Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 19
ISSUE 2
December
2006

Structure and magnetic properties of amorphous and nanocrystalline $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy

S. Lesz [a,*], D. Szewieczek [a], J.E. Frąckowiak [b]
[a] Division of Nanocrystalline and Functional Materials and Sustainable Pro-ecological Technologies, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Institute of Physics and Chemistry of Metals, Silesian University, ul. Bankowa 12 , 40-007 Katowice, Poland
* Corresponding author: E-mail address: sabina.lesz@polsl.pl

Received in revised form 15.07.2006; accepted in final form 30.10.2006

Properties

ABSTRACT

Purpose: The forming of magnetic properties of the nanocrystalline Fe-based are different than those in conventional ferromagnetic materials that is: the soft magnetic properties increase with decreasing of grain size of crystalline phase
Design/methodology/approach: The nanocrystalline Fe-based alloys could be obtain by many different methods, in this work first amorphous ribbons were obtained by planar-flow casting method and after that amorphous precursor were heat treated. The changes of structure associated to crystallization was investigated by X-ray diffractometry, the analysis of Mössbauer spectra made it possible to determine the average hyperfine field and volume fractions of α Fe crystalline phase. The changes of coercive force (H_c) of tapes were investigated using coerciometer with the terrestrial magnetic field compensation.
Findings: The obtained results of investigations shows that crystallization process of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ allowed to form nanocrystalline structure. This crystallization process has two-stages character and exhibit redistribution of the phases stages. The changes of magnetic properties has been observed with increasing the temperature annealing of investigated alloy. The coercive force is decreasing and minimum H_c is obtained at temperature 523 K. The obtained results showed clearly that for examined alloy is possible to determine the specific thermal treatment conditions (T_{op}) causing an improvement of the magnetic properties.
Practical implications: The possibility of optimization of soft magnetic properties is obtaining by the use of controlled crystallization of amorphous alloys.
Originality/value: It has been found that the $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloys consisting of a mostly single bcc structure with nanoscale grains exhibit much better soft magnetic properties than in example well-known nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$. The group of Fe – M – B alloys is called NANOPERM™. From a viewpoint of industrial application they are very attractive materials especially because of the highest B_S among the nanocrystalline alloys
Keywords: Magnetic properties; Amorphous materials; Nanomaterials; Electron microscopy; Heat treatment

1. Introduction

Over the past few years nanocrystalline materials which structure is formed in nanoscale have aroused researchers interest. The nanocrystalline Fe-based alloys obtaining by controlling crystallization of amorphous alloys are a large group among this class of materials. Ones of the basic are two phase soft magnetic materials which exhibit good properties combining high saturation induction, high permeability, low coercive, vanishing magnetostriction and low core losses [1-7].

The investigated $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy belongs to this class of materials. The main parameters of two phase nanocrystalline ferromagnetic materials are:
- the grain size
- volume fraction of the crystalline phase after annealing.

The nanocrystalline structure is obtaining by the use of controlling crystallization of amorphous alloys. However optimal soft magnetic properties are obtaining by applying heat treatment, defined as annealing at temperature T_{op}, which corresponds with maximum value of permeability [8-10]. The structure obtaining by this method in the investigated ferromagnetic materials is two-phase and consisted of αFe nanocrystalline phase and amorphous matrix.

The forming of magnetic properties of this type of alloys are different than those in conventional ferromagnetic materials that is: the soft magnetic properties increase with decreasing of grain size of crystalline phase.

In the present work influence of structure evolution of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy involved by controlled crystallization on magnetic properties has been undertaken.

2. Materials and methods

Investigations were carried out on amorphous tapes having the chemical composition: Fe – 85.4, Hf – 1.4, B – 13.2% at. Tapes obtained by planar-flow casting method were 0.024 mm thickness and 10.0 mm width. The samples of 120 mm long were annealed in temperature range from 373÷1023 K (denotes as T_a) in vacuum. The annealing time was constant and equal 1 h, with step of 50 K. The crystallization temperatures (T_{x1} i T_{x2}) and resistivity of amorphous alloy were determined from isochronous curve ρ of samples, using the linear heating rate 0.007 K/s with measurement "in situ".

The changes of structure associated to crystallization was investigated by X-ray diffractometry with the use of filtered Co K_α radiation. In order to conduct structural study, the high-resolution electron microscope (HRTEM) JEM – 3010 in the range of $1.0 \cdot 10^5\times$ to $1.5 \cdot 10^6\times$ magnitude was used.

The conventional Mössbauer measurements were performed by means of a constant acceleration spectrometer. The ^{57}Co in Rh source with an activity of about 20 mCi was used. The analysis of Mössbauer spectra made it possible to determine the average hyperfine field and volume fractions of αFe crystalline phase. The average hyperfine field was evaluated from the hyperfine field distribution obtained according to the Hesse-Rübartsch method [11,12].

Ductility test of as-quenched and annealed tapes was carried out by bending the tapes of 180° angle. Then value of ε=2g/h, were g-sample thickness, h-distance between micrometer jaws in moment of appearing the fracture, was determined. Fracture surfaces after decohesion in tensile testing were observed by means of OPTON DSM 940 scanning electron microscope (SEM).

The measurements of initial permeability $\mu_i(T_a)$ (at force H≈0.5 A/m and frequency f≈1 kHz) and the intensity of magnetic after effect $\Delta\mu/\mu(t_1)$ ($\Delta\mu=\mu(t_1=30\text{ s})-\mu(t_2=1800\text{ s})$), where μ is the initial magnetic permeability measured at time t after demagnetisation, have been done.

The investigations of tapes in as quenched state and after annealing in temperature range 373÷1023 K by 1 h were performed with the use of automatic device for measurements magnetic permeability.

The changes of coercive force (H_c) of tapes annealed in the mentioned above temperature range and time were investigated using coerciometer with the terrestrial magnetic field compensation.

The magnetisation primary curves for the tapes as well in as quenched state as after optimal annealing were examined by system equipped with fluxmeter.

All magnetic measurements were carried out at room temperature.

3. Results

It was found from the obtained results of structural studies performed by X-ray diffraction, transmission electron microscopy and Mössbauer spectroscopy, that in as quenched state $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy has amorphous structure (Fig. 1,2, Table 1).

Obtained Mössbauer spectrum (Fig. 2a,b) consists of broadened lines typical for the amorphous state.

The investigated $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy in as quenched state has excellent plasticity and in bending test value ε=1 (Table 2) and high value resistivity ρ equal 1.120 μΩm (Fig. 3).

Investigations of tapes fractures after decohesion in tensile test showed their ductile character with vein pattern morphology, typical for amorphous alloys of high ductility (Fig. 4). The magnetic properties of investigated alloy in as quenched state are following: μ_i≈150 (Fig. 5), $\Delta\mu/\mu$≈9% (Fig. 6) and H_c≈23 A/m (Fig. 7).

Basing on isochronous curves of electric resistivity ρ as function of temperature annealing T_a, it was found that crystallization of investigated alloy was two-stage: primary and polymorphous (Fig. 3). The characteristic crystallization temperature of the first stage (T_{x1}) and the second one (T_{x2}) was equal 533 K and 707 K, respectively (Fig. 3).

Annealing of the alloy at temperature 523 K leads to change in the Mössbauer spectrum (Fig. 9). As can be seen from Fig. 9, the transmission spectrum consists of the spectral component with the hyperfine field B equal about 33 T and isomer shift δ=0.00 mm/s, characteristic for the αFe phase (Fig. 9a,b).

Increase the temperature of annealing from 623 K up to 1023 K involves the changes in phase composition of investigated alloy.

The existence of Fe_2Hf, Fe_2B, FeB and HfB_2 phases together with αFe phase has been identified on X-ray diffraction pattern for tapes annealed at temperature from T_a=623 K (Table 1). Increase the temperature annealing involves changes in the Mössbauer spectrum (Fig. 10a,b) too.

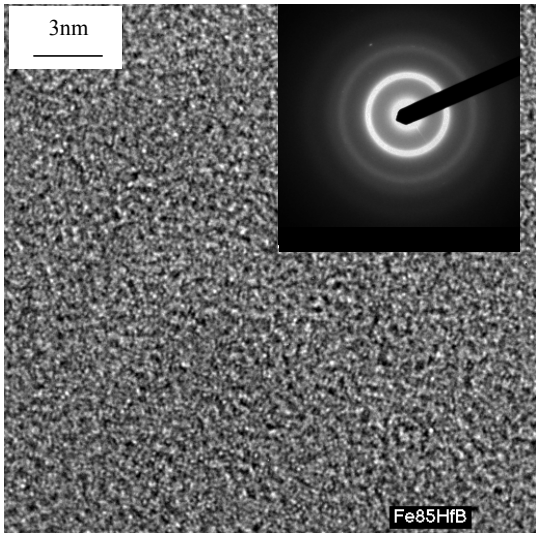
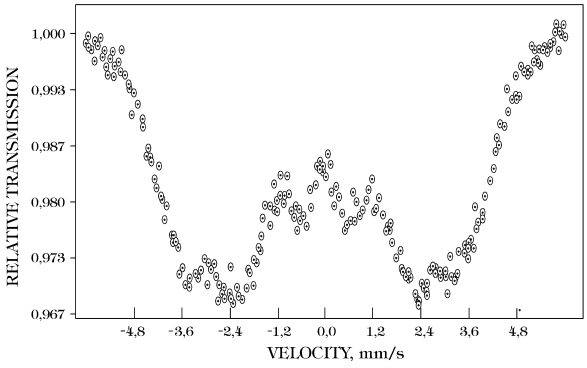


Fig. 1. HRTEM micrograph for $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy in as quenched state

a)



b)

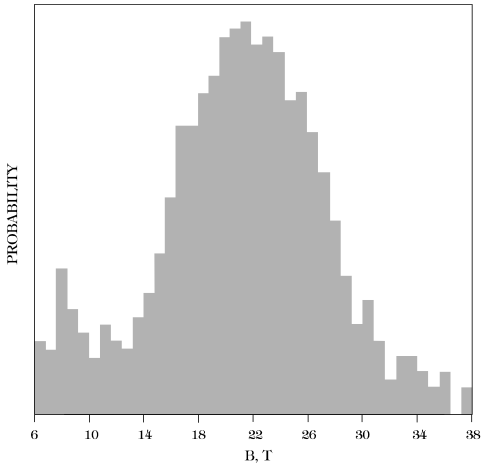


Fig. 2. The Mössbauer spectrum (a) and hyperfine field distributions (b) at room temperature for the samples of the $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy in as quenched state

At T_a=773 K the additional lines in the Mössbauer spectrum corresponding to the crystalline phases appear (probably from the phases of Fe_2Hf, Fe_2B, FeB, HfB_2).

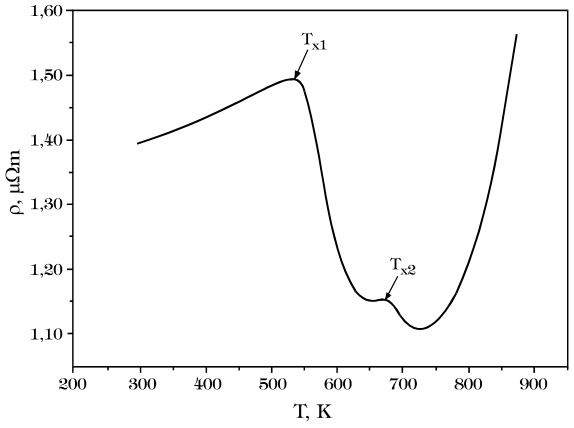


Fig. 3. The isochronal resistivity curve of $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy determined for the heating rate 0.007 K/s

Table 1.
Influence of heat treatment on phase composition of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy

Heat treatment parameters		Phase composition
Temperature T_a, K	Time, h	of alloy
As quenched		
373		
423		A[1)]
473		
498		
523		
548		A[1)]+αFe
573	1	
623		
673		
723		
773		αFe, Fe_2B,
823		HfB_2,
873		FeB, Fe_2Hf
923		
973		
1023		

[1)] A – amorphous phase

The last stage of annealing, in the temperature range from 823K up to 1023 K, is characterized by decrease of magnetic permeability (Fig. 5) with the decrease of $\Delta\mu/\mu$ (Fig. 6) of investigated alloy.

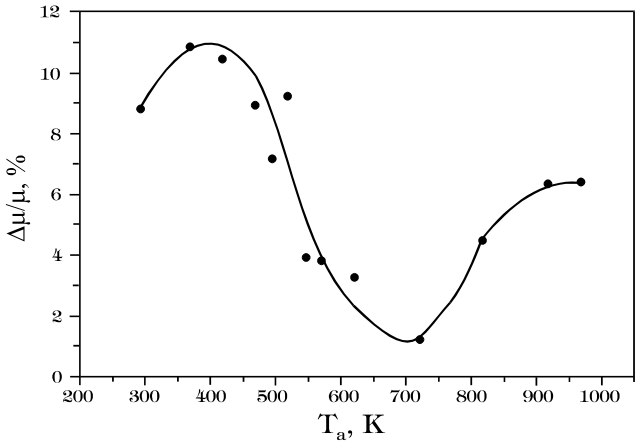


Fig. 6. Magnetic after effect $\Delta\mu/\mu$ ($\Delta\mu=\mu(t_1=30\ s)-\mu(t_2=1800\ s$ after demagnetisation) measured at room temperature for $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy after 1 h annealing at temperature T_a

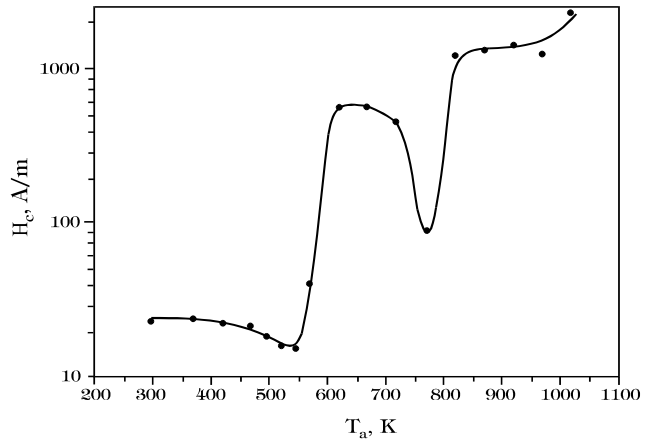


Fig. 7. Coercive force H_c measured at room temperature for $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy after 1 h annealing at temperature T_a

Changes in magnetic permeability achieved from the primary curves of magnetisation for the alloy in as quenched state and after optimal annealing shows that the optimal annealing for examined alloy allows to achieve $\mu_{max}\approx37700$ at intensity of magnetic force $H_{\mu max}\approx1$ A/m. (Fig. 12).

Described process of crystallization based on analysis of isochronal resistivity curves exhibits in general the correlation between proceeding of alloy crystallization determined in X-ray diffraction method, Mössbauer spectroscopy and magnetic properties. Heat treatment process at annealing temperature T_a, near the crystallization temperature T_{x1} ($T_a=T_{x1}\pm20$ K) in time of 1 h which was applied in present work is mainly use method forming nanocrystalline structures from amorphous alloys. The aim of controlling crystallization was transformation of some amorphous phase volume into nanocrystalline phase without presence of boron phases, which are forming in second stage of crystallization process. The temperature of the optimisation annealing (T_{op}=523 K) of investigated alloy is lower then crystallization temperature and temperature difference is equal about 10 K.

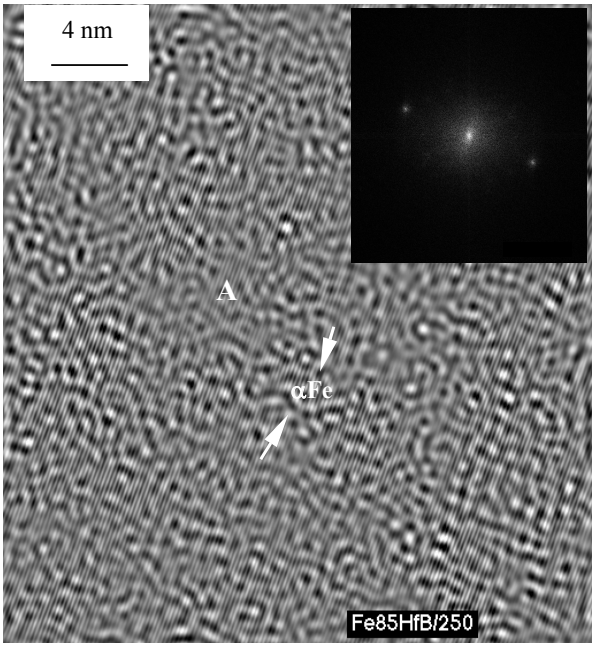


Fig. 8. HRTEM micrograph for $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy after annealing at T_{op}=523 K by 1 h

The obtained results of investigations shows that crystallization process of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ allowed to form nanocrystalline structure. This crystallization process of investigated alloy has two-stages character and exhibit redistribution of the phases stages. The temperature difference T_{x2}-T_{x1} is equal 170 K (Fig. 3) and the crystallization process exhibits low transformation rate. This effect is benefit from the point of view of controlled crystallization process, which aim is forming two-phase structure consisted of αFe crystalline phase and amorphous matrix. It makes easier proceeding of nanocrystallization process and reducing the risk of forming the undesirable borides.

The first stage of crystallization process can be related to the formation of αFe crystalline phase and amorphous phase (primary crystallization) as well the second stage due to the formation of borides (polymorphous crystallization) [13-15].

The αFe hafnium-free phase formed in the second stage of crystallization process can suggest that the diffusion of hafnium from crystallization front to residual amorphous phase takes place [16].

The addition of hafnium results in reduced crystal growth rate of αFe crystalline phase due to the small diffusivity of hafnium in Fe investigated alloy at crystallization temperature range.

The phase composition of investigated alloy after annealing at optimisation temperature is composed of amorphous phase and αFe crystalline phase. From the obtained results of the structural studies it was found that the structure is consisted in major part of intergranular amorphous phase (Fig. 9a,b). Therefore the volume fraction of the αFe crystalline phase is 1.5% and it's grains size is from 5 to 25 nm (Fig. 8).

As well quantity as grains size of crystalline phase are different from acknowledge in the literature as optimal values for the ferromagnetic nanocrystalline materials [17,18].

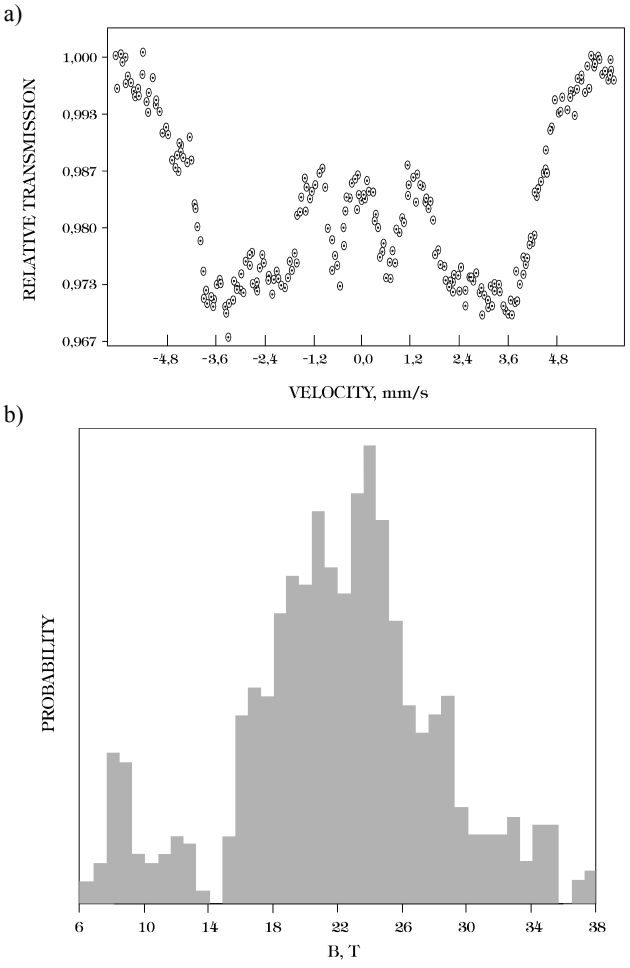


Fig. 9. The Mössbauer spectrum (a) and hyperfine field distributions (b) at room temperature for the samples of the $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy after annealing at T_{op}=523 K by 1 h

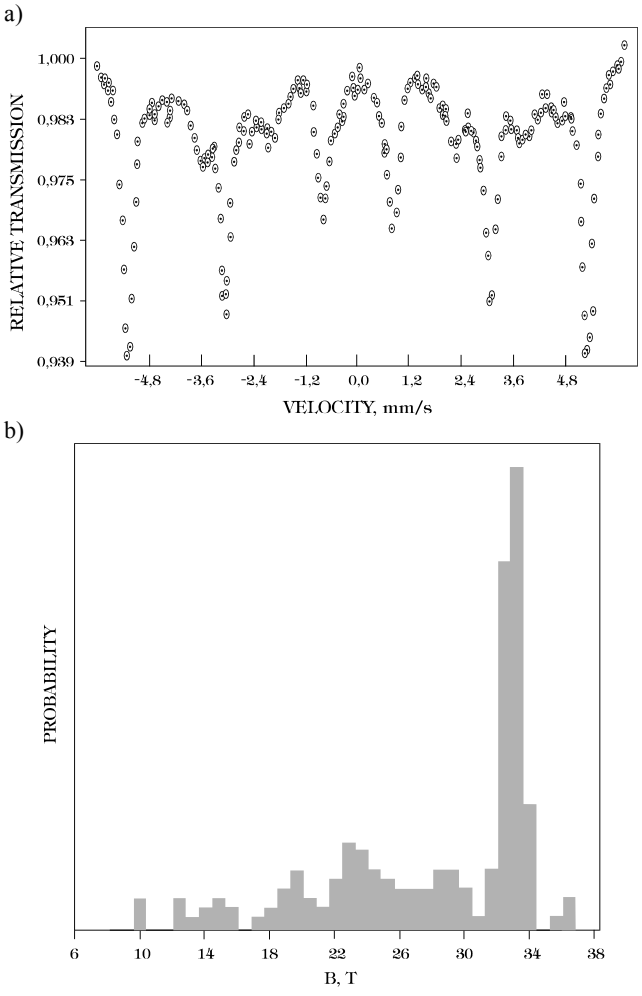


Fig. 10. The Mössbauer spectrum (a) and hyperfine field distributions (b) at room temperature for the samples of the $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy after annealing at 773 K by 1 h

For example in paper [17] the optimal volume fraction of crystalline phase equal 70-75% and grains size smaller than 25 nm were given. The obtained magnetic properties ($\mu_i \approx 240$ and $H_c \approx 16$ A/m) after annealing at optimisation temperature are connected with a quantity and grains size of crystalline phase in investigated alloy (Fig. 8,9). The volume fraction is probably not enough to proceeding the effect of averaging of magnetocrystalline anisotropy.

The result of this is high value of coercive force H_c in investigated alloy. Too small of volume fraction of crystalline phase leads to high magnetostriction value.

The obtained results showed clearly that for examined alloy is possible to determine the specific thermal treatment conditions (T_{op}) causing an improvement of the magnetic properties.

In compare to as quenched state has been achieved increase of magnetic properties after annealing of $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy at T_{op}. For examined alloy in the as quenched state the initial permeability μ_i and coercive force H_c is about 150 and 23 A/m, respectively whereas after annealing at T_{op} is $\mu_i \approx 240$, $H_c \approx 16$ A/m (Fig. 5,7) and $\mu_{max} \approx 37700$ (Fig. 12).

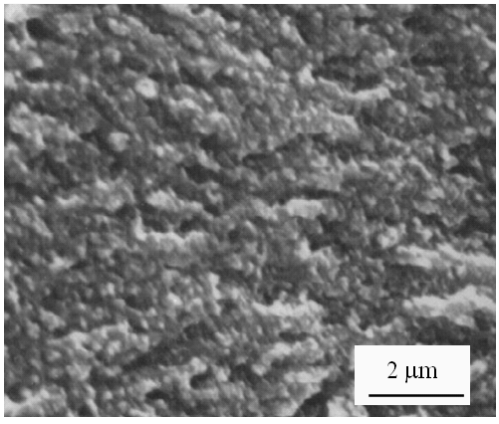


Fig. 11. SEM image of fracture of $Fe_{85.4}Hf_{1.4}B_{13.2}$ tapes after decohesion in tensile test – annealing temperature 723 K/1 h; brittle intercrystalline fracture

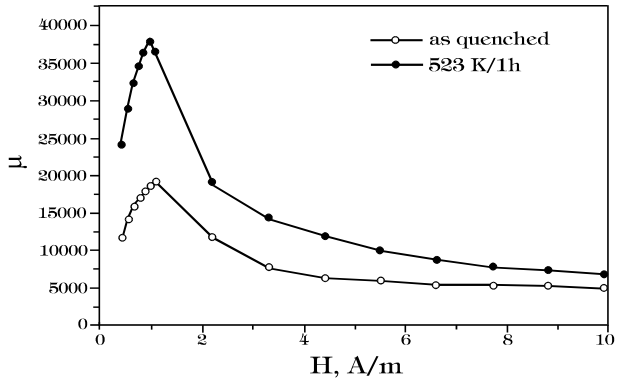


Fig. 12. The maximum permeability μ_{max} for amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy in as quenched state and after annealing at temperature T_{op}= 523 K by 1 h

4. Conclusions

It has been showed that the obtaining of nanocrystalline structure in the investigated alloys, consisted of αFe grains and amorphous phase is possible by the use of controlling primary crystallization of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy.

The obtained results of investigations showed that crystallization process of amorphous $Fe_{85.4}Hf_{1.4}B_{13.2}$ allowed to form nanocrystalline structure consisted of αFe crystalline phase and amorphous matrix.

This crystallization process of investigated alloy has two-stages character and exhibits redistribution of the phases stages i.e. primary and polymorphous crystallization. Temperature which allowed to achieve nanocrystalline structure is near the crystallization temperature i.e. $T_a=T_{x1}\pm20$ K.

The possibility of optimisation of soft magnetic properties is obtaining by the use of controlled crystallization of amorphous alloys. This process can be explained by forming αFe crystalline phase in amorphous matrix and is connected with thermal activation. The structure of $Fe_{85.4}Hf_{1.4}B_{13.2}$ alloy which is characterised by excellent soft magnetic properties ($\mu_{max}\approx37700$ and $H_c\approx16$ A/m) consists of αFe crystalline phase (in volume fraction 1.5%) of grains changing from 5 to 25 nm and amorphous matrix.

Acknowledgements

This work was partially supported by the Committee for Scientific Research under Grant No. 7 T08A 029 16.

References

[1] M.E. McHenry, M.A. Willard, D.E. Laughlin, Amorphous and nanocrystalline materials for applications as soft magnets Progress in Materials Science. 44 (1999) 291–433.
[2] T. Mizushima, A. Makino, A. Inoue, Structure and magnetic properties of Fe-based glassy alloys Materials Science and Engineering, A Volume, 226-228 (1997) 721-725.
[3] K. Suzuki, A. Makino, A. Inoue, T. Masumoto, Soft magnetic properties of nanocrystalline bcc Fe-Zr-B and Fe-M-B-Cu (M=transition metal) alloys with high saturation magnetization, Journal of Applied Physics 70 (1991) 6232-6237.
[4] A. Makino, A. Inoue, T. Masumoto, Nanoctystalline soft magnetic-Fe-M-B (M=Zr, Hf, Nb) alloys produced by crystallization of amorphous phase, Materials Transaction JIM 36 (1995) 924-930.
[5] Y. Naitoh, T. Bitoh, T. Hatanai, A. Makino, A. Inoue, T. Masumoto, Applications of nanocrystalline soft magnetic Fe-M-B (M = Zr, Nb) alloys, NanoStructured Mater. 8, 8 (1997) 987-995.
[6] P. Kwapuliński, J. Rasek, Z. Stokłosa, G. Haneczok, Magnetic properties of $Fe_{14}Cu_1Cr_xZr_{3-x}Si_{13}B_9$ amorphous alloy, Journal of Magnetism and Magnetic Materials, 2003, 413.
[7] S. Lesz, D. Szewieczek, Optymalization of magnetic properties of amorphous and nanocrystalline Fe – Hf – B alloy, Proceedings of the third Scientific Conference M^3E'2005, Gliwice–Wisła 2005, 373-380.
[8] S. Lesz, R. Szewczyk, D, Szewieczek, A. Bieńkowski, The structure and magnetic properties of the Fe-based amorphous alloy with Hf addition, Proceedings of 11 th Internation Scientific Conference AMME'02, Gliwice-Zakopane 2002, 311-318.
[9] K. Suzuki, J. M. Cadogan, Critical behaviour in the temperature dependence of the coercivity for nanocrystalline soft-magnetic materials, Philosophical Magazine Letters 77 (1998) 371-379.
[10] P. Kwapuliński, J. Rasek, Z. Stokłosa, G. Haneczok, Optimisation of soft magnetic properties in Fe–Cu–X–$Si_{13}B_9$ (X=Cr, Mo, Zr) amorphous alloys Journal of Magnetism & Magnetic Materials 234 (2001) 218-226.
[11] P. Kwapuliński, A. Chrobak, G. Haneczok, Z. Stokłosa, J. Rasek, J. Lelątko, Optimatization of soft magnetic properties in nanoperm type alloys, Materials Science and Engineering C 23 (2003) 71-75.
[12] A. Oleś, Experimental methods of solid state physics, WNT, Warsaw, 1998 (in Polish).
[13] A. Makino, T. Bitoh, J.T. Murakami, T. Hatanai, A. Inoue, T. Masumoto, Nanocrystalline soft magnetic Fe-M-B (M = Zr, Hf, Nb) alloys " NANOPERM " with high magnetic induction Journal De Physique IV, 8 (1998) 103-107.
[14] R. Grossinger, D. Holzer, C. Kussbach, H. Sassik, R. Sato Turtelli, J.P.Sinnecker, E.Wittig, High temperature behaviour of FINEMET ribbons in the amorphous and in the nanocrystalline state, IEEE Transactions on magnetics, 31, November (1995) 3883-3885.
[15] P. Kwapuliński, A. Chrobak, J. Rasek, Z. Stokłosa, G. Haneczok, The influence of zirconium on magnetic properties and crystallisation of amorphous alloys based on iron, Proceedings of the 10th Jubilee International Scientific Conference AMME'01, Gliwice–Cracow–Zakopane, Poland 2001, 333-336.
[16] P. Kwapuliński, J. Rasek, Z. Stokłosa, B. Zegrodnik, The influence of heat treatment on magnetic and electric properties of Fe-based metallic glasses, Proceedings of the 7th International Scientific Conference AMME'98, Gliwice–Zakopane, Poland (2001) 305-308.
[17] P. Kwapuliński, J. Rasek, Z. Stokłosa, G. Haneczok, Magnetic properties of amorphous and nanocrystalline alloys based on iron, Journal of Materials Processing Technology 157–158, (2004) 735–742.
[18] Y. Yoshizawa, S. Oguma, Y. Yamauchi, New Fe-based soft magnetic alloys composed of ultrafine grain structure Journal of Applied Physics 64 (1988) 6044-6046.