Journal of Optoelectronics and Advanced Materials Vol. 5, No. 3, September 2003, p. 709 - 711

METASTABLE PHASES AND CRYSTALLIZATION PRODUCTS IN NANOCRYSTALLINE FINEMET-TYPE ALLOYS WITH *RE* ADDITION

A. D. Crisan[a], J. M. LeBreton[b], O. Crisan[a,c*], G. Filoti[c]

[a] Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[b]GPM, UMR 6634 CNRS, Université de Rouen, 76801 Saint Etienne du Rouvray, France
[c]National Institute of Materials Physics, MG-7, 76900 Bucharest, Romania

The melt spun nanocrystalline alloys such as $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (FINEMET) have attracted great deal of interest in recent years due to their excellent soft magnetic properties mostly related to the exchange coupling between nanograins, through the amorphous matrix. The microstructural evolution of both nanocrystalline and amorphous residual phases during annealing of the ribbons give rise to crystallization products that determine the expected magnetic properties for specific applications. Upon addition of the rare earth (RE), the evolution of the crystalline phases which emerge from metastable precursors during annealing is investigated. It is expected that the RE presence should strongly modify both the phase structure via new ternary metastable precursors and the magnetic properties of the ribbons by inducing enhanced exchange correlation due to novel ternary crystalline phases.

(Received July 11, 2003; accepted July 31, 2003)

Keywords: Nanocrystalline alloys, Metastable precursors, Ternary crystalline phases

1. Introduction

Amorphous alloys are good candidates for soft magnetic materials because of the lack of crystal anisotropy [1].

The melt spun nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ribbons have outstanding potential as soft ferromagnets or magnetostrictive materials. This alloy obtained after annealing the as-cast amorphous ribbons in strictly controlled conditions such as temperature and time, consist of α-Fe(Si) nanocrystalline grains dispersed into an amorphous residual Fe-Nb-B matrix, and exhibit thus excellent soft magnetic properties (high permeability, high saturation magnetization and low magnetostriction) that are related to the exchange coupling between nanocrystalline grains, through the amorphous matrix, if the exchange correlation length does not exceed the nanocrystalline grain size [2]. Recently, Szewczyk et al. [3] have shown that carefully annealed FINEMET material of the same composition exhibits high stress sensitivity in nanocrystalline sensors.

On the other side RE containing alloys (usually RE-Fe-B) obtained in amorphous state by melt-spinning technique and subsequently annealed, have been considered since enhanced magnetic properties, comparing to traditional permanent magnets, were predicted [4,5]. The enhanced remanence and coercivity of these alloys are related to the interphase exchange coupling within the composite system. The hard magnetic grains – most commonly $RE_2Fe_{14}B$ - are magnetically coupled through the soft magnetic ones – such as α-Fe, Fe_3B or Fe_2B - if the size of the soft magnetic regions is in the range of the exchange correlation length. Changes in the alloy chemical composition may promote different intermediate metastable phases during the annealing treatment and consequently, the resulting phase structure would be definitely different. The idea behind the present work is that, starting with a commonly known extremely soft material, such as FINEMET, to promote the co-existence with a hard magnetic phase by RE addition. In some previous works [6-8] we have reported

* Corresponding author: ocrisan@yahoo.com; crisan@physics.auth.gr

on the crystallization products and the phase microstructure of fully crystallized $Sm_xFe_{80-x}B_{20}$ ribbons and we have shown that below a critical Sm content x_c = 8 at% the co-existence of the hard magnetic phase $Sm_2Fe_{14}B$ together with the soft magnetic ones α-Fe and Fe_2B is promoted. Phase composition in the nanocrystalline state is nevertheless strongly dependent on the metastable precursors, occurring during crystallization process that depends on the crystallization path, i.e. rates of nucleation and growth. The matter of intermediate metastable phases that appear during the crystallization of RE-Fe-B ribbons and lead to different crystallization products still remains a controversial issue, being strongly related to the local chemical composition of the ribbons.

2. Experimental

The amorphous ribbons that have the nominal composition $Fe_{73.5}Cu_1Gd_5Nb_3Si_{8.5}B_9$ (hereafter denoted C sample, the 5 at% Gd being substituted to the Si from the standard FINEMET composition) have been prepared by rapid quenching of the melt. The primary alloys were prepared from high purity elements by arc melting under Ar atmosphere (10^{-1} torr) and then three times re-melted. The amorphous ribbons were prepared by melt spinning, as described hereafter. Pieces of the primary alloys (total mass per experiment: 5 g) were remelted under Ar atmosphere (normal pressure) in a quartz crucible with circular nozzle (Φ=1 mm) made using a CO_2 laser. The ribbons were obtained by evacuating the melt with an over pressure gas (4 x 10^4 Pa) on a 40 cm diameter Cu wheel that rotates at 1600 rot/min. (linear speed: 33.5 m/s, corresponding to a 10^6 K/min cooling rate). The crystallization processes have been monitored using the differential scanning calorimetry (DSC). DSC thermoanalysis have been performed with a Setaram DSC 111 system with a heating rate of 5 K/min up to 1085 K. The XRD analysis was performed with a fast curved detector in an evacuated chamber using Co Kα radiation (λ = 0.17902 nm).

3. Results and discussions

The DSC study of the sample has revealed that there are several exothermic events during the crystallization. These events occur as follows: a pre-peak prior to the main one, at 565 ºC, the main exothermic peak assimilated to the temperature of primary crystallization, at 632 ºC and another exothermic peak that may be attributed to the secondary crystallization and/or transformation of metastable phases formed in the first stage, at 753 ºC. Considering these values, another DSC run has been made and the heating has been stopped successively at 600 ºC, 650 ºC and 810 ºC, in order to investigate the phase structure after every exothermic event. The resulting samples were submitted to XRD and the corresponding spectra are shown in Fig. 1. At 600 ºC the sample is still mainly amorphous but the presence of broad peak at around 26º is the sign of the onset of crystallization. At 650 ºC, the sample is mostly crystallized but there still is an amorphous remainder. The bcc α-Fe(Si) and the metastable precursor $Gd_2Fe_{23}B_3$ (hereafter denoted 2:23:3) phase are indexed predominantly. At 810 ºC the sample is fully crystallized, the bcc α-Fe(Si) is fully formed (all the 3 Bragg reflections are well defined) and the 2:23:3 has started to decompose into $Gd_2Fe_{14}B$ (hereafter denoted 2:14:1) and Fe_2B. The paramagnetic $Gd_{1.1}Fe_4B_4$ (hereafter denoted 1:4:4) is also indexed in the sample at higher annealed temperature. Thus, the following crystallization sequence can be inferred:

a) At 600 ºC: Amorphous + onset of crystallization
b) At 650 ºC: Amorphous → amorphous' + α-Fe(Si) + 2:23:3
c) At 810 ºC: Amorphous' + α-Fe(Si) + 2:23:3 → α-Fe(Si) + 2:14:1 + Fe_2B + 1:4:4

It should be noted that if the 5 at% Gd is substituted not to the Si but to the Fe, i.e. for the composition $Fe_{68.5}Cu_1Gd_5Nb_3Si_{13.5}B_9$ we have shown that the metastable phase formed during primary crystallization is $Gd_3Fe_{62}B_{14}$ [8] and the final crystallization products were strongly dependent upon chemical composition.

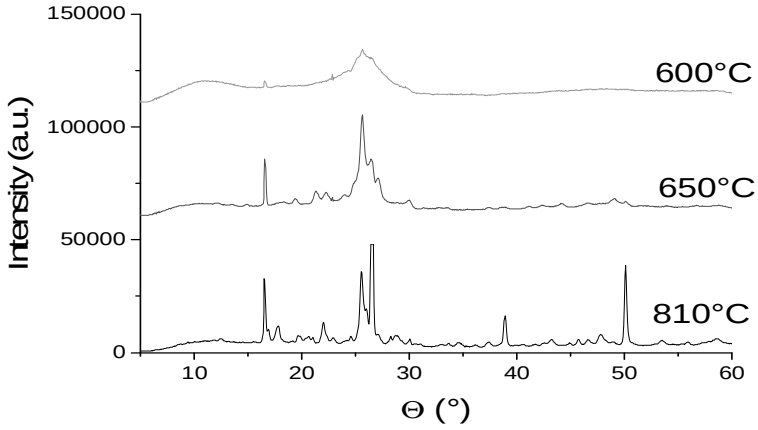

Fig. 1. XRD spectra for the sample C annealed during DSC at: a) 600ºC, b) 650 ºC and c) 810 ºC.

4. Conclusions

The effect of the RE addition to the FINEMET type alloys obtained by a melt spinning technique has been investigated. It was shown that the DSC exothermic events correspond to different crystallization stages. Whereas primary crystallization occurs at about 635 ºC with the promotion of α-Fe(Si) and metastable $Gd_2Fe_{23}B_3$, the secondary crystallization stage give rise to decomposition of the metastable precursor into hard magnetic $Gd_2Fe_{14}B_1$ and soft magnetic Fe_2B with further increase of degree of crystallinity also for the α-Fe(Si). Thus, the co-existence of hard and soft magnetic phases, a prerequisite for enhanced remanence in permanent magnets, is promoted. It is also shown that the occurrence of metastable precursors is highly sensitive to the initial chemical composition and to the crystallization path, with direct impact of the phase structure and the final crystallization products.

Acknowledgements

The help provided by A. Jianu, Bucharest, for preparing the samples and F. Machizaud, Nancy, for DSC studies are gratefully acknowledged.

References

[1] S. Roth, H. Grahl, J. Degmova, N. Schloreke de Boer, M. Stoica, J. M. Borrego, A. Condé, N. M. Mitrovic, J. Eckert, J. Optoelectron. Adv. Mater. **4**(2), 199 (2002).
[2] G. Herzer, in: Buschow K H J (ed), Handbook of Magnetic Materials 10, Elsevier Science (1997).
[3] R. Szewczyk, A. Biénkowski, J. Salach, E. Fazakas, L. K. Varga, J. Optoelectron. Adv. Mater. **5**(3), 659 (2003).
[4] R. Skomski, J. Appl. Phys. **76**, 7059 (1994).
[5] R. Fischer, T. Schrefl, H. Krönmuller, J. Fidler, J. Magn. Magn. Mater. **150**, 329 (1995).
[6] O. Crisan, J. M. Le Breton, F. Machizaud, Y. Labaye, G. Filoti, J. Magn. Magn. Mater. **242-245**, 1299 (2002).
[7] O. Crisan, J. M. Le Breton, M. Noguès, F. Machizaud, G. Filoti, J. Phys.: Condensed Matter **14**, 12599 (2002).
[8] O. Crisan, J. M. Le Breton, A. Jianu, J. Teillet, G. Filoti, J. Alloys & Comp. **262-263**, 381 (1997).