

ION-INDUCED FORMATION OF MICROPOLYCRYSTALLINE $Nb_{1-x}C_x$ ($0 \leq x < 0.3$) THICK COATINGS WITH QUASI-TERNARY PHASE STRUCTURE

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Структура и сверхпроводимость толстых поликристаллических ниобий-углеродных покрытий ($Nb_{1-x}C_x$, $0 \leq x < 0,3$), осажденных из низкоэнергетических самоионных-атомных Nb- и C- потоков на подложки в температурном интервале 500...650 К, были изучены рентгеноструктурным анализом (XRD), просвечивающей электронной микроскопией (ТЕМ), дифракцией электронов, просвечивающей микроскопией окисных реплик и методом измерений идеального сопротивления при низкой температуре. Было установлено, что $Nb_{1-x}C_x$ покрытия с концентрацией углерода в интервале 9...15 ат.% обладают необычно высокой температурой сверхпроводящего перехода $T_c \sim 12$ К. Зависимость критической плотности этих покрытий от температуры не является монотонной и обнаруживает крутой изгиб около $T_c \approx 9,5$ К. Структурный анализ этих покрытий показал, что они имеют квазитройной фазовый состав, состоящий из Nb (ОЦК), субкарбида Nb_2C (ГПУ) и метастабильного карбида NbC_x с ГЦК-структурой. Полученные результаты обсуждаются с точки зрения NbC_x -фазы, формирующейся на поверхности раздела Nb- и Nb_2C - фаз. Показано также, что $Nb_{1-x}C_x$ покрытия с концентрацией углерода ниже 5 ат.% обнаруживают перенасыщенный твердый раствор и имеют $T_c \approx 9,5$ К. Была также исследована кинетика диффузного разложения ниобий-углеродных покрытий в процессе изотермического отжига.

Структура та надпровідність товстих полікристалічних ніобій-вуглецевих покриттів ($Nb_{1-x}C_x$, $0 \leq x < 0,3$), осаджених із низкоенергетичних самоіонних-атомних Nb- и C- потоків на підкладки у температурному інтервалі 500...650 К були вивчені за допомогою рентгеноструктурного аналізу, просвічуючи електронної мікроскопії окисних реплік та методом вимірювання питомого опору при низькій температурі. Було встановлено, що $Nb_{1-x}C_x$ покриття з концентрацією вуглецю в інтервалі 9...15 ат.% мають надзвичайно високу температуру надпровідного переходу $T_c \approx 12$ К. Залежність критичної щільності цих покриттів від температури не є монотонною і виявляє крутий згін величин біля $T_c \approx 9,5$ К. Структурний аналіз цих покриттів показав, що вони мають квазіпотрійний фазовий склад, що складається із Nb(ОЦК), субкарбида Nb_2C (ГПУ) та метастабільного карбиду NbC_x з ГЦК-структурою. Отримані результати обговорюються з точки зору NbC_x -фази, яка утворюється на поверхні розподілу Nb та Nb_2C -фаз. Показано також, що $Nb_{1-x}C_x$ покриття з концентрацією вуглецю нижче 5 ат.% виявляють пересичений твердий розчин і мають $T_c \approx 9,5$ К. Була також досліджена кінетика фаз дифузного розкладу ніобій-вуглецевих покриттів у процесі ізотермічного відпалу.

Structure and superconductivity of thick polycrystalline niobium-carbon coatings ($Nb_{1-x}C_x$, $0 \leq x < 0.3$) deposited from low-energy self-ion-atomic Nb- and C- fluxes onto substrates with the temperature range 500...650 K were studied by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), electron diffraction, TEM of oxidic replicas and resistivity measurement method at low temperature. It is founded, that $Nb_{1-x}C_x$ coatings with carbon concentration range 9...15 at.% have an unusual high superconducting transition temperature $T_c \sim 12$ K. Dependency of critical current density of these coatings on temperature is not monotonous and have a sharp bend near $T_c \approx 9.5$ K. Structural analysis of these coatings has revealed they have a quasi-ternary phase composition consisting of Nb(b.c.c.), subcarbide Nb_2C (c.p.h.) and metastable carbide ' NbC_x ' with f.c.c. structure. The results obtained are discussed from a point of view of ' NbC_x ' phase forming at Nb and Nb_2C phases interface. It is also shown, that $Nb_{1-x}C_x$ coatings with carbon concentration less than 5 at.% revealed supersaturated solid solution and have $T_c \approx 9.5$ K. Kinetics of diffusive decomposition of niobium-carbon coatings during isothermal annealing was also investigated.

1. INTRODUCTION

Thick coatings and thin films of carbides and nitrides of transitional refractory metals have found wide applications in different industrial branches, since they possess both high protective properties and unique electrophysical characteristics which are stable in wide temperature region [1-5]. These coatings, as a rule, are synthesized in vacuum by simultaneous deposition of ion and atomic fluxes of metal and metalloid (carbon and/or nitrogen) onto substrates with temperature $T_s < 0.3T_m$, where T_m is the melting temperature of condensable material [6-12].

At present a great amount of investigations of the

influence of ion irradiation on the kinetics of coatings formation have been carried out with the purpose of optimization of operational characteristics of metal-metalloid coatings. It was established, that ion irradiation induces formation of polycrystalline coatings with nonequilibrium metastable structures (supersaturating solid solutions [13-16], new phases [17-21], polymorphic modifications [22-27] etc.), which are absent on equilibrium state diagrams.

Supersaturating solid solutions of metalloid atoms in metal matrix are the object of increased interest of many researchers. It was found, that these solid solutions can decay with the formation of precipitates of dispersion carbides (or nitrides) depending on

conditions of coatings syntheses. In turn, these precipitates can induce either polymorphous transformation of metal matrix [22,23,24] or formation of a new metastable metal-metalloid phases [10,16,19,26,28]. As a result of such structural transformations, micropolycrystalline heterophase coatings are formed. These coatings, as a rule, have anomalously high mechanical properties as well as electrophysical ones.

High values of superconducting transition temperature $T_C = 11.5 \dots 12.5$ K were discovered during investigation of superconductivity parameters of niobium-carbon coatings in carbon concentration range 6...20 at.% which were prepared by ion-atomic sputtering method [26,29]. Authors [29] suppose, that high T_C values can be connected with a high-stoichiometric phase of niobium carbide which forms in these coatings.

In the present work, we report a study carried out on microstructure, composition and superconductivity parameters of niobium-carbon ($Nb_{1-x}C_x$, $0 \leq x < 0.3$) coatings prepared by simultaneous deposition of self-ion-atomic Nb and C fluxes. X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), electron diffraction, electron microscopy of oxidic replicas and resistivity measurement method at low temperature were used in these investigations. The results thus obtained are discussed.

2. EXPERIMENTAL DETAILS

Niobium-carbon coatings (100...110 μm) were prepared onto copper substrates (30 mm \times 30 mm \times 2 mm) by condensation of self-ion-atomic fluxes of metal and carbon using an atom-ionic sputtering method [30,31]. A purity of used materials was better than 99.91 at.%. The substrates were polished mechanically to give a final mirror-like surface using 1 μm particle size alumina powder. Cleaning of substrates has been carried out by following a well-known procedure with a final rinse in alcohol. The substrates were located in multi-position heating holder, which allows to support and measure the substrates temperature during coatings deposition in the region from 500 to 650 K. The vacuum system was pumped down to 1.3×10^{-4} Pa. Ion energy of both metal and carbon was 250 eV and a ratio of ion-to-vapor fluxes was equal to 0.1 ± 0.01 . The deposition rate was (5.5 ± 0.3) nm/sec. The detailed description of coatings deposition can be found in [31,32].

Composition of deposited coatings was determined by means of nuclear reactions using electrostatic proton accelerator with energy beam 4.5 MeV [33]. Nuclear reactions $^{13}\text{C}(p,\gamma)^{14}\text{N}$, $^{12}\text{C}(p,\gamma)^{13}\text{N}$ and $^{13}\text{C}(\alpha,n)^{16}\text{O}$ were used for determination of carbon concentration. Nitrogen, oxygen and hydrogen concentrations were obtained with using nuclear reactions $^{15}\text{N}(p,\alpha,\gamma)^{12}\text{C}$, $^{18}\text{O}(\alpha,p,\gamma)^{21}\text{Ne}$ and $^1\text{H}(\alpha,\gamma)^{12}\text{C}$ respectively [34]. The measurement accuracy of concentrations of carbon, nitrogen, oxygen and hydrogen was better 1×10^{-2} at. %.

Investigations of crystal structure and phase composition of niobium-carbon coatings in initial state and after thermal annealing ($T = 1000$ K for $t = 0.3, 0.5$ and 1–5 hours) were carried out using DRON-3M X-ray

diffractometer (Cu K_{α} - radiation) and electron microscopes EVM-100L and JEM-100CX both operated at 100 kV. Lattice constants of both niobium and carbides phases of deposited $Nb_{1-x}C_x$ coatings were evaluated from the XRD patterns which have been obtained during examination of coatings in a free state ($Nb_{1-x}C_x$ coatings, detached from a substrate). The intrinsic oriented microstrains (ϵ) of niobium matrix in the direction parallel to the substrate surface were determined for samples in free state by well-known $\sin^2\psi$ method [35, 36]. Mechanical and chemical polishes of the coatings were performed to study of coatings structure into the depth. TEM of oxidic replicas [37] was used to determine size, morphology and volume fraction of carbide phase particles.

The superconductivity parameters measurements of samples were conducted by standard four-probe DC technique in a helium cryostat. Temperature dependencies of resistivity of $Nb_{1-x}C_x$ samples were obtained in the interval 4.2...300 K. Measurement accuracy of superconducting transition temperature T_C was better than 0.01K. Critical current density (J_C) was determined from the volt-ampere dependence at fixed temperature in the interval 7...15 K in zero magnetic field.

3. RESULTS AND DISCUSSION

Investigation results of superconducting transition temperature of niobium-carbon coatings are shown in Fig. 1. As may be seen in Figure 1 dependence of superconducting transition temperature has a nonmonotonous behavior as the C/Nb composition ratio increases. In the region $0 \leq C/Nb \leq 0.1$ temperature T_C depends weakly on carbon concentration and equals to (9.35 ± 0.15) K. Transitional width $\Delta T_C = (0.6 \pm 0.01)$ K in this concentration interval. T_C behavior has bell-shape with a maximum $T_C = 12.01$ K at $C/Nb \approx 0.14$ in the region $0.1 < C/Nb < 0.2$. In this concentration interval transitional width increases in 2 times and it is equal to (1.2 ± 0.11) K. When the composition ratio increases above $C/Nb > 0.16$ the values of both T_C and ΔT_C fall drastically to ~ 9.5 K and ~ 0.5 K respectively. The values of superconductivity parameters do not change in the region $0.2 \leq C/Nb < 0.3$. It may be noted that the results obtained are very near to values published in works [26, 29].

It is known that electrophysical properties of superconducting films unambiguously are determined by their structure [38-45]. Therefore, detail investigations of $Nb_{1-x}C_x$ coatings structure have been carried out for the interpretation of their superconducting parameters. The results of these investigations have discovered unusual behavior of both phase state and microstructure of the $Nb_{1-x}C_x$ coatings on carbon content. These results can be described as follows. Examinations of the niobium-carbon coatings in the region $0 \leq C/Nb < 0.05$ ($0 \leq C < 5$ at.%) by TEM and XRD revealed a polycrystalline single phase b.c.c. structure having (211) and (111) preferred orientations. Figure 2 depicts the electron micrographs of $Nb_{1-x}C_x$ coatings with various carbon concentration. No extra reflections in electron diffraction pat-

tern are observed, indicating that a carbide phase does not form under these conditions. The structure with no well-defined carbide precipitate often is named as 'mottled' structure [28]. As the carbon concentration increases the weight of crystallographic planes with preferred (111) orientation rises, an average size of blocks ($\langle D \rangle$) of grains decreases from (61 ± 3) nm to (42 ± 5) nm, microdeformation value of crystal lattice grows from 0.025% to 0.042%, and the lattice constant of Nb-matrix varies in the interval $a = (0.33002_{\pm 2} - 0.33005_{\pm 3})$ nm.

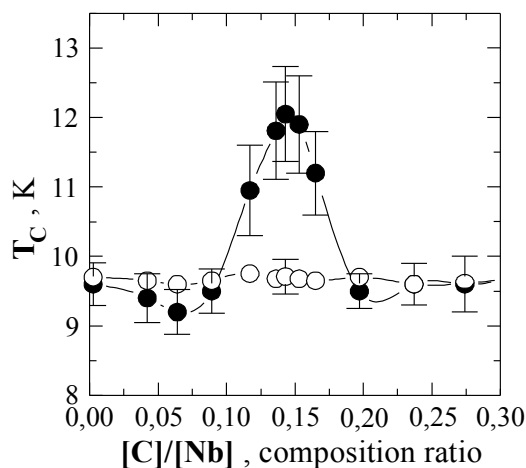


Fig. 1. Dependence of a superconducting transition temperature of niobium-carbon coatings prepared at $T_s = (550 \pm 10)$ K vs. composition ratio C/Nb. Vertical bars show a width of superconducting transition temperature ΔT_c . (●) - initial state of $Nb_{1-x}C_x$ coatings; (○) - state of $Nb_{1-x}C_x$ coatings after thermal annealing at $T = 1000$ K for $t = 2$ h

Elemental analysis showed the concentration of gases impurities are 0.1 at.% N, 0.08 at.% O and 0.51 at.% H in all coatings. The dependence of lattice constant on concentration of metalloid impurity (c_x in at.%) can be written as

$$a(\text{nm}) = 0.33000 \times (1 + k_x \times c_x),$$

where k_x is a constant for each impurity: $k_o = 0.0006_{\pm 2}$, $k_H = 0.00015_{\pm 2}$ [5,46], $k_N = 0.0008_{\pm 2}$ [5,46,47] and $k_C = 0.00044$ [48] – $0.0012_{\pm 2}$ [5,28,46,47].

Estimation of the lattice constant of Nb-matrix with account of given relation and concentrations of metalloid impurities allows to conclude that gases atoms can be partially in solid solution, and the highest possible carbon content in solid solution can not exceed 0.2 at.%. The latter does not contradict the experimental results of works [28,46,49]. Therefore, carbon excess can form very fine (≤ 1 nm) carbide precipitates (not detectable by TEM) in the host matrix as well as at the boundaries of blocks (grains). The latter case really takes place in coatings so far as the density of blocks boundaries increases in ~ 2 times with carbon concentration growth.

XRD examinations of the carbon-doped niobium coatings prepared in the composition ratio region $0.05 \leq C/Nb < 0.2$ ($5 \leq C < 17$ at. %) showed a heterophase mi-

cropolycrystalline structure which consists of Nb-matrix and Nb_2C precipitates. Fig. 3 shows a typical θ - 2θ scan for a niobium-carbon coating obtained at substrate temperature below 600 K. It is necessary to note, that a noticeable broadening of diffraction peaks of both phases as well as an increased background have been observed for $Nb_{1-x}C_x$ samples with carbon concentration 9...15 at.%.

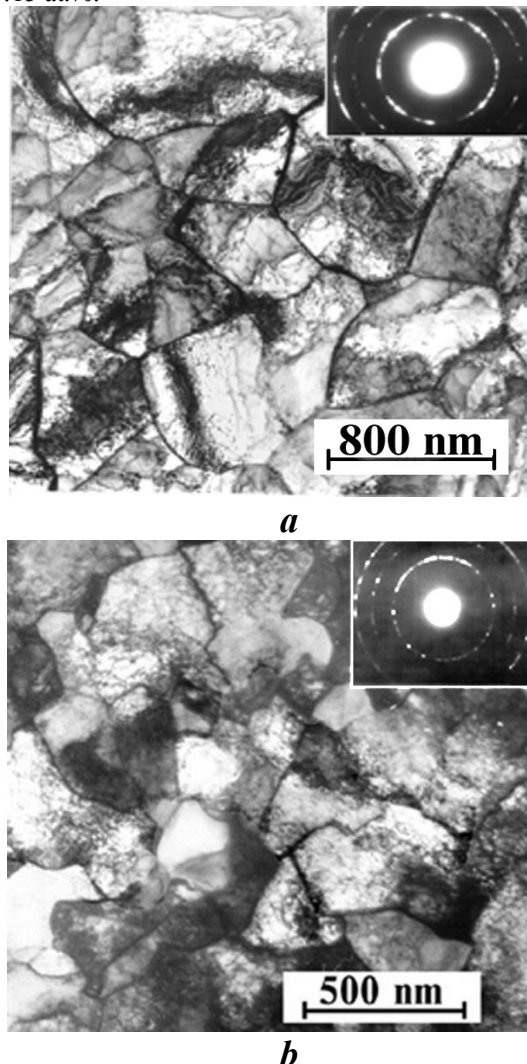


Fig. 2. A bright-field electron micrograph and corresponding electron diffraction pattern of $Nb_{1-x}C_x$ coatings deposited onto substrate with temperature (550 ± 10) K. a - 0.53 at.% C; b - 3.54 at.% C

The precipitates have a hexagonal W_2C -type structure with the lattice constants $a = 0.31262_{\pm 4}$ nm and $c = 0.4968_{\pm 2}$ nm which are very near to published values [1,2,49]. The lattice constant of Nb matrix does not change in this concentration region and equals to $a = 0.33005_{\pm 4}$ nm. Crystallographic planes (110) and (111) are preferred orientation planes for Nb_2C and Nb phases respectively. Microdeformation value of Nb-matrix rises from 0.05% to 0.3% as the carbon concentration rises up to ~ 12 at.%. Further increase of carbon concentration leads to decrease of ε -value down to $\sim 0.06\%$. Average size of blocks of Nb grains is $\langle D \rangle = (40 \pm 5)$ nm and depends weakly on carbon contents in coatings.

However, $\langle D \rangle$ for the Nb_2C precipitates depends on carbon concentration as follows: (36 ± 3) , (17 ± 3) and (32 ± 3) nm for ranges $5 \leq C < 9$ at. %, $9 \leq C \leq 15$ at. % and $15 < C < 17$ at. % consequently. Layerwise analysis of structure of $\text{Nb}_{1-x}\text{C}_x$ coatings using oxidic replicas method and electron diffraction has allowed to detail and supplement XRD analysis data. The results of these investigations have confirmed the formation of two polycrystalline Nb and Nb_2C phases in the region $5 \leq C < 9$ at.% (see Fig. 4).

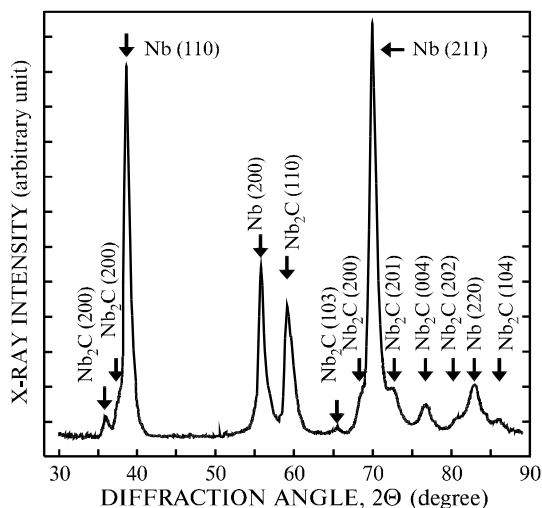


Fig. 3. XRD pattern from a $\text{Nb}_{1-x}\text{C}_x$ (7.5 at.% C) coating deposited onto substrate with temperature (550 ± 10) K. The major X-ray diffraction peaks are indexed to the Nb and Nb_2C phases

Furthermore, it was established that for this concentration region a volume fraction of Nb_2C phase increases from ~ 0.18 up to 0.23 with rising of the carbon concentration. TEM of oxidic replicas of $\text{Nb}_{1-x}\text{C}_x$ ($9 \leq C \leq 15$ at. %) coatings has revealed the extended areas of a new phase around Nb_2C precipitates in Nb-matrix such as that depicted in Fig. 5. The micrograph shows that area width of the new phase increases as the size of Nb_2C precipitates decreases. Electron diffraction examinations of this phase showed f.c.c. NaCl-type structure with the lattice constant 0.445 nm. Moreover, in this concentration region great deviation ($\sim 40\%$) of volume fraction of the Nb_2C phase from an equilibrium value was found. The similar deviations were also revealed in [29]. It may be noted that the formation of such structure occurs in the region of an eutectic composition $C = (12 \pm 2)$ at.% [1,2,5,49].

The structure of $\text{Nb}_{1-x}\text{C}_x$ ($17 \leq C < 23$ at.%) coatings is qualitatively similar to niobium-carbon coatings with the concentration $C = 5 \dots 9$ at.%. Volume fraction of Nb_2C phase in these coatings is close to a thermodynamic equilibrium value at carbon contents more than 18 at.%.

Let's discuss obtained results. It is known, that superconducting transition temperature of Nb_2C phase is ~ 9.1 K [4,44,45], and T_C of niobium changes from ~ 5 to ~ 9.7 K and depends on purity of niobium matrix [4,38-41]. As shown in [4,42,43], increasing of dispersity of niobi-

um matrix leads to increase T_C on $0.3 \dots 0.5$ K, and formation of high-dispersion metal-metalloid precipitates in Nb-matrix

induces the increasing of ΔT_C and J_C . Then, on the basis of these data and obtained experimental results it is possible to conclude that $T_C \sim 9.5$ K for $\text{Nb}_{1-x}\text{C}_x$ coatings in concentration regions $C/\text{Nb} < 0.05$ and $C/\text{Nb} > 0.16$ corresponds to the superconducting transition temperature of niobium matrix. High value $\Delta T_C \sim 0.5$ K can be stipulated by strain of a matrix lattice as a result of nucleating of Nb_2C phase for $C/\text{Nb} < 0.05$ region and as a result of the increasing of volume fraction of the subcarbide precipitates for $C/\text{Nb} > 0.16$ region.

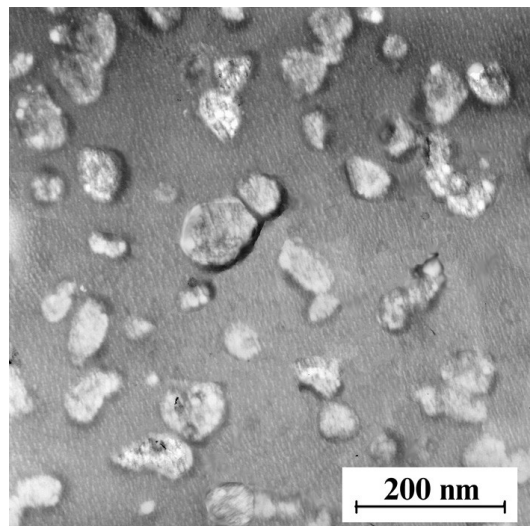


Fig. 4. A bright-field electron micrograph of oxidic replica from a $\text{Nb}_{1-x}\text{C}_x$ (7.2 at.% C) coating deposited onto substrate with temperature (550 ± 10) K. Bright formations are attributed to Nb_2C precipitates and gray field is a niobium matrix

In the region $0.11 \leq C/\text{Nb} \leq 0.175$ ($9 \leq C \leq 15$ at.%), as it is shown above, considerable growth of T_C and ΔT_C values are observed. High-dispersion precipitates with f.c.c. structure ($a = 0.445$ nm) were detected in the same region. It is known [1,2,49], there is only carbide NbC_x ($0.72 \leq x \leq 1$) with f.c.c. structure in Nb-C system. For this phase superconducting temperature and lattice constant increases ($T_C = 0.32 \dots 14$ K and $a = (0.4430 \dots 0.44707)$ nm) as carbon concentration grows from ~ 42 to 50 at.% [1-4,44, 45, 49,50]. Then, obtained experimental results allow to conclude, that founded high-dispersion f.c.c. phase is a nonequilibrium ' NbC_x ' phase. The formation of this phase can explain decreasing of volume fraction of Nb_2C precipitates, on the one hand, and increasing of microdeformation of Nb-matrix, on the other hand. It is necessary to note, the formation of metastable ' NbC_x ' phase was founded by authors [51] in 'low-carbon' alloy obtained by high-velocity quenching and this phase was indexed as tetragonal distortion of the cubic NbC_x structure. Moreover, the formation of nonequilibrium phase with f.c.c. structure at the interface of Nb-matrix and Nb_2C precipitates is like the polymorphous transformation of host matrix Nb(b.c.c.) \rightarrow Nb(f.c.c.) which can be induced by high-dispersion

metal-metalloid precipitates [22,24].

However, this process takes place when metal-metalloid precipitates have a f.c.c. structure [22]. In our case, the Nb₂C precipitates, as shown above, have a hexagonal structure. Moreover, as shown in [22], the system consisting of three phases Nb(b.c.c.) + Nb(f.c.c.) + Nb₂C(c.p.h.) cannot be realized because its free volume energy is higher than the energy of Nb(f.c.c.) + NbC(f.c.c.) system.

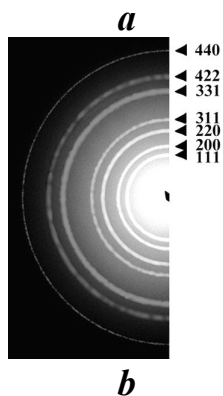
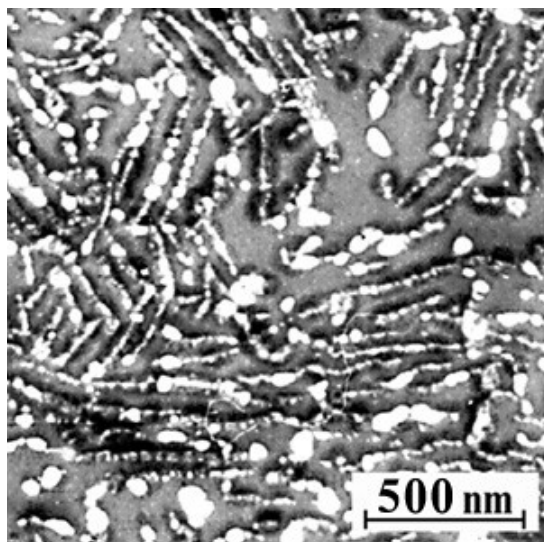


Fig. 5 A bright-field electron micrograph of an oxidic replica from a Nb_{1-x}C_x (11.2 at.% C) deposited onto substrate with temperature (550±10) K. Bright formations are attributed to precipitates of a Nb₂C phase, gray field is a Nb-matrix and dark fields around precipitates correspond to a nonequilibrium phase(a).

Electron diffraction pattern of a nonequilibrium phase with the f.c.c. NaCl-type structure (b)

The measurements data of critical current density as well as the investigations results of both microstructures and superconducting temperature of Nb_{1-x}C_x samples after high-temperature annealing are additional arguments confirming 'NbC_x' phase presence in coatings with concentration (9...15) at.% C. Temperature dependencies of critical current density of Nb_{1-x}C_x coatings are presented in Fig. 6. As may be seen in Fig. 6, for niobium-carbon coating with 'NbC_x' phase there is a 'stair' on J_c(T) dependence which is allocated near superconducting temperature of niobium matrix. Such effect takes place in heterophase systems which have superconduct-

ing phases with different values T_c and J_c [3,4].

Isothermal annealing of Nb_{1-x}C_x coatings leads to change of their structural state and superconducting parameters. For example, aging of coatings with 1...5 at.% C at T= 1000 K for t= 0.3 h induces the decay of solid solution and the formation of very fine (~2 nm) precipitates visible through structure factor contrast. The precipitates grow up to ~4 and ~15 nm for the annealing time 0.5 and 2 h respectively. At the same time thermal annealing of samples with C = 9...15 at.% causes dissolution of 'NbC_x' phase, growth of Nb₂C precipitates (<D> = 45 nm for t = 1 h, <D> = 63 nm for t = 5 h) and increasing of their volume fraction. 'NbC_x' phase is disappearing completely after annealing for t = 1 h (see Fig. 7).

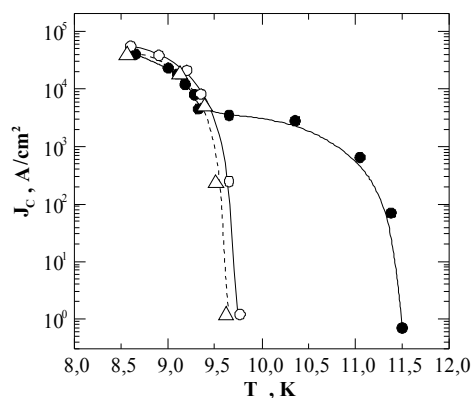


Fig. 6. Dependencies of a critical current density of the Nb_{1-x}C_x coatings on temperature. (□) - Nb_{1-x}C_x coating with 11.2 at.% C at the initial state; (Δ) - Nb_{1-x}C_x coating with 11.2 at.% C after thermal annealing at T = 1000 K for t = 1 h and (○) - Nb coating with the residual carbon content 0.2 at.%

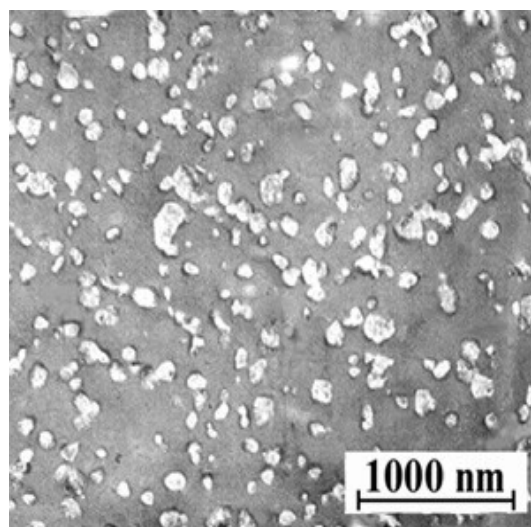


Fig. 7. A bright-field electron micrograph of an oxidic replica from a Nb_{1-x}C_x (11.2 at.% C) coating which has been annealed at T = 1000 K for t = 1 h. Bright formations are attributed to precipitates of a Nb₂C phase and gray field is a Nb-matrix

As a result the superconducting temperature of coatings is falling down to ~9.5 K (see Fig. 1) and the

'stair' on $J_c(T)$ dependence is disappearing (see Fig. 6). The detailed description of kinetics of diffusive decomposition of $Nb_{1-x}C_x$ (9...15 at.% C) coatings will be presented in the next report.

4. CONCLUSION

Results of this investigation can be summarized as follows:

1. High-rate condensation of self-ion-atomic fluxes of niobium and carbon onto substrates with $T_s = (500...650)$ K forms polycrystalline single phase coatings with b.c.c. structure when carbon concentration does not exceed 5 at.%. Isothermal annealing of samples at $T = 1000$ K for $t < 1$ h does not lead to formation of a well-defined carbide phase.

2. The heterophase polycrystalline structure consisting of Nb (b.c.c.) matrix and Nb_2C (c.p.h.) precipitates is formed in the intervals 5...8 at.% C and 16...23 at.% C. Volume fraction of Nb_2C phase in these concentration regions is close to a thermodynamic equilibrium value.

3. The structure of $Nb_{1-x}C_x$ ($9 \leq C \leq 15$ at.%) coatings represents a quasi-ternary micropolycrystalline composition consisting of Nb(b.c.c.), Nb_2C (c.p.h.) and ' NbC_x '(f.c.c.) phases. Metastable ' NbC_x ' phase is formed at Nb and Nb_2C phases interface.

4. Formation of ' NbC_x ' phase leads to increasing of superconducting transition temperature of niobium-carbon coatings up to ~12 K and explains considerable decreased (~40%) of Nb_2C volume fraction in comparison with a thermodynamic equilibrium value. Thermal annealing of these coatings at $T = 1250$ K for $t \geq 1$ h causes dissolution of ' NbC_x ' phase and growth of both the volume fraction and the precipitates size of Nb_2C phase.

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