

# Structure and Phase Composition of Niobium–Copper Deposited Films

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**Abstract**—Solid solutions of Nb + 9 at % of Cu and Cu + 12 at % of Nb are obtained by ion-plasma sputtering and the codeposition of ultrafine particles of niobium (less than 11 nm) and copper (less than 1.7 nm), which is confirmation of the theory of the thermal-fluctuation melting of small particles and the coalescence of quasi-liquid clusters of subcritical size. The film coating consists of an amorphous phase in the concentration range 22.7–80.2 at % of Cu. Upon the annealing of amorphous systems of all compositions at 600–850°C, a new phase, presumably, of an orthorhombic system is found and its approximate lattice parameters are determined. At specific dimensional ratios of ultrafine particles of niobium and copper, nanoclusters with an ordered superlattice are formed. The appearance of a superstructure is a result of the size factor.

**Keywords:** niobium–copper solid solutions, phase composition, nanocluster superlattice

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## INTRODUCTION

Information concerning the phase diagram of the niobium–copper system is contradictory [1]. Peritectic equilibrium and segregation in the concentration range 5–33 at % of niobium are found in this system [2, 3]. Other authors have revealed eutectic equilibrium and a shallow liquidus line in this system [4, 5]. We used the phase diagram [2], according to which the solubility of niobium in copper in the liquid state at a temperature of 1050°C does not exceed 0.14 at % [2], and the solubility of copper in niobium is 0.9 at %. The field of solid solutions based on niobium at this same temperature is degenerate. The maximum solubility of niobium in copper in the solid state is 0.28 at %, and the field of copper solid solutions becomes degenerate at ~800°C. At room temperature, the components of the system are virtually insoluble.

It is known that the formation of materials by the deposition of flows of ultrafine particles gives the means to obtain alloys of metals that are immiscible in the case of conventional melting, which is accompanied, as a rule, by an increase in the concentration of the solid-solution fields [6–8]. This can be explained from the standpoint of the theory of the thermal-fluctuation melting of small particles [9, 10], in which a small particle is in a quasi-liquid state and is capable of coalescence with another particle of similar size.

A change in the melting point of the films with decreasing thickness is similar to that of small particles [11] because their formation occurs by the island growth mechanism. In the case of this mechanism of film formation on a substrate, growth in the size of

particles is determined by the coalescence of islands. That is, the coalescence of small islands of different metals in the liquid state occurs until the island has reached the critical size, which causes its crystallization. This process can be used in the preparation of coatings of alloys consisting of metals with different physical properties.

The goal of the present work is to determine the possibility of forming alloys of the niobium–copper system, taking into account the size factor and the concentration limits of the existence of solid solutions and other phases and to determine the structure of the resulting film coating materials.

## EXPERIMENTAL

In the experiments, we used niobium (99.96 wt %) and copper (99.99 wt %) 40 mm in diameter and 4 mm in thickness as targets. Argon, purified with a getter (atomized titanium), was used in the magnetron-sputtering system as the plasma gas.

The procedure for obtaining the coating samples involved the ion-plasma sputtering of niobium and copper and their codeposition in the form of sublayers less than 1 nm in thickness up to some total film thickness to the substrate moving relative to the plasma flows. The speed was  $5 \times 10^{-2} \text{ m s}^{-1}$ . Deposition was carried out simultaneously with two oppositely positioned magnetrons, the space between which was split by a device for moving the substrates made of polycrystalline  $\alpha\text{-Al}_2\text{O}_3$ . The substrate temperature did not exceed 200°C.

**Table 1.** Composition of coatings, thickness of individual layers, and structure of coatings

Concentration of copper, at %	Concentration of niobium, at %	Thickness of Nb layer, nm	Thickness of Cu layer, nm	Lattice parameter $a$ , nm (BCC, solid solution of Cu in Nb)	Lattice parameter $a$ , nm (FCC, solid solution of Nb in Cu)
9.0	91.0	1.0	0.1	$0.3314 \pm 0.0003$	—
22.7	77.3	1.0	0.2	Amorphous phase	
29.7	70.3	1.0	0.3	Amorphous phase	
40.9	59.1	1.0	0.5	Amorphous phase	
52.6	47.4	1.0	0.7	Amorphous phase	
73.5	26.5	0.5	1.0	Amorphous phase	
80.2	19.8	0.4	1.2	Amorphous phase	
88.2	11.8	0.3	1.2	—	$0.3637 \pm 0.0012$
95.0	5.0	0.1	1.5	—	$0.3619 \pm 0.0004$

In studying the effect of the size factor, the thickness of alternating layers of niobium and copper was varied. The procedure of the study included a gradual decrease in the thickness of the layers of niobium and copper after each time the metal-plasma flow intersected with the moving substrate. The thickness of the layers was varied by alternately switching on the magnetrons, wherein the substrate was coated by layers of a certain thickness, increasing or decreasing it for each of the metals, transitioning eventually to deposition from simultaneously spraying nozzles.

The coating composition was controlled by varying the ratio of the powers supplied to the magnetrons sputtering niobium and copper. The ratio of the deposited metals was monitored gravimetrically by the amounts of each of the metals sputtered and deposited. The film thickness was determined by Rutherford proton backscattering using a UKP-2-1 tandem accelerator and calculated from the amount of deposited metals. Isochronal annealing was performed in a vacuum oven, created on the basis of a URVT-2500 installation with oil-free pumping using an NMD-0.4-1 diode magnetic-discharge pump. Before annealing, the oven was evacuated to a pressure of  $3 \times 10^{-4}$  Pa.

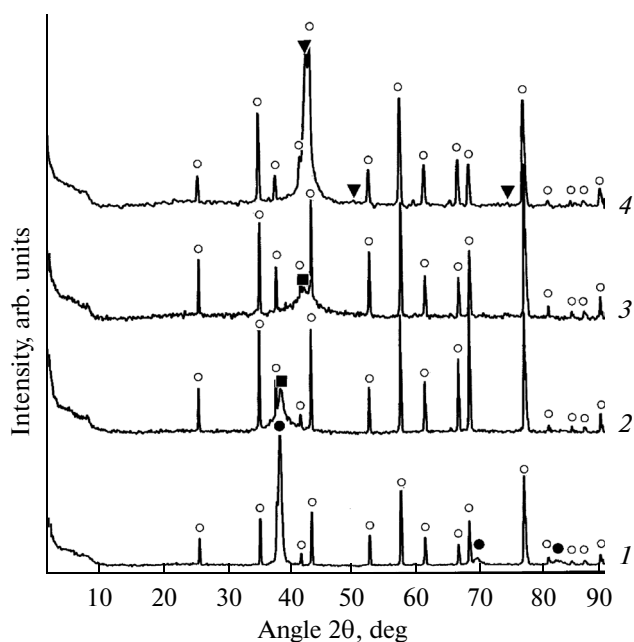
X-ray diffraction studies were carried out according to the procedure in [12] using a Bruker D8 Advance diffractometer (Bruker) equipped with a copper anode,  $\lambda_{K\alpha} = 0.154051$  nm, and a graphite monochromator. The value of the lattice parameters was calculated as an average using all of the diffraction lines of the phase under study. To detect superstructures, small-angle X-ray diffraction analysis ( $2\theta$  less than  $5^\circ$ ) was used.

## RESULTS AND DISCUSSION

It was found in preliminary studies that at a thickness of the sublayers deposited of less than 10.9 nm for

niobium and 1.7 nm for copper, the metals in the coating are not observed in the form of individual phases, which indicates the formation of a solid solution. To study the effect of the concentration of components on the structure of the film system, coatings were prepared, the composition of which, as well as the thickness of the individual layers and the lattice parameter are shown in Table 1.

Diffraction patterns of the samples, the compositions of which correspond to a change in the coating structure, are shown in Fig. 1. X-ray diffraction studies of the obtained samples show that in the initial state,



**Fig. 1.** Diffraction patterns of the Nb–Cu film coatings containing (1) 9.0, (2) 22.7, (3) 80.2, and (4) 88.2 at % of Cu: (●) solid solution of Cu in Nb, (▼) solid solution of Nb in Cu, (■) amorphous structure, and (○) polycore.

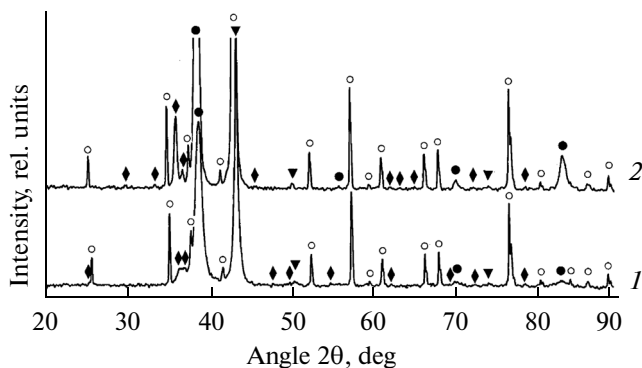
**Table 2.** Lattice parameters of solid solutions after annealing at 600°C

Concentration of copper, at %	Concentration of niobium, at %	Lattice parameter $a$ , nm (BCC, solid solution of Cu in Nb)	Lattice parameter $a$ , nm (FCC, solid solution of Nb in Cu)	X phase, number of reflections
9.0	91.0	$0.3286 \pm 0.0006$	—	—
22.7	77.3	$0.3277 \pm 0.0002$	—	3
29.7	70.3	$0.3285 \pm 0.0003$	$0.3620 \pm 0.0009$	4
40.9	59.1	$0.3278 \pm 0.0004$	$0.3610 \pm 0.0002$	3
52.6	47.4	$0.3275 \pm 0.0050$	$0.3610 \pm 0.0003$	3
73.5	26.5	$0.3280 \pm 0.0006$	$0.3607 \pm 0.0009$	3
80.2	19.8	$0.3278 \pm 0.0080$	$0.3617 \pm 0.0009$	5
88.2	11.8	0.3286 (trace amount)	0.3606	—
95.0	5.0	—	$0.3614 \pm 0.0004$	—

**Table 3.** Lattice parameters of solid solutions after annealing at 850°C

Concentration of copper, at %	Concentration of niobium, at %	Lattice parameter $a$ , nm (BCC, solid solution of Cu in Nb)	Lattice parameter $a$ , nm (FCC, solid solution of Nb in Cu)	X phase, number of reflections
9.0	91.0	$0.3287 \pm 0.0001$	$0.3628 \pm 0.0003$	4
22.7	77.3	$0.3285 \pm 0.0003$	$0.3624 \pm 0.0001$	3
29.7	70.3	$0.3281 \pm 0.0001$	$0.3611 \pm 0.0002$	4
40.9	59.1	$0.3278 \pm 0.0001$	$0.3614 \pm 0.0001$	3
52.6	47.4	$0.3274 \pm 0.0002$	$0.3615 \pm 0.0004$	2
73.5	26.5	$0.3271 \pm 0.0002$	$0.3606 \pm 0.0002$	5
80.2	19.8	$0.3265 \pm 0.0002$	$0.3608 \pm 0.0001$	5

the coatings are solid solutions with a concentration of copper in niobium of up to 9 at % and a concentration of niobium in copper of up to 12 at %. Coatings containing from 22.7 to 80.2 at % of copper have an amorphous structure. The preparation of solid solutions of this concentration is confirmation of the formation of alloys as a result of the thermal-fluctuation melting of ultrafine particles.



**Fig. 2.** Diffraction patterns of the film coating with 52.6 at % of Cu after annealing at (1) 600°C and (2) 850°C: (●) the solid solution of Cu in Nb, (▼) the solid solution of Nb in Cu, (◆) X phase, and (○) polycore.

To examine the thermal stability of the phases in the film, the coatings were isochronically annealed at temperatures of 600°C and 850°C for 1 h. At 600°C, the amorphous phase decomposes into a mixture of a solid solution of copper in niobium and a solid solution of niobium in copper, the lattice parameters of which are presented in Table 2. It should be noted that the lattice parameters of the solid solutions based on niobium ( $a_{av} = 0.3281$  nm) and copper ( $a_{av} = 0.3612$  nm) are rather constant within measurement error. In the X-ray diffraction patterns of the samples with a copper concentration of 22.7 to 80.2 at %, reflections of an unknown phase, denoted as the X phase, were detected alongside the Bragg reflections of the phases of a solid solution of copper in niobium and a solid solution of niobium in copper.

With increasing annealing temperature to 850°C, similar results were obtained. In this case, the lattice parameters of the solid solutions (Table 3) remained practically constant (for Nb and Cu,  $a_{av}$  was 0.3277 and 0.3615 nm, respectively), but the presence of the X phase was found even in the sample with an initial concentration of copper of 9.0 at %. The diffraction patterns of the sample with a copper concentration of 52.6 at % after annealing at (1) 600°C and (2) 850°C for 1 h are presented in Fig. 2. It follows from analysis

of the diffraction pattern of the sample annealed at 600°C that the *X* phase is poorly crystallized, and the reflections from this phase overlap each other. Angles  $2\theta$  for the reflections of the unknown phase and the corresponding interplanar distances observed in the sample with 73.5 at % of Cu after annealing at 850°C are given in Table 4.

With the use of the RTP program, the crystal structure that best fit with the observed set of reflections was determined. The unknown phase belongs, most likely, to the orthorhombic system, and at a dispersion of  $2\theta = 0.038$ , the lattice parameters have the following values:  $a = 0.7720$  nm,  $b = 0.7361$  nm, and  $c = 0.6690$  nm. Since these reflections sit alongside the more intense reflections of niobium and copper, as well as the substrate, no reliable data on the relative intensity of the reflections of the unknown phase can be obtained from the available X-ray diffraction patterns. It follows from the analysis of the set of X-ray diffraction patterns recorded for the samples annealed at 850°C that with increasing concentration of copper in the coating, the formation conditions of an unknown phase are improved. In accordance with this, it was suggested that its composition might correspond to NbCu or Nb<sub>2</sub>Cu<sub>3</sub>. More research is required to determine the exact stoichiometry of the detected compound.

In the case of the preparation of coatings by the codeposition of sputtered ultrafine metal particles with decreasing particle size, there is always a state of the system when there are neither separate metal phases nor a solid solution. Ordered ensembles of nanoclusters often form in such systems, yielding superstructure reflections. To study the effect of such an intermediate state of the system on the film structure, we prepared coatings consisting of alternating layers of niobium and copper with increasing thickness of Cu layers on a substrate of monocrystalline silicon (Table 4).

It was found in X-ray studies that the coating containing 18.7 at % of Cu is represented by a solid solution of copper in niobium with a parameter of the body-centered cubic (BCC) lattice of the solid solution of  $a = 0.3294 \pm 0.0002$  nm. Poorly defined cubic superstructure with a lattice parameter of  $a = 6.0079 \pm 0.1396$  nm was observed upon recording at small angles (Fig. 3, curve 1). The low intensity of the superlattice peaks indicates, apparently, the lack of clear boundaries between the niobium and copper nanoclusters.

The panoramic diffraction pattern of the sample with a copper concentration of 46.7 at % recorded in the angular range of  $2\theta = 2^\circ$ – $100^\circ$  showed the presence of a strongly amorphized phase based on niobium with a lattice parameter of  $a = 0.3286$  nm and a strongly amorphized phase based on copper with a lattice parameter of  $a = 0.3640$  nm. The grain size was estimated by the Debye–Scherrer method; the resulting value was less than 10 nm. In the diffraction pat-

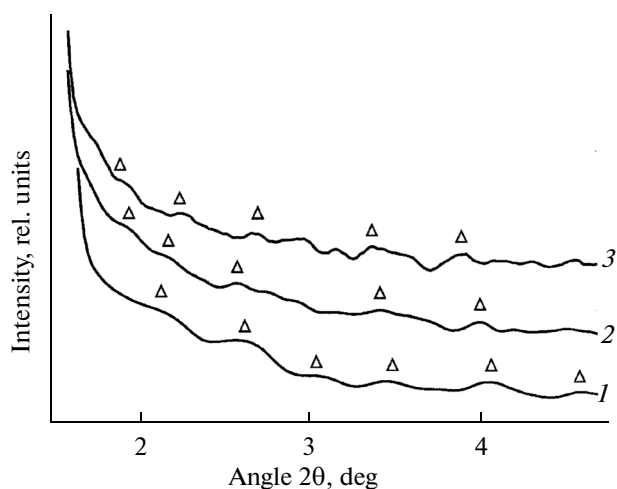


Fig. 3. Diffraction patterns of the coatings containing (1) 18.7, (2) 46.7, and (3) 67.5 at % of Cu; ( $\Delta$ ), superstructure reflections.

tern recorded in the grazing-incidence small-angle mode, poorly defined reflections of a superstructure formed by nanoclusters of niobium and copper were observed (Fig. 3, curve 2). Calculations performed with the program Index show that the given set of reflections corresponds to a tetragonal lattice formed of copper nanoclusters within the niobium matrix with the parameters  $a = 4.6319$  nm and  $c = 5.1209$  nm. The

X-ray diffraction analysis of a niobium–copper sample with 67.5 at % of Cu proves that the coating consists of fine crystalline phases of niobium and copper with the parameters  $a_{\text{Nb}} = 0.3324 \pm 0.0003$  nm and  $a_{\text{Cu}} = 0.3615$  nm, and the grain size of niobium and copper is 40 and approximately 20 nm, respectively. In the diffraction pattern of the sample recorded in the grazing-incidence small-angle mode, a tetragonal superstructure with the parameters  $a = 4.7037$  nm and  $c = 5.2910$  nm was detected (Fig. 3, curve 3). The superstructure in this coating is represented by poorly defined reflections; a peak corresponding to  $d_{hkl} =$

Table 4. Angle  $2\theta$  for reflections of the unknown phase and the corresponding interplanar distances

Angle $2\theta$ , deg	$d_{hkl}$ , nm	Miller indices ( <i>hkl</i> )
21.36	0.4156	111
26.62	0.3346	002
29.11	0.3065	102
29.98	0.2978	121
31.52	0.2836	112
33.61	0.2664	220
36.30	0.2473	221
37.02	0.2426	310
38.47	0.2338	130
44.35	0.2041	302
44.92	0.2015	321

**Table 5.** Thickness of alternating sublayers and composition of the niobium–copper coatings

No.	Thickness of alternating sublayers, nm		Coating composition, at %	
	niobium	copper	niobium	copper
1	7.5	1.2	81.3	18.7
2	5.1	2.9	53.3	46.7
3	4.0	5.5	32.5	67.5
4	2.6	4.7	26.5	73.5
5	1.3	2.5	25.3	74.7

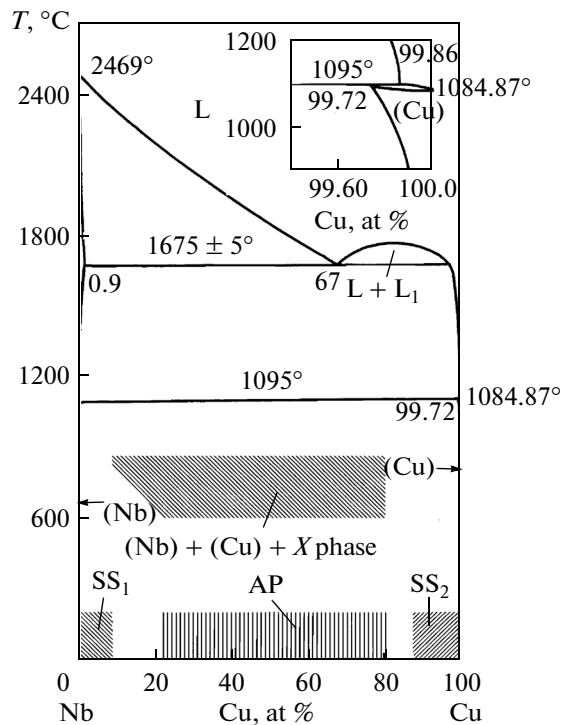
5.1185 nm is distinguished among them. This value correlates with the thickness of the copper layers, and, therefore, we may consider that in this coating, the niobium nanoclusters are arranged in layers in the copper matrix.

The X-ray diffraction analysis of the sample with a copper content of 74.7 at % (Table 4) shows that the coating is completely amorphized, but in the small-angle region, superstructure peaks are visible, corresponding to a cubic superlattice with the parameter  $a = 3.1050 \pm 0.0108$  nm. This value matches the thickness of one copper layer plus a niobium half layer. This implies that under these conditions, the coating con-

sists of niobium nanoclusters, regularly arranged in a matrix of copper and similar to each other in shape and size, and that in this case, the self-organization of nanostructures occurs during ion-plasma deposition of the coating.

The niobium–copper phases found in the film system in the concentration and temperature ranges of this study were applied to the equilibrium phase diagram of Nb–Cu [1] for visual reference (see Fig. 4); although, it is obvious that these phases are nonequilibrium.

The presence of the fields of solid solutions with high concentration of copper in niobium and niobium in copper and an amorphous phase and the appearance of the unknown phase at a high temperature indicate a fundamental difference between the structure of the materials obtained by melting and formed by metal nanoparticles.



**Fig. 4.** Phase diagram of the niobium–copper system: SS<sub>1</sub>, solid solution of a high concentration of copper in niobium; SS<sub>2</sub>, solid solution of niobium in copper; and AP, amorphous phase.

## CONCLUSIONS

It is found in the study that upon the layer-by-layer deposition of coatings with a thickness of layers of niobium and copper of less than ~11 and 1.7 nm, respectively, mutual dissolution of the components occurs with the formation of a solid solution of one metal in another.

The codeposition of plasma-sputtered ultrafine particles of niobium and copper yields solid solutions of copper in niobium to a concentration of 9.0 at % of Cu and of niobium in copper to 12 at % of Nb. The formation of solid solutions of high concentrations directly during the process of codeposition is confirmation of the theory of the thermal-fluctuation melting of small particles and the coalescence of quasi-liquid particles of subcritical size. In the concentration range of 22–80 at % of Cu, the system is X-ray amorphous.

Upon the annealing of amorphous samples of all compositions at 600–850°C, a new phase, presumably, of an orthorhombic system is found and its approximate lattice parameters are determined. The range of characteristic sizes of metal particles (thickness of

sublayers) is determined, in which the dispersion structures no longer form solid solutions of a high concentration due to thermal-fluctuation melting, but also do not fall into the two coexisting phases of the individual metals. In this range of particle sizes (thicknesses of individual sputtered layers), ordered distributions of nanoclusters of one metal in the matrix (crystalline or amorphous) of the other metal appear. It was also found that the cause of the formation of superstructures is the size factor.

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