Materials Letters 229 (2018) 36–39

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Fe-Zr-N films: Effect of nitrogen content and nitrogen-to-zirconium concentration ratio on saturation induction

E.N. Sheftel, E.V. Harin *

Baikov Institute of Metallurgy and Materials Science RAS, Leninsky pr. 49, Moscow 119334 Russia

ARTICLE INFO

Article history:
Received 24 May 2018
Received in revised form 21 June 2018
Accepted 24 June 2018
Available online 25 June 2018

Keywords:
Crystal structure
Deposition
Magnetic materials
Nanocrystalline materials
Thick films
X-ray techniques

ABSTRACT

Films $Fe_xZr_9N_y$ (x = 86 ÷ 77, y = 5 ÷ 14, at.%) prepared by rf reactive magnetron sputtering were used to study the effect of nitrogen content and nitrogen-to-zirconium concentration ratio on their phase composition and saturation induction B_s. It was shown that the films containing 9 at.% Zr and characterized by the nitrogen-to-zirconium ratio ≥1 have the two-phase structure, which forms during deposition and comprises α-Fe(N) solid solution and ZrN nitride. The B_s dependence on the nitrogen content in α-Fe(N) solid solution was found to be linear.

1. Introduction

Nanocrystalline Fe-Zr-N system films prepared by magnetron sputtering can provide the unique combination of magnetic and mechanical properties, which exceed those of majority of soft magnetic materials and are required for their application in advanced miniature microelectronic devices. The chemical composition of these films comprises 10–12 at.% Zr and is characterized by the ratio C_N/C_{Zr} = 1 (where C_N and C_{Zr} are the nitrogen and zirconium concentration, at.%, respectively), which corresponds to the composition range of eutectic alloys of the equilibrium quasi-binary Fe-ZrN phase diagram [1].

Previous studies [2–6] showed that nitrogen, being the alloying element, determines the phase and structural state of the films to a certain degree. Under suitable deposition conditions, depending on the nitrogen content and C_N/C_{Zr} ratio, either single phase or phase combination, such as amorphous, α-Fe(N) solid solution supersaturated with nitrogen, ZrN and Fe_xN_y nitrides form. So the phase composition of the films determines their saturation induction B_s.

The aim of the present study is to estimate the effect of nitrogen content and C_N/C_{Zr} ratio in the $Fe_xZr_9N_y$ (x = 86 ÷ 77, y = 5 ÷ 14, at.%) films on their B_s.

2. Material and methods

The chemical composition of the studied films (about 1 μm thick) corresponds to the formula $Fe_xZr_9N_y$ (x = 86 ÷ 77, y = 5 ÷ 14, at.%). They were prepared by rf reactive magnetron sputtering and subsequently subjected to annealing in vacuum $2\cdot10^{-6}$ Torr at temperatures from 300 to 750 °C using 30-, 60-, 120-, and 180-min holdings. Deposition conditions and detailed data on the phase composition and structure of the films, which were studied by X-ray diffraction (XRD), are available in our works [7–8].

The chemical composition of the films was determined in vacuum 10^{-5} Torr using a scanning electron microscope equipped with an X-ray energy-dispersion analyzer. B_s of the films was measured at room temperature in applied magnetic fields up to 7 kOe using a vibrating-sample magnetometer. The results of the measurements are given in Table 1.

3. Results and discussion

According to the data given in Table 1, depending on the nitrogen content and C_N/C_{Zr} ratio, two two-phase states can be formed; these are (1) the nanocrystalline ferromagnetic phase (the grain size is 6–23 nm), which is an α-Fe-based solid solution, plus ferromagnetic Fe-based amorphous (in XRD terms) phase and (2) nanocrystalline α-Fe-based phase (with a grain size of 4–12 nm) plus nanocrystalline nonferromagnetic ZrN phase.

* Corresponding author.
E-mail address: harin-eugene@ya.ru (E.V. Harin).

https://doi.org/10.1016/j.matlet.2018.06.110
0167-577X/

Table 1
Annealing conditions, chemical composition, B_s, phase composition, and lattice parameter of α-Fe-based phase.

No.	Annealing temperature (°C), holding time	Chemical composition, at.%			C_N/C_{Zr} ratio	B_s, T	α-Fe-based phase, vol.%	Other phases, vol.%	Lattice parameter of α-Fe, Å
		Fe	Zr	N					
1	as-sputtered	–	–	–	–	1.20	50 ± 4	amorphous, 50 ± 4	2.908 ± 0.005
2	as-sputtered	–	–	–	–	1.87	45 ± 4	amorphous, 55 ± 5	2.915 ± 0.005
3	200, 1 h	78.8	9.2	12	1.31	1.42	96 ± 5	ZrN, 4 ± 4	2.903 ± 0.001
4	300, 1 h	78.3	9.2	12.5	1.36	1.42	55 ± 5	amorphous, 45 ± 4	2.903 ± 0.005
5	300, 1 h	78.3	9.2	12.5	1.36	1.42	96 ± 5	ZrN, 4 ± 3	2.896 ± 0.001
6	300, 1 h	–	–	–	–	1.40	50 ± 4	amorphous, 50 ± 4	2.914 ± 0.005
7	475, 0.5 h	79.5	8.7	11.8	1.37	1.44	84 ± 5	ZrN, 16 ± 4	2.880 ± 0.001
8	475, 1 h	80.4	8.8	10.8	1.23	1.48	88 ± 5	ZrN, 12 ± 4	2.870 ± 0.001
9	475, 2 h	80.9	8.8	10.3	1.16	1.55	89 ± 5	ZrN, 11 ± 4	2.869 ± 0.001
10	475, 3 h	82.2	8.8	9	1.02	1.99	95 ± 5	ZrN, 5 ± 4	2.869 ± 0.001
11	500, 1 h	86.5	8.4	5.1	0.61	1.51	54 ± 5	amorphous, 46 ± 4	2.892 ± 0.005
12	600, 1 h	–	–	–	–	1.30	55 ± 5	amorphous, 21 ± 4; ZrN, 24 ± 4	2.857 ± 0,005
13	600, 1 h	83.3	8.8	7.9	0.90	1.54	95 ± 5	ZrN, 5 ± 4	2.868 ± 0.001
14	600, 0.5 h	81.7	8.4	9.9	1.19	1.73	92 ± 5	ZrN, 8 ± 4	2.868 ± 0.001
15	600, 1 h	82.6	8.6	7.8	0.92	1.71	96 ± 5	ZrN, 4 ± 4	2.862 ± 0.001
16	600, 2 h	82.9	8.3	8.8	1.06	1.95	91 ± 5	ZrN, 9 ± 4	2.860 ± 0.001
17	600, 3 h	83.1	8.5	8.4	1.00	1.74	97 ± 5	ZrN, 3 ± 3	2.863 ± 0.001
18	650, 1 h	83.3	8.9	7.8	0.88	1.40	57 ± 5	amorphous, 43 ± 4	2.858 ± 0.005
19	700, 1 h	84.7	8.8	6.5	0.74	1.46	74 ± 4	ZrN, 3 ± 1; Fe_4N, 23 ± 5	2.863 ± 0.004
20	750, 1 h	81.7	9.2	9.1	0.99	1.40	69 ± 5	amorphous, 31 ± 4	2.857 ± 0.005

To analyze the obtained results, we used the following fundamental concepts. Since B_s is the magnetic moment density per unit volume of a material, B_s of multiphase material comprising one ferromagnetic phase is determined by the phase volume fraction in the material. For the material comprising several ferromagnetic phases, B_s of the material is determined by the sum of saturation inductions of ferromagnetic phases, fractions of which correspond to volume fractions of the phases in the material.

When phase state of the studied films is characterized by the presence of α-Fe ferromagnetic phase, B_s of these films is calculated by the linear dependence

$$B_s = B_s^{\alpha-Fe} \cdot V_{\alpha-Fe}, \quad (1)$$

where $B_s^{\alpha-Fe}$ is the saturation induction of single-crystal α-Fe equal to 2.15 T; $V_{\alpha-Fe}$ is the volume fraction of ferromagnetic α-Fe phase; the phase fraction was determined by XRD (Table 1). The dependence (1) is given in Fig. 1 by solid line.

The symbols in Fig. 1 correspond to the studied films with different α-Fe volume fractions (Table 1). So the experimentally measured B_s values mainly correspond to two ranges.

One of the groups of values corresponds to the volume fractions of α-Fe-based phase, which are less than 60 vol%. The phase composition of these films is represented by two ferromagnetic phases, namely, α-Fe-based solid solution and amorphous Fe-based phase (Table 1), the saturation induction of which [9] is known to be lower than α-Fe-based nanocrystalline phase. The measured B_s values belonging to this group are lower (~1.2–1.8 T) than the values calculated by Eq. (1).

The possible cause for this fact is follows. It is known that wide XRD reflection can indicate amorphous, cluster, and nanocrystalline (with extreme small grain size ≤1.5 nm) states. The

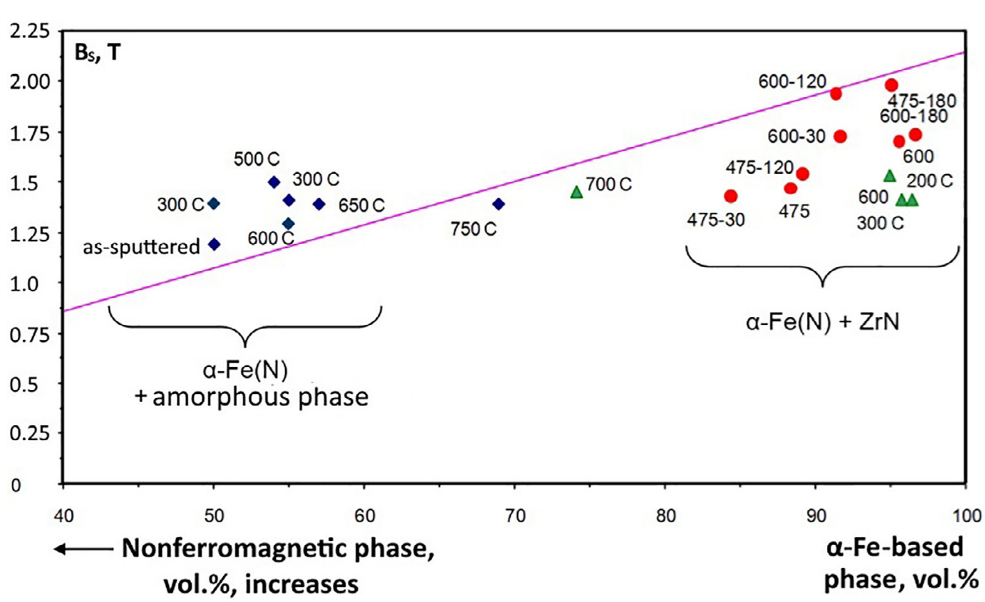

Fig. 1. Saturation induction vs the volume fraction of α-Fe-based phase. Solid line corresponds to the dependence calculated by Eq. (1). Symbols correspond to measured values. Digits shown near symbols indicate either the annealing temperature (°C) and time (min) or temperature (°C) of annealing for 60 min.