Study of nanocrystalline nickel films deposited in a nitrogen atmosphere

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It is shown that high-speed condensation methods can be used to prepare nickel nitride films in the nanocrystalline state. The phase composition of the condensate formed exhibits a strong dependence on the substrate temperature. © *1998 American Institute of Physics.*
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The study of the structural–energy state of nitrogen in solid solution and in nonstoichiometric metal nitrides Me–N of the ''interstitial phase'' type based on fcc metals (Me stands for Fe, Ni, etc.) continues to be an urgent metallophysical task in the development of high-nitrogen alloys. Such metal nitrides remain the subject of extended study as model objects on which information can be obtained about the correlation of crystal structure, electronic structure, and physical properties as a function of the nitrogen concentration. At the same time, limitations of the experimental data about the structure and properties of Me–Ni alloys force the authors of these models to turn to the works of the 1940s.[1,2]

In recent years in connection with the development of methods of preparing nanocrystalline materials,[3] the possibilities of creating large amounts of various alloys have broadened. First of all, this is a function of the fact that the chemical activity of these materials manifests a strong dependence on the size of the crystallites.[4]

The present paper examines the properties of films of nickel nitride and the processes accompanying their synthesis. To prepare these films, we used the method of pulsed plasma sputtering. Earlier we showed that with the help of this technique it is possible to prepare nanocrystalline films of 3d metals with unusual properties.[5–8] The starting vacuum was 10^{-6} Torr. Spectrally pure nitrogen, whose pressure was varied from 5×10^{-5} to 10^{-2} Torr, was then admitted to the sputtering chamber. The substrate temperature at the outset of sputtering was always 20 °C. The condensation rate of the Ni films in a pulse of 100 μs duration was $10^4 - 10^5$ A/s. We used cover glasses of 0.2 mm thickness as the substrate. The thickness of the investigated films varied within the range 45.0–70.0 nm.

We studied the phase composition and magnetic properties (magnetization M_s) in the prepared samples as functions of the nitrogen partial pressure in the chamber. The results obtained are presented in Table I. We also determined the state of the substrate after the preparation process. The magnetization was measured at room temperature.

The films prepared at $P = 10^{-6}$ Torr had a metallic lustre, an undeformed surface, and zero magnetization. At $P = 10^{-4}$ Torr the samples also had a metallic lustre, but were strongly deformed, and $M_s = 415$ Js. Starting from a pressure of 2×10^{-4} Torr, two pronounced regions were ob-

served on the sample: in its center a light-colored region, with metallic luster but strongly deformed, and along its edges, a dark, undeformed region [Fig. 1a]. The light-colored region had a large magnetization while the dark region was practically nonmagnetic. The films prepared at $P = 10^{-2}$ Torr were homogeneous and nonmagnetic. Samples with similar properties were prepared at 10^{-3} Torr, when sputtering is performed with interruptions.

To examine the structure of the films, we performed an electron-microscope analysis. Figure 1b displays electron diffraction patterns and photographs of the microstructure from different regions of film 3, prepared at 10^{-3} Torr. The central part of the film has fcc structure with lattice parameter $a = 0.352$ nm, and size of the crystallites $0.2 - 0.4$ μm. Taking into account the large magnetization, it is possible to identify this region as a phase of pure Ni. The second part of the sample has hcp structure with lattice parameters $a = 0.266$ mm and $c = 0.429$ nm, and size of the crystallites < 10.0 nm. The lattice parameters and zero magnetization suggest that this region is nickel nitride with the formula Ni_3N (Ref. 1).

Film 1 had a hcp phase with lattice parameters $a = 0.264$ nm and $c = 0.433$ nm. We identified it as a phase of pure Ni. The properties of these films are discussed in Ref. 8. In sample 2 we observed fcc structure with lattice parameters characteristic of pure Ni. Films 4 and 5 are nickel nitride with the formula Ni_3N.

As was noted above, in some of the samples the substrate was strongly deformed, which speaks of the presence of a high temperature at the time of formation of the conden-

TABLE I.

Sample No.	P_N, Torr	Phase composition	M_s, Js	State of substrate
1	10^{-6} (without nitrogen)	hcc (Ni)	0	Not deformed
2	10^{-4}	fcc (Ni)	415	Deformed
3	10^{-3}	fcc (Ni)	415	Partially deformed
		hcc (Ni_3N)	0	
4	10^{-3} *	hcc (Ni_3N)	0	Not deformed
5	10^{-2}	hcc (Ni_3N)	0	Not deformed

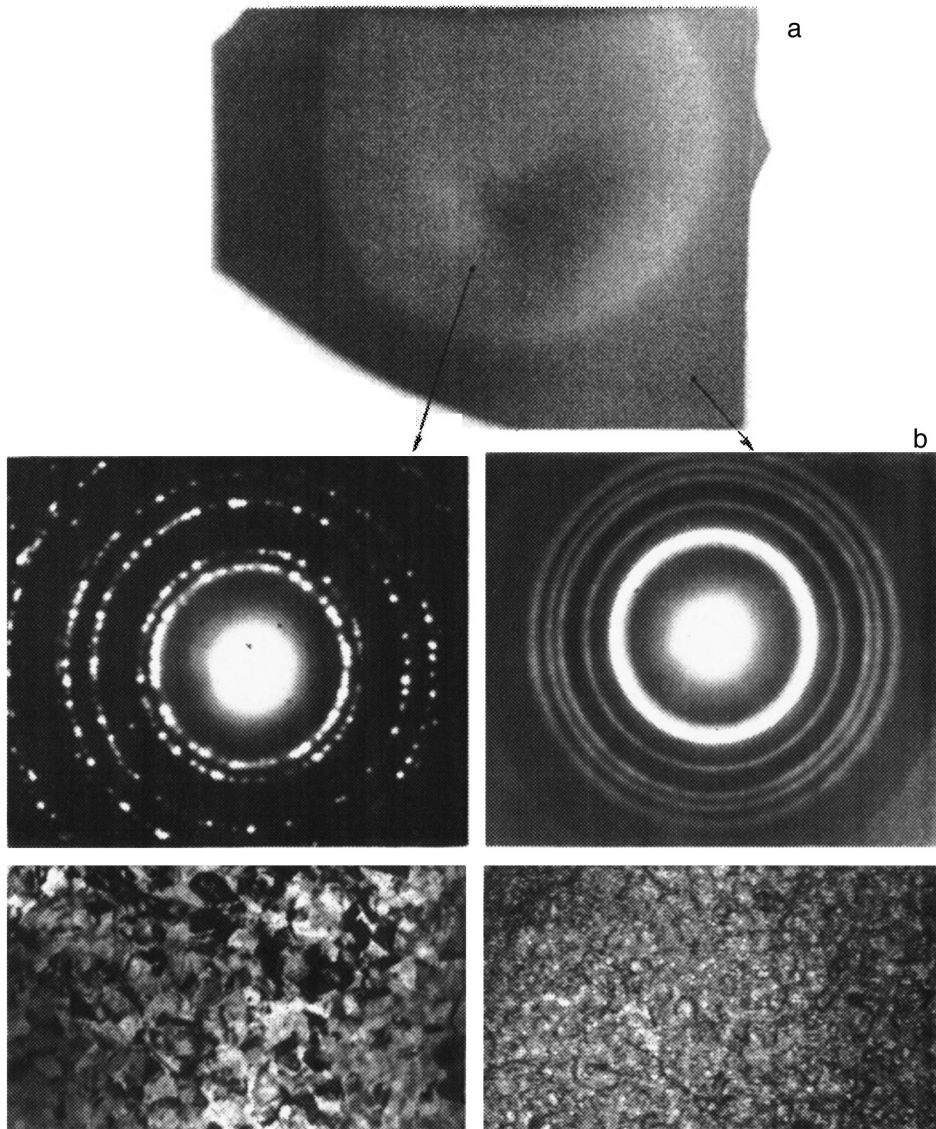*The film was prepared with evaporation interruption every $15 - 20$ s.

FIG. 1. Electron-microscopic analysis of a Ni–N$_2$ film prepared at a pressure of 10^{-3} Torr: a — photograph of the sample; b — electron diffraction patterns and microphotographs; left — of the central part, right — from the periphery of the sample.

sate. In order to pursue this question in more detail, we performed an analysis of the temperature dynamics in the substrates during the film deposition process. Toward this end, we sputtered Pd–Cu film thermocouples on the substrate. The results are plotted in Fig. 2. During the first few minutes, when deposition of the condensate takes place, the substrate temperature was raised to $T = 470-570$ K. This is because the high flux density of the evaporated material carries with it a large amount of heat, which is then liberated to the substrate. After switching off the plasma the substrate temperature stays unchanged for some time and then begins to fall according to an exponential (films 1 and 4).

A different picture is observed for film 2: as the temperature is raised to $T \sim 470$ K, a jumplike increase in the temperature occurs. Due to the finite response time of the thermocouple it was not possible to measure it exactly. However, the strong deformation of the substrate indicates that $T > 770$ K. We attribute this sudden increase in the temperature to the liberation of heat accompanying the decomposition of nickel nitride. As follows from Ref. 1, the phase transition Ni$_3$N–Ni$_4$N takes place at $T = 460-470$ K. Due to
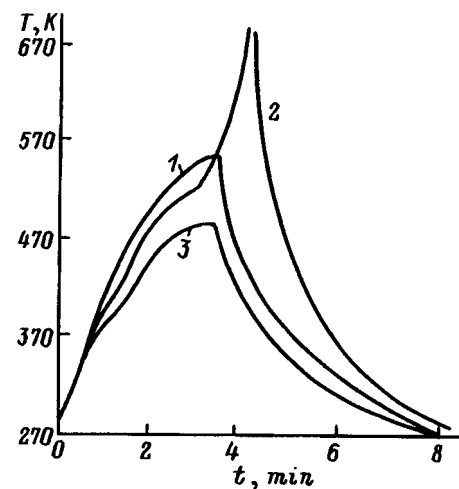

FIG. 2. Time scans of the temperature in nickel films deposited in a 10^{-6} Torr vacuum (*1*) and in a nitrogen atmosphere at a pressure of 10^{-4} (*2*), 10^{-2} (*3*).

the accompanying liberation of heat, an abrupt growth of the temperature takes place, and at $T = 610 - 620$ K the nickel nitride decomposes with liberation of the fcc phase of Ni.

Thus, in order to prepare nickel nitride (Ni_3N) films using the proposed technique, it is necessary to avoid raising the substrate temperature to temperatures $T > 460$ K. In our case, this was achieved both by raising the nitrogen pressure in the vacuum chamber (film 5), which leads to a decrease in the condensation rate and a corresponding decrease in T, and by interrupting the sputtering process (film 4). In film 3, in which we simultaneously observed regions with different structure, the decomposition temperature was reached only in the center of the sample. Thus, on the periphery of the film the nickel nitride phase was preserved. The small size of the crystallites on the periphery (< 10.0 nm) would seem to in-

dicate that the nanocrystallinity of the films is one of the reasons for the formation of the nickel nitride phase.

[1] R. Bernier, Ann. Chim. (Paris) No. **66**, 104 (1951).
[2] N. Terao, J. Phys. Soc. Jpn. **15**, No. 2, 227 (1960).
[3] W. Siegel, Nanostruct. Mater. No. **3**, 1 (1993).
[4] M. L. Cohen and W. D. Knight, Phys. Today **43**, No. 12, 42 (1990).
[5] G. I. Frolov, O. A. Bayukov, V. S. Zhigalov *et al.*, JETP Lett. **61**, 63 (1995).
[6] V. G. Myagkov, L. I. Kveglis, and G. I. Frolov, Izv. Ross. Akad. Nauk **59**(2), 152 (1995).
[7] G. I. Frolov, V. S. Zhigalov, A. I. Pol'skiĭ *et al.*, Fiz. Tverd. Tela (St. Petersburg) **38**, 1208 (1996) [Phys. Solid State **38**, 668 (1996)].
[8] S. M. Zharkov, V. S. Zhigalov, and G. I. Frolov, Fiz. Met. Metalloved. **81**, 170 (1996).

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