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ON THE INFLUENCE OF Zr AND Hf ADDITION ON THERMAL AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE Fe-Co-Hf-Zr-Cu-B ALLOYS

M. Kowalczyk — J. Ferenc — T. Kulik[*]

One of the most rapidly developing groups of magnetically soft materials are the nanocrystalline, iron-based alloys. Special interest concerns the materials obtained by partial crystallization of metallic glasses, with better magnetic properties than those found for the amorphous counterparts. Nanocrystalline magnetically soft materials are divided into three main groups: Finemets, Nanoperms and Hitperms. The first two groups of materials exhibit very soft magnetic behavior, however, their application is limited to relatively low temperatures, due to low situated Curie point of their amorphous matrix. The useful method of increasing the Curie temperature of both phases of the alloys is the addition of cobalt. A partial replacement of Fe by Co results in an extension of application temperature to 500-600°C. The modification with Co is the most effective for NANOPERM, and hence these Co-modified alloys bear the name of HITPERM. The disadvantage of this modification is that the excellent magnetically soft properties of Nanoperm's alloys are slightly deteriorated. Magnetically soft nanomaterials for high-temperature applications have to fulfill two basic requirements: (i) very soft magnetic behavior at elevated temperatures, and (ii) stable performance at elevated temperatures for the time of application.

This paper describes the results of the study of $(Fe_{0,5}Co_{0,5})_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$ alloys, where x = 5, 6, 7 and 9 (at. %) and v = 0, 0.5 and 1. The influence of Hf and Zr on the crystallization process and magnetic properties was investigated. Differential thermal analysis (DTA), X-ray diffraction (XRD) and quasistatic hysteresis loop tracing were used. Isothermal annealing at various temperatures for 1 h was carried out and magnetic properties of the alloys after such heat treatment were studied.

Partial replacement of Hf by Zr reduces the temperature of the 2nd crystallization stage, reducing the thermal stability of nanocrystalline alloys. All the alloys, if annealed between 450 and 600°C for 1 h exhibit the desired two-phase structure, and if the annealing temperature exceeds 600°C, other phases appear and magnetically soft properties are lost. The lowest coercive field, H_c, of 23 A/m, was obtained for the nanocrystalline alloy containing 7% of Hf. An increase of the Hf or Zr total content increases the coercive field, H_c, of the nanocrystalline alloys. Zr used instead of Hf also increases H_c of the studied materials. However, the content of Zr or Hf does not have a significant influence on the annealing temperature that enables obtaining the lowest coercive field. Such common optimum annealing temperature is 550°C.

Keywords: hitperm, nanocrystalline alloys, soft magnetic alloys, coercive field, thermal stability

1 INTRODUCTION

Since several years lots of studies concerning nanocrystalline magnetically soft materials have been carried out. Special interest concerns the materials obtained by partial crystallisation of metallic glasses, with better magnetic properties than those found for the amorphous counterparts. Nanocrystalline magnetically soft materials are divided into three main groups: Finemets [1], Nanoperms [2] and Hitperms [3-5]. The first two groups of materials exhibit very soft magnetic behavior, but their application is limited to temperatures below 200°C. This is caused by low situated Curie point of the amorphous matrix. This limitation may be overcome by a partial replacement of iron by cobalt, which increases the Curie temperature of the amorphous matrix up to about 700°C. Such high Curie temperature of the matrix ensures preservation of good soft magnetic properties at elevated temperatures. Such a Nanoperm's alloys containing cobalt are so called Hitperm's.

For materials designed to work at elevated temperatures, it is very important that their properties are stable for the lifetime of the equipment where they are applied. The latter condition is met when structure and magnetic properties are stable over time and at temperature of application. It is very important to consider in the design process of a material, the influence of the crystallization temperatures and magnetization dependency versus temperature. Those mentioned properties depend mainly on chemical composition of alloys, and also on their manufacturing process, usually controlled by crystallization of the amorphous precursor.

In this study, structure, magnetic and thermal properties of Hitperm alloys with different amount of refractory metals *RM* (Hf, Zr) were investigated in order to optimise the chemical composition and heat treatment from the viewpoint of high-temperature application.

2 EXPERIMENTAL

Six alloys were molten from pure elements and melt-spun in the form of amorphous ribbons. The chemical compositions (in at. %) of the ribbons were: $(Fe_{0.5}Co_{0.5})_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$, where x = 7 or 9 and v = 0, 0.5 or 1. Crystallisation temperatures of the amorphous alloys were investigated using a continuous heating in Perkin Elmer DSC 7 and Setaram Labsys DSC/DTA calorimeters, with scanning rate 20 K/min. 100 mm long pieces of ribbons were subjected to isothermal annealing at temperatures between 300 and 650°C in quartz ampoules with vacuum after argon

[*] Warsaw University of Technology, Faculty of Materials Science and Engineering, ul. Wołoska 141, 02-507 Warsaw, Poland,
E-mail: tkulik@inmat.pw.edu.pl

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flushing. Value of coercive field for samples annealed at different temperatures was measured by quasistatic histeresis loop tracer, where maximal magnetic field H_{max} 660 A/m was used [6]. For samples, representing each alloy and the lowest values of coercive field, long term annealing was carried out. The long term annealing was done in three different temperatures (500°C, 550°C, 600°C) and for different time, from 3 up to 3000 hours. Structure of alloys after heat treatment and long-term annealing was investigated with X-Ray Diffractometry (XRD) and Transmission Electron Microscopy (TEM).

3 RESULTS AND DISCUSSION

As the first part of this study the thermodynamic behaviour of investigated alloys was carried out. The results of differential thermal analysis are shown on figures 1 and 2. Correlation between the crystallisation temperatures of the studied materials and their chemical compositions can be observed.

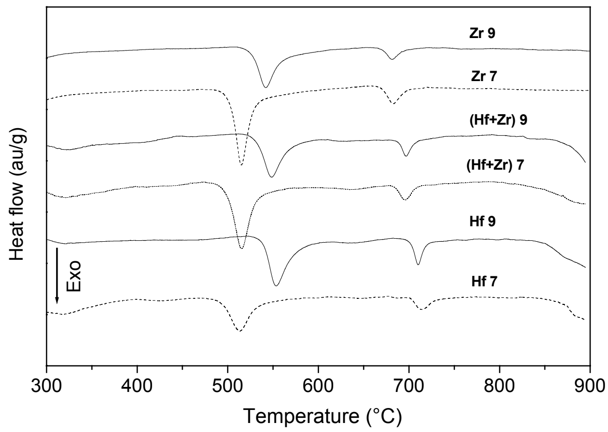

Fig. 1. DTA curves for variable amount of refractory metals

The onset temperature of the first crystallisation stage, T_{x1}, depends on the amount of refractory metals and for the same amount is almost independent on the type of refractory metals. For example for 7 at. % of hafnium or zirconium this temperature is about 500°C (dashed lines on figure 1). It does not matter if there is only hafnium or zirconium, or both of them in the alloy, important is only the total amount of those two elements. The alloys containing 9 at. % of refractory elements have the temperature of the first crystallisation situated on the level of 550°C.

In the case of the second crystallisation stage there is another dependency. Not amount, but kind of the element used in the alloy is important. It is visible that for both alloys with hafnium only, the temperature corresponding to the second crystallization peak, T_2 is situated at the highest level. Partial substitution of hafnium by zirconium slightly moves the second crystallisation peak to lower temperatures. Full substitution of hafnium by zirconium confirms this tendency and manifests with further temperature decrease. This suggests that Hf is a preferred choice from the standpoint of stability of amorphous matrix after nanocrystallization

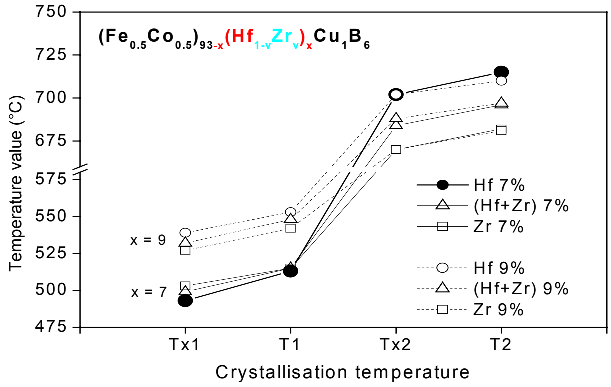

Fig. 2. Crystallisation temperatures *vs* alloy composition

To determine the optimum nanocrystallisation temperatures $T_{opt.}$ of the studied alloys, pieces of ribbons were subjected to annealing for one hour at temperatures between 300 and 650°C, with step of 25°C. The values of the coercive field H_c of the ribbons after annealing are shown in figure 3. It can be assumed that the annealing at the temperatures from the range between 525 and 600°C results in good magnetic properties. The value of H_c is not higher then 75 A/m after annealing at the whole, above mentioned, temperature range. Although, the alloy containing 7 % of hafnium exibits the lowest value of the coercive field in as-nanocrystallised state. Partial replacement of Hf by Zr or an increase of RM content (or both) result in an increase of the coercive field. Finally, it can be assumed that for all the alloys studied, the optimum temperature of 1 hour long annealing is 550-575°C.

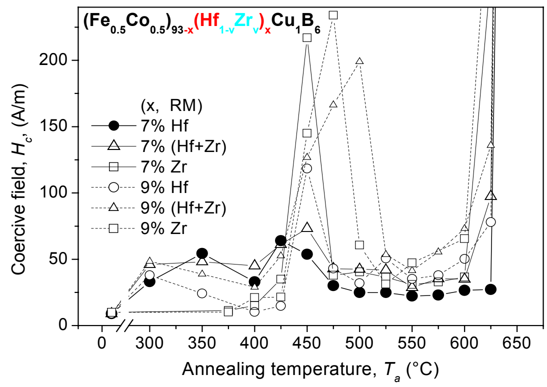

Fig. 3. Coercive field after annealing for 1 hour in different temperatures

After finishing the nanocrystallization process, the ribbons were subjected to long term annealing at several temperatures and several times. The results of magnetic measurements after the long term annealing are presented on figures 4, 5 and 6.. There is clear influence of the annealing temperature on the magnetic behavior of the alloys studied. In the case of annealing at 500°C an increase of H_c is quite slow. Even for 3000 h and for the worst alloy ($(Fe_{0.5}Co_{0.5})_{94}(Hf_{0.5}Zr_{0.5})_9Cu_1B_6$) the value of H_c is below 120 A/m. The most stable material, containing only 7 % of hafnium, exhibits after annealing for 3000h the coercive field on the same level as before the long term annealing. The situation becomes different when temperature of the long term annealing is increased. Higher temperature causes structural changes and at the same time the magnetic properties are changed. The all alloys shown on the figures 5 and 6 loose their magnetic softness. For example the alloy containing 9 % of hafnium and zirconium after 300 h of annealing at 550°C exhibits the same value of coercive field as when annealed for 3000 h at temperature 50 degrees lower. Only the material containing 7% of hafnium is rather resistant for the temperature of 550°C. After 300 h of annealing at 550°C the H_c is below 40 A/m. The results shown on figure 6 prove that none of the investigated materials can be used at 600°C. Annealing at so high temperature causes rapidly (after several hours) structural changes, which results in dramatic changes of the magnetic properties. The nanocrystalline structure is damaged and the materials loose their softness. The structural changes are confirmed by the results of the X-Ray Diffraction (figure 7). Since 600°C new fhases are visible.

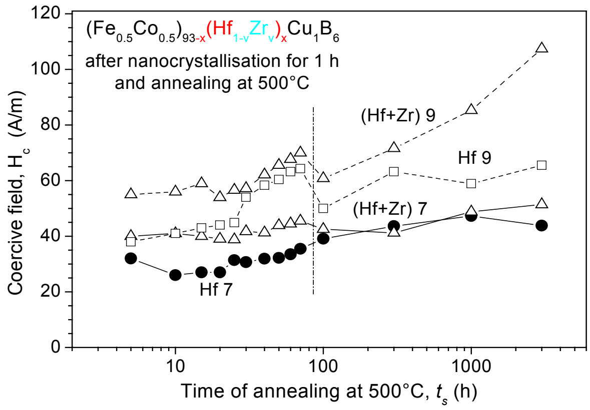

Fig. 4. Coercive field H_c after long time annealing at 500°C

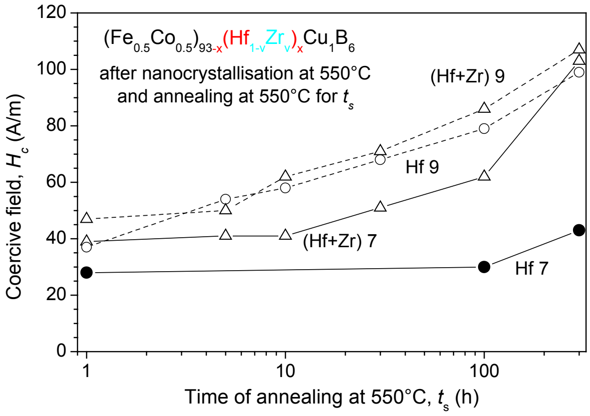

Fig. 5. Coercive field H_c after long time annealing at 550°C

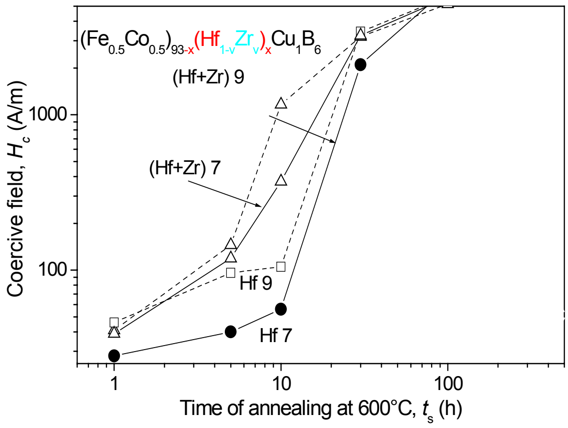

Fig. 6. Coercive field H_c after long time annealing at 600°C

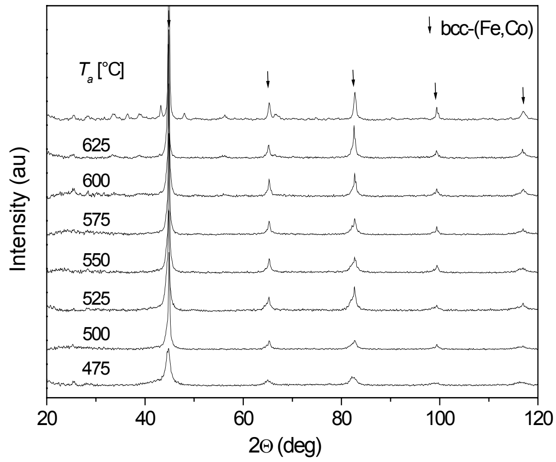

Fig. 7. X-Ray Diffraction patterns of Hf 7 alloy after 1 hour annealing at different temperatures

To investigate the structural changes during the long term annealing Transmission Electron Microscopy for samples before and after long term annealing, were done. The graphs in figures 8 and 9 present grain size distribution of Hf 7 and (Hf+Zr) 9 alloys. It is well seen that for both materials before annealing the mean value of grain diameter is comparable, but after 3000 h of annealing the grain size distribution of Hf7 alloys is almost unchanged. This is in different comparing to (Hf+Zr) 9 alloy, for which the grain growth tendency is visible. The mean value of the grain size is shifted to the values higher by about 50 %, from 10.6 to 15.2 nm.

4 CONCLUSIONS

The optimum chemical composition of Hitperm-type alloys is $(Fe_{0.5}Co_{0.5})_{86}Hf_7Cu_1B_6$. This alloy presents the lowest coercive field at room temperature in as-nanocrystallized state and after long term annealing at elevated temperature (3000h, 500°C). The values of H_c for this alloy do not exceed 50 A/m, what can make it useful for high temperature application.

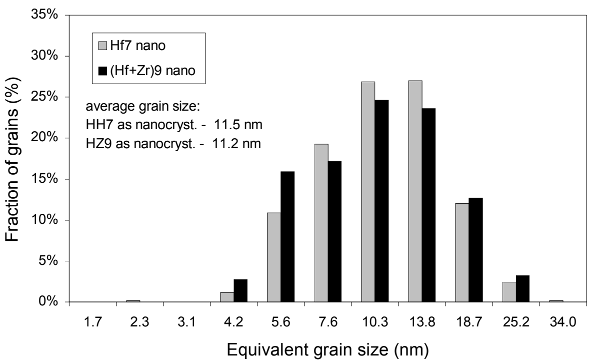

Fig. 8. Grain size distribution of Hf7 and (Hf+Zr)9 alloys after nanocrystallization

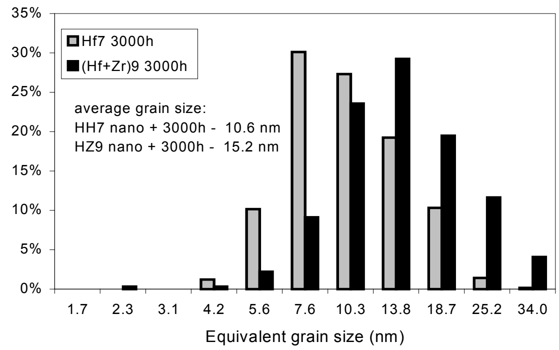

Fig. 9. Grain size distribution of Hf7 and (Hf+Zr)9 alloys after long term annealing, after 3000 h at 500°C

A partial replacement of Hf by Zr, as well as an increase of Hf or Zr content result in an increase of the coercive field. There is an influence of an amount of RM elements on the crystallisation process of the alloys. Higher amount of RM manifests itself by a shift of temperature of the first crystallisation stage. Addition of hafnium increases the temperature of the second crystallisation process, hence material with 7 at.% of Hf has the most stable magnetic and structural properties at elevated temperatures.

Acknowledgement

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