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Original article

Preparation, structure and magnetic properties of the nanostructural Ni@C films obtained by magnetron deposition

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ABSTRACT Three series of films were obtained by magnetron sputtering of the composite C-Ni target with different ratios C/Ni (vol.%) = 60/40; 40/60; 30/70. The effect of the substrate temperature on the structure and the size of film-forming nickel nanocrystallites with a carbon shell was studied with using X-ray diffraction analysis. The cluster nature of film deposition on the growth surface was established by using atomic force microscopy. The saturation magnetization of nickel nanoparticles 4πMS was measured by the inductive-frequency method and the substrate temperature dependence was studied. It has been shown that the films with a high carbon content exhibit magnetism only when deposited on hot substrates. The films with the minimum carbon concentration exhibit ferromagnetic behavior even when deposited on a relatively cold substrate.

KEYWORDS magnetron deposition, nucleation processes, nanoclusters, saturation magnetization

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1. Introduction

After the discovery of carbon nanostructured materials (nanotubes, nanofibers, etc.), a significant part of the research is aimed at studying the mechanisms of their growth [1–3]. From the point of view of applications, nanotubes are the objects of particular interest when they are filled with various materials like special magnetic metals. In this case, the nanotube plays the role of a kind of shell for a metal nanowire/nanorod, which is in a magnetically ordered state.

The classical methods [4, 5] for producing carbon nanotubes filled with transition metal atoms usually require the use of metal-catalysts, fairly high (600 – 800 °C) growth temperatures, and technologically complex processing of the resulting structures. At the same time, the necessary activation of carbon and nitrogen during the growth of such materials is also possible in low-temperature plasma. This fact allows combination of these materials with polymers and other objects characterized by low operating temperatures in order to expand the application area.

Around 2010s, we developed a low-temperature technology for producing columnar nanostructures of the C–N system that grow perpendicular to the substrate surface and do not require the use of a metal catalysts. This technology is based on magnetron sputtering of carbon in low-temperature plasma at substrate temperatures of ∼150 – 200 °C. We established that columnar carbon nanostructures were formed at low substrate temperatures and nitrogen concentrations up to 10 at.% [6, 7]. Hybrid nanocolumn structures consisting of core-shell nanoclusters (magnetic metals (Ni, Fe, Co) coated with carbon) were of special interest. The structure and the properties were intensively studied due to their promising potential applications. So, further studies showed the possibility of obtaining metal-containing nanocolumn structures of the Ni–C–N system in low-temperature plasma [2, 8, 9]. However, it should be noted that the structural and phase composition of "metal core-carbon shell" nanoobjects has not been enough studied. The main reason is the diversity of synthesis processes affecting the structure of these composites.

The present work contains some materials not included in our earlier published work [10] and is aimed at studying structure and magnetic properties of hybrid nickel-carbon films synthesized at low temperature magnetron deposition of Ni-C clusters.

2. Experimental technique

Nanostructural Ni@C films were obtained by the method of magnetron sputtering of a nickel-carbon target in argon atmosphere with small nitrogen admixture onto quartz glass substrates. The target-substrate distance was 2.0 cm, the substrate holder was grounded. The planar DC magnetron with a flat cathode and a ring anode was used. Magnetron discharge power did not exceed 20 W. Working gas pressure was 26 Pa. The pressure was almost an order of magnitude higher than that typically used in magnetron sputtering experiments at low magnetron plasma power [11]. The substrate temperature varied in the range 100 – 350 °C. The films growth time varied in the range 10 s up to 10 min.

A double disk structure was used as a target: a nickel disk with apertures was imposed onto a solid graphite disk. Three series of films were grown in the following C/Ni-ratios (vol.%): 30/70 – A group; 40/60 – B group; 60/40 – C group. The film thickness was up to 100 nm.

The surface morphology of the films was analyzed with the atomic force microscope (AFM). The relative content of atoms in the samples was registered by the energy dispersive X-ray (EDX) spectroscopy with using INCA Penta FETx3 (Oxford Instruments) attachment. The structure of samples was studied with the X-ray diffraction (XRD) on a DRON-3 instrument using Co$K\alpha$ radiation. The saturation magnetization of the film material was studied with using an inductive-frequency device, in which a change in the resonance frequency $\Delta F \propto \Delta M = f(H)$ was measured for an oscillatory circuit with a sample placed into the induction coil [12].

3. Main results and discussion

Nucleation processes and growth dynamics of nanostructural nickel-carbon films on a substrate were studied with AFM. Polished quartz glass substrates with small roughness were used, so the control the complicated morphology of sample surfaces with accuracy ~ 1 nm was allowed.

Fig. 1 shows the AFM-images of the Ni-C nanostructures surface after 30 and 300 s growth. After 30 s growth the whole surface of the substrate is covered with cluster elements of about 10 nm in size.

Thus, we can talk about the cluster nature of the films deposition. As a result, the formed clusters of the sputtered material are deposited on the substrate surface. Formation of clusters in plasma is presumably caused by sufficiently high buffer gas pressure (let's remember that we used pressure of 26 Pa). So, a small plasma area has a high concentration of sputtered atoms. This fact is the reason of starting self-organizing processes: formation of clusters from the atoms of target material and buffer gas in plasma at rather low temperature. The speed of buffer gas flow is small as compared to thermal speeds of the target atoms and the atoms of buffer gas. It has no influence on the concentration and distribution of the sputtered atoms. Also, the presence of carbon in the structure of films indicates existence of a carbon cover around of nickel nanocrystallites/nanoclusters as it is shown in works [1,2].

Such results require reconsideration of the processes of nanostructure deposition with using magnetron sputtering and the development of new nucleation models, in particular the growth of nanotubes/nanofibres from small charged clusters in the gas phase [13].

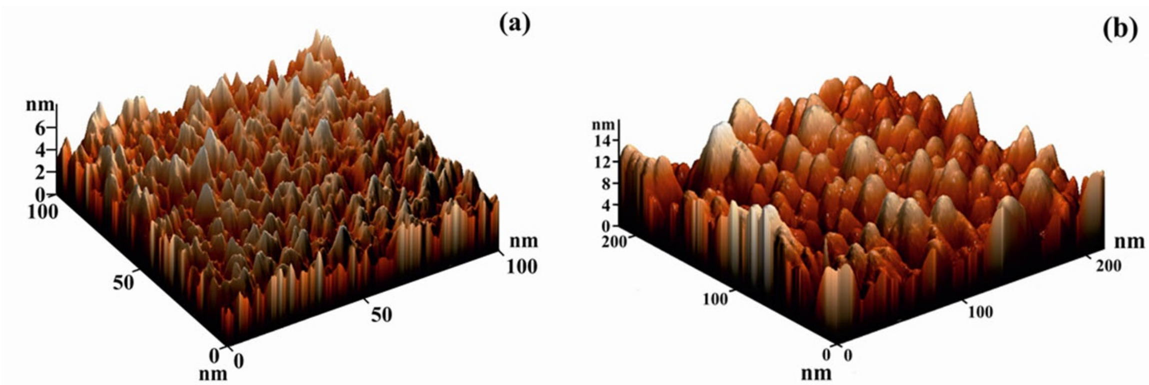

FIG. 1. AFM-images of hybrid Ni-C nanostructures surfaces at growth time, s: (a) - 30 s, (b) - 300 s

The rest of the studies except nucleation processes were performed on the films of three series (A, B, and C) with the growth time above 10 min.

The X-ray diffraction patterns of A group films (Fig. 2) show the reflexes corresponding to the FCC-lattice of nickel only. The lattice constant has appeared to be 3,53 Å that is close to the value for bulk nickel (3,56 Å). At the same time, some line broadening is observed in the X-ray reflexes that indicates rather small size of Ni-crystallites making the films up.

Being estimated by broadening of X-ray reflexes, the size of the Ni-nanocrystallites of the films of group A smoothly increases with substrate temperature T_S increase. The values for reflexes (111) and (200) are different. It should be noted that the distinction is not present at low temperatures. Hence, the clusters deposited on a substrate at low temperatures have a spherical form.

The B-group films (C/Ni=40/60 vol.%) demonstrate nickel FCC-phase at average and high substrate temperatures (see X-ray diffraction patterns in Fig. 3a). At the same time, the reflexes of the NiO phase are registered at substrate temperatures < 160 °C (see Fig. 3a, too).

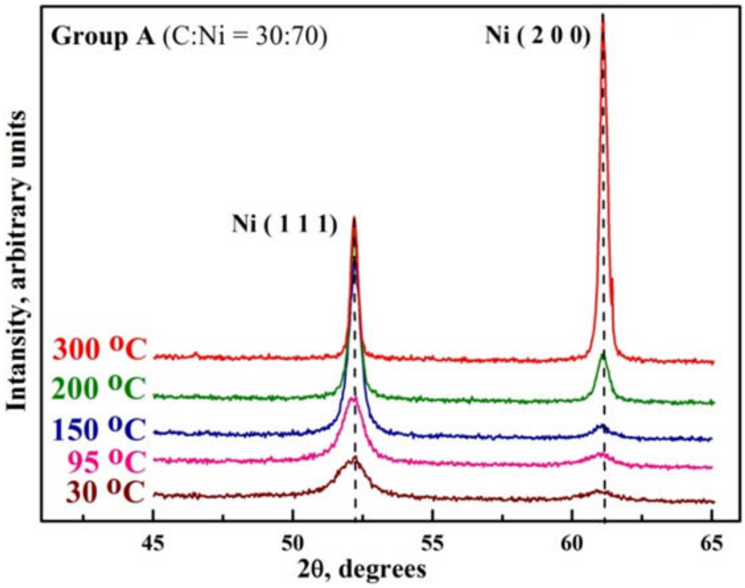

FIG. 2. Influence of substrate temperature T_S on X-ray diffraction of the A-group films

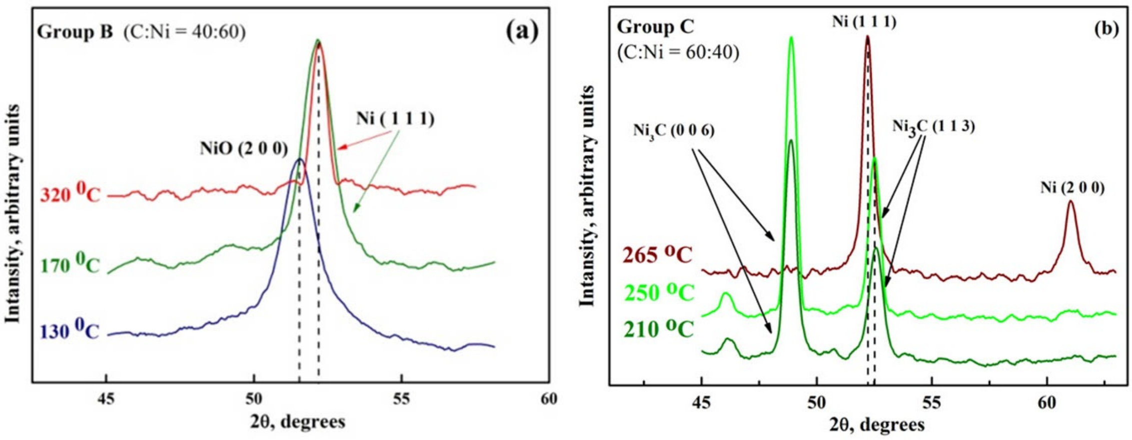

FIG. 3. Influence of substrate temperature T_S on X-ray diffraction of B (a) and C (b) groups films

It is possible to assume, that the increase in concentration of carbon in the films results in a change of carbon structure covering the nickel nanocrystallites. At low carbon concentrations in the Ni-C nanoclusters, the carbon shells around the metal nanocrystallites are mostly unclosed and composed by imperfect curved fragments with pores. It is obvious that nickel oxidation takes place under the interaction of the nanoclusters with atmosphere. At the same time, an increase in the substrate temperature results in a sharp increase of ordering of curved carbon fragments and provides protection of the Ni-crystallites against oxidation.

The C-group films (C/Ni=60/40 vol.%) demonstrate the nickel carbide Ni_3C HCP phase at the substrate temperature below 250 °C (see X-ray diffraction patterns in Fig. 3b). However, the reflexes corresponding to the FCC-lattice of nickel (111) and (200) are registered only at increasing temperature.

Fig. 4 shows substrate temperature T_S dependences of Ni-nanocrystallites size D of the B-group films. With T_S increase, the Ni-crystallites size increases, too. There is some critical temperature of the substrate T_{cr} nearby 80 °C, below which the nickel particles size tends to zero. This fact is the proof of amorphous nature of nanoclusters deposited onto a substrate.

In Fig. 4, there are also substrate temperature dependences of the nickel carbide Ni_3C nanocrystallites size D of the C-group films in direction (113). With T_S increase from 170 to 250 °C, the crystallites size sharply increases. The nickel carbide particles size tends to zero below the critical temperature of the substrate T_{cr} nearby 150 °C.

Application of the inductive-frequency method allows measuring directly the saturation magnetization of ferromagnetic samples $4\pi M_S$ [8, 12]. The presence of nonmagnetic impurities (for example, carbon) does not distort the result of measurements. Saturation magnetization of all samples was measured at room temperature. Fig. 5 shows the effect

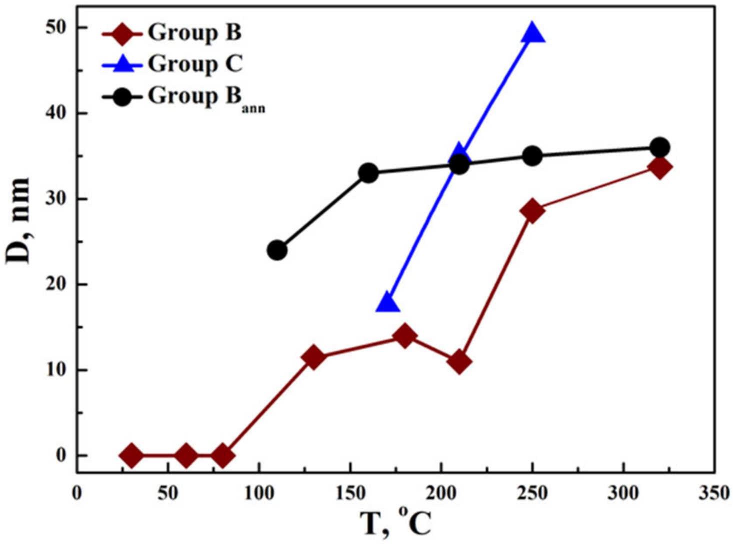

FIG. 4. Substrate temperature T_S dependence of size D of Ni- and Ni_3C-nanocrystallites of B- and C-groups films. B_{ann} – B-group films after annealing

of substrate temperature T_S on saturation magnetization $4\pi M_S$ of the ferromagnetic component for nickel-carbon films during growth. It is shown that the films of A-group characterized by the minimal content of carbon demonstrate ferromagnetism even at deposition onto a cold substrate. This result confirms the data of X-ray diffraction presented above in Fig. 2, where the Ni phase is fixed already for the lowest substrate temperatures. An increase of $4\pi M_S$ with the rising substrate temperature T_S can be explained by dimensional effect [8] due to increasing crystallite size D. These data are in good agreement with the conclusion that the deposited clusters have the structure of the "Ni core/C shell" type at low carbon concentration. They are formed directly in the magnetron plasma by crystallization of nickel atoms inside the nickel-carbon cluster. As the substrate temperature rises, the size of a cluster's nickel-core grows due to diffusive processes and saturation magnetization of such crystallites $4\pi M_S$ is increased, too. We can see in Fig. 5 that $4\pi M_S$ comes nearer to magnetization of bulk nickel when the Ni crystallite size reaches macroscopic values at the substrate temperature $T_S \approx 300\,^\circ$C.

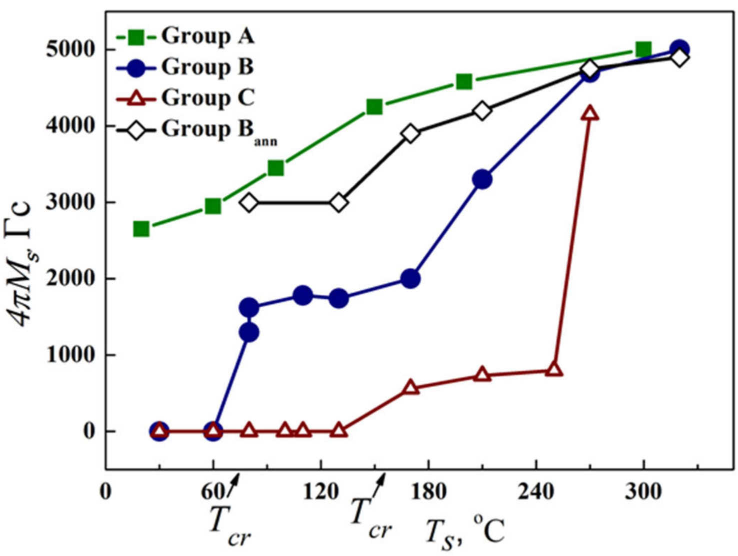

FIG. 5. Dependences of saturation magnetization $4\pi M_S$ on substrate temperature T_S for A-, B-, C-groups films of Ni–C system. B_{ann} – B-group films after annealing

At the same time, the films of B- and C-groups characterized by a larger content of carbon appear nonmagnetic in the case of deposition onto a cold substrate. They demonstrate ferromagnetism when deposited directly onto hot substrates. The critical temperature T_{cr} of ferromagnetism occurrence rises with an increase of the carbon – nickel ratio: for C/Ni = 40/60 vol.% $T_{cr} \approx 80\,^\circ$C, for C/Ni = 60/40 vol.% $T_{cr} \approx 150\,^\circ$C. At a higher substrate temperature, magnetization of deposited clusters grows quickly until it approaches magnetization of bulk nickel at $\sim$300 °C. This behavior of ferromagnetism in the films of B- and C-groups may be explained by the dissolution of carbon atoms in the nickel crystallites of deposited clusters. As a result, weakly magnetic solid solution of carbon in nickel can be formed and nonmagnetic carbide phase can be registered at large concentration of carbon.

It should be noted that we have observed a similar behavior of the ferromagnetic moment in the nickel-nitrogen films [14]. Besides, the magnetization depends on the crystallite size of nickel phase in the center of the deposited cluster. It is shown in Fig. 5 that increasing carbon concentration is accompanied by the increased substrate temperature at which the mentioned critical size is reached. In Fig. 5, we can see that the magnetization is decreased with increasing carbon concentration. This fact agrees with the model assuming the formation of an increasingly saturated solid solution of carbon in nickel. Further, with increase in substrate temperature, there is a crystallization of a nickel phase in separate clusters at first. When the carbon concentration in cluster becomes higher, the magnetization of nickel crystallite and its size is less [14]. The same process obviously takes place in the range of substrate temperatures T_S 80…180 °C for B-group films and 150…250 °C for C-group films. At higher T_S , there is an increase of the magnetization and confluence of separate clusters with increased nickel core and with general carbon shell, due to diffusive processes on a substrate and extraction of carbon from nickel phase.

To verify the model, we have carried out annealing of the B-group samples. The experiment was carried out on air at the temperature about 370 °C during 10 min. We can see increasing magnetization after annealing for the samples obtained at low substrate temperatures (see Fig. 5, B_{ann} curve). This fact confirms the diffusive mechanism of nickel crystallites growth at high substrate temperatures. The X-ray data also give evidences of an increase in Ni-crystallites size for the samples of B-group subjected to annealing (see Fig. 4, B_{ann} curve).

The results of the study allow us to make the following conclusions. At high C/Ni ratios, the nickel-carbon clusters formed in the plasma are amorphous formations in the form of a mixture of Ni and C atoms. Being deposited on a cold substrate, the clusters compose nonmagnetic films. Forming of nickel ferromagnetic crystallites starts for the substrate temperatures above T_{cr}. The higher the C/Ni ratio, the higher the value T_{cr}. It should be noted that if the carbon concentration is not high enough (imperfect carbon shell around the nickel core), oxidation of some of the Ni-crystallites and the appearance of the NiO phase is possible in the case of exposing samples to air. Similar situation is observed in the B-group films at the substrate temperature 130 °C (Fig. 3). In the films of C-group, clusters containing the hexagonal phase of nickel carbide Ni_3C are formed basically at the substrate temperature within the range of 170 – 250 °C due to the high content of carbon in magnetron plasma. The ferromagnetic crystallites of nickel phase are of small size and well protected by carbon shell. Nickel carbide is decomposed at the substrate temperature above 250 °C and deposited clusters have ordinary structure, namely “a crystal Ni-core/carbon shell”.

4. Conclusion

Three series of Ni@C films were grown with different ratios C/Ni (vol.%) = 30/70 (group A); 40/60 (group B); 60/40 (group C). Using atomic force microscopy, it is shown that Ni-C clusters with a characteristic dimension about $\sim$10 nm are formed in the plasma and deposited onto the growth surface of the film. Thus, magnetron deposition of the films is of predominant cluster’s nature. For the samples of A-group, X-ray diffraction analysis reveals the nickel phase and the increase in the size of its crystallites with increasing substrate temperature. For the samples of B- and C-groups, the nickel phase is observed only at relatively high substrate temperature, while the films with nanocrystalline nickel carbide Ni_3C are formed on relatively cold substrates. The research results show that the samples of A-group (low carbon content) exhibit ferromagnetic properties even when deposited on a cold substrate, while for B- and C-groups (average and high carbon content), ferromagnetism occurs only under conditions of sample growth at temperatures higher than certain critical substrate temperatures: 80 and 150 °C, respectively.

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Conflict of interest: the authors declare no conflict of interest.