STRUCTURAL AND MAGNETIC INVESTIGATION OF MECHANICALLY ALLOYED Fe-M-B (M = Nb, Zr, Hf) POWDERS[*]

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Nanocrystalline $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) alloys consisting of a supersaturated bcc phase and a small amount of amorphous phase were prepared by high-energy ball milling of elemental powders, in argon atmosphere. The structural and magnetic properties are discussed as a function of milling time. The X-ray diffraction patterns show that the $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders, obtained after 250 h of milling, are nanocrystalline with the final crystallite sizes between 8 and 14 nm. An improvement in the magnetic properties of the mechanically alloyed powders, by controlled heat treatments, can be noticed. A comparison between the magnetic properties of the $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) and $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ (FINEMET) mechanically alloyed powders is also reported.

1. Introduction

During the last years, the mechanical alloying technique has been found to be very effective in producing powders with interesting properties. By this tool it is possible to synthesise alloys or composite materials with highly dispersed components, far away from the equilibrium state. Mechanical alloying generates extreme fine grain sizes and has the ability to produce a variety of non-equilibrium phases, ranging from supersaturated solid solutions to nanocrystalline or amorphous phases, thus improving the ductility and providing a better balance of properties in challenging new materials. The development of soft magnetic materials with high saturation magnetization combined with good soft magnetic properties continues to be in demand for high performance and miniaturised magnetic devices such as transformers, inductors, magnetic recording heads and others [1].

The $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) nanocrystalline alloys consisting of a mostly bcc structure exhibit excellent soft magnetic properties combined with the highest saturation magnetization values among the nanocrystalline soft magnetic materials, much higher than those of the representative Fe-Cu-Nb-B-Si nanocrystalline soft magnetic alloy [2]. The nanocrystalline materials in powder shape have the advantage to be compacted to any configuration, being very interesting for the technological applications in which the ribbon and wire shapes are not adequate.

In this work the nanocrystallization process induced by high-energy ball milling of elemental powder mixtures with the overall composition $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) has been studied as a function of milling time. A comparison between the magnetic properties of the as-milled $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders and $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ (FINEMET) mechanically alloyed powders is also reported.

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2. Experimental details

The elemental crystalline Fe, Nb, Hf, Zr and B powders with purity between 99.5 % - 99.9 % and particle sizes under 100 µm, were used as starting materials. Elemental blends with compositions $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) at. % were mechanically alloyed, under purified argon atmosphere, in high energy planetary ball mill, with stainless steel vial and balls. Balls with diameter of 12 mm were used and the ball to powder weight ratio was 5:1. The vial temperature was kept constant during the experiments, by air cooling. A rotational speed of 250 rpm was employed for the processing. At selected times, the milling process was interrupted to avoid excessive warming up of the powder and to extract samples to study the structure by XRD and DTA. The X-ray diffraction patterns were performed by a diffractometer using MoK_α radiation (λ = 0.71069 Å). Separation of the size and strain components of line broadening for the milled powders was accomplished by Warren and Averbach method [3]. The thermal stability of the mechanically alloyed powders was characterised by means of DTA at a heating rate of 10 ^{o}C/min. The magnetic properties of the as-milled and annealed samples were measured by a vibrating sample magnetometer, in an external magnetic field of 14.9 kOe, at room temperature.

3. Results

The X-ray diffraction patterns of the initial mixtures and $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders milled for 250 h are reported in Fig. 1. After 250 h of milling the peaks corresponding to the elemental Nb, Zr and Hf disappear indicating the complete transformation of the initial mixture to nanocrystalline bcc phases with an average grain size depending on composition.
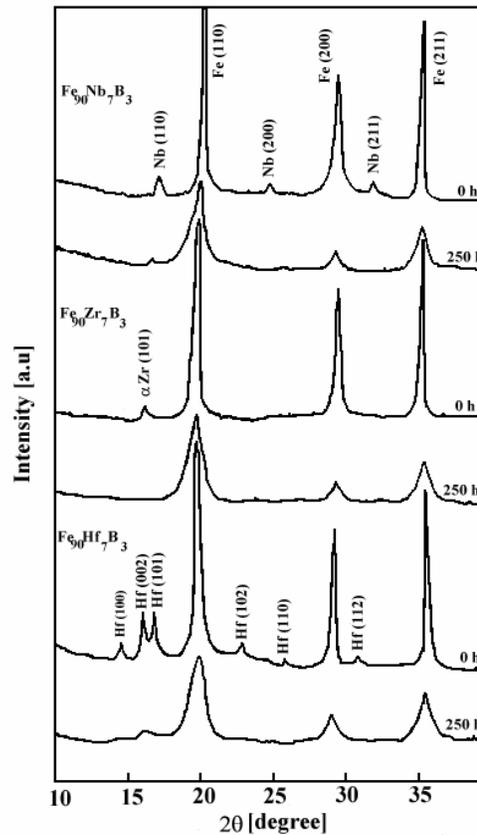

Fig. 1. X-ray diffraction patterns of the initial mixtures and $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders milled for 250 h.

Fig. 2 shows the dependence of the average grain size on the milling time. Within the first 100 h of milling, the grain size rapidly decreases from tens of microns, for the un-milled material, to 25 - 45 nm.
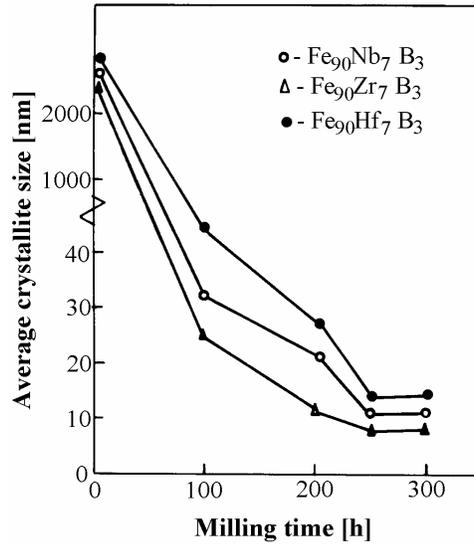

Fig. 2. The dependence of the average grain size of the $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders on the milling time.

After 250 h of milling, the values of the crystallites size are 10 nm, 8 nm and 14 nm for $Fe_{90}Nb_7B_3$, $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ powders, respectively.

The results obtained from the XRD analysis for the as-milled powders are summarised in Table 1.

Table 1. Mean crystallite sizes and mean strains for the as-milled $Fe_{90}M_7B_3$ (M=Nb, Zr, Hf) Powders.

Milling time (h)	Mean crystallite size (nm)			Mean strain (10^{-3})		
	$Fe_{90}Nb_7B_3$	$Fe_{90}Zr_7B_3$	$Fe_{90}Hf_7B_3$	$Fe_{90}Nb_7B_3$	$Fe_{90}Zr_7B_3$	$Fe_{90}Hf_7B_3$
50	> 2000	> 200	> 2000	3.86	3.65	3.98
100	32	25	45	4.25	4.12	4.71
200	21	11	27	5.17	4.87	5.27
250	10	8	14	4.03	3.95	4.12
300	11	10	15	4.15	3.14	4.20

The results of the DTA measurements for $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders after 250 h of milling are shown in Fig. 3. During heating of the as-milled powders, many exothermic peaks appear: broadened peaks between 240 - 275 °C, sharp ones between 400 - 460 °C and broadened peaks between 540 - 570 °C.
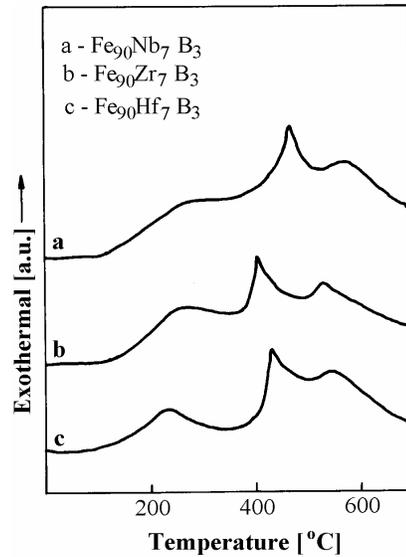
Fig. 3. The DTA curves for the $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders after 250 h of milling.

Fig. 4 shows the variations of room temperature saturation magnetization (Ms) and coercivity (Hc) with milling time for $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders comparatively to those of the $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ mechanically alloyed powders.

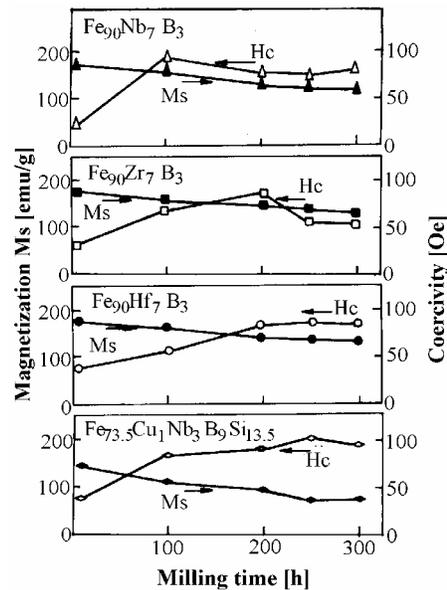

Fig. 4. The dependence of the saturation magnetization and coercivity on the milling time for
$Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) and $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ powders.

Fig. 5 shows the saturation magnetization and coercivity of $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders milled for 250 h, after thermal treatments of 1 h in vacuum, at temperatures between $100 - 400^{o}$ C.
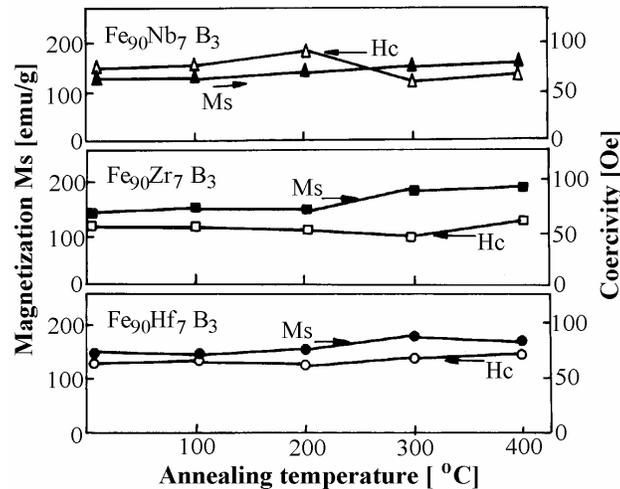
Fig. 5. The saturation magnetization and coercivity of $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders
milled for 250 h, after thermal treatments.

4. Discussions

The Bragg peak intensity corresponding to the initially powder mixtures decreases and the peaks become broader as the milling progresses, indicating a decrease of the crystallites size as well as an increase of the internal stresses due to the deformations and the alloying effect (Fig. 1).

For milling time over 100 h the peak corresponding to Zr is not detected, this behaviour indicating that $Fe_{90}Zr_7B_3$ solid solution with bcc structure is forming more rapidly than $Fe_{90}Nb_7B_3$ and $Fe_{90}Hf_7B_3$ alloys because Zr atoms together with B atoms diffuse easier into Fe.

The appearance of new phases can not be observed and within the capabilities of the peak analysis method we find that the crystallites size remains approximately constant after 300 h milling time. New phases could exist but the crystallites size being very small, the maximum of the newly formed phases could constitute a background that presents only the (110) maximum corresponding to the α-Fe bcc structure. The $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders obtained after 250 h of milling additionally consist of small fractions of amorphous phase. This is not indicated by XRD, but is proved by the thermomagnetic measurements and DTA.

After 250 h of milling, the values of the crystallites size are 10 nm, 8 nm and 14 nm for $Fe_{90}Nb_7B_3$, $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ powders, respectively.

The heating of the $Fe_{90}Nb_7B_3$ powders (see the DTA curves from Fig. 3) leads to the appearance of many exothermic peaks: the first peak, at 275 ^{o}C, may be due to the release of the strain energy during the heating process; the peaks at 460 ^{o}C and 570 ^{o}C are related to the crystallisation of α-Fe and amorphous phase, respectively. Quite similar DTA curves were obtained for $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ powders, the peaks related to the release of the strain energy during the heating process appearing at 250 ^{o}C and 240 ^{o}C, respectively and the peaks determined by the crystallisation of the α-Fe and amorphous phase appearing at 400 ^{o}C and 440 ^{o}C and at 540 ^{o}C and 550 ^{o}C, respectively.

The decrease in saturation magnetization of $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) powders during the milling process (Fig. 4) is due to the alloying and amorphization processes, and its small variation as a function of milling time may be related to the changes in the microstructure of the powders. The saturation magnetization values of the $Fe_{90}Nb_7B_3$, $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ powders milled 250 h were 148 emu/g, 149 emu/g and 147 emu/g, respectively. The fragmentation of the magnetic particles during the milling process and the appearance of internal strain lead to an increase of the coercivity with increasing the milling time. The coercivities remain approximately constant after 250 h of milling. The values of the coercivity for $Fe_{90}Nb_7B_3$, $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ mechanically alloyed powders after 250 h of milling were 75 Oe, 52 Oe and 76 Oe, respectively. The saturation magnetization and coercivity values of the obtained $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) nanocrystalline

powders are better than those corresponding to $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ mechanically alloyed nanocrystalline powders (Ms = 48 emu/g and Hc = 102 Oe) [4].

It can be noticed an improvement of the soft magnetic properties of $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) nanocrystalline powders annealed 1 h at 300°C due to the microstructure rearrangements at the atomic level and to the strain relaxation (Fig. 5). The values of the saturation magnetization and coercivity for $Fe_{90}Nb_7B_3$, $Fe_{90}Zr_7B_3$ and $Fe_{90}Hf_7B_3$ powders annealed in vacuum for 1 h at 300°C were 156 emu/g and 65 Oe, 158 emu/g and 48 Oe and 155 emu/g and 65 Oe, respectively.

The thermal treatment of the nanocrystalline samples over 400 ^{o}C deteriorates the magnetic properties, probably due to the appearance of incipient crystallization phases of different compounds (Fe_2B, Fe_2Nb, Fe_3Zr, Fe_2Hf).

5. Conclusions

The mechanically alloying has proven to be a versatile technique for the preparation of $Fe_{90}M_7B_3$ (M = Nb, Zr, Hf) soft magnetic nanocrystalline powders with the crystallites size between 8 and 14 nm, obtained after 250 h of milling. The cyclic heavy cold deformation leads to internally strained nanostructures so that additional heat treatment for stress relaxation is required. An improvement in the soft magnetic properties after annealing at 300 ^{o}C for 1 h, in vacuum, was observed.

References

[1] A. Kojima, H. Horikiri, Y. Kawamura, A. Makino, A. Inoue, T. Masumoto, J. Magn. Magn. Mater. **162**, 95 (1996).
[2] D. Wexler, R. Bennet, M. Emr, K. P. Gilleard, Proc. of Internat. Symp. on Metastable Mechanically Alloyed and Nanocrystalline Materials, Rome, 729 (1996).
[3] H. P. Klug, L. E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd edition (Wiley, N. Y.), 665 (1974).
[4] H. Chiriac, A. E. Moga, M. Urse, C. Hison, Nanostructured Materials **12**, 495 (1999).