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Magnetically soft nanomaterials for high-temperature applications

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Abstract

The paper summarizes the current status of research in the field of magnetically soft nanocrystalline materials especially highlighting the influence of alloy composition on structure and magnetic properties as well as their stability at elevated temperature during very long time annealing (several thousand hours at temperature up to 550 °C). Modification of the alloys allows to tailor their chemical composition and manufacturing process to particular application temperature requirements. FINEMET is the most suitable material for application at temperature up to 300 °C, FINEMET modified by cobalt $(Fe_{0.6}Co_{0.4})_{73.5}Cu_1Nb_3Si_{13.5}B_9$ for 300 °C < T < 350 °C, NANOPERM for 350 °C < T < 400 °C, and HITPERM $(Fe_{0.6}Co_{0.4})_{86}Hf_7B_6Cu_1$ for 400 °C < T < 550 °C.

Keywords: Nanostructured materials; High-temperature alloys; Rapid-solidification; Quenching; Magnetic measurements

1. Introduction

The newest class of magnetically soft materials are the nanocrystalline iron and cobalt-based alloys produced by partial crystallisation of metallic glasses. The first developed alloy was the well known FINEMET (Fe–Nb–Cu–Si–B) [1]. The other group of this type of materials were NANOPERMs (Fe–Zr–Nb–Cu–B) [2]. Their outstanding properties made them an attractive replacement of the conventional ferrites, crystalline and amorphous alloys in many applications. However, their application is limited to the temperatures close to the Curie point of an amorphous matrix, because the magnetic coupling between the single crystals is necessary for preserving the excellent soft magnetic behaviour. As the result, FINEMET-type alloys as an example, are usually used at temperature not higher than 230 °C, otherwise their coercivity and core losses are very high, and the available induction is too low. The possible way to improve the soft magnetic properties at elevated and high temperatures is the partial substitution of iron with cobalt. It is intended that this increases the Curie temperature of both, amorphous and crystalline, phases and the whole materials is still ferromagnetic at elevated temperature. The Co-modified NANOPERM alloys are known as HITPERM, and were shown to be suitable for temperature up to 600 °C [3]. The nanocrystalline materials for high-temperature applications must meet two basic requirements: good soft magnetic properties at working temperature and stability of structure and properties upon exposure to high temperature for a prolonged time. In order to develop the new materials for the high-temperature work regime, it is necessary to determine the influence of chemical composition and structure on magnetic properties at the working conditions and thermal stability of structure and properties of the alloys.

This work presents the overview of the results of studies of FINEMET and NANOPERM alloys modified with cobalt. In particular, the high-temperature properties and their stability are presented. On the basis of the obtained results, the ranges of application temperature are shown, and the suggestions of materials selection for high-temperature applications are proposed.

2. Experimental

Two series of alloys were prepared: FINEMET-type $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (at.%) (x = 0–1) and NANOPERM-type $(Fe_{1-z}Co_z)_{93-x}(Hf_{1-v-u}Zr_vNb_u)_xCu_1B_6$ (x = 7 and 9 at.%, v = 0, 0.5 and 1, u = 0, 0.5 and 1, z = 0–1). They were melt-spun into the form of amorphous ribbons. Isothermal crystallisation was performed for 1 h at temperature from 350 to 650 °C. Prolonged annealing was performed at 200 and 300 °C for FINEMET alloys, and at 500, 550 and 600 °C for NANOPERM alloys. Crystallisation temperatures were established with Setaram LABSYS DTA/DSC (differential thermal analysis mode) with the heating rate of 20 °C/min. Quasistatic coercive field

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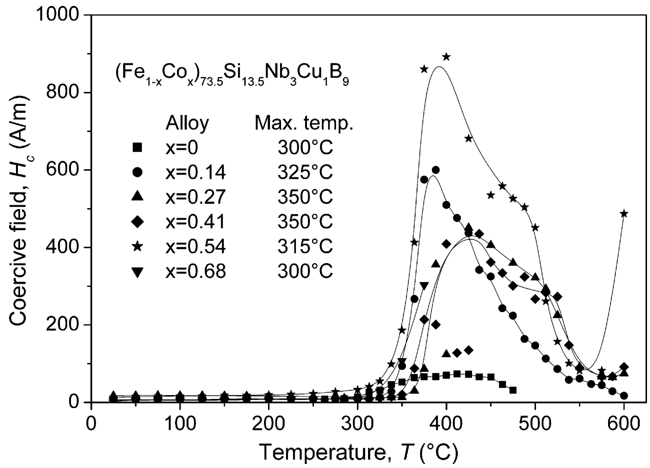

Fig. 1. Dependence of coercive field of the optimally annealed $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys on temperature. The maximum allowable temperature for each alloy is indicated, based on the abrupt rise of H_c.

(H_c) of the 150 mm long samples was assessed with the high-temperature hysteresis loop tracer (self-made, based on [4]) from room temperature to 600 °C. Additionally, the magnetic loss for FINEMET toroidal samples was established with the REMACOMP C-100 apparatus at 200 and 300 °C, at 50 kHz, with the maximum induction of 0.4 T.

3. Results and discussion

The crystallisation temperatures of the FINEMET-type $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys modified with cobalt, called also Co-FINEMET, depend on the Co content: the more Co, the lower the temperatures of both crystallisation stages. However, this dependence is weak—the crystallisation onset temperature decreases from 545 to 500 °C when x changes from 0 to 1. From the manufacturing viewpoint it is more important what temperature of isothermal annealing should be selected to obtain the best soft magnetic properties. Here, it is observed that the increase of cobalt content lowers the optimum annealing temperature, from 540 to 460 °C (annealing for 1 h) [5]. The comparison of the optimum structure for each of the alloys proves that the more Co in an alloy, the less nanocrystalline bcc-Fe(Co,Si), although the first stage of crystallisation is not completed. The reason for this may be the balance of contribution of magnetocrystalline anisotropy and magnetoelastic anisotropy to the overall anisotropy of the alloys. The coercive field, H_c, of the FINEMET alloys modified with Co, measured at room temperature, increases with the Co content. However, from the viewpoint of the high-temperature applications, room temperature coercive field is not the key criterion for the selection of the alloys and for the determination of the application temperature range. Fig. 1 shows the dependence of the coercive field of nanocrystalline FINEMET-type alloys modified with cobalt on temperature. For all the alloys, H_c is relatively low up to 300–350 °C, but above this temperature the values of H_c significantly increase. The reason for this maybe the weak magnetic coupling between the crystalline grains, due to the low Curie temperature of an amorphous matrix. Surprisingly, the addition of Co to FINEMET only slightly improves the high-temperature performance of these alloys—the highest application temperature is of about 350 °C (x = 0.27–0.41), compared to about 300 °C for original FINEMET (x = 0). Therefore, FINEMET-based alloys should not be considered as useful for applications above 350 °C.

The other important issue is the stability of properties at application temperature. The *in situ* measurements of magnetic loss were made after annealing at 200 and 300 °C for a longer time. The results are presented in Fig. 2. It shows that annealing at 200 °C for 150 h does not change the properties of the studied alloys. Probably this temperature is too low to provoke any structural changes. For 300 °C, a gradual increase of magnetic loss and decrease of permeability (not shown here) are observed at the initial stage of annealing, and the properties become stable after about 80 h. Such behaviour may be explained by slow occurrence of crystallisation during this prolonged heat treatment. The optimum annealed alloys are in a metastable condition and, as pointed out before, may further crystallise until the first stage of crystallisation is finished. The alloys, subjected to annealing at 300 °C, undergo the slow crystallisation (an increase of crystals volume fraction and crystals size), and therefore are shifted out of their optimum structure. This results in the observed deterioration of the magnetic properties. Subsequently, it may be

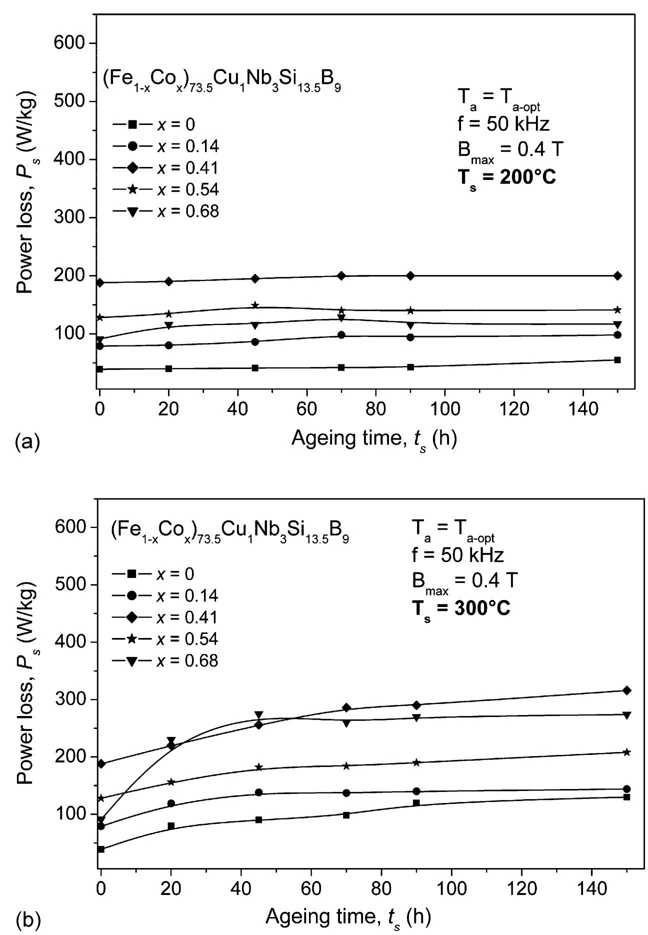

Fig. 2. Dependence of magnetic loss of $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys on Co content, temperature and time of prolonged annealing. Measurements performed *in situ* at the respective annealing temperature, T_s. Frequency: 50 kHz, maximum induction: 0.4 T.

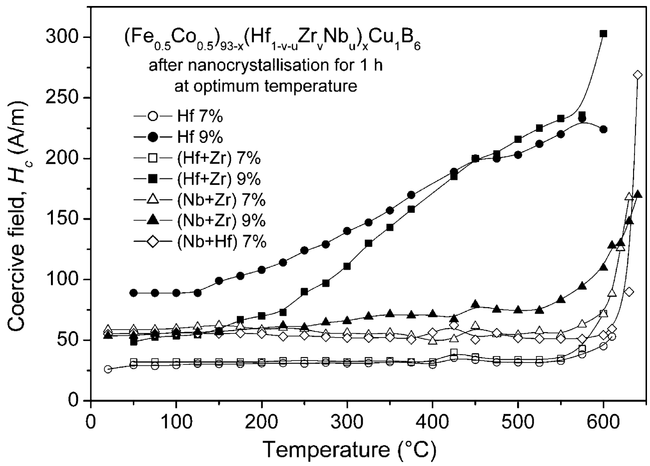

Fig. 3. Dependence of coercive field of nanocrystalline $(Fe_{0.5}Co_{0.5})_{93-x}(Hf_{1-v-u}Zr_vNb_u)_xCu_1B_6$ alloys on temperature and Hf, Zr and Nb content.

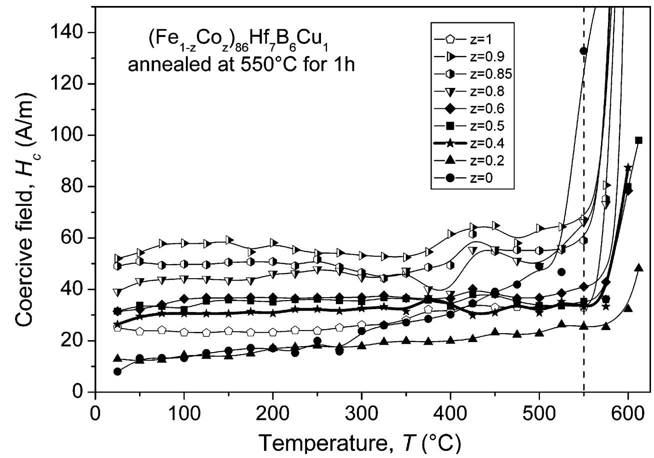

Fig. 4. Coercive field of the optimally annealed $(Fe_{1-z}Co_z)_{86}Hf_7Cu_1B_6$ alloys vs. temperature.

suggested that the application of optimum nanocrystallisation conditions (i.e. the creation of desired structure) is immaterial, because the structure may further evolve at high-application temperature, such as 300 °C. The nanocrystallisation process should rather lead to the completion of the first crystallisation stage. However, it may be expected that the temperature of 350 °C will not provoke the second stage of crystallisation (the crystallisation temperature of an amorphous matrix is of about 700 °C) and the properties will remain similar to these found after annealing for 150 h also after much longer time.

The other group of nanocrystalline alloys suitable for high-temperature applications, are NANOPERMs, also modified with cobalt: $(Fe_{0.5}Co_{0.5})_{93-x}(Hf_{1-v-u}Zr_vNb_u)_xCu_1B_6$ ($x=7$ and 9 at.%, $v=0$, 0.5 and 1, $u=0$, 0.5 and 1). In this case, the chemical composition was adjusted to optimise the magnetic properties and stability, by changing Co, Zr, Hf and Nb content. These nanocrystalline alloys, with optimum soft magnetic properties, are obtained by isothermal annealing of amorphous precursors at 550–600 °C for 1 h. The room temperature coercive field of the alloys depends on Co content (the more Co, the higher H_c) [6] and on Zr, Hf and Nb (called refractory metals, RM) content [7]. The lowest H_c (of about 22 A/m) was observed for the alloy containing 7 at.% of Hf, and the increase of RM concentration, or replacement of Hf with Zr, resulted in an increase of coercive field [7]. Here, similarly to the Co-FINEMETs, the behaviour at working temperature should be taken into account as the major criterion. The coercive field of these alloys measured at high temperature, presented in Fig. 3, proves that the increase of Hf or Zr content worsens the soft magnetic properties at the application conditions. For the alloys containing 7 at.% of RM, H_c is constant until 550 °C, whereas for 9% of RM alloys, H_c monotonously increases with temperature. For this reason, the alloys containing only 7 at.% of RM element are preferred for high-temperature applications.

For the $(Fe_{1-z}Co_z)_{86}Hf_7Cu_1B_6$ ($z=0$–1) alloys, the temperatures of both crystallisation stages depend on the Co content, and, similarly to Co-FINEMETs, are lower for higher cobalt content [6]. In this case, however, the optimum annealing temperature shows a weak dependence on the Co content—in most of the cases 550 °C gives the best coercive field [6]. The investigations of magnetic behaviour at high temperature of the series of HITPERM alloys with variable cobalt content proved that the addition of Co improves the magnetic properties at high temperature, as compared to the 0% of Co alloy, as presented in Fig. 4. For the latter, a monotonous increase of H_c with temperature is observed, although until 275 °C its values are lower than for the Co-containing alloys. Similarly to the results of room temperature measurements, H_c of the alloys at high temperature increases with the increase of Co content, but the differences are insignificant. The lowest values of H_c of all the studied HITPERM alloys exhibits the alloy with $z=0.2$, but it should be born in mind that this alloy also exhibits significantly lower saturation magnetisation than the $z=0.4$–0.6 alloys [8]. The combination of the satisfactorily good magnetic properties is found in the case of the alloys, where the Fe:Co ratio of about 1:1. From the above presented results the preliminary conclusion may be drawn that these alloys may be practically used at 500–600 °C, depending on the chemical composition.

The investigations of thermal stability of HITPERM alloys were carried out by the prolonged annealing at 500–600 °C, and the H_c measurements were carried out at room temperature. All the alloys subjected to the annealing at 600 °C exhibit the significant increase of H_c after a relatively short time, so this temperature is too high for these alloys. The investigations of stability of these alloys at 550 and 500 °C show that the increase of Co content in the alloys reduces the stability of magnetic properties. The highest cobalt content in an alloy with satisfactory stability is $z=0.5$ (Fig. 5a). Also, when RM content is considered, the best stability of properties and structure is found for the alloys with 7% of Hf (Fig. 5b and c). An increase of RM content, or partial replacement of Hf with Zr, result in the increase of H_c after prolonged annealing, meaning the worse thermal stability. The values of H_c after annealing at 550 °C for 1000 h are satisfactory, therefore this temperature may be considered as the maximum temperature of application of HITPERM-type alloys.

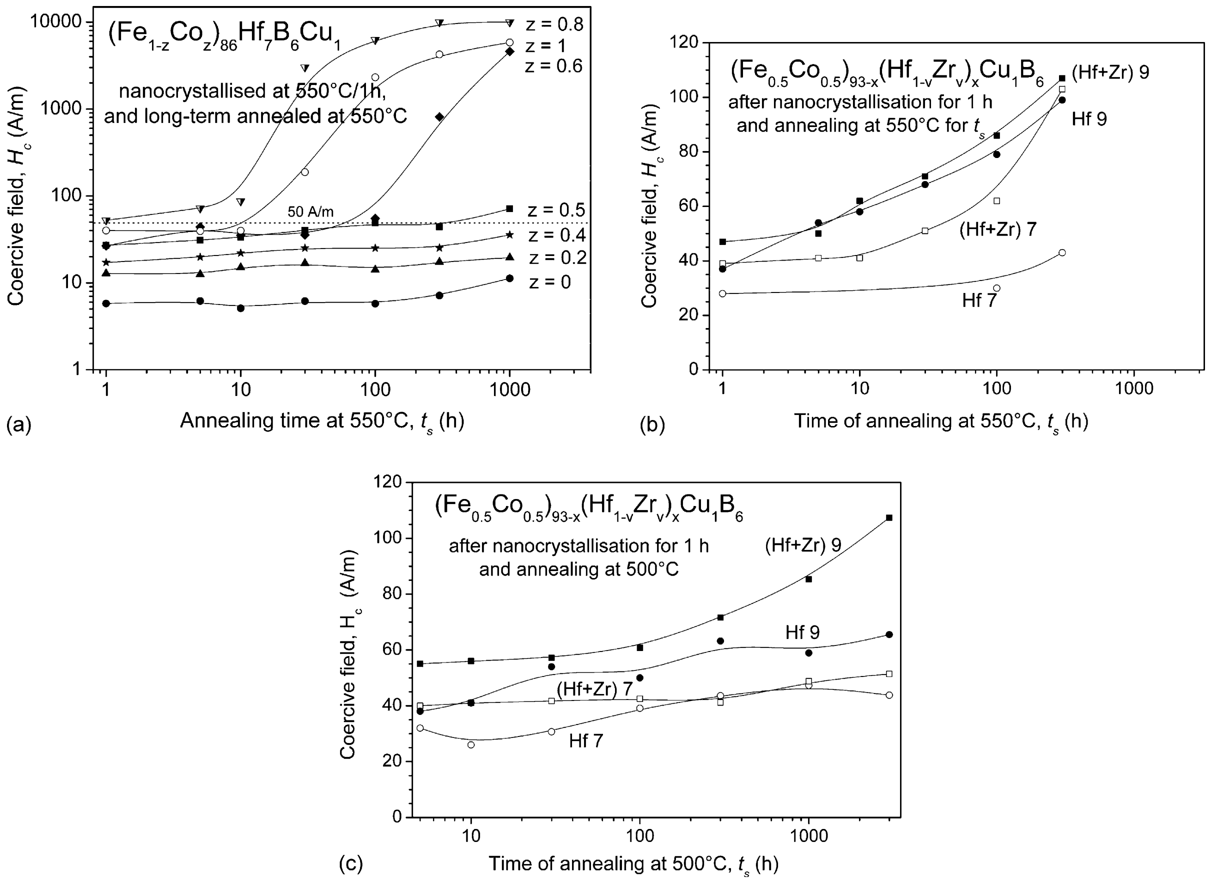

Fig. 5. Dependence of coercive field of $(Fe_{1-z}Co_z)_{93-x}(Hf_{1-v}Zr_v)_xCu_1B_6$ alloys on their chemical composition, temperature and time of long-term annealing.

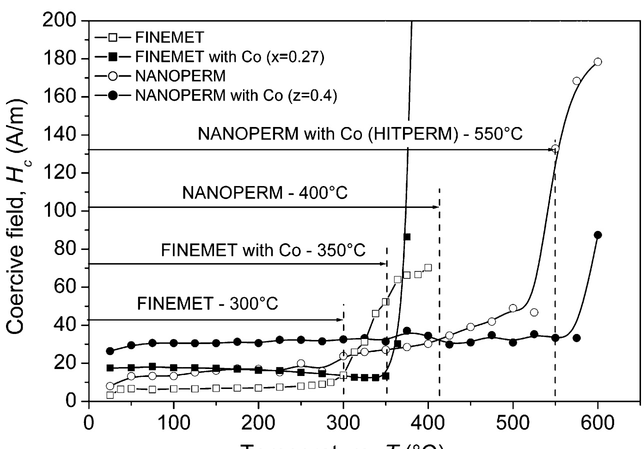

Fig. 6. Temperature ranges of applicability of nanocrystalline soft magnetic alloys.

4. Summary

The magnetic properties of the studied Co-FINEMET and HITPERM alloys measured at elevated and high temperature indicate that each of these groups of alloys is suitable for different working conditions. For FINEMET-type alloys, the coercive field is relatively low, being of 5–30 A/m, up to about 300 °C. Also the magnetic properties are worsened with time during annealing at 300 °C, proving that these alloys are not thermally stable above approximately 250 °C. In the case of FINEMET-type alloys, addition of Co does not improve the properties at high temperature significantly. For the higher temperature band, NANOPERM and HITPERM alloys, e.g. doped with hafnium, should be used. These alloys exhibit good soft magnetic properties up to 550 °C, as well as their properties and structure stability is satisfactory up to this temperature. As the result of this study, the proposed application temperature bands are presented in Fig. 6.

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