



Films of immiscible systems obtained by three-electrode ion-plasma sputtering

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Introduction

Recently, interest in materials based on components with limited mutual solubility in the liquid state has increased significantly. It is known that in systems with positive mixing energy, the energy barriers for the formation of homogeneous structures are rather high. To overcome them, it is necessary that the kinetic energy of the atoms that fall on the substrate exceed the height of these barriers. According to the calculated estimates the mixing energy values for Ag-Fe alloys are 94 kJ/mol, Fe-Bi - 80 kJ/mol, Co-Ag - 63 kJ/mol, Ni-Ag - 52 kJ/mol. Therefore, films were prepared using the method of modernized three-electrode ion-plasma sputtering (MTIPS) of composite targets. The kinetic energy of the deposited atoms using the MTIPS method can vary from 100 to 200 eV with a decrease in the pressure of the plasma-forming gas to 16 mPa. According to theoretical estimates, the relaxation rate of the energy of deposited atoms at different sputtering regimes reaches 10^{12} – 10^{14} K/s. This allows you to talk about quenching from vapor state (QVS).

Materials and Methods

As targets, parallelepipeds were used with a dimension of $20 \times 20 \times 5$ mm of pure components (99.99 %) separated by barrier cells performing like electrostatic lens, which 5-7-fold increase in the velocity of sputtered atoms before a collision with the substrate. Deposition was carried out on the sital substrates, as well as on a fresh cleavage of NaCl single crystal. To evaluate the compositions of the resulting films, a technique was used, which considered the relationship between the relative sputtering area the element occupies and its content in the deposited film. This technique makes it possible to determine the film composition to within ± 0.5 at.%. The thickness of the films was varied by the deposition time in the range 0.02-2.9 μm . Films deposited on NaCl single crystal substrates after dissolving the salt were used for structural studies by transmission electron microscope (TEM) and X-ray diffraction analysis in filtered cobalt $K\alpha$ -radiation. Films obtained under identical sputtering conditions on the glass-ceramic substrates were used to investigate the physical properties of nonequilibrium structures. Measurements of the change in the electrical resistivity of the films upon heating were carried out in a vacuum of ~ 13.3 mPa by a four-probe method. Measurements of the coercive force H_c of films were carried out on a vibrating magnetometer in a maximum magnetizing field of 0.5 T applied parallel and perpendicular to the surface of the films. The objects of investigation in the present paper were films of alloys of the following compositions: Ni- (21 - 88) at.% Ag; Fe- (12 - 49) at.% Ag, Fe- (5 - 18) at.% Bi; Co-(24 - 28) at.% Fe-(7 - 24) at.% Ag; Fe-(11.5 - 21) at.% Ag- (4 - 4.5) at.% Bi. Equilibrium phase diagrams of the investigated binary systems Ni-Ag, Fe-Ag, Fe-Bi, Co-Ag are characterized by extremely low mutual solubility of the components even at eutectic temperatures and the presence of wide temperature-concentration separation intervals.

Results

Table. Phase composition of freshly sputter-deposited and heat-treated films (Fe, Co) – (Ag, Bi)

Composition. (at.%)	Phase composition of films	
	The freshly sputter-deposited state	After heating
Fe-12%Ag	a mixture of SSS based on fcc silver ($a=0.4085$ nm, $L=15$ nm) and bcc α -Fe ($a=0.2894$ nm $L=20$ nm)	910 K a mixture of fcc silver ($a=0.4087$ nm, $L=1000$ nm) and bcc α -Fe ($a=0.2871$ nm $L=1000$ nm)
Fe-23%Ag	a mixture of SSS Ag ($a=0.4083$ nm, $L=90$ nm) and NCP iron ($a=0.2889$ nm $L=12$ nm).	910 K a mixture of fcc silver ($a=0.4087$ nm) and a solid solution of iron ($a=0.2889$ nm)
Fe-49%Ag	a mixture of fcc Ag ($a=0.4082$ nm $L=18$ nm) and NCP iron ($L=9$ nm).	910 K a mixture of fcc silver ($a=0.4087$ nm) and bcc solid solution of iron ($a=0.2884$ nm)
Fe-5%Bi	a mixture of α -Fe ($a=0.2887$ nm), rhombohedral lattice Bi ($c/a=2.6$) and traces of cubic Bi ($a=0.3795$ nm)	800 K a mixture of α -Fe ($a=0.2886$ nm) and rhombohedral lattice Bi ($c/a=2.605$)
Fe-10%Bi	a mixture of α -Fe ($a=0.2887$ nm), rhombohedral lattice Bi ($c/a=2.59$) and cubic Bi ($a=0.3795$ nm)	780 K a mixture of α -Fe ($a=0.2886$ nm) and rhombohedral lattice Bi ($c/a=2.605$)
Fe-18%Bi	a mixture of NCP iron ($a=0.2830$ nm $L=6$ nm), rhombohedral lattice Bi ($c/a=2.50$) and of cubic Bi ($a=0.378$ nm)	780 K a mixture of α -Fe ($a=0.2855$ nm) and rhombohedral lattice Bi ($c/a=2.605$)
Co-28% Fe-7% Ag	a mixture of amorphous Ag and dispersed phase FeCo_3 , $a=0.2841$ nm	870 K a mixture of Ag ($a=0.40862$ nm) + FeCo_3 with constant lattices almost coinciding with tabulated values $a=0.2857$ nm
Co-24%Fe-14% Ag	a mixture of a dispersed solid solution of Ag and a phase of FeCo_3	870 K a mixture of Ag ($a=0.40862$ nm) + FeCo_3 with constant lattices almost coinciding with tabulated values
Co-24%Fe-20% Ag	a mixture of Ag solid solution ($a=0.4068$ nm) and a phase of FeCo_3	870 K a mixture of Ag ($a=0.40862$ nm) + FeCo_3 with constant lattices almost coinciding with tabulated values
Fe-11.5%Ag-4.5%Bi	a mixture of dispersed solid solutions α -Fe ($a=0.2880$ nm) and Ag ($a=0.4079$ nm).	870 K a mixture of α -Fe ($a=0.28664$ nm) Ag ($a=0.40862$ nm) and traces of rhombohedral Bi
Fe-16.5%Ag-4.5%Bi	a mixture of NCP Fe ($L=6$ nm) and Ag ($L=12$ nm)	890 K a mixture of α -Fe ($a=0.2870$ nm), Ag ($a=0.4067$ nm) and traces of rhombohedral Bi
Fe-21%Ag-4 %Bi	a mixture of NCP Fe ($L=11$ nm) and Ag ($L=5$ nm)	870 K a mixture of α -Fe ($a=0.2872$ nm) and Ag ($a=0.4086$ nm)

Note: SSS - supersaturated solid solution; NCP - is the nanocrystalline phase, and L is the size of the coherent scattering region (CSR)

In freshly deposited Ni-Ag films with a content of (0-21) at.% Ag, the X-ray patterns show predominantly Ni lines. In the Ag-Ni films and with the content and (42-100) at.% Ag, Ag lines were fixed. Calculations of the periods of fcc Ni and Ag lattices have shown that in these concentration intervals, supersaturated solid solutions form in the films, the saturation of which increases with increasing doping level. Diffraction patterns of Ni- (21-42) at.% Ag films contained a diffuse halo. The presence of such a halo indicates the formation of an amorphous phase. The dimensions of the coherent scattering regions for films of this composition are ~ 1.6 nm, which is characteristic of metal alloys with an amorphous structure. The results of X-ray phase investigations of binary alloys Fe-Ag, Fe-Bi and ternary Co-Fe-Ag, Fe-Ag-Bi alloys in the freshly sputter-deposited state and after heating are summarized in Table. The presence in the film structure of the nanocrystalline phase is indicated by the presence on the X-ray diffraction patterns of the first line with the effective size of the coherent scattering regions (CSR) $L = 2$ -12 nm. The fixed interplanar distance makes it possible to assume that the short-range order in the arrangement of atoms in the microcrystalline phase is close to the bcc orientation of iron-based atoms. In the films of Fe-Ag binary alloys with a positive mixing energy of ~ 94 kJ/mol, a mixture of two solid solutions based on the components was formed. The average size of these structural components tended to decrease with increasing Ag concentration. The size of α -Fe crystals decreased from 200 to 9 nm, and Ag - to 18 nm. The Fe-Bi system also is characterized by a high (~ 80 kJ/mol) positive mixing energy. A somewhat unexpected result was obtained when studying the structure of sputtered films of Fe- (5-18) at.% Bi alloys.

As the concentration of Bi was increased to 18 at.%, The size of the CSR of α -Fe decreased to 6 nm, and additional weak reflections appeared in the diffraction patterns of the films, the angular position of which corresponded to the bcc phase with a period of 0.378 ± 0.0001 nm. The formation of a similar phase was observed earlier at elevated pressures ($a = 0.3795$ nm). To clarify the phase composition of the Fe-Bi films, a pure Bi film with a thickness of ~ 2900 nm was obtained. An analysis of the x-ray pattern of this film showed that, in addition to the diffuse lines of rhombohedral Bi, it contains reflections of the bcc phase with a period of 0.379 nm. The thermal treatment of the films (heating to a temperature of 613 K) leads to the disappearance of the bcc phase lines, which indicates its metastable nature. In Co-28% Fe-7% Ag films, when a mixture of amorphous Ag and a dispersed phase FeCo_3 is formed, $a = 0.2841$ nm, the presence of diffuse maxima is observed. The CRS estimates for this film showed that they are about 3 nm, which indicates the nanocrystalline nature of its microstructure. With an increase in the silver content and a decrease in the cobalt content (Co-24% Fe-14% Ag and Co-24% Fe-20% Ag), a dispersed solid solution Ag and a FeCo phase with an ordered bcc structure are formed in the films. In the films Fe-16.5% Ag-4.5% Bi and Fe-21% Ag-4% Bi nanocrystalline phase is formed. This is evidenced by the presence at small angles of X-ray diffraction patterns and electron diffraction patterns of only one diffuse line. It can be seen that the addition of immiscible elements (Ag, Bi, Ag + Bi) more than 18, 21, 23 at.%, respectively, leads to the formation of amorphous phase or NCP iron in freshly sputter-deposited films with MIPS.

When the $\text{Ni}_{64}\text{Ag}_{36}$ film with an amorphous structure is heated, its electrical resistance practically does not change before the crystallization begins. Because alloys with low TCR are of great practical interest, for the films of this system, there were made measurements of the electrical resistivity (RS) and its temperature dependence. Both these characteristics, depending on the composition, vary non monotonically, which indicates the essential role of the structural state. In particular, the formation of an amorphous phase in films leads to a marked increase in the RS (up to ~ 6 Ohm/sq) and a sharp decrease in TCS (up to $3 \cdot 10^{-6}$ K $^{-1}$). Since the investigated films contain atoms of ferromagnetic components, it was interesting to evaluate their saturation magnetization and coercive force H_c , which is a structure-dependent quantity. The measurements, the results of which are shown selectively in Fig., showed that the deposited films have a relatively high coercive force. An increase in the concentration of the diamagnetic component in the alloy leads to a decrease in the magnetization, and holding for 5 min at the temperatures of decomposition completion leads to an increase in the coercive force up to 150 kA/m in the $\text{Fe}_{77}\text{Ag}_{23}$ film when the external field is directed perpendicular to the film plane. For Fe-23% Ag films after heat treatment, hysteresis curves are observed when the external field is directed both parallel and perpendicular to the film plane. The most probable reason for the significant magnetic anisotropy is the predominant orientation of nanocrystals formed during quenching, which increases with their growth.

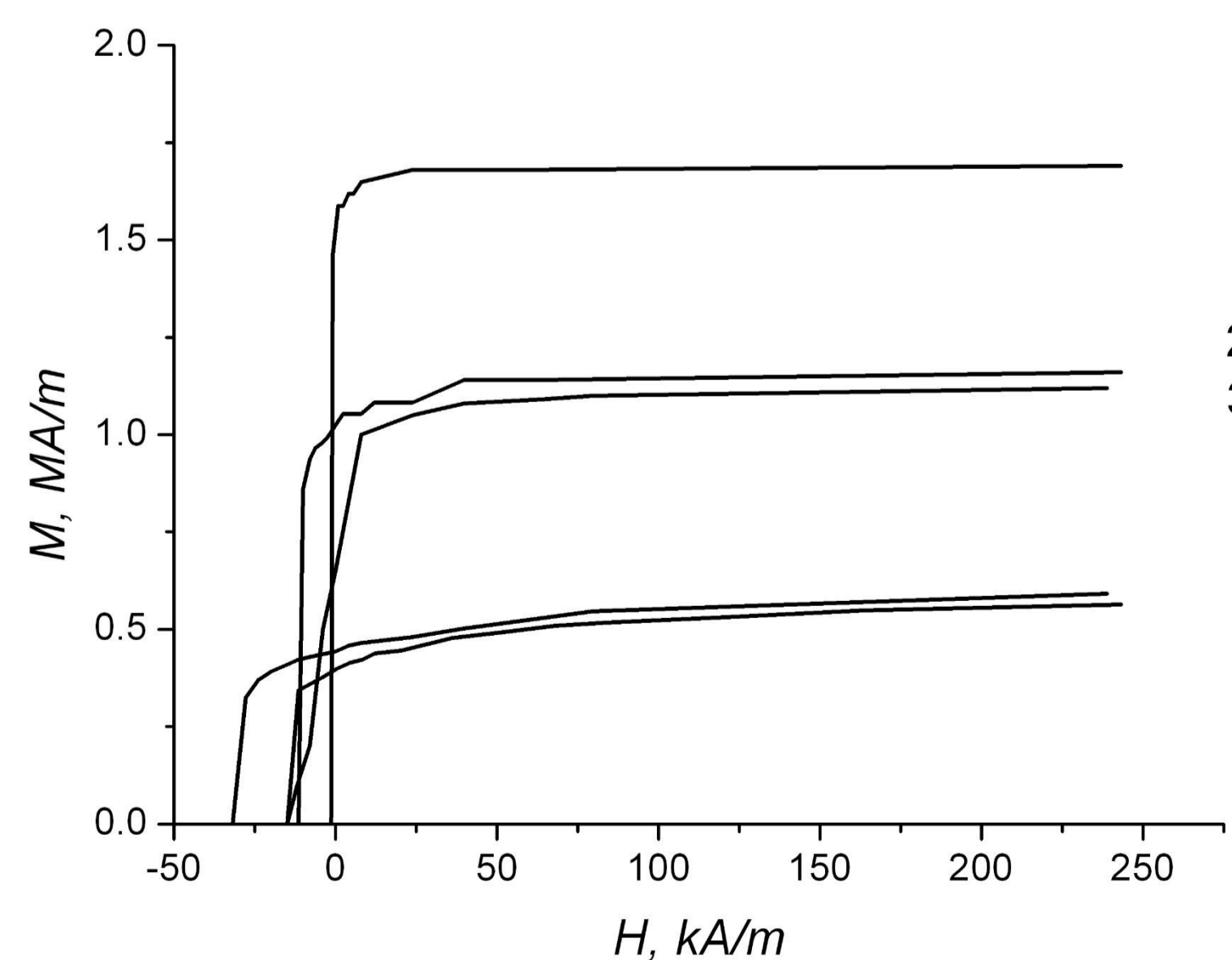


Fig. Demagnetization curves for heat-treated films oriented parallel to the field: 1) Fe ($d=80$ nm); 2) Fe-49%Ag; 3) Fe-10% Bi; 4) Co-24%Fe-20% Ag 5) Fe-16.5%Ag-4.5%Bi

Conclusions

It is shown that amorphous and nanocrystalline structures are formed in glories characterized by the immiscibility of components in the liquid state when quenching from the vapor state by the method of modernized ion-plasma sputtering. The maximum degree of homogeneity of metastable structures correlates with the value of the mixing energy of the components. In particular, as the mixing energy decreases from 94 to 52 kJ/mol in the series of Fe-Bi, Ag-Fe, Ag-Co, and Ag-Ni systems, the minimum size of nanoscale crystallites decreases from 9 to 3 nm (in the Ag-Fe- Co), and in Ag-Ni alloys an amorphous phase with dimensions of coherent scattering region of 1.6 nm is formed. It is shown that the electrical and hysteresis magnetic properties of the sputtered films vary widely, depending on the composition and structural state. The compositions and conditions for obtaining films with low ($\sim 10^{-5}$ K $^{-1}$) values of the temperature coefficient of resistance and high coercive force (≥ 150 kA/m) are promising for use as thin-film precision resistors and data carriers, respectively.