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Thermal degradation of hard alloys of the niobium-cadmium system at low pressure

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Abstract. Due to the lack of data on the double film Nb-Cd system thermal stability, the effect of thermo-vacuum treatment of cadmium solid solutions in niobium, in intermetallic compound $NbCd_2$ and in cadmium-based alloys on the structure of materials was studied. A step-by-step isochronous annealing at a temperature of 300 and 500°C and a pressure of $1 \cdot 10^{-3}$ Pa was used as the research method followed by tracking changes in the composition and structure by comparing the diffractometric data before and after heat treatment. The amount of cadmium in the coating, the sublimation (evaporation) rate of cadmium from film coatings was determined based on the previously established dependence of the lattice parameter of the body-centered cubic lattice of solid solutions on the composition. As a result, the heating of film coatings (49.0 - 64.5 at % Cd) represented by solid solutions in high vacuum up to 300°C was founded to be accompanied by the onset of intense degradation of the crystalline niobium-cadmium system due to the diffusion of cadmium atoms to the solid phase-vapor interface and its subsequent sublimation. Coatings from the $NbCd_2$ intermetallic compound which is a degenerate semiconductor and cadmium-based solid solutions (72.5 and 76.8 at % Cd) including the amorphized phase of the intermetallic compound, after exposure at this temperature are degraded due to the complete transfer of cadmium to the vapor phase by evaporation. Upon thermal exposure to a temperature of 200°C, the structure of solid solutions of cadmium in niobium and the $NbCd_2$ intermetallic compound was stable.

Keywords: niobium, cadmium, solid solution, intermetallic compound, diffractometry, sublimation.

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Introduction

The nanotechnology development has sparked a surge of interest in materials science, including knowledge about the effect of ultrafine formations on the properties of materials. Roduner E. [1, 2], when considering the thermodynamics of small systems, noted several key points, in particular: for sufficiently small systems, ideas about the phase state and phase transitions lose their meaning; for very small and isolated systems, fluctuations begin to play a huge role; in such systems, a reasonable definition of the concept of temperature becomes impossible; the melting and boiling points of liquid nanoscale droplets of a substance always fall below the corresponding values in the bulk phase of the same material, etc. The use of the dimensional factor involves obtaining new materials with unusual properties.

In this regard, to date, a very significant amount of work has been done on the effect of particle size on the melting temperature [3-13], the thermodynamics of small formations [13-17], material structure, process design, etc. Such studies entailed the production of new materials with unusual properties, including those applied to the considered niobium-cadmium system [18].

However, studies on the thermal stability of such systems are sporadic [19], and similar information on the binary Nb-Cd system is absent.

Taking into account the foregoing, the aim of this research was to study the thermal stability of solid solutions and the intermetallic $NbCd_2$ compound discovered, at low pressure.

Research object and technique

Film coatings with a cadmium content of 49.0; 64.5; 68.0; 72.5 and 76.8 at. % (53.76; 68.74; 72.0; 76.13 and 80.02 wt. %, respectively) were used as the object of study; the rest was niobium. Samples were obtained by layer-by-layer (with a small number of crystal lattice periods) coprecipitation of sputtered metals on a substrate moving relative to low-pressure plasma flows. Composition with 68.0 at. % cadmium corresponded to the $NbCd_2$ compound. Coatings are applied to substrates made of polycor-polycrystalline α-Al_2O_3 of 6×12 mm in size. The coating thickness ranged from 1.5 to 1.8 μm. The film thickness was determined by the method of Rutherford backscattering of protons at the UKP-2-1 tandem accelerator (Institute of Nuclear Physics) and by calculation based on the amount of deposited metals and their density.

An isochronous (1 hour) step-by-step annealing at a temperature of 300 and 500°C and a pressure of 1·10-3 Pa was chosen as a research method. The sample was subjected to primary annealing at 300°C, then secondary treated at 500°C. Annealing was carried out on a high-temperature vacuum furnace manufactured on the basis of the URVT-2500 plant. The change in composition and structure was monitored by comparing diffractometric data before and after heat treatment.

X-ray diffraction studies of the niobium system with cadmium were carried out on a D8 Advance diffractometer (Bruker) with copper radiation $\lambda_{K\alpha}$ = 0.154051 nm and graphite monochromators. The value of the lattice parameter was calculated as the average, using all diffraction lines from this phase.

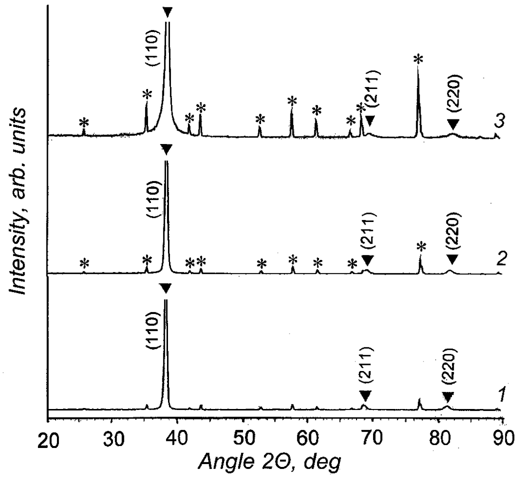
Since cadmium expectedly escaped during thermo-vacuum exposure of samples, we attempted to quantify the rate of evaporation of the volatile component from solid solutions. The calculation is based on a change in the parameter of the body-centered cubic lattice of solid niobium-based solutions before and after thermal exposure at low pressure. Due to the fact that the dependence of the lattice parameter on the composition, the amount of cadmium in the coating was established by us [13], it became possible to quantitatively establish the loss of the latter from the alloy by evaporation over a certain period of time, i.e. process intensity. Moreover, given that the coating thickness is extremely small compared to other measurements, in the calculation it was considered that the sample is two-dimensional, i.e. evaporation proceeds from the film surface. The specific evaporation rate was obtained due to the relation of the calculated velocity to the evaporation surface, i.e substrate area.

Electron microscopic studies of the film coatings of the niobium-cadmium system were performed on a JSM-8230 electron probe microanalyzer (JEOL).

Experiment results and discussion

X-ray diffraction patterns of the initial and thermo-vacuum-treated samples with a content of 49.0 and 64.5 at.% are shown in Figures 1 and 2.

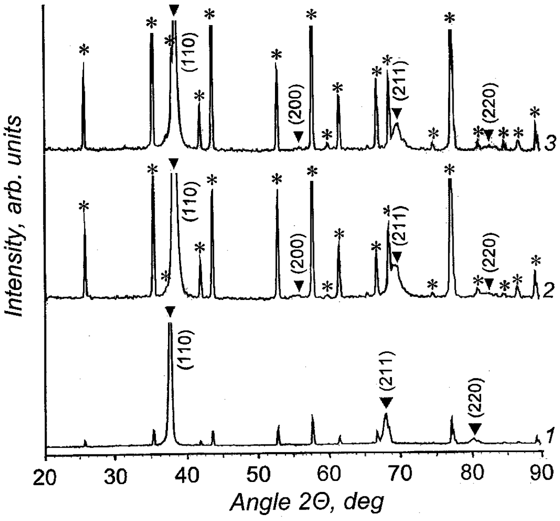
Analysis of the diffraction patterns showed that in the initial state the lattice parameter of the cadmium solid solution in niobium with 49.0 at.% Cd is 0.3348 ± 0.0003 nm; after annealing at 300°C, it is 0.3336 ± 0.0006 nm; and after annealing at 500°C it is 0.3311 ± 0.0002 nm. Similarly, the change in parameters for the sample with 62.4 at.% Cd is 0.3383 ± 0.0002; 0.3326 ± 0.0006 and 0.3313 ± 0.0004 nm, respectively. A similar dynamics of the change in the lattice parameter upon annealing in vacuum indicates a diffusion loss of cadmium in the solid solution.



1 – in initial state; 2 – after annealing at 300 °C; 3 – at 500 °C; ▼ - solid solution of cadmium and niobium; * - substrate - α-Al_2O_3

Figure 1 Diffraction patterns of the coating with the initial cadmium concentration of 49.0 at %

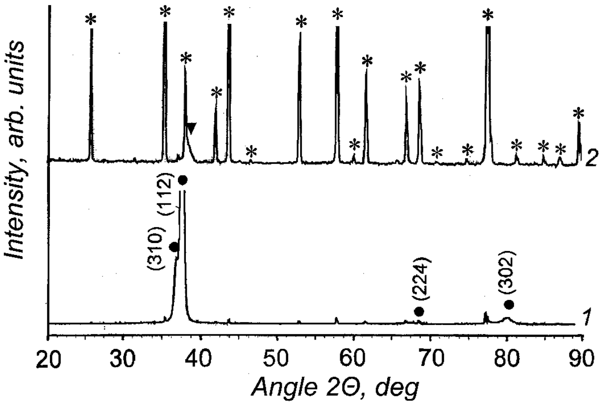
The cadmium atoms diffuse to the interface of the condensed phase, vapor, followed by sublimation (evaporation at 500°C). This is accompanied by a decrease in the cadmium concentration in the coating and a decrease in the lattice parameter of the solid solution.



1 – in initial state; 2 – after annealing at 300 ºC; 3 – at 500 ºC; ▼ - solid solution of cadmium and niobium; ∗ - substrate - α-Al_2O_3

Figure 2 Diffraction patterns of the coating with the initial cadmium concentration of 64.5 at %

Vacuum annealing at 200°C and 300°C ws conducted to determine the thermal stability of solid niobium-based solutions (having crystal lattice of niobium) and the phase of the intermetallic $NbCd_2$ compound (68.0 at.% Cd). The heat treatment at 200°C did not lead to any changes in the samples, and at 300°C, the $NbCd_2$ compound loses cadmium due to its sublimation with the appearance of the niobium phase (Figure 3).



1 – in initial state; 2 – after annealing at 300 ºC; ● – $NbCd_2$; ▼ - solid solution of cadmium and niobium; * - substrate - α-Al2O3

Figure 3 Diffraction patterns of the coating with the initial cadmium concentration of 68.0 at %

In this case, the coating was represented by ultrafine particles that are not bonded to each other (Figure 4). The sizes of individual formations range from 2 microns to 100 nm.

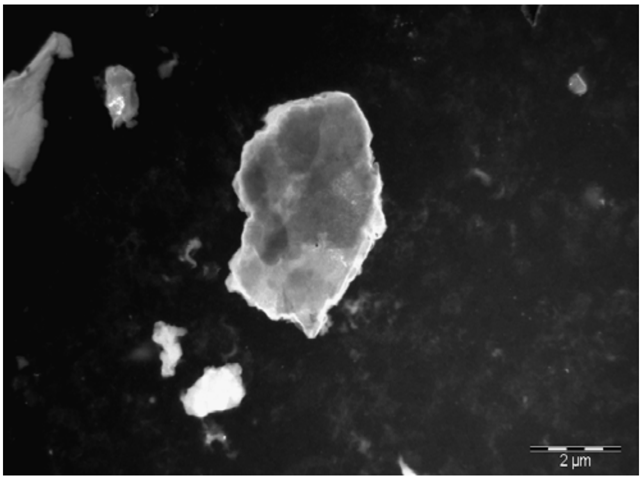


Figure 4 Electron microscopic image of the coating particles upon sublimation of cadmium from a sample with a cadmium concentration of 68.0 at %

On the diffraction pattern after annealing at 300°C, trace manifestations of reflections of a solid niobium-based solutions were observed.

The results of the study of the thermal stability of the coatings of the film system of niobium-cadmium with a concentration of the latter of 72.5 and 76.8 at. % showed complete degradation of the coatings at 300°C followed by the formation of dispersed niobium and the transfer of cadmium to the vapor phase.

Based on the dependences of the lattice parameter of the solid solution on the concentration of cadmium in the film coating in the range 0 - 50.0 at. % and 50.0 - 64.5 at. % Cd described by the equations a [nm] = $8\cdot10^{-5}x_{Cd}$ +0,3306 and a [nm] = $3\cdot10^{-4}x_{Cd}$ +0,3218 [13] (where xCd is the cadmium content in the alloy, at. %), and changes in the lattice parameters of the samples after annealing, the average rate of sublimation (evaporation) of cadmium was calculated (Table 1) by us. For comparison, the evaporation rate of liquid elemental cadmium under the same conditions determined by us earlier [20], is also given there. When calculating the material flow, the coating density of the Nb-Cd system was found additively in accordance with the composition, and the density of niobium and cadmium were taken from the reference publication [21].

The data on the intensity of cadmium removal from its solutions in niobium show that the cadmium sublimation rate at 300°C is comparable to the evaporation rate at 500°C with a slightly lower cadmium content in the sample at the beginning of the heat treatment process. An increase in the amount of cadmium in solid solutions from 40.0 to 64.5 at.%

upon annealing at 300°C and from 30.0 to 32.5 at.% at 500°C is expected to increase the rate of transfer of the volatile component to the vapor phase, since the diffusion process of cadmium to the sublimation surface (evaporation) is derived from the concentration gradient.

Table 1 Sublimation (evaporation) rate of cadmium from the coatings of the niobium-cadmium system

The cadmium content, at.% (Wt.%)	Annealing temperature, ° C	The residual cadmium content, at.% (Wt.%)	Evaporation rate, $kg\cdot m^{-2}\cdot s^{-1}$	Annealing temperature, ° C	The residual content of cadmium, at.%	Evaporation rate, $kg\cdot m^{-2}\cdot s^{-1}$
49.0 (53.76)	300	30.0 (34.15)	$7.06\cdot10^{-8}$	500	7.5 (9.65)	$8.78\cdot10^{-8}$
64.5 (68.74)	300	32.5 (36.81)	$1.25\cdot10^{-7}$	500	8.75 (10.40)	$1.03\cdot10^{-7}$
68.0 (72.0)	300	0 (0)	$3.11\cdot10^{-7}$	-	-	-
100*	-	-	-	500	-	$3.65\cdot10^{-2}$
* - elemental cadmium						

Comparison of the evaporation rate of elemental cadmium from a liquid bath and a solid solution with 30.0 - 32.5 at. % (34.15 - 36.81 wt.%)

Cd showed a significant (by 5 orders of magnitude) decrease in the intensity of the process of degradation of solid solutions.

Conclusions

As a result, of the study, it was found that the heating of film coatings (49.0 - 64.5 at. % Cd) represented by solid solutions in high vacuum up to 300°C was founded to be accompanied by the onset of intense degradation of the crystalline niobium-cadmium system due to the diffusion of cadmium atoms to the solid phase-vapor interface and its subsequent sublimation. Coatings of the intermetallic compound $NbCd_2$ (68.0 at % Cd) and cadmium-based solid solutions, including the amorphized phase of the intermetallic compound, were completely degraded upon exposure at this temperature. The structure of solid solutions of cadmium in niobium and the $NbCd_2$ intermetallic compound is stable ip to a temperature of 200 °C.

The intensity of the process of evaporation of cadmium from solid solutions at 500 °C is comparable to that at 300 °C, indicating the limiting stage of the process of diffusion of cadmium to the evaporation surface.

Such studies may be useful in developing new technologies for the production of metals and materials [22-25].

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Төмен қысымда ниобий-кадмий жүйесіндегі қатты қорытпалардың термиялық құлдырауы

Володин В. Н., Тулеушев Ю. Ж., Кенжалиев Б. К., Требухов С. А.

Түйіндеме. Nb - Cd қос қабатты жүйенің жылу тұрақтылығы туралы ақпараттың болмауына байланысты, ниобийдегі кадмий қатты ерітінділерін термо-вакуумдық өңдеудің әсерін зерттеу үшін $NbCd_2$ материалдардың құрылымына және кадмий негізіндегі қорытпалардың интерметалдық қосылыстарына зерттеу жүргізілді. Зерттеу әдісі ретінде изохронды кезең-кезеңмен тазарту 300 және 500 ° С температурада және 1 · 10-3 Па қысымында қолданылды, термиялық өңдеуден бұрын және кейінгі дифрактометриялық деректерді салыстыру арқылы құрамы мен құрылымындағы өзгерістер бақыланды. Қатты ерітінділердің корпустық центрлік кубтық торының тор параметрінің тәуелділігі негізделе - құрамдағы кадмий мөлшеріне байланысты кадмийдің қабықшадан сублимация (булану) жылдамдығы анықталды. Нәтижесінде, қатты қабатты қыздыру (49.0 - 64.5 ат. % Cd), қатты

ерітінділермен ұсынылған, жоғары вакуумда 300 ° С-қа дейін, ол ниобий-кадмий кристалды жүйесінің қарқынды деградациясының басталуымен қатар жүреді, ол кадмий атомдарының қатты-бу фазалар интерфейсіне таралуына байланысты және одан кейін сублимациялануымен жүреді. $NbCd_2$ интерметалдық қосылыстың жабыны пайда болғанынан жартылай өткізгіш болуы және кадмий негізіндегі қатты ерітінділер (72.5 және 76.8 ат. % Cd), аморфталған интерметалдық фазаны қосылатындықтан, осы температурада болғаннан кейін олар кадмийдің булану арқылы бу фазасына толық ауысуына байланысты нашарлайды. 200 ° С температураға термиялық әсер еткенде, ниобий мен $NbCd_2$ интерметалдық қосылыстағы кадмийдің қатты ерітінділерінің құрылымы тұрақты.
Түйінді сөздер: ниобий, кадмий, қатты ерітінді, интерметалдық қосылыс, дифрактометрия, сублимация.

Термическая деградация твердых сплавов системы ниобий-кадмий при низком давлении

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Аннотация. В связи с отсутствием сведений о термической стабильности двойной пленочной системы Nb – Cd, выполнено исследование по изучению влияния термо-вакуумной обработки твердых растворов кадмия в ниобии, интерметаллического соединения $NbCd_2$ и сплавов на основе кадмия на структуру материалов. В качестве метода исследования использован изохронный пошаговый отжиг при температуре 300 и 500 °С и давлении $1{\cdot}10^{-3}$ Па, с последующим отслеживанием изменения состава и структуры сравнением дифрактометрических данных до и после термообработки. На основании ранее установленной зависимости параметра решетки объемно-центрированной кубической решетки твердых растворов от состава - количества кадмия в покрытии, определена скорость сублимации (испарения) кадмия из пленочных покрытий. В результате установлено, что нагрев пленочных покрытий (49.0 - 64.5 ат. % Cd), представленных твердыми растворами, в высоком вакууме до 300 °С сопровождается началом интенсивной деградации кристаллической системы ниобий – кадмий вследствие диффузии атомов кадмия к поверхности раздела твердая фаза – пар с его последующей сублимацией. Покрытия из интерметаллического соединения $NbCd_2$, являющегося вырожденным полупроводником, и твердых растворов на основе кадмия (72.5 и 76.8 ат. % Cd), включающих аморфизованную фазу интерметаллида, после экспозиции при этой температуре деструктурированы из-за полного перевода кадмия в паровую фазу испарением. При термическом воздействии до температуры 200 °С структура твердых растворов кадмия в ниобии и интерметаллида $NbCd_2$ стабильна.
Ключевые слова: ниобий, кадмий, твердый раствор, интерметаллид, дифрактометрия, сублимация.

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