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Ion Irradiation of Oxidized FeCoZr–CaF_2 Nanocomposite Films for Perpendicular Magnetic Anisotropy Enhancement

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The paper is focused on the results of Xe ions irradiation of nanocomposite FeCoZr-CaF_2 films synthesized in the oxygen-containing atmosphere. Combined influence of nanoparticles partial oxidation and ion irradiation with different fluences on the crystalline structure, phase composition and magnetic anisotropy is analysed by X-ray diffraction, the Mössbauer spectroscopy and vibrating sample magnetometry. The origin of the detected progressive enhancement of perpendicular magnetic anisotropy as the result of films oxidation and irradiation is discussed in the context of formation of nanoparticles oxide shells and ion tracks along the films normal.

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1. Introduction

Shape anisotropy of elongated magnetic nanoparticles is the origin of perpendicular magnetic anisotropy (PMA) of nanocomposite materials which are of industrial interest for designing high density recording media, magnetic field sensors and systems for visualization of magnetic fields distribution. Such type of magnetic anisotropy was previously reported to be characteristic of the FeCoZr-CaF_2 nanocomposite films with a high concentration of metallic fraction [1, 2]. Nanostructurization of the films occurs due to the growth of elongated (columnar) metallic nanoparticles along the films normal demonstrating anisotropic ferromagnetic properties and separated by the CaF_2 matrix. PMA of the films is of critical dependence on nanocolumns shape, growth orientation and ordering inside the matrix. Any deviations of nanoparticles growth orientation from the films normal provided by stochastic distribution lead to decrease in PMA. Additionally, strong magnetostatic interaction between the nanocolumns through the thin matrix layers results in PMA reduction and corresponding increase in the planar component of magnetic anisotropy. Decrease in the dispersion of nanoparticles orientations as well as increase in the thickness of non-magnetic barriers between the nanoparticles preventing their interaction are the problems under consideration in the present work. Partial oxidation of nanoparticles leading to the formation of "ferromagnetic metallic core-non- or weak-magnetic oxide shell" structures and subsequent films irradiation with heavy ions in the direction of their normal is proposed as the promising way for PMA enhancement.

2. Experimental

Granular nanocomposite films $(Fe_{45}Co_{45}Zr_{10})_{74}(CaF_2)_{26}$ are deposited by ion-beam sputtering in the oxygen-free (Ar) and oxygen-containing (Ar+O_2) atmosphere on the Al foil [1, 3]. The partial pressure of oxygen in the mixed ambient is 4.3 mPa. Irradiation is carried out by 167 MeV Xe^{26+} with the fluence D in the range 5×10^{12}–2.5×10^{13} ion/cm^2 generated by the IC-100 heavy ion cyclic accelerator (JINR, Dubna). Orientation of ion beam is along the normal to the films plane.

X-ray diffraction (XRD) analysis is performed by an Empyrean PANalytical diffractometer using a diffracted beam graphite monochromator and an X'Celerator linear detector (Cu K_α radiation). The data are collected with divergent-beam optics (using 1/32" divergence and 1/16" anti-scatter slits) at a grazing incidence of 5 degrees with respect to the sample surface, with the detector scanning the 2Θ space over the 10–120 degree range.

The room temperature (RT) ^{57}Fe transmission Mössbauer spectroscopy measurements were performed using a conventional constant acceleration type spectrometer with a 20 mCi ^{57}Co in Rh source. The spectra were analysed with the MOSMOD software basing on Rancourt procedure [4]. Accuracy of estimation of α angle characterizing average deviation of magnetic moments from the

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films normal (deviation angle) available from spectra fit is found to be 0.5°.

Magnetic moments (μ) of the films are studied using the Vibrating Sample Magnetometer (VSM) option of a Quantum Design PPMS in the range of magnetic fields $H = 0{-}90$ kOe and temperature $T = 2{-}300$ K. External magnetic field is applied in the direction parallel ($H_\parallel$) or perpendicular ($H_\perp$) to the films surface.

3. Results and discussion

Figure 1 summarizes the XRD patterns of $(FeCoZr)_{74}(CaF_2)_{26}$ films obtained under different experimental conditions-the initial film obtained in Ar ambient, the one deposited in the oxygen-containing atmosphere and the oxidized films irradiated subsequently with Xe ions of $D = 5$ and 25×10^{12} ion/cm^2. As it can be seen from Figure 1, the initial oxygen-free film contains the crystalline α-FeCo(Zr) phase characterizing nanoparticles [1], whereas the initial oxidized film contains the same phase in a highly disordered state. Additionally, the broadened line at $2\Theta \sim 32°$ indicates the presence of oxide in the film prepared in the mixed ambient. Phase analysis of the film carried out in [5] allows its interpretation as hematite α-Fe_2O_3, the oxide being at the surface of nanoparticles that forms their shells. Ion irradiation of the oxidized films appears to improve crystalline structure of α-FeCo(Zr) nanoparticles which becomes similar to that in the non-oxidized film. Moreover, insignificant narrowing of diffraction line characterizing α-Fe_2O_3 is also detected. It should be noted that irradiation was carried out with the fluences $D = 5, 7, 10, 20$ and 25×10^{12} ion/cm^2, but there is no significant difference in the influence of irradiation with an alternating dose on the phase composition and crystalline structure of the studied film. This phenomenon differentiates the oxidized composites from the oxygen-free films with the same composition which demonstrate the improvement of α-FeCo(Zr) crystallinity only in the range of $D = 7{-}8 \times 10^{12}$ ion/cm^2, whereas the higher fluences of $D \geq 10^{13}$ ion/cm^2 introduce disordering of nanoparticles crystalline structure [6].

The Mössbauer spectra of the oxygen-free, oxidized and irradiated $(FeCoZr)_{74}(CaF_2)_{26}$ films are collected in Figure 2. The initial non-oxidized film demonstrates a single Fecontaining phase corresponding to α-FeCo(Zr) nanoparticles and revealing magnetic splitting of spectral lines that indicates α-FeCo(Zr) ferromagnetic ordering (Figure 2a). The spectrum of the film sputtered in the oxygen-containing atmosphere (Figure 2b) additionally contains a sextet related to the Fe^{3+} oxide phase (α-Fe_2O_3) with significantly broader spectral lines due to structural disordering. Line broadening is characteristic also of the sextet describing the α-FeCo(Zr) phase in the oxidized film as compared with the non-oxidized one, the quantity of non-oxidized phase being about 40 %. Thus oxygen from the synthesis atmosphere disorders nanoparticles crystalline structure in the sputtered films and

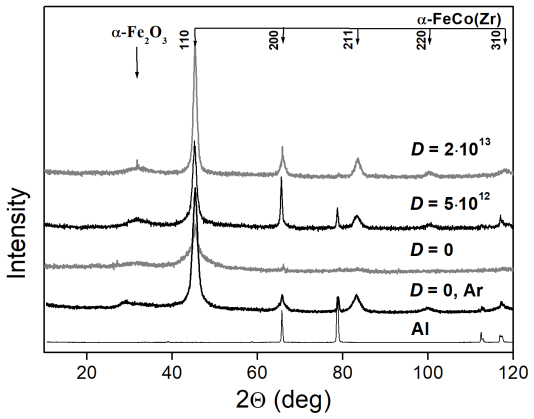

Fig. 1. XRD patterns of $(FeCoZr)_{74}(CaF_2)_{26}$ films obtained in the Ar atmosphere and oxygen-containing ambient and irradiated with different fluences D; reference XRD pattern of Al substrate is shown at the bottom of the figure.

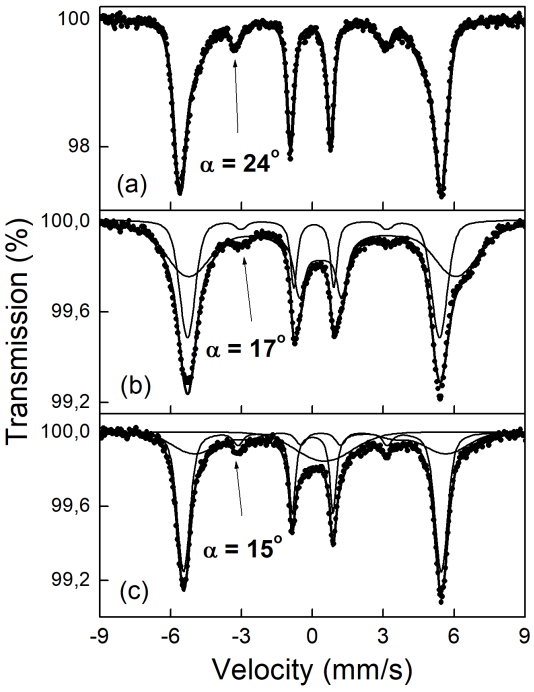

Fig. 2. Mössbauer spectra of $(FeCoZr)_{74}(CaF_2)_{26}$ films deposited in the oxygen-free (a), oxygen-containing atmosphere (b)–(c), as well as irradiated by Xe ions with the fluence $D = 7 \times 10^{12}$ ion/cm^2 (c).

leads to their partial oxidation at $P_O = 4.3$ mPa with the conserved α-FeCo(Zr) non-oxidized cores and formation of oxide shells [5]. Analysis of magnetic anisotropy of the studied films based on the spectral lines relation according to [1] allows detection of significant oxidation-induced decrease in the average angle α of α-FeCo(Zr) nanoparticles magnetic moments deviation from the films normal that varies from 24° for the non-oxidized film to 17° for the oxidized sample.

As can be seen from the spectra shape changes in Figure 2, irradiation of partially oxidized $(FeCoZr)_{74}(CaF_2)_{26}$ film provides further decrease in deviation angle α. Mössbauer spectrum of the film irradiated with $D = 7 \times 10^{12}$ ion/cm^2 presents maximal decrease in α down to 15° that is illustrated in Figure 2c. Similar parameters are characteristic also of the spectrum of the film irradiated with $D = 25 \times 10^{12}$ ion/cm^2, the data obtained for the films irradiated with other fluences being almost the same. Some changes in the angle characterizing deviation of magnetic moments in the oxide phase from the films normal are also detected. It decreases from 26° in the non-irradiated film to 20−22° in the irradiated samples. Additionally, α-FeCo(Zr) phase demonstrates spectral line narrowing after irradiation in agreement with the XRD data and increase in its contribution from 41 % for the non-irradiated film to 64 % maximally in the film treated by Xe ions with $D = 10^{13}$ ion/cm^2. Simultaneously, considerable reduction of the sextet characterizing the α-Fe_2O_3 phase (from 45 to 20%) accompanied with appearing of a superparamagnetic singlet (or doublet) takes place in the spectra of the irradiated films. The latter indicates size reduction of oxide nanoparticles or shells. The described phenomena point out to the decrease in nanoparticles oxidation after irradiation with improving their crystalline structure.

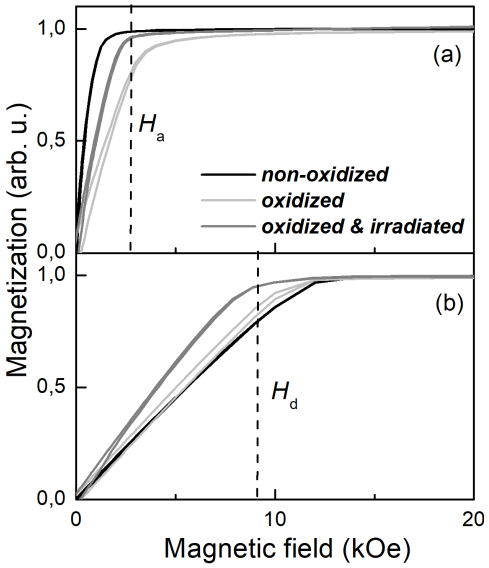

Fig. 3. Magnetization curves of $(FeCoZr)_{74}(CaF_2)_{26}$ films deposited in the oxygen-free and oxygen-containing atmosphere, as well as irradiated by Xe ions with the fluence $D = 2 \times 10^{13}$ ion/cm^2; magnetic field is applied in the films plane (a) and along the films normal (b).

Field dependences of the studied $(FeCoZr)_{74}(CaF_2)_{26}$ films magnetic moments μ vs. the applied magnetic field H are presented in Figure 3 for two orthogonal orientations of H. The magnetization curves $\mu(H_\parallel)$ measured in the films plane and depicted in Figure 3a clearly demonstrate a quite sharp inflection point near saturation corresponding to the anisotropy field H_a and separating two almost linear regions of μ $(H_\parallel)$ dependences. It is evident that H_a significantly increases in the partially oxidized film as compared to the non-oxidized sample from 1.4 to 3.4 kOe. Additionally, decrease in the demagnetizing field H_d corresponding to the inflection point of $\mu(H_\perp)$ curves from 11.3 to 10.4 kOe compared with the non-oxidized film is detected (see Figure 3b). The obtained data indicate clearly the nanocomposites PMA enhancement as the result of oxidation.

Irradiation of partially oxidized $(FeCoZr)_{74}(CaF_2)_{26}$ film provides further significant decrease in H_d which reaches 7.5 kOe after both oxygen and ions treatment with $D = 10^{13}$ ion/cm^2 (see Figure 3b). The latter is in the full agreement with the reduction of angle α down to 15° (Figure 2) obtained by Mössbauer spectroscopy for magnetic moments deviation from the film normal, in spite of some decrease in H_a. The origin of detected PMA enhancement is supposed to be formation of nanoparticles oxide shells and ion tracks along the films normal. Both shells and tracks can be considered as non-magnetic (or weakly magnetic) barriers arising between the α-FeCo(Zr) nanocolumns and preventing or minimizing their interaction. Application of two combined types of treatment is proved to improve crystalline structure of metallic nanoparticles and simultaneously release it from oxygen decreasing oxide contribution. Such modification promotes nanoparticles magnetic moments ordering. The normal to the films plane orientation of ion beam at irradiation assists homogenization of magnetic nanostructure sizes and orientations leading to their alignment inside the matrix perpendicularly to the films surface.

4. Summary

A comprehensive study of crystalline structure, phase composition and magnetic anisotropy in the nanocomposite $(FeCoZr)_{74}(CaF_2)_{26}$ films obtained under different synthesis and treatment conditions has been carried out. It is established that the initial film obtained in pure Ar ambient demonstrates PMA provided by columnar shape of α-FeCo(Zr) nanoparticles oriented near the film normal direction and characterized by the anisotropy field $H_a = 1.4$ kOe and the demagnetizing field $H_d = 11.3$ kOe. Partial oxidation of nanoparticles realized by deposition of $(FeCoZr)_{74}(CaF_2)_{26}$ film in the oxygen-containing atmosphere with $P_O = 4.3$ mPa leads to significant increase in H_a up to 3.4 kOe and decrease of H_a to 10.4 kOe. Additionally, considerable decrease in the deviation of nanoparticles magnetic moments from the films normal from $\alpha = 24°$ to 17° is detected in the oxidized film by Mössbauer spectroscopy. The above mentioned changes clearly indicate PMA increase as the result of nanoparticles partial oxidation and formation of "metallic core–oxide shell" structures. Being weak- or non-magnetic, oxide shells prevent interaction between the α-FeCo(Zr) nanoparticles.

Irradiation of the oxidized $(FeCoZr)_{74}(CaF_2)_{26}$ film by Xe ions provides further significant decrease in H_d which reaches 7.5 kOe and the reduction of the deviation angle α down to 15°. Moreover, the improvement of α-FeCo(Zr) crystallinity accompanied by the decrease in the oxide contribution in nanoparticles is detected for the irradiated films in the whole range of applied ion fluences $D = 5{-}25 \times 10^{12}$ ion/cm^2. Ion tracks appearing as the result of treatment are believed to form additional non-magnetic barriers preventing α-FeCo(Zr) nanocolumns interaction. Being oriented normally to the films, ion tracks lead to homogenization of magnetic nanostructure orientations and their alignment inside the matrix in this direction.

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