Journal of Magnetics 9(2), 65-68 (2004)

Magnetically Soft Nanomaterials Obtained by Devitrification of Metallic Glasses

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(Received 15 June 2004)

Magnetically soft nanomaterials obtained by controlled crystallisation of metallic glasses are the newest group of materials for inductive components. In particular, research is carried out in the field of alloys for high temperature applications. This kind of materials must meet two basic requirements: good magnetic properties and stability of properties and structure. In the present work the magnetic properties and structure of Fe-Co-Hf-Zr-Cu-B (HITPERM-type) alloys were investigated, as well as their stability. Differential thermal analysis, (DTA), X-ray diffractometry (XRD), transmission electron microscopy (TEM), magnetometry (VSM) and quasistatic hysteresis loop recording were used to characterise structure and properties of the alloys investigated. Optimisation against properties and their stability was performed, resulting in formulation of chemical composition of the optimum alloy, as well as its heat treatment.

Key words : soft magnetic materials, nanocrystalline materials, HITPERM, stability, magnetic properties

1. Introduction

Amongst the magnetically soft materials, the newest class are the alloys with nanocrystalline structure, obtained by partial crystallisation of metallic glasses. These alloys exhibit the combination of interesting properties typical of various groups of conventional and amorphous magnetic materials. By means of proper selection of chemical composition and their manufacturing process, nanocrystalline alloys may be produced so as to satisfy specific requirements. One of the groups of nanocrystalline alloys are HITPERM alloys, first developed by Willard *et al.* [1, 2] in 1998, suitable for application at high temperatures. These alloys were elaborated on the basis of nanocrystalline NANOPERM alloys [3], where half of iron content was substituted by cobalt. This modification allowed to increase Curie temperature of amorphous matrix, and therefore to increase significantly the application temperature range, intentionally up to 600 °C [4]. At such elevated temperatures structural changes are likely, so the stability of structure and - more important - of magnetic properties becomes a primary question in the application of HITPERM alloys. This work is aimed at finding the chemical composition of an alloy that is thermally stable at temperatures of 500 °C and possesses good magnetically soft properties.

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2. Experimental

Master alloys with composition of $(Fe_{1-z}Co_z)_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$ (x = 7 and 9; v = 0, 0.5 and 1, z = 0-1) were prepared by arc melting, and subsequently amorphous ribbons were produced by melt-spinning. The crystallisation process of amorphous alloys was investigated with LABSYS DTA/DSC calorimeter, and crystallisation temperatures were determined applying constant heating rate of 20 °C/min. Heat treatment of pieces of ribbons, 100 mm long, was performed in vacuum, in isothermal mode. Amorphous alloys were crystallised for 1 hour at various temperatures, and long term annealing was carried out at 500 °C for times up to 3000 h. Magnetic hysteresis loop of the alloys was recorded in quasistatic conditions (H_{max} = 660 A/m and 27.8 kA/m) with the hysteresis loop tracer [5]. The dependence of saturation magnetisation on temperature was measured with vibrating sample magnetometer (VSM). The structure of nanocrystalline alloys was investigated with X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

The process of crystallisation of amorphous alloys upon continuous heating was investigated in order to define relationship between the chemical composition and crystallisation temperatures, as well as to select the range of annealing temperatures leading to partial crystallisation. Fig. 1 presents the dependence of crystallisation temperatures of the alloys on their chemical composition.

For the investigated alloys it is clearly seen that the temperatures of the first stage of crystallisation (T_{x1}, T_1) depend rather on the refractory metal (RM) content than on the type of the RM added to the alloy. The more RM added, the higher crystallisation temperature. On the other hand, the second crystallisation stage temperatures (T_{x2}, T_2) depend on the type of the alloying element, and the content of this element is immaterial. Having in mind that the ultimate structure of the investigated alloys is obtained when the primary crystallisation is completed, and the major limitation of use of the alloys is the temperature of operation, we should focus on the second stage of crystallisation. Therefore, it is expected that among the alloys investigated herein, the alloys containing only hafnium will exhibit the highest stability of two-phase structure. From this point of view, the most suitable are the alloys containing Hf.

The initially amorphous alloys were annealed for 1 hour at temperatures ranging from 300 to 650 °C in order to find the conditions enabling the lowest coercive field of the alloys. Partial crystallisation of the alloys changes the value of coercive field, as presented in Fig. 2.

Each of the investigated alloys exhibits minimum of H_c,

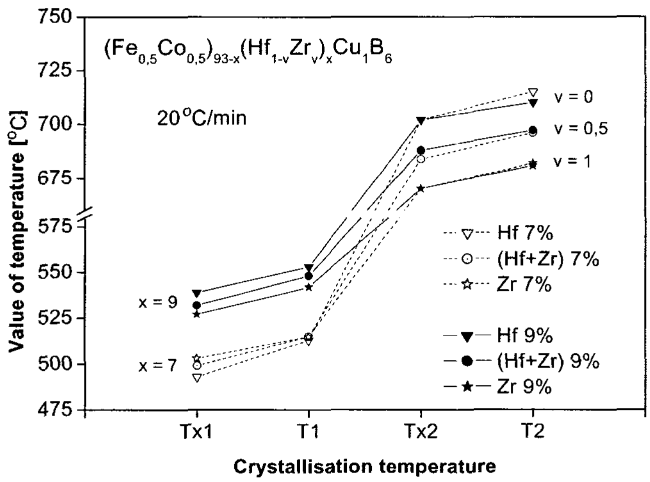

Fig. 1. Dependence of crystallisation temperatures on chemical composition of $(Fe_{0.5}Co_{0.5})_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$ alloys (T_{xn} - onset temperature of n[th] stage of crystallisation, T_n - peak temperature of n[th] stage of crystallisation).

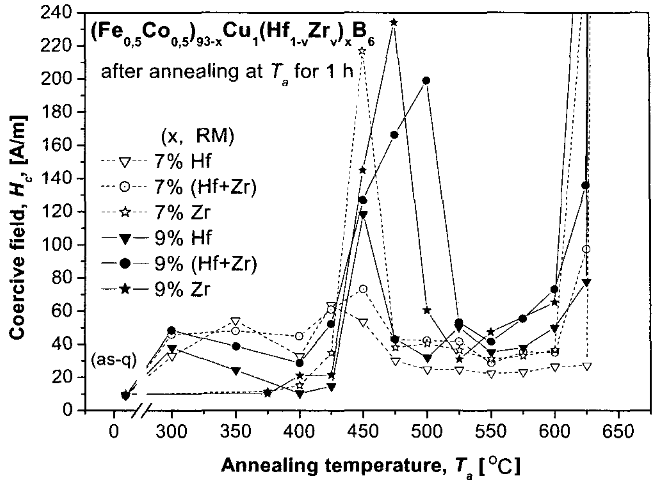

Fig. 2. Dependence of coercive field of $(Fe_{0.5}Co_{0.5})_{93-x}$-$(Hf_{1-v}Zr_v)_xCu_1B_6$ alloys after annealing for 1 hour on annealing temperature and on content of refractory metals (RM).

and the temperature related to the lowest value of H_c is called the optimum temperature of annealing, T_{opt}. For most of the alloys, optimum annealing should be carried out at temperatures of about 575 °C. Fig. 2 proves that the value of H_c after annealing depends on chemical composition of the alloys. The lowest value of H_c is observed for the alloy containing 7% of Hf, and the addition of more hafnium results in an increase of H_c of the alloys after annealing. Partial replacement of Hf by Zr also results in an increase of coercive field. Therefore, from the magnetic properties viewpoint, the preferred alloying element seems to be hafnium, and it should not be overdosed.

The series of alloys with varying ratio of cobalt to iron were subjected to isothermal nanocrystallisation at 550 °C for 1 h. The temperature of nanocrystallisation was chosen as the common temperature ensuring nanocrystalline structure and good magnetic properties in all the alloys. Dependence of saturation magnetisation versus temperature of the nanocrystalline alloys was measured with VSM, and is presented in Fig. 3.

The investigated alloys are supposed to work at elevated temperature, therefore properties at operation temperature are more important than these at room temperature. The operation temperature of the alloys was assumed at the level of 500 °C. For this temperature, the highest value of magnetisation is observed for the alloys containing approximately equiatomic proportion of Fe and Co.

Selected alloys were subjected to nanocrystallisation at their optimum temperatures and, subsequently, to long-term annealing at 500 °C. The coercive field of the alloys after nanocrystallisation and after long-term annealing

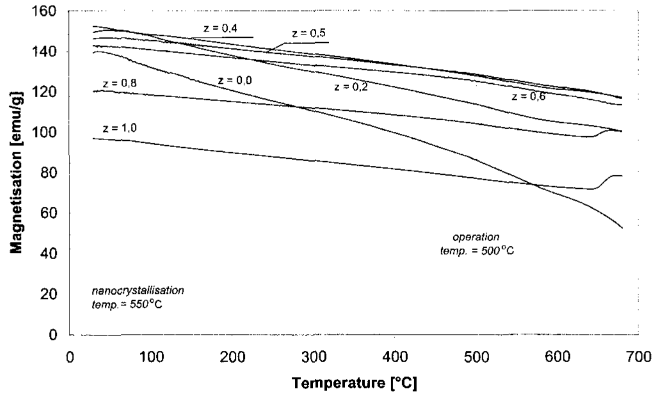

Fig. 3. Saturation magnetisation of nanocrystalline $(Fe_{1-z}Co_z)_{86}$-$Hf_7Cu_1B_6$ alloys vs. temperature.

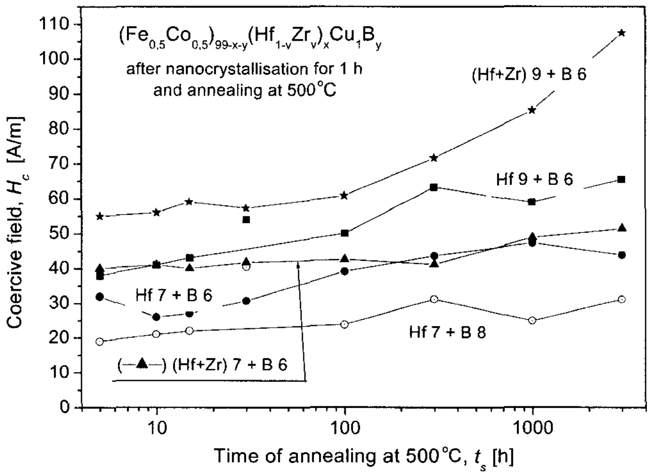

Fig. 4. Dependence of coercive field of nanocrystalline $(Fe_{0.5}Co_{0.5})_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$ alloys on chemical composition and duration of long-term annealing at 500 °C.

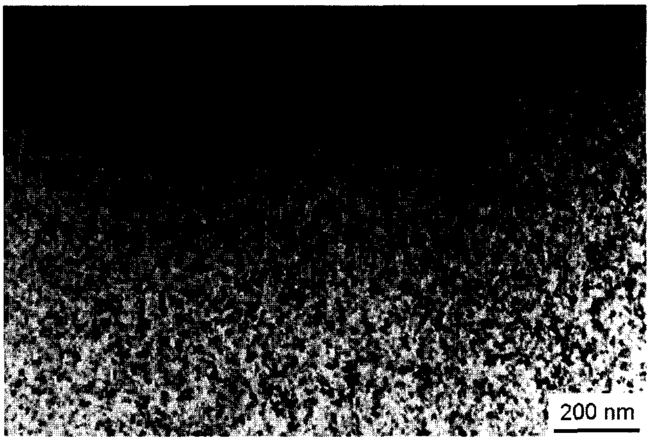

Fig. 5. Structure of $(Fe_{0.5}Co_{0.5})_{86}Hf_7Cu_1B_6$ alloy just after nanocrystallisation at 575 °C. Bright field image.

Fig. 6. Structure of $(Fe_{0.5}Co_{0.5})_{86}Hf_7Cu_1B_6$ alloy after nanocrystallisation at 575 °C and long-term annealing at 500 °C. Bright field image.

was measured at room temperature. The dependence of the coercive field on the annealing time and chemical composition of the alloys studied is presented in Fig. 4.

The alloys containing 7% hafnium exhibit the most stable coercive field over the time of annealing, and its value of Hc increases by only about 10 A/m after 3000 hours of annealing at 500 °C. Addition of zirconium causes that the coercive field increases slightly faster. In the case of the alloys containing 9% of refractory metals, the coercive field increases relatively quickly, after 3000 h of annealing exceeding the level of 100 A/m in the case of 9% of Hf and Zr, which disqualifies this alloy as the magnetically soft material. This relationship is consistent with the results obtained for the alloys after nanocrystallisation - the best performance is observed for the alloy containing 7% Hf.

Stability of properties of the selected alloys suggests that also their structure is stable after application of long-term annealing at 500 °C. XRD investigations prove that there were no significant changes of qualitative and quantitative phase composition in the most stable alloy. TEM study of the structure of the alloy after nanocrystallisation and after subsequent long-term annealing revealed that the morphology of the alloys did not change. In particular, the grain size remained not affected - the average grain size was equal to about 11 nm before and after long-term annealing. The structure of $(Fe_{0.5}Co_{0.5})_{86}$-$Hf_7Cu_1B_6$ alloy is presented in Figs. 5 and 6.

4. Summary

The best magnetic properties, amongst the alloys investigated, are observed for the $(Fe_{0.5}Co_{0.5})_{86}Hf_7Cu_1B_6$ alloy. Also, this alloy exhibits the best stability of magnetic properties at the planned temperatures of operation - its coercive field does not exceed 50 A/m, even after annealing at 500 °C for 3000 h. The structure of this alloy is also stable in these conditions. Partial replacement of hafnium by zirconium results in deterioration of the magnetic properties of the alloys, and adversely affects the alloys' stability of magnetic properties. If the alloys contain more Hf or Zr than the necessary 7%, their properties, and especially their stability, are worse as compared to 7% Hf alloy. The highest saturation magnetisation at room temperature is observed for the alloy with Fe:Co ratio equal to 4:1, but at the operation temperature (500 °C) the highest magnetisation exhibits the alloy with equiatomic Fe:Co ratio.

Acknowledgments

This work is supported by the EC GROWTH programme, research project "HiT-Fcore", contract n° G5RD-CT-2001-03009.

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