

**COMMENT**Worldwide Congress on  
Materials and Manufacturing  
Engineering and Technology16<sup>th</sup> - 19<sup>th</sup> May 2005  
Gliwice-Wiśła, PolandCOMMITTEE OF MATERIALS SCIENCE OF THE POLISH ACADEMY OF SCIENCES, KATOWICE, POLAND  
INSTITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS OF THE SILESIA UNIVERSITY  
OF TECHNOLOGY, GLIWICE, POLAND  
ASSOCIATION OF THE ALUMNI OF THE SILESIA UNIVERSITY OF TECHNOLOGY, MATERIALS  
ENGINEERING CIRCLE, GLIWICE, POLAND**13<sup>th</sup> INTERNATIONAL SCIENTIFIC CONFERENCE  
ON ACHIEVEMENTS IN MECHANICAL AND MATERIALS ENGINEERING**

## Temperature of nanocrystallisation of magnetically soft alloys for high-temperature applications

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**Abstract:** The newest class of magnetically soft materials are the nanocrystalline iron alloys obtained by partial crystallisation of metallic glasses. Within this group, FINEMET (Fe-Si-Nb-Cu-B) and NANOPERM (Fe-Zr-Cu-B) alloys exhibit the unique combination of interesting magnetic properties. These materials may be used at temperature below 230°C. For high temperature applications, the HITPERM alloys (Fe-Co-Zr-Cu-B) are used. Their optimisation should lead to (i) good magnetic properties at working temperature and (ii) good thermal stability of structure and properties. The alloys' properties are the function of their chemical composition and heat treatment. This work is related to the optimisation of heat treatment of HITPERM alloys. High operating temperature may induce further crystallisation of an amorphous matrix. It is suggested that the nanocrystallisation temperature should be as high as possible, and the optimisation of HITPERM-type alloys should focus on their chemical composition.

**Keywords:** Nanomaterials; Soft magnetic materials; HITPERM; Stability of magnetic properties; Crystallisation;

### 1. INTRODUCTION

Nanocrystalline alloys obtained by partial crystallisation of metallic glasses are the newest class of magnetically soft materials. These alloys combine the advantageous properties of cobalt-based metallic glasses and of conventional crystalline materials. The lowest coercive field,  $H_c$ , below 1 A/m, was observed for the FINEMET alloy (Fe-Si-Cu-Nb-B) with the saturation induction,  $B_s$ , of 1.24 T [1]. Another group of alloys, NANOPERM (Fe-Zr-Nb-Cu-B) [2], exhibit  $H_c$  at the level of 2 – 3 A/m and  $B_s$  of 1.65 T. Both types of alloys may be used at temperature not higher than 230°C. In order to extend the temperature range of applications, cobalt is added. This way, HITPERM alloys (Fe-Co-(Zr,Nb,Hf)-Cu-B) were developed, and they may work up to 600°C [3]. In these conditions, important are: (i) good soft magnetic properties at high temperature and (ii) stability of structure and properties for the extended period of time. The properties of the magnetically soft nanocrystalline alloys are the function of their chemical composition and structure: crystalline grain size,  $d$ , and the volume fraction of crystals  $V_{cr}$  [4]. The structure depends on the conditions of heat treatment

of the amorphous precursor. This work treats on the temperature of nanocrystallisation process of HITPERM-type alloys and its impact on the magnetic properties and their stability.

## 2. EXPERIMENTAL

Series of amorphous alloys:  $\text{Fe}_{45}\text{Co}_{43}\text{Cu}_1\text{B}_{3.6}\text{Zr}_{7.4-x}\text{RM}_x$ , ( $x = 0, 3.7$  and  $7.4$ ,  $\text{RM} = \text{Nb}$  and  $\text{Hf}$ ) and  $(\text{Fe}_{0.5}\text{Co}_{0.5})_{93-x}(\text{Hf}_v\text{Zr}_{1-v})_x\text{Cu}_1\text{B}_6$  ( $x = 7$  and  $9$ ;  $v = 0, 0.5$  and  $1$ ), all in at. %, were prepared by melt-spinning. The crystallisation process was observed with the Setaram Labsys calorimeter working in thermal analysis (DTA) mode, with the heating rate of  $20^\circ\text{C}/\text{min}$ . Heat treatment was carried out in isothermal conditions, in vacuum. Nanocrystallisation process lasted for 1 h, and prolonged annealing was up to 3000 h long. The structure of the alloys was observed with the X-ray diffractometer Philips PW1830 (XRD) and the transmission electron microscope Philips EM300 (TEM). Grain size distribution was performed with image analysis software on the basis of TEM images. Magnetic properties were measured at room temperature with the quasistatic hysteresis loop tracer [5].

## 3. RESULTS AND DISCUSSION

The series of HITPERM-type amorphous alloys,  $\text{Fe}_{45}\text{Co}_{43}\text{Cu}_1\text{B}_{3.6}\text{Zr}_{7.4-x}\text{RM}_x$ , was prepared and subjected to isothermal crystallisation for 1 hour at various temperature,  $T_a$ . It was found that relatively low values of  $H_c$  can be obtained at the  $T_a$  range from  $500$  to  $600^\circ\text{C}$ . Therefore, these two extreme annealing conditions were used to produce the nanocrystalline alloys. The alloys, nanocrystallised at  $500$  and  $600^\circ\text{C}$ , were subjected to prolonged annealing at  $T_s = 500^\circ\text{C}$  (assumed as the working conditions), and after the long-term annealing the coercive field was measured. The results for all the studied alloys are similar, and the  $\text{Fe}_{45}\text{Co}_{43}\text{Cu}_1\text{B}_{3.6}\text{Zr}_{3.7}\text{Hf}_{3.7}$  alloy will be presented as the example. The dependence of  $H_c$  of the alloy on the nanocrystallisation

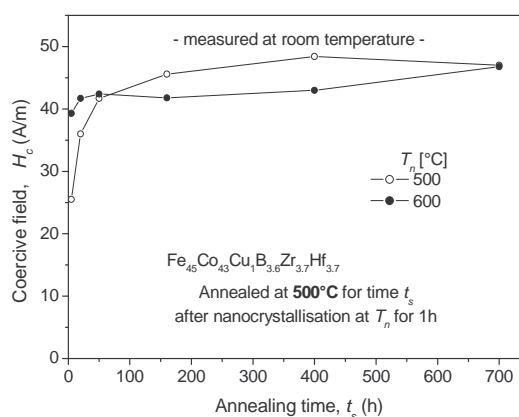


Figure 1. Coercive field of  $\text{Fe}_{45}\text{Co}_{43}\text{Cu}_1\text{B}_{3.6}\text{Zr}_{3.7}\text{Hf}_{3.7}$  alloy after nanocrystallisation at  $500^\circ$  and  $600^\circ\text{C}$  for 1 h and prolonged annealing at  $500^\circ\text{C}$

temperature,  $T_n$ , and on long-term annealing time,  $t_s$ , is shown in Fig. 1. In the case of lower  $T_n$ , the coercive field is initially low (about 26 A/m) and within 160 h increases until it reaches a plateau at the level of 47 A/m. This suggests that crystallisation at  $T_n = 500^\circ\text{C}$  for 1 h is insufficient to obtain a stable structure, and working conditions cause further crystallisation of the amorphous matrix until the 1<sup>st</sup> stage of crystallisation is complete. For the alloy annealed at  $T_n = 600^\circ\text{C}$ , the value of  $H_c$  directly after nanocrystallisation is of 39 A/m, and over the next 50 h of annealing at  $500^\circ\text{C}$  the coercive field increases to 43 A/m and reaches a relatively stable level. Regardless of the nanocrystallisation conditions, the stable values of  $H_c$  are observed at the same level. This means that for the given alloy, working at temperature high enough to allow further crystallisation, the coercive field will eventually reach a stable level that refers to the completion of the first stage of crystallisation.

Obviously, the working conditions must not promote the second stage of crystallisation, because it increases the coercive field by several orders of magnitude.

The amorphous  $(\text{Fe}_{0.5}\text{Co}_{0.5})_{93-x}(\text{Hf}_{1-v}\text{Zr}_v)_x\text{Cu}_1\text{B}_6$  ( $x = 7$  and  $9$ ,  $v = 0, 0.5$  and  $1$ ) alloys were subjected to isothermal annealing for 1 h, and coercive field in the crystallised state was measured. The results of the measurements are presented in Fig. 2 (the alloys with Zr only were skipped for the graph clarity). Additionally, XRD studies were carried out in order to assess the structure of the crystalline alloys. Low values of  $H_c$  are found unless  $T_a$  exceeds  $625^\circ\text{C}$ . The optimum nanocrystallisation temperature was determined as  $575^\circ\text{C}$ . For  $T_a = 650^\circ\text{C}$ , stronger lines of the metastable phases appear in the XRD patterns, and therefore the coercive field increases over a thousand A/m.

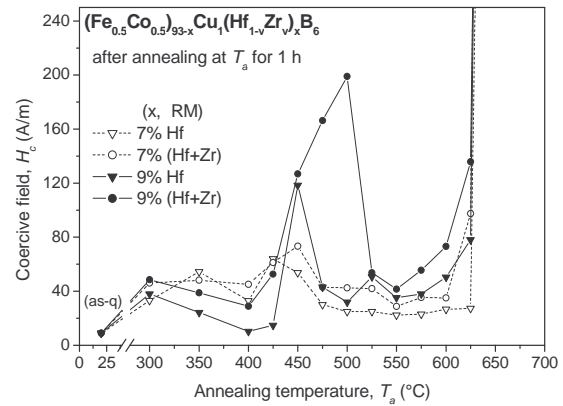


Figure 2. Coercive field of  $(\text{Fe}_{0.5}\text{Co}_{0.5})_{93-x}(\text{Hf}_{1-v}\text{Zr}_v)_x\text{Cu}_1\text{B}_6$  alloys vs. annealing temperature,  $T_a$ , and Hf and Zr content. Annealing time: 1 h

It should also be noted that for the alloys with 9% RM, the optimum range of isothermal crystallisation is quite narrow (see Fig. 2), meaning that annealing over  $T_{opt}$  results in a substantial increase of  $H_c$ , although the alloy still has a two-phase structure. Much more flexible are the alloys with 7% RM, as they offer wider range of crystallisation temperature that ensures the low values of coercive field. In particular, the alloy containing 7% of Hf is insensitive to the selection of nanocrystallisation temperature – between  $500$  and  $625^\circ\text{C}$  any will do. The 7% Hf alloy exhibits the widest temperature span between both crystallisation stages [6], so there are no significant differences in structure, and hence in the properties, of this alloy in the mentioned temperature range.

The  $(\text{Fe}_{0.5}\text{Co}_{0.5})_{93-x}(\text{Hf}_{1-v}\text{Zr}_v)_x\text{Cu}_1\text{B}_6$  alloys after nanocrystallisation at optimum temperature ( $575^\circ$  and  $600^\circ\text{C}$ , depending on the alloy) were subjected to prolonged annealing at  $500^\circ$  and  $550^\circ\text{C}$ . Fig. 3 presents the dependence of the coercive field of the alloys on the annealing time and on their chemical composition. The best stability of the magnetic properties exhibits the alloy with 7% Hf, and the worst stability we observe for the alloy with

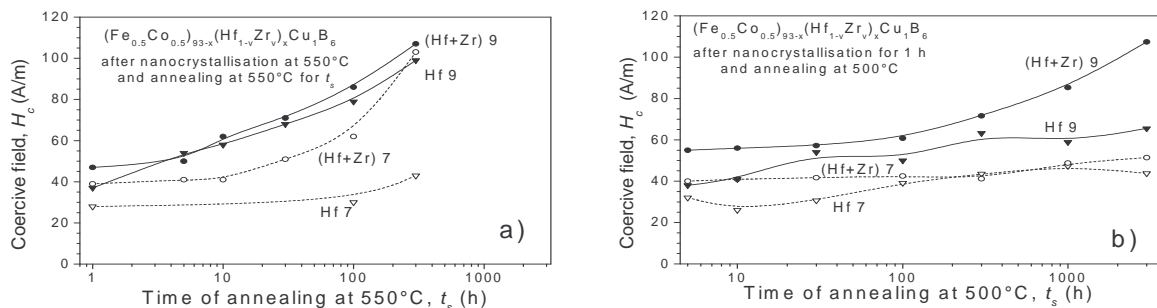


Figure 3. Dependence of the coercive field of the  $(\text{Fe}_{0.5}\text{Co}_{0.5})_{93-x}(\text{Hf}_{1-v}\text{Zr}_v)_x\text{Cu}_1\text{B}_6$  alloys on the time of long-term annealing at a)  $550^\circ\text{C}$  and b)  $500^\circ\text{C}$ , and on their chemical composition.

9% (Hf+Zr). Since the XRD patterns of the two extreme alloys are similar, morphology of the crystalline phase was studied with TEM. The average grain size in the 7% Hf alloy, estimated from the TEM images, was 11.5 nm in as-nanocrystallised state and 10.6 nm after subsequent annealing at 500°C for 3000 h. The respective values for the 9% (Hf+Zr) are 11.2 and 15.2 nm. According to the random anisotropy model [7], the increase of the crystals size during prolonged annealing in the 9% (Hf+Zr) alloy is the reason for gradual increase of  $H_c$ . Another reason may be the increase of crystalline volume fraction from the optimum value to a higher value due to prolonged exposure of the alloy to high temperature. For the 9% (Hf+Zr) alloy, a little increase of  $V_{cr}$  results in a significant increase in the coercive field, as pointed out in the comments to Fig. 2.

On the basis of structural investigations, for the 7% Hf alloy it may be assumed that the selected nanocrystallisation temperature, 575°C, was high enough to ensure the formation of the structure stable at 500°C, *i.e.* the first crystallisation stage was almost completed. This is confirmed by the behaviour of the magnetic properties. On the contrary, for the 9% (Hf+Zr), long-term annealing provokes further devitrification of an amorphous matrix and much worse stability of magnetic properties is observed. One of the reasons for this is the incomplete occurrence of the first stage of crystallisation during the nanocrystallisation annealing.

The results obtained allow to suppose that the best thermal stability of two-phase structure and properties will be obtained for the alloys exhibiting a wide temperature span between the crystallisation stages. This enables the completion of the first crystalline stage without the danger of occurrence of the second stage.

#### 4. SUMMARY AND CONCLUSIONS

The results obtained for the HITPERM-type alloys working at temperature close to the crystallisation temperature suggest that during the prolonged exposure of the alloys to high temperature, structural changes may occur due to incomplete first stage of crystallisation. To avoid these effects, crystallisation of amorphous precursors should be carried out at the highest possible temperature which yet allows obtaining the two-phase, nanocrystalline structure. Neglecting this will result in the instable performance of the final product. This requirement limits the space for optimisation of the HITPERM-type alloys for specific application to the modification of the chemical composition only. This is unlike in the case of the nanocrystalline alloys working around room temperature, which allow tailoring the properties also with the variable heat treatment conditions.

#### ACKNOWLEDGEMENT

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

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