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Magnetic structure and magnetic properties of nanocrystalline and amorphous Fe–Zr–N films

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ABSTRACT

Data on the magnetic structure and magnetic properties of Fe–Zr–N films, which were prepared by reactive magnetron sputtering of a heated target and deposited on glass substrates, are reported. Depending on the Zr content (from 3 to 35 at%), the film compositions are characterized by Zr-to-N (at%) ratio from 0.3 to 36.5. The magnetic properties (saturation magnetization M_s, coercive field H_c) and magnetic structure (effective local magnetic anisotropy field $D^{1/2}H_a$, grain size $2R_c$, effective anisotropy field of stochastic domain $D^{1/2}\langle H_a\rangle$, relative stochastic domain size R_L/R_c) of the films are discussed in interrelation with their phase and structural states. The coercive field of the studied ferromagnetic nanocrystalline films was shown to obey the relationship $H_c \sim (2R_c)^6$ and depends on not only the grain size but also the local magnetic anisotropy field $D^{1/2}H_a$. As the grain size of ferromagnetic phase decreases, the contribution of the magnetoelastic component to the coercive field decreases. It was shown, by examples of weak ferromagnetic and superparamagnetic films with amorphous and mixed (amorphous+nanocrystalline) structures containing a nonferromagnetic phase, that the magnetic properties reflect the real structural and phase state of the films, which cannot be revealed by the X-ray diffraction analysis.

1. Introduction

Unique magnetic properties of nanocrystalline ferromagnets were demonstrated experimentally at the late 80s of the last century [1,2]. This fact, to a great extent, stimulated revolutionary changes in magnetic electronics, which have started in 90s, in particular, in the field of designing miniature, sensitive to low magnetic fields, quick-operating, high-density recording devices for microelectronics. Therefore, it demanded soft magnetic materials characterized by a combination of properties, such as low coercive field, high magnetic permeability over a wide frequency range, maximum possible saturation magnetic induction, high electrical resistivity, high mechanical properties, and thermal stability.

In this relation, nanocrystalline films prepared by magnetron sputtering followed by annealing, the compositions of which are close to the quasi-binary eutectic of the two-phase αFe-$M_{IV}X$ system, are of substantial interest. Such new class of films, due to nano-structured state and dispersion strengthening of the α-Fe ferromagnetic phase by hard nonferromagnetic $M_{IV}X$ phases (nitrides, carbides, and borides of elements of the IVA Group in the Periodic Table) can provides the combination of magnetic and mechanical properties, which exceed those of all existing modern soft magnetic alloys [3,4].

The level of soft magnetic properties (low coercive field and high magnetic permeability) of a ferromagnet is known to be determined by its effective magnetic anisotropy energy and formed micromagnetic structure. Quantitative estimations of the micromagnetic structure of a ferromagnet in interrelation with its magnetic properties, chemical composition and phase structural states are the important stage of investigations related to designing magnetic materials with given properties.

Almost no data on similar studies for new class of the two-phase αFe-$M_{IV}X$ films are available in the literature. In this relation, the aim of the present study is to investigate the interrelation of phase and structural states with the micromagnetic structure and static magnetic properties of the Fe–ZrN films, which are among the aforementioned new class of film materials.

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2. Experiment

The Fe–Zr–N films for the investigation were prepared by reactive magnetron sputtering of a $FeZr_x$ target, which was heated above the Curie temperature of iron [5]. The target was manufactured in the form of Fe disc with iodide Zr chips, which are uniformly distributed over the disc surface. During magnetron training, the contact melting of Fe and Zr in the vacuum chamber (at residual pressure of no more than $\sim 10^{-3}$ Pa) takes place, and the Fe–Zr phases having various composition (depending on the number of Zr chips) are formed in the erosion zone. Before each of sputtering cycles, the target was heated above the Curie temperature of iron. This allowed the target to be successfully sputtered thanks to suppression of interaction between magnetic fields of magnetron system and those of ferromagnetic target. The films were deposited in Ar or mixed $Ar+N_2$ (with 5 and 15 vol % N_2) atmosphere. Glass plates were used as the substrates. The films were subjected to 1 h vacuum annealing (residual pressure of $\sim 10^{-4}$ Pa) at 300, 400, 500, and 600 °C.

The element composition of the sputtered films was determined by X-ray energy dispersive spectroscopy using a Hitachi S-3400N microscope equipped with a Noran 7 Thermo attachment and 10 kV accelerating voltage. The analysis of each film was performed for from 3 to 5 points in the film cross section. To accurately determine the contents of light elements (O and N) in the films, we used a Profiler–2 (Horiba YJ) optical emission glow-discharge spectrometer, which allows one to obtain the element distribution in depth; the error of estimating is less than 1 at %. According to SEM data, the thickness of films was of from 0.8 to 1.7 μm.

The phase composition and structural state of the films were studied by X-ray diffraction (XRD) analysis using a Rigaku Ultima IV diffractometer and CuK_α radiation. Data on the lattice parameters, grain sizes, and microdeformation magnitudes for phases formed in the films were obtained using the X-ray diffraction patterns and original software utilizing full-profile Rietveld analysis [6].

Magnetic properties of the films were measured at room temperature in the applied magnetic fields in the film plane up to 16 kOe using a LakeShore 7407 vibrating-sample magnetometer. The error of measurements of the saturation induction was related to differences in the shape and sizes of a standard nickel ball (3 mm in diameter) and the samples and did not exceed ~10%. Parameters of the magnetic structure of films were estimated by correlation magnetometry [7].

3. Results and discussion

3.1. Phase composition and structure

According to element analysis data, the prepared films (see Table 1) contain ~3–4 at % Zr (series I, II, IV, V, VI), ~9 at% Zr (series III) and ~33–35 at% Zr (series VII, VIII). The equilibrium Fe–Zr phase diagram [8] shows that the compositions are hypoeutectic, near-eutectic, and hypereutectic respectively. The films are characterized by the following Zr-to-N (at%) ratios: 0.3 (VI), 0.5–0.6 (IV, V), 1.3 (III), 2.8 (VII), 36.5 (VIII) (see Table 1, Fig. 1). The presence of oxygen in the films is likely to be due to insufficient vacuum ($\sim 10^{-3}$ Pa) in the magnetron sputtering chamber.

The single phase nanocrystalline structure, which consists of α-Fe(Zr,N), nitrogen and zirconium solid solution in iron, and has bcc crystal structure, is formed in the $Fe_{90.4}Zr_{2.9}N_{4.7}O_{2.0}$ and $Fe_{75.8}Zr_{8.7}N_{6.8}O_{8.7}$ (II, III) films prepared under argon atmosphere with 5 vol% N_2 (Table 1, Fig. 1). The formation of the solid solution is testified by the fact that the lattice parameter of the bcc phase

Table 1
Chemical and phase compositions of the as-sputtered and annealed films.

Film series [vol% N][a]	Element composition (at%)	Phase composition [vol%] and grain size (nm) after annealing				
		As-sputtered	300 °C	400 °C	500 °C	600 °C
I [0]	$Fe_{81.1}Zr_{3.2}N_{2.1}O_{13.6}$	α-Fe[65] (28.4)ZrO_{2-x}[35](2.9)	[b]	[b]	[b]	[b]
II [5]	$Fe_{90.4}Zr_{2.9}N_{4.7}O_{2.0}$	α-Fe(Zr,N) [~100](13.6)	α-Fe(Zr,N) [~100] (14.0)	α-Fe(Zr,N) [~100](14.8)	α-Fe(Zr,N) [~100](18.4)	α-Fe(Zr,N) [~100](21.4)
III [5]	$Fe_{75.8}Zr_{8.7}N_{6.8}O_{8.7}$	α-Fe(Zr,N) [~100](3.5)	α-Fe(Zr,N) [~100](4.1)	α-Fe(Zr,N) [~100](3.8)	α-Fe(Zr,N) [~100](4.0)	α-Fe(Zr,N) [~100](6.9)
IV [15]	$Fe_{82.5}Zr_{3.1}N_{6.4}O_{8.0}$	α-Fe(Zr,N)[58](7.5) Fe_4N [42](8.1)	[b]	α-Fe(Zr,N)[53](8.2) Fe_4N [47](8.3)	α-Fe(Zr,N)[48](8.6) Fe_4N [52] (8.5)	[b]
V [15]	$Fe_{86.0}Zr_{4.3}N_{6.7}O_{2.9}$	α-Fe(Zr,N)[58](2.0) Fe_4N [42](5.5)	[b]	α-Fe(Zr,N) [61](2.0) Fe_4N [39](6.7)	α-Fe(Zr,N)[51](2.9) Fe_4N [49] (6.1)	α-Fe[28](14.6) Fe_3N [57](3.4) ZrO_2 [15](3.7)
VI [15]	$Fe_{87.3}Zr_{2.4}N_{7.4}O_{2.9}$	α-Fe(Zr,N)[31](4.5) Fe_4N [64](7.6) Fe_3N [5](9.1)	[b]	α-Fe(Zr,N)[34](2.3) Fe_4N [56](10.2) Fe_3N [10](11.3)	[b]	[b]
VII [15]	$Fe_{43.3}Zr_{34.8}N_{12.4}O_{9.5}$	amorphous [~50] ZrN [~50](5.3)	[b]	amorphous [~50] ZrN [~50](5.2)	[b]	[b]
VIII [0]	$Fe_{61.9}Zr_{32.9}N_{0.9}O_{4.3}$	amorphous [~100]	amorphous [~100]	amorphous [~100]	amorphous [~50] ZrO_2 [~50](16.5)	amorphous [~50] ZrO_2[~50] (22.7)

[a] Nitrogen content in argon atmosphere.
[b] Annealing was not performed.