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STRUCTURE AND PHYSICAL PROPERTIES OF ION-PLASMA DEPOSITED (Fe, Co, Ni)-C FILMS

The formation conditions of metastable structures and phase transformations during heat treatment of (Fe, Co, Ni) − C films, obtained through the upgraded method of three-electrode ion-plasma sputtering, are researched via X-ray analysis, transmission electron microscopy, the building of temperature dependences of the electrical resistance. It is shown that the films have a metastable structure in the initial state. The transition of Fe−C film structure from amorphous to equilibrium state during annealing occurs through the formation and subsequent decay of an intermediate metastable hexagonal close-packed-phase with variable composition. This phase has enlarged lattice parameters of hcp-phase in comparison with parameters of the phase produced by melt quenching. In as-deposited films the lattice parameters of the hcp Ni_3C carbide decrease as compared to those of Ni_3C produced by melt quenching. The precise values of the temperature coefficient of resistance, 5 10^{-5} K^{-1} - 10^{-6} K^{-1} , are fixed in the (Fe,Ni)−C films.

Keywords: (Fe ,Co, Ni)−C films, ion-plasma sputtering, X-ray diffraction, transmission electron microscopy, temperature coefficient of resistance, amorphous phase, metastable state.

Методами рентгеноструктурного аналізу, електронної мікроскопії і побудови температурних залежностей електроопору вивчались умови формування різних метастабільних структур і фазові перетворення в процесі нагріву в плівках (Fe, Co, Ni) − C, які були отримані модернізованим методом трьохелектродного іонно-плазмового розпилення. Показано, що плівки в свіжонапиленому стані мають метастабільну структуру. Перехід із аморфного в рівноважний кристалічний стан у плівках Fe−C проходить крізь стадію утворення та наступного розпаду проміжної, метастабільної гексагональної щільно упакованої фази змінного складу, яка характеризується зменшеними параметрами решітки у порівнянні з ГЩУ-фазою, яка отримана при гартуванні з розплаву. У свіжонапилених плівках Ni-20…61%C параметр решітки ГЩУ-карбиду Ni_3C зменшений у порівнянні з ГЩУ- Ni_3C після гартуванні з розплаву У плівках (Fe,Ni)−C зафіксовані прецизійні значення температурного коефіцієнту опору на рівні 5 10^{-5} K^{-1} - 10^{-6} K^{-1}.

Ключові слова: (Fe, Co, Ni)−C плівки, іонно-плазмове розпилювання, рентгеноструктурний аналіз, електронна мікроскопія, температурний коефіцієнт електроопору, аморфна фаза, метастабільній стан.

Методами рентгеноструктурного анализа, электронной микроскопии и построения температурной зависимости электросопротивления изучались условия формирования разных метастабильных структур и фазовые превращения в процессе нагрева в пленках (Fe,Co,Ni)−C, полученных модернизированным методом трехэлектродного ионно-плазменного распыления. Показано, что пленки в свеженапыленном состоянии имеют метастабильную структуру. Переход из аморфного в равновесное кристаллическое состояние в пленках Fe−C проходит через стадию образования и последующего распада промежуточной, метастабильной гексагональной плотноупакованной фазы переменного состава, характеризующейся уменьшенными значениями параметра решетки по сравнению с ГПУ-фазой, полученной при закалке из расплава. В свеженапыленных пленках Ni-20…61%C параметр решетки ГПУ-карбида Ni_3C уменьшен по сравнению з ГПУ- Ni_3C после закалки из расплава. В пленках (Fe,Ni)−C зафиксированы прецизионные значения температурного коэффициента сопротивления на уровне 5 10^{-5} K^{-1} - 10^{-6} K^{-1}.

Ключевые слова: (Fe,Co,Ni)−C пленки, ионно-плазменное распыление, рентгеноструктурний анализ, электронная микроскопия, температурный коэффициент электросопротивления, аморфная фаза, метастабильное состояние.

1. Introduction

The use of traditional techniques of high rates of cooling allows realization of a number of metastable states, the solid amorphous state among them, to be fixed in many systems, in particular, in transition metal–carbon (TM–C) alloys. Often, the rapidly cooled materials exhibit a combination of unique physical properties. However, the most detailed experimental data presented in the literature [1–3] are related to the preparation of materials by melt quenching (MQ) at cooling rates of 10^6–10^8 K/s. At the same time, the structure and properties of metastable phases in TM–C films produced at higher cooling rates (to 10^{12} K/s) are of great theoretical and technological interest [3]. The aim of this work was to study the effect of ultrahigh cooling rates (to 10^{14} K/s) on the peculiarities of the formation, stability, and properties of metastable phases in (Fe,Co,Ni)–C alloys.

2. Materials and methods

The ultrahigh cooling rates were reached through using a modified three-electrode ion-plasma sputtering of composite targets [4]. Films intended for X-ray diffraction (XRD) studies of their phase composition and physical properties were deposited in 4–6 cycles for 5–6 min, whereas films intended for transmission electron microscopy (TEM) analysis were deposited in one 2–4-min cycle at the voltage applied to the target U_M = 2 kV and anode current I_A = 1-2 A. Prior to the filling the chamber with the working gas (high-purity Ar – State Standard 10167-79, O_2 content – 0.0004%), it was pumped out to 1,3 mPa. After that the chamber was filled with argon up to working pressure of 1.2-5.3×10^{-2} Pa. In this case, the cooling rate related to the relaxation time of an individual atom at the substrate is estimated to be 10^{12}–10^{14} K/s [5], i.e., really, the quenching from the vapor (VQ) occurs. The films were deposited under the same conditions on either dielectric pyroceramics (sitall) substrates or on a fresh cleavage plate of a NaCl single crystal. The rate of the increasing coatings was 0.3–0.5 nm/s. The phase composition of the deposited films was studied by both XRD photometric analysis, which was performed with using Co radiation and a Debye camera; and by TEM. The films used for the phase-composition studies were separated from the surface of NaCl single crystals through a standard procedure, which consists in the dipping of the single crystal in distilled water. The X-ray diffraction and electron diffraction patterns obtained were scanned. Then, we selected an axis, along which the degree of blackening and the distance to the reference point were determined via using a special program [6]; thus, we plotted a profile along the selected axis. The program for the analysis of profiles was developed on the basis of Microsoft Windows, which is a sufficiently simple and commonly used operating system. As the programming language, we used C++; the coding was realized with using object-oriented programming procedures and Borland C++ Builder 6.0 library facilities. The profile so built was used to perform the phase analysis and to determine lattice parameters accurately. With allowance for the extrapolation of the angle to 90°, the accuracy of the lattice parameter determination was $\pm3\times10^{-4}$ nm. The electrical properties and thermal stability of the films deposited on glass ceramic substrates were studied via using temperature dependences of the electrical resistivity measured during the continuous heating and cooling of a sample at the rate of 0.3 K/s in vacuum of ~1.33×10^{-2} Pa. The thermal stability of the arising metastable states was estimated on the basis of points of inflection in the temperature dependences. To estimate the composition of the films, we used a special technique allowed us to determine the film composition accurately to ± 2 at. % of C. We studied the structure and properties of the Fe (20, 31, 43, 55, 69, and 84 at.

% C), Co (5, 11, 18, 26, and 52 at. % C), and Ni (7, 15, 13, 18, 20, 24, 35, and 61 at. % C) films.

3. Results and duscussion

X-ray and TEM analysis results of the initial and heat treated films are shown in Table 1. The formation of metastable states upon VQ is characterized by a number of peculiarities.

(1) The mixture of two phases is formed in the structure of as-deposited films of 20-55 at. % C compositions (Table 1). It is AP-1 based on specific close-packed coordination of Fe and C atoms and a carbonic amorphous phase AP-2 surrounding the last one. The AP-1 probably consists of the clusters based on HCP-coordination of iron atoms. The size of coherent domains (~2.5 - 2.8 nm) was estimated by the Selyakov-Sherer formula. Refinement of coherent domain size up to 1.5 nm is observed at increased contents of carbon up to 31%. It can testify about forming of amorphous structure in the sputtered Fe-55 % C films.

Table 1

Phase composition of (Fe, Co, Ni) – C films in the as-deposited and annealed states produced by quenching from the vapor

Composition at. % C	Phase composition of films			
	As-deposited	After heating to		
		300 °C	500 °C	630 °C
Fe-20%C;	AP-1, (L=2,8нм)	AP-1, (L=2,8нм)	α′-Fe+Fe_3C	α-Fe+Fe_3C
Fe-31%C	AP-1 (L=2,5nm)+AP-2	$Fe_{2-X}C_X$	α′-Fe+Fe_3C	α-Fe+Fe_3C
Fe-43%C	AP-1 (L=1,2nm)+AP-2	$Fe_{2-X}C_X$+AP-2	α′-Fe+Fe_3C	α-Fe+Fe_3C
Fe-55%C	AP-1 (L=1,5nm)+AP-2	$Fe_{2-X}C_X$+AP-2	α′-Fe+Fe_3C	α-Fe+Fe_3C
Fe-69%C	$Fe_{2-X}C_X$ +AP-2	α′-Fe+Fe_3C+C	α′-Fe+Fe_3C+C	α-Fe+Fe_3C+C
Fe-84%C	$Fe_{2-X}C_X$ +AP-2	α′-Fe+Fe_3C+C	α′-Fe+Fe_3C+C	α-Fe+Fe_3C+C
Co-5%C	α′-Co (a=0.3570 nm)			
Co-11%C	α′-Co (a=0.3581 nm)+Co_3C			
Co-18%C	NCP (L=12 nm)			
Co-26%C	AP-1 (L=3.5 nm)			
Co-52%C	Co_2C (a=0.2864 nm; b=0.4509nm; c=0.4395 nm)+C			
Ni-7%C	α′-Ni (*a*=0,3573 nm, L=7 nm)		α′-Ni (*a*=0,353 nm, L=12 nm)	
Ni-13%C	α′-Ni (*a*=0.3617 nm, L=5 nm)		-	
Ni-15%C	NCP (L=4,5 nm)		α′-Ni (*a*=0,353 nm, L=14,5 nm)	
Ni-18%C	AP-1 (L=2,5 nm)		-	
Ni-20%C	α′-Ni (*a*=0,3605 nm, L=7 nm) +Ni_3C(*a*=0,269nm,*c*=0,433nm)		-	
Ni-24%C	Ni_3C (*a*=0,2697 nm, *c*=0,4334 nm L=12 nm)		α′-Ni (*a*=0,3524 nm, L=13 nm)+ AP -2	
Ni-35%C	Ni_3C (*a*=0,2727 nm, *c*=0,4357 nm L=10 nm)+ AP -2		α′-Ni (*a*=0,3522 nm, L=11 nm)+ AP -2	
Ni-61%C	Ni_3C (*a*=0,2747 nm, *c*=0,436 nm L=12 nm)+ AP -2		Ni (*a*=0,3522 nm, L=13 nm)+ AP -2	
Ni	Ni (*a*=0,353 nm, L=9 nm)		Ni (*a*=0,3528 nm, L=12,5nm)	

Note: α′ is the highly supersaturated solid solution (HSS) of carbon in bcc Fe, fcc Co, and fcc Ni; NCP is a nanocrystalline phase; AP is an amorphous phase; and L is the size of coherent domains.

During the annealing of amorphous films the comparatively wide lines of metastable $Fe_{2-X}C_X$ phase are observed on the diffuse halo from the side of smaller angles. This phase has enlarged lattice parameters of hcp-phase (a=0.2635 nm, c=0.4283 nm, c/a=1.63) in comparison with parameters of the phase produced by melt quenching. The lattice parameters depend on carbon content within the limits of a=0.2810…0.2871 nm, c=0.4371…0.4474 nm, c/a=1/56. The iron volume per atom in $Fe_{2-X}C_X$ phase varies within 0.015…0.016 nm^3/atom. It is 15-20% higher than identical parameter fixed in melt-quenched Fe–C alloys. Obtained values of HCP-lattice parameters allow to assume that nanocrystals of metastable $Fe_{2-X}C_X$ phase are formed at the early decomposition stage at annealing of the amorphous phase. Under nonequilibrium condensation not only the high cooling rates but also the Laplace pressure significantly influences the metastable phase formation in the films with the thickness of 40…45 nm and coherent domain sizes of 2…3 nm. At the sputtering process the probable mechanism of crystallization is "vapor-liquid-solid phase" type. In this situation the Laplace surface pressure on the particle is about 10^4-10^5 atm. It is quite enough for the formation of high-pressure phases in the sputtered films, especially with small thickness [7]. HCP-modification of iron is a high-pressure phase. The alteration of lattice parameters of metastable hcp-phase in the films (Table 1) is due to the formation of solid solutions based on HCP-phase with different saturation rate depending on carbon content and sputtering conditions. The saturation rate of hcp-phase with carbon decreases droningly with increasing of annealing temperature. The lattice parameters of bcc solid solutions alter similarly at annealing temperature 500 ^oC and 630 ^oC (a=0.2873 nm and a=0.2870 nm, accordingly) depending on carbon content (Table 1). Depending on carbon content, the structure of equilibrium heat treated (973 K) Fe–C films consists of phase mixture: α-Fe (a=0.2867 nm)+cementite (Fe_3C) or α-Fe (a=0.2867 nm)+Fe_3C+free carbon partly as carbon clusters. So transition from amorphous to equilibrium state occurs through the formation and following decomposition of the metastable HCP-phase. It agrees with the thermodynamic Ostvald's rule of stages. Electron-microscopic photographs (enlargement is 23000) corroborate the most refinement of structure in the films with carbon content nearly 55% (Fig. 1). This film structure has more "unstructured" form. It confirms the amorphous character of structure.

(2) The highly supersaturated solid solution of carbon in HCP Co is formed in the structure of as-deposited films of Co–5at%C compositions (Table 1), NCP (L=12 nm) and AP-1 (L=3.5 nm) are formed in the structure of as-deposited films of Co–18 - 26 at. % C compositions.

(3) As the lattice parameters of the HCP Ni_3C carbide (a = 0.2697– 0.2747 nm and c = 0.4334 – 0.4360 nm) decrease as compared to those of Ni_3C produced by melt quenching, the c/a ratio decreases to ~1.61 – 1.59. In the composition range of 13 – 18 at. % C, a metastable amorphous phase is formed. According to X-ray diffraction data, the phase undergoes partial crystallization during condensation, which is accompanied by the formation of a Ni-based α′ with a lattice parameter a = 0.3617 nm, which corresponds to the maximum supersaturation of nickel with carbon of about 11 at. %. The formation of two-phase mixtures was found in the as-deposited Ni–C films containing from 20 to 61 at. % C; these are either the metastable Ni_3C carbide with variable lattice parameters (see Table) and Ni-based HSS containing about 9 at. % C (a = 0.3605 nm) or the Ni_3C carbide and free amorphous carbon. Fig. 2 shows the most typical temperature dependence of the film's resistivity during heating and cooling. The Fe–C films containing <20 at. % C

exhibit the thermal stability to ~540 °C; the Fe–69…84%C films containing a metastable HCP-phase exhibit the lowest thermal stability (~170 °C). Measuring the temperature coefficient of resistance (TCR) showed that films Fe–69%C after heat treatment at 630 °C had minimal TCR ($\pm 10^{-6}$ K^{-1}) in the wide temperature interval. A change of TCR sign at this carbon concentration evidences the domination of covalent over metallic bond between atoms.

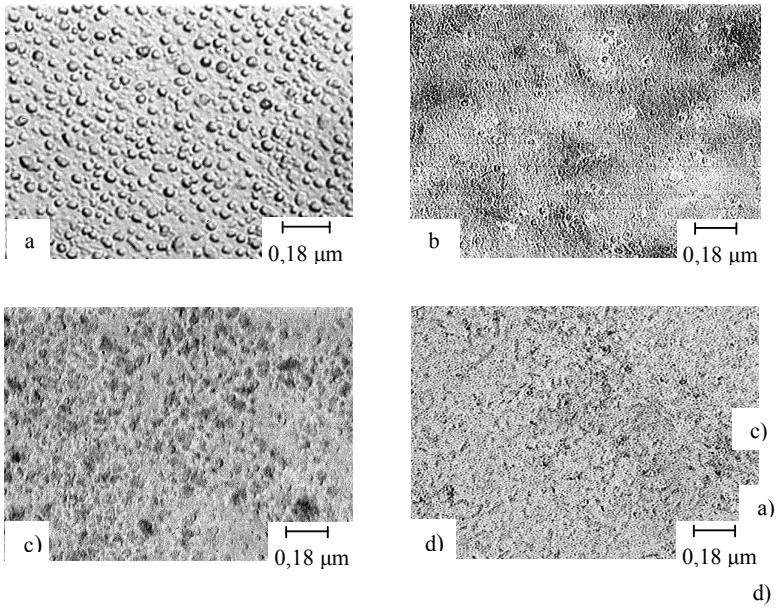

Fig. 1. Electron micrographs (×23000) of initial Fe–C films (at. %): a) Fe–20% C; b) Fe–31% C; c) Fe–55% C; d) Fe–69% C;

The Ni–C films containing 24.1–34.6 at. % C exhibit the highest thermal stability (~540 °C); the films containing a nanocrystalline phase exhibit the lowest thermal stability (~470 °C). Our analysis of the temperature dependences (Fig. 2) indicates that the nanocrystalline state was reached in the as-deposited Ni–C films containing ~15 at. % C.

This is confirmed by both the low positive temperature coefficient of resistance (TCR) that equals to 1.2×10^{-4} K^{-1} and the size of coherent domains determined by Selyakov–Sherer equation (L ~ 4.5 nm). The temperature dependences of the electrical resistivity for all films under study are characterized by points of inflection indicating the decomposition of metastable phases and transition to a more equilibrium state. The identical character of transformations occurring in these alloys allows us to conclude that, as the carbon content increases, the thermal stability of arising metastable phases increases by 70 K as compared to that of the nanocrystalline state. The formation of metastable Ni–C phases saturated with carbon positively affects the electrical properties of the films. For example, the Ni–34.6 at. % C and Ni–61.4 at. % C films are characterized by low values of TCR that equal to ~5 10^{-5} K^{-1} and by a high electrical resistivity reaching 200 Ω/sq., which can be increased by several orders of magnitude (on the retention of the above TCR magnitude) by decreasing the film thickness.

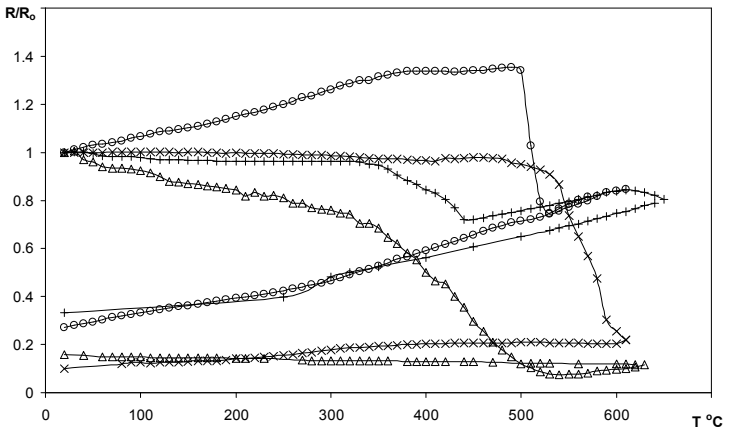

Fig. 2. The temperature dependence of the resistivity of the film: + - Fe–20%C; Δ - Fe–69%C; o - Co–52%C; × - Ni–61%C

5. Conclusions

The quenching from the vapor was found to result in a substantial expansion of the range of metastable states as compared to that obtained upon quenching from the melt. Carbon concentrations, which correspond to the formation of metastable states, such as HSS, amorphous and nanocrystalline phases, and metastable carbide, in the (Fe,Co,Ni)–C alloys upon quenching from the vapor, have been determined. Temperature ranges of the stability of metastable phases obtained during melt quenching have been determined. The use of the ion plasma sputtering allows us to prepare high-carbon (Fe,Ni)–C films, which can be recommended for the practical use in microelectronic devices as high-resistance corrosion-resistant film resistors characterized by a temperature coefficient of resistance of about $\leq 5 \times 10^{-5}$ K^{-1}.

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