment in the crystalline fraction, the Fe content in the matrix did not vary significantly. This is an important fact in order to maintain a good ferromagnetic intergranular amorphous matrix to ensure the soft magnetic properties. However, on the other hand, there was an increase on the content of B and Nb + Mo in the matrix that could detriment the soft magnetic properties.

Nevertheless, a decrease in H_C with Nb partial replacement was measured: Mo0 (0.58 ± 0.50 A/m) < Mo1.5 (0.53 ± 0.10 A/m) < Mo2 (0.41 ± 0.05 A/m). We associated it to: (1) a decrease of magnetocrystalline anisotropy due to the increase of Si % in the grains and, (2) a reduction on the magnetostriction constant of the alloy when Mo was added [5]. Both factors reduce the effective anisotropy constant $\langle K \rangle$ and consequently increment the soft magnetic properties of the nanocrystalline alloy.

4 Conclusions

A new contribution was made to the comprehension of the FINEMET system with the partial replacement of Nb by Mo. By means of the Mössbauer technique we were able to obtain the crystalline and amorphous mass fractions of nanocrystallized alloys and their chemical composition, as well as to make a correlation with magnetic properties. We noticed an increment on crystalline fraction when Mo content ascended from 1.5% to 2%, possibly related to the decrease of the thermal stability [8]. Nanocrystals Si content was estimated on ∼20.5 for both alloys (error: 0.3%), which represented ∼1% more than in our FINEMET composition alloy (Mo0). The interesting thing was that the increase of Si was attained by the balance of refractory elements whilst keeping Fe, Si and B contents in the alloy constant, as well as the heat treatment.

With respect to the intergranular amorphous matrix, because of the increase on the crystalline fraction, the content of B and Nb + Mo—that could deteriorate the soft magnetic properties of the material—rose, but on the contrary, the Fe content remained nearly the same as in Mo0. Moreover, such adverse effect could be counteracted. Our results and the ones reported in [7] agreed on the decrease of H_C with the partial substitution of Nb by Mo. We explain the good soft magnetic properties in terms of a reduction on the effective anisotropy constant via the decreasing on both, the magnetocrystalline anisotropy of the nanocrystals due to the higher Si content and on the magnetostriction constant. Further work will be made in order to clarify these preliminaries results.

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