FeCo-BASED SOFT MAGNETIC NANOCRYSTALLINE ALLOYS

Ivan ŠKORVÁNEK[*], Jozef MARCIN[*], Jana TURČANOVÁ[*], Jozef KOVÁČ[*], Peter ŠVEC[**]
[*]Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
[**]Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 842 28 Bratislava, Slovak Republic

ABSTRACT

The influence of microstructure on the magnetic properties is studied in series of of FeCoNbB, FeCoZrB and FeCoMoBCu amorphous and nanocrystalline alloys with different amount of crystalline phase.V arious thermomagnetic treatments have been used in order to tailor the soft magnetic characteristics of these alloys for potential applications. We report on a beneficial effect of both longitudinal and transverse magnetic field applied during annealing. A heat treatment under the presence of longitudinal magnetic field results in squared hysteresis loops that are characterized by very low coercivities. Sheared loops with good field linearity and low coercivity were achieved for all alloys after annealing in transverse magnetic field. Such characteristics are of particular interest for the high frequency transformers and the magnetic sensors.

Keywords: *soft magnetic materials, nanocrystalline alloys, magnetization, coercivity, induced anisotropy*

1. INTRODUCTION

The reduction of the grain sizes to the nanometer range may vary drastically the functional properties of materials, including the magnetic behavior. Typical examples of such systems are nanocrystalline Fe-based alloys prepared by devitrification of melt-spun amorphous precursors, which belong to an important group of soft magnetic materials [1]. The properties of these materials can vary widely, depending on the size and volume fraction of the nanocrystalline grains as well as on the magnetic properties of the intergranular amorphous matrix. It has been shown that the crucial role in the marked improvement of their soft magnetic behaviour is played by the reduction of the effective magnetic anisotropy, which occurs when the size of nanocrystals become comparable with the magnetic exchange length [2].

The discovery of the excellent soft magnetic properties in the nanocrystalline alloys based on FeCuNbSiB, and Fe(Zr,Nb)B(Cu), called FINEMET and NANOPERM, as well as the later development of the nanocrystalline (Fe,Co)MBCu alloys (M=Zr, Nb and Hf), named HITPERM, has stimulated an enormous research activity in these systems [1]. The HITPERM alloys, display usually less favorable soft magnetic properties as compared to the FINEMET or NANOPERM alloys. However, they exhibit a higher saturation magnetic flux density and they are capable of operation at higher temperatures [3,4].

In order to enhance the application potential of the FeCo-based nanocrystalline alloys it is important to deepen knowledge about the available processing techniques that can be used to tailor their magnetic properties. One possible way, which could be employed for this purpose, is the thermal processing under the presence of external magnetic field, called also „magnetic annealing". The effect of heat treatment under a presence of magnetic field is to superpose on the material an extra annealing-induced magnetic anisotropy in addition to whatever anisotropies may have been present originally. This induced anisotropy is almost always uniaxial, i.e. it creates an easy axis of magnetization, which complies with the direction of magnetization during annealing. In the case of the soft magnetic nanocrystalline alloys, it was shown that the local random magnetocrystalline anisotropies are strongly suppressed by exchange interactions, and thus, they can be easily overcome by the long ranged macroscopic anisotropy induced by field annealing.

Our previous study on the magnetic field annealing effects in the FeCoNbB-type nanocrystalline alloys with various ratios of Fe/Co atoms has clearly demonstrated that the improvement of the soft magnetic characteristics due to field annealing is most significant for the $Fe_{1-x}Co_x$ concentrations close to x=0.5 [5,6]. Such behavior strongly indicates that the operative mechanism of induced anisotropy in these alloys is the magnetic atoms pair ordering.

In this work, a controllable field-induced magnetic anisotropy is produced in the sesies of nanocrystalline $Fe_{44.5}Co_{44.5}Zr_7B_4$, $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and $Fe_{38}Co_{38}Mo_8B_{15}Cu$ samples with different amount of crystalline phase. We report on the beneficial effects of both longitudinal and transverse magnetic field applied during the heat treatment process on the application-oriented magnetic characteristics of these soft ferromagnets.

2. EXPERIMENTAL

Master alloys have been prepared by arc-melting from elements of 99.95 % purity. Amorphous ribbons 6 mm wide and ~ 25 μm thick were produced by planar flow casting. Chemical composition of the ribbons was checked by inductionally coupled plasma spectrometer and found to be as indicated to the accuracy of 3% of the nominal content of each element. In order to prepare the nanocrystalline samples with preferred direction of induced anisotropy, the pieces of amorphous ribbons (6 cm long) were isothermally annealed under a high vacuum for 1 hour at different temperatures above the crystallization temperature in the presence of transverse (TF) or longitudinal (LF) magnetic field. In the case of TF-annealed samples, the furnace was placed inside the commercial permanent magnet system (Magnetic Solutions LTD) producing a magnetic field of 640 kA/m directed in the plane of the ribbon and perpendicular to its length. In the LF-annealed samples, the same furnace was inserted into the water-cooled solenoidal coil that provided a magnetic field of 20 kA/m oriented along the ribbon length. After such annealing, the specimens were slowly cooled to room temperature in a presence of the magnetic field. A typical cooling rate was 3 K/min. The reference samples were annealed and cooled in a zero magnetic field (ZF).

The changes of microstructure upon annealing were investigated by transmission electron microscopy (TEM), and X-ray diffraction (XRD). Samples for transmission electron microscopy were thinned, after corresponding heat treatment, by ion beam milling; TEM and electron diffraction observations were performed using JEM1200 EX microscope. The X-ray measurements were performed using CuKα radiation in Bragg-Brentano configuration with a graphite monochromator in the diffracted beam. The magnetization measurements have been performed by vibrating sample magnetometer (VSM) over the temperature range from 300 K to 1100 K, in a field 240 kA/m and with a heating rate 10 K/min. The soft magnetic behavior was investigated by using a Forster type B-H loop tracer.

3. RESULTS AND DISCUSSION

Fig. 1 shows the DSC thermograms of the as-quenched samples measured in the temperature range where the primary crystallization takes place. The exothermal peaks with onset at T_{x1} and the peak position at T_{p1} correspond to the formation of the nanocrystalline bcc-FeCo. An increase of the onset and peak crystallization temperatures from T_{x1} = 695 K and T_{p1} = 719 K for $Fe_{38}Co_{38}Mo_8B_{15}Cu$ to T_{x1} = 745 K and T_{p1} = 764 K for $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and to T_{x1} = 769 K and T_{p1} = 788 K for $Fe_{44.5}Co_{44.5}Zr_7B_4$ has been detected.

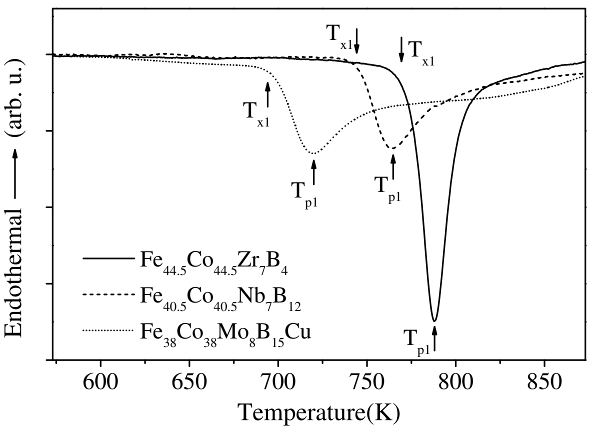

Fig. 1 DSC thermograms of the amorphous samples

The changes in microstructure upon annealing were examined by TEM. Ultrafine grains were observed for $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and $Fe_{38}Co_{38}Mo_8B_{15}Cu$ where typical grain dimensions ranged from 5-10 nm. In the case of $Fe_{44.5}Co_{44.5}Zr_7B_4$, formation of bigger nanograins that show a tendency towards the grain clustering is observed [4].

The temperature dependencies of magnetization for the as-quenched sample and the nanocrystalline samples annealed for 1 hour at indicated temperatures are shown in Fig. 2. The thermomagnetic plots were obtained by using a constant heating rate of 10 K/min. The magnetization of both amorphous samples shows a monotonic decrease with an increase of temperature.

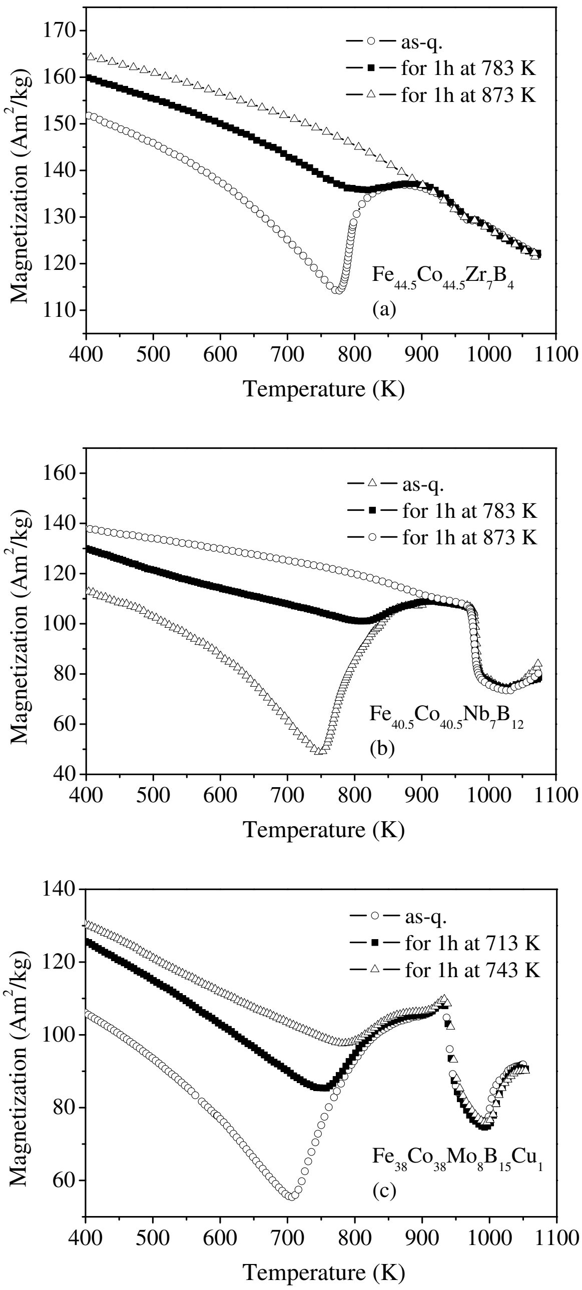

Fig. 2 Thermomagnetic plots of the amorphous and partially crystallized (a) $Fe_{44.5}Co_{44.5}Zr_7B_4$, (b) $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and (c) $Fe_{38}Co_{38}Mo_8B_{15}Cu_1$ samples

After overcrossing the crystallization temperature of bcc-FeCo phase, a strong increase in the magnetization due to formation of crystalline particles with higher Curie temperature is observed. The magnetization starts to decrease again when the process of primary crystallization is finished. The magnetization of the nanocrystalline sample is higher as that of as-quenched sample due to a presence of bcc-FeCo particles. The thermomagnetic plots in Fig 3 indicate that the primary crystallization is finished for the $Fe_{44.5}Co_{44.5}Zr_7B_4$ and $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ samples annealed at 873 K while in the case of all other samples the primary crystallization process is not completed yet.

A main attention of this work has been devoted to the study of the effects of annealing under presence of external magnetic field in order to induce controllable uniaxial anisotropy in the samples. The effect of field annealing on the hysteresis loops of $Fe_{44.5}Co_{44.5}Zr_7B_4$, $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and $Fe_{38}Co_{38}Mo_8B_{15}Cu$ alloys is demonstrated in Figs. 3-5. The shape of the hysteresis loop is dictated by the relative importance of domain wall displacement and magnetic moment rotation processes in the sample. According to direction of the induced anisotropy, the magnetization curves with large or small squareness ratio could be obtained. The rotation processes tend to dominate after annealing in the transverse magnetic field, and consequently, the sheared loops with relatively good field linearity are achieved. Such characteristics are of particular interest for high frequency transformers and magnetic sensors. A heat treatment under the presence of longitudinal magnetic field results in squared hysteresis loops that are characterized by a significant reduction of the coercivity. The coercive field values for Nb- and Mo-containing samples are in the range of 2 – 8 A/m, i.e. they are markedly lower than those previously reported for the field annealed HITPERM-type alloys [6-8].

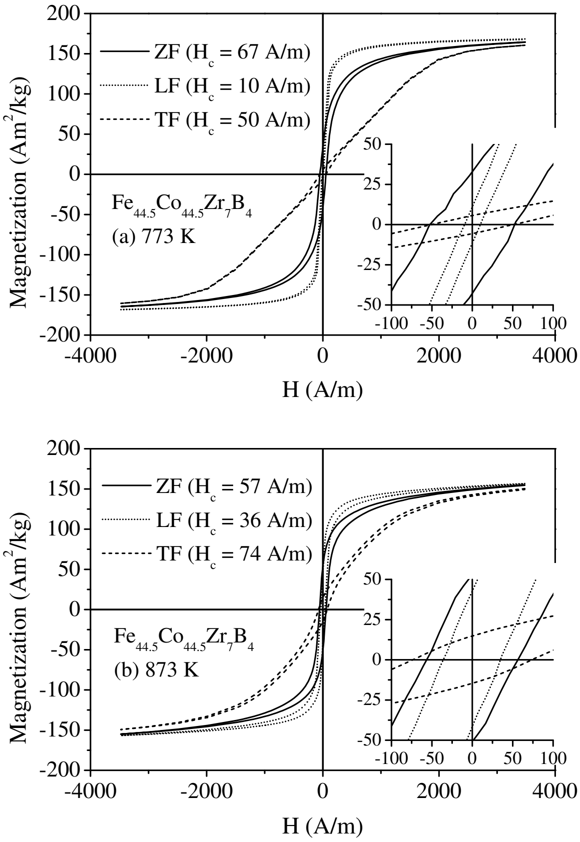

Fig. 3 Hysteresis loops for $Fe_{44.5}Co_{44.5}Zr_7B_4$ after different field annealing for 1 hour at indicated temperature

From the area in the first quadrant between the loops corresponding to TF samples (hard direction) and LF samples (easy direction), the values of induced anisotropy constant, K_u, can be determined. The maximum value of induced anisotropy constant $K_u \sim 1350$ J/m^3 is observed for the $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ annealed at 773 K. The induced anisotropy constant for the $Fe_{44.5}Co_{44.5}Zr_7B_4$ annealed at 773 K reaches the value of $K_u \sim 1240$ J/m^3. The lower value of K_u (935 J/m^3) is observed for $Fe_{38}Co_{38}Mo_8B_{15}Cu$ annealed at 743 K, which is attributed to a decrease of the saturation magnetization due to higher amount of non magnetic elements in this sample.

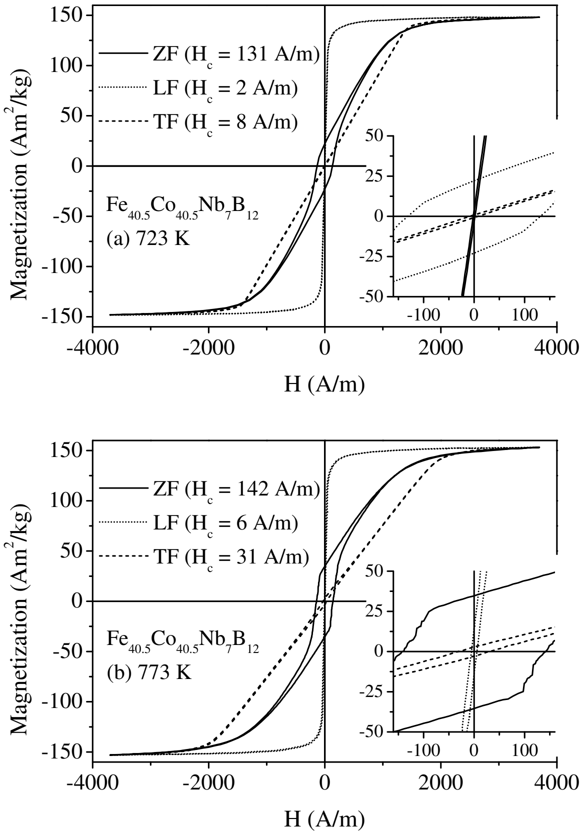

Fig. 4 Hysteresis loops for $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ after different field annealing for 1 hour at indicated temperature

Directional order theory predicts the dependence of induced anisotropy for binary alloys with two constituent magnetic elements A_xB_{1-x} to go as $x^2(1-x)^2$ [9]. The composition of the nanocrystalline alloys studied in the present paper are very close to the equiatomic FeCo concentration, which explains the observed strong influence of the magnetic field annealing treatment. Directional ordering effects can occur even if the alloy is heat treated below its Curie temperature in the absence of an external magnetic field. In this case, the internal magnetic field of each domain will influence the directionality of diffusion. The consequence of this „self magnetic annealing“ is that the domains and domain walls tend to be stabilized in the positions they occupied during the annealing, which results often in undesirable increase of coercive field. The fact that the field annealed samples reveal a smaller coercivity than the samples annealed without field can thus be understood from more simple domain configuration due to the uniform induced anisotropy, which in addition suppress the effects of the angular dispersion of the easiest magnetic axis from one region of exchange coupled grains to the other as it was recently observed for the field annealed FINEMET alloys [10].

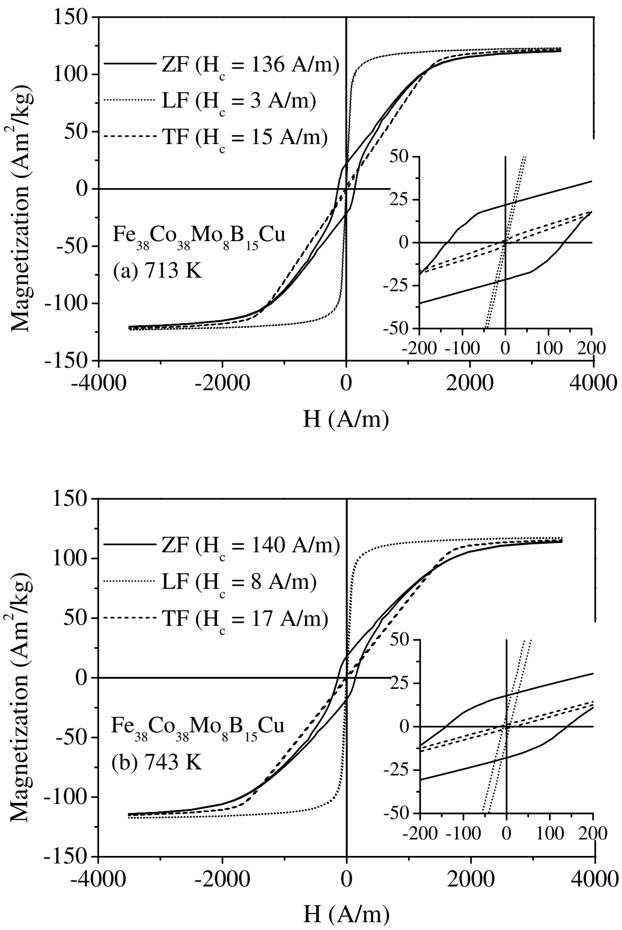

Fig. 5 Hysteresis loops for $Fe_{38}Co_{38}Mo_8B_{15}Cu$ after different field annealing for 1 hour at indicated temperature

4. CONCLUSIONS

The influence of the heat treatment under an external magnetic field on the magnetic properties of annealed material has been investigated in the $Fe_{44.5}Co_{44.5}Zr_7B_4$, $Fe_{40.5}Co_{40.5}Nb_7B_{12}$ and $Fe_{38}Co_{38}Mo_8B_{15}Cu$ nanocrystalline alloys. We have shown that the crystallization of amorphous material in the longitudinal or transverse magnetic field is very powerful tool to tailor the shape of the hysteresis loops of these nanocrystalline alloys. Sheared loops with good field linearity and low coercive field were achieved after annealing in transverse magnetic field. A heat treatment of the samples under the presence of longitudinal magnetic field results in squared hysteresis loops characterized by the values of the coercive field in the range of 2 – 8 A/m. These H_c values are superior to those reported previously for HITPERM alloys. A marked response of the magnetic properties of FeCo-based nanocrystalline alloys to the magnetic field annealing can be utilized in their better adaptation to the potential electromagnetic applications.

ACKNOWLEDGMENTS

This work was realized within the frame of the project „Centre of Excellence for Advanced Materials with Nano- and Submicron - Structure“, which is supported by the Operational Program “Research and Development” financed through European Regional Development Fund.

REFERENCES

[1] McHENRY, M. E. – WILLARD, M. A. – LAUGHLIN, D.E.: Amorphous and nanocrystalline materials for applications as soft magnets, *Progress in Materials Science*, vol. 44 , no. 4, pp. 291-433, Oct. 1999.

[2] HERZER, G.: Creep induced magnetic anisotropy in nanocrystalline Fe-Cu-Nb-Si-B alloys, *IEEE Transactions on Magnetics*, vol. 30, no. 6, pp. 4800-4802, Nov. 1994.

[3] WILLARD, M. A. – LAUGHLIN D. E. – McHENRY, M.E. – THOMA, D. – SICKAFUS, K. - CROSS, J. O. – HARRIS, V. G.: Structure and magnetic properties of $(Fe_{0.5}Co_{0.5})_{88}Zr_7B_4Cu_1$ nanocrystalline alloys, *Journal of Applied Physics*, vol. 84, no. 12, pp. 6773-6777, Dec. 1998.

[4] ŠKORVÁNEK, I. – ŠVEC, P. – MARCIN, J. – KOVÁČ, J. – KRENICKÝ, T. – DEANKO, M.: Nanocrystalline Cu-free HITPERM alloys with improved soft magnetic properties, Physica Status Solidi A, vol. 196, no. 1, pp. 217-220, Mar. 2003.

[5] ŠKORVÁNEK, I. – MARCIN, J. – KRENICKÝ, T. – KOVÁČ, J. – ŠVEC, P. – JANIČKOVIČ, D.: Improved soft magnetic behaviour in field-annealed nanocrystalline Hitperm alloys, *Journal of Magnetism and Magnetic Materials*, vol. 304, no. 2, pp. 203-207, Sep. 2006.

[6] ŠKORVÁNEK, I. – MARCIN, J. – TURČANOVÁ, J. – WOJCIK, M. – NESTERUK, K. – JANIČKOVIČ, D. – ŠVEC, P.: Field induced anisotropy and stability of soft magnetic properties towards high temperature in Co-rich nanocrystalline FeCoNbB alloys, *Journal of Magnetism and Magnetic Materials*, vol. 310, no. 2, pp. 2494-2496, Mar. 2007.

[7] JOHNSON, F. – GARMESTANI, H. – CHU, S. Y. – McHENRY, M. E. – LAUGHLIN, D. E.: Induced anisotropy in FeCo-based nanocrystalline ferromagnetic alloys (HITPERM) by very high field annealing, *IEEE Transactions on Magnetics*, vol. 40, no. 4, pp. 2697-2699, Jul. 2004.

[8] SUZUKI, K. – ITO, N. – GARITAONANDIA, J. S. – CASHION, J. D.: High saturation magnetization and soft magnetic properties of nanocrystalline $(Fe,Co)_{90}Zr_7B_3$ alloys annealed under a rotating magnetic field, *Journal of Applied Physics*, vol. 99, no. 8, pp. 08F114, Apr. 2006.

[9] O`HANDLEY, R. C.: Modern Magnetic Materials, *Principles and Applications*, John Wiley & Sons, Inc., New York, 1999.

[10] FLOHRER, S. – SCHAFER, R. – POLAK, C. – HERZER, G.: Interplay of uniform and random anisotropy in nanocrystalline soft magnetic alloys, *Acta Materialia*, vol. 53, no. 10, pp. 2937-2942, Jun. 2005.

Received January 15, 2010, accepted July 9, 2010

BIOGRAPHIES

Ivan Škorvánek was born on 4. 10. 1957. He graduated from the Faculty of Science P.J.Šafarik University, Košice in 1982. He defended his PhD in 1988. He is head of the Laboratory of Nanomaterials and Applied Magnetism, which belongs to the Institute of Experimental Physics, Slovak Academy of Sciences in Košice.

Jozef Marcin was born on 10. 10. 1971. He graduated from the Faculty of Science P.J.Šafarik University, Košice in 1996. He defended his PhD in 2003. He is working as researcher in the Laboratory of Nanomaterials and Applied Magnetism, which belongs to the Institute of Experimental Physics, Slovak Academy of Sciences in Košice.

Jana Turčanová was born on 28. 6. 1982. She graduated from the Faculty of Science P.J.Šafarik University, Košice in 2005. She defended his PhD in 2009. She is working as researcher in the Laboratory of Nanomaterials and Applied Magnetism, which belongs to the Institute of Experimental Physics, Slovak Academy of Sciences in Košice.

Jozef Kováč was born on 3. 4. 1954. He graduated from the Faculty of Science P.J.Šafarik University, Košice in 1977. He defended his PhD in 1989. He is working as senior researcher in the Laboratory of Nanomaterials and Applied Magnetism, which belongs to the Institute of Experimental Physics, Slovak Academy of Sciences in Košice.

Peter Švec was born on 4. 1. 1955. He graduated from the Faculty of Electrical Engineering, Slovak Technical University, Bratislava in 1979. He defended his PhD in 1985 and DrSc. in 2003. He is head of the Department of Metal Physics, which belongs to the Institute of Physics, Slovak Academy of Sciences in Bratislava.