ISSN 2616-6445 (Online), ISSN 2224-5243 (Print)
Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a №1.2019 (30-35)

UDC 541.1+669. 73’293.112.5
IRSTI 81.09.03
https://doi.org/10.31643/2019/6445.04

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CONCENTRATION LIMITS OF NIOBIUM AND CADMIUM ALLOYS EXISTENCE, FORMED BY ULTRAFINE PARTICLES

Cite this article as: Volodin V.N., Tuleushev Yu. Zh, Nitsenko A.V. Burabaeva. N.M. Concentration limits of niobium and cadmium alloys existence, formed by ultrafine particles. Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a. **2019**. *1*. 20-25. https://doi.org/10.31643/2019/6445.04

Received: 26 October2018 / Peer reviewed: 08 January 2019 / Accepted: 01 February2019

Abstract. Cd metals are established to form an alloy with a body-centered cubic structure up to a 64.5 at. % concentration as a result of determining the limits existence of Cadmium in Niobium solid solutions, obtained by plasma-assisted ion sputtering and ultrafine particles co-precipitation to a critical size. At this, two linear dependence sections in the range of 0 - 50.0 at. % and 50.0 - 64.5 at. % of Cadmium (the rest is Niobium) are found described by the equations a [nm] = $8 \cdot 10^{-5}$x +0.3306 and a [nm] = $3 \cdot 10^{-4}$x +0.32188 (respectively), where x is the Cadmium content in the alloy, at. %. At 68 at. % of Cadmium, an unknown phase was identified; no solid solutions of Niobium in the Cadmium were detected. The growth of the lattice parameter is due to the fact, that Cadmium atoms have a larger radius than Niobium atoms: $(r_a)_{Cd}$ = 0,1727 нм, $(r_a)_{Nb}$ = 0,1625 nm. The kink on the linear dependence of the lattice parameter of the Cadmium in Niobium solid solution as a result of Cadmium concentration in the alloy is explained by the fact that Cadmium first replaces the Niobium atom in the center of the unit cell, then is also embedded in the Niobium lattice with increasing its concentration replacing the Niobium atom in one of the cube vertices. The latter causes a more intense increase in the size of the unit cell. The possibility of the alloys formation in a wide range of concentrations as a result of thermal-fluctuation melting and the merging of very small unlike particles that have significant differences in physical properties, metal particles was confirmed, which is unattainable with the traditional thermal production method.

Keywords: ultrafine particle, Niobium, Cadmium, diffractogram, unit cell, solid solution, alloy.

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УЛЬТРАДИСПЕРСТІ БӨЛШЕКТЕР БОЛЫП ҚАЛЫПТАСҚАН НИОБИЙ МЕН КАДМИЙ БАЛҚЫМАЛАРЫНЫҢ ҚАТАР ЖҮРУІНІҢ КОНЦЕНТРАЦИЯЛЫҚ ШЕКАРАЛАРЫ

Түйіндеме. Ультрадисперсті бөлшектерді тұндыру және ионды-плазмалы тозаңдату арқылы алынған ниобийдегі кадмий қатты ерітінділерінің қатар жүру шекараларын анықтау жайлы жүргізілген зерттеулердің нәтижесінде, Cd 64,5 ат. % концентрациясына дейін металдар көлемді-орталықтандырылған кубдық құрылымды балқымаға айналатындығы анықталған. Сонымен қатар сызықтық тәуелділігі 0 – 50,0 ат. % және 50,0 – 64,5 ат. % интервалда кадмий (қалғаны ниобий) болатын екі аумақ анықталған, олар мынадай теңдеумен сипаталады: a[нм]=$8 \cdot 10^{-5}x$ +0,3306 және a[нм]=$3 \cdot 10^{-4}x$ +0,3218 (тиісінше), x – кадмийдің балқымадағы құрамы, ат. %. 68 ат.% - да кадмий белгісіз фаза біріздестірілген, кадмийдегі ниобийдің қатты ерітінділері анықталмады. Тор өлшемдерінің өсуі, кадмий атомының атомдық радиусы ниобий атомының атомдық радиусынан үлкендігімен түсіндіріледі: $(r_a)_{Cd}$= 0,1727 нм, $(r_a)_{Nb}$ = 0,1625 нм. Балқымадағы кадмий концентрациясынан ниобийдегі кадмийдің қатты ерітіндісінің торының сызықтық тәуелділіктерінің параметрлерінің сынуы, былай түсіндіріледі, кадмий алдымен ниобий атомын элементарлы ұяшықтың ортасында орнын басады, содан кейін концентрациясы ұлғайған кезде ниобийдің торына енеді, ниобийдің атомын кубтың бір шыңына ығыстырады. Соңғысы элементарлы ұяшықтың өлшемінің белсенді ұлғаюына акеліп соқтырады. Физикалық қасиеттерде едәуір айырмашылықтар бар, аттас емес метал бөлшектерінің термофлуктуациялық балқуынан және өте аз мөлшерде біріктірілуінің нәтижесінде концентрацияның кең ауқымында қорытпалардың пайда болу мүмкіндігі расталды, бұған дәстүрлі жылу әдісімен қол жеткізу мүмкін емес.

Түйінді сөздер: ультра-бөлшектер, ниобий, кадмий, дифрактограмма, бірлік жасушасы, қатты ерітінді, қорытпа.

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КОНЦЕНТРАЦИОННЫЕ ГРАНИЦЫ СУЩЕСТВОВАНИЯ СПЛАВОВ НИОБИЯ С КАДМИЕМ, СФОРМИРОВАННЫХ УЛЬТРАДИСПЕРСНЫМИ ЧАСТИЦАМИ

Резюме. В результате определения границы существования твердых растворов кадмия в ниобии, полученных ионно-плазменным распылением и соосаждением ультрадисперсных частиц до критического размера, установлено, что до концентрации 64,5 ат. % Cd металлы образуют сплав с объемно-центрированной кубической структурой. При этом обнаружены два участка с линейной зависимостью в интервале 0 – 50,0 ат. % и 50,0 – 64,5 ат. % кадмия (остальное ниобий), описываемых уравнениями a [нм] = $8\cdot10^{-5}x$ +0,3306 и a [нм] = $3\cdot10^{-4}x$ +0,3218 (соответственно), где x – содержание кадмия в сплаве, ат. %. При 68 ат. % кадмия идентифицирована неизвестная фаза, твердых растворов ниобия в кадмии не обнаружено. Рост параметра решетки обусловлен тем, что атомы кадмия имеют больший радиус, чем атомы ниобия: $(r_a)_{Cd}$ = 0,1727 нм, $(r_a)_{Nb}$ = 0,1625 нм. Излом на линейной зависимости параметра решетки твердого раствора кадмия в ниобии от концентрации кадмия в сплаве объясняется тем, что кадмий сначала замещает атом ниобия в центре элементарной ячейки, затем при увеличении его концентрации еще встраивается в решетку ниобия, замещая атом ниобия в одной из вершин куба. Последнее вызывает более интенсивное увеличение размеров элементарной ячейки. Подтверждена возможность образования сплавов в широком интервале концентраций в результате термофлуктуационного плавления и слияния весьма малых разноименных, имеющих значительные различия в физических свойствах, частиц металлов, что недостижимо при традиционном термическом способе получения.

Ключевые слова: ультрадисперсная частица, ниобий, кадмий, дифрактограмма, элементарная ячейка, твердый раствор, сплав.

Introduction. The thermal-fluctuation effect of particles melting appears not only at the temperature of phase transitions and transformations reducing [1, 2], the synthesis capability of various chemical entities and materials [3], but also in a significantly increasing solubility limits, including in the solid state. Despite the relatively large amount of researches regarding impact simulation of the nanoparticles surface energy on their properties [4], there is currently no single approach to predict the course of chemical and physical processes to acquire the double alloys.

The author [5, 6] has specified the change in the melting temperature of thin films with a decrease in their thickness is similar to that for the small particles, due to the fact that they are formed according to the "island like" principle, that is, ultrafine formations are placed on the substrate in the form of islands.

The authors have pointed out the importance of studying the phase transitions in the highly dispersed materials and nanocomposite structures with a purpose of a fundamental realizing of nucleation during melting and crystallization, as well as the limits of appearance of stable and metastable phases [7].

We [8] used the method of consistently reducing of the sublayers thickness during the formation of the total coating thickness to fix the critical sizes of Niobium (less than 2 nm) and Cadmium (less than 3 nm) clusters, whereby the metals alloy is produced at a low temperature.

The study was aimed to obtain Niobium and Cadmium alloys by co-precipitation of ultrafine clusters at a low temperature, in particular, determination of the concentration limits of the alloys appearance obtained in a similar way.

Research Methods. The method of samples forming of different concentrations alloy coatings lied in plasma-assisted ion sputtering of Niobium and Cadmium and their joint deposition on unheated substrates moving relative to plasma flows, with a thickness less than the critical size for each of the metals.

The process was localized on the substrate surface owing to the streams with unlike metals particles have been separated by 180° relative to each other. The time interval of substrate moving from the axial line of one spraying eguipment to the second was 3 s, which is enough for crystallization of the very small particles on the theory of this process existence. The solid solution formation, in this case, became a confirmation of the metal particles being initially in the liquid state, their merger and subsequent crystallization. In the experiments, the Niobium containing 99.95 wt. % (Irtysh

Metallurgical Plant) of the main element and Cadmium - 99.98 wt. % obtained by the vacuum distillation from a rough metal [9, 10] were used.

The substrates’ moving velocity relative to plasma flows is $5 \cdot 10^{-2}$ $m \cdot s^{-1}$. The ratio of electric power supplied to the Niobium and Cadmium sputtering magnetrons were changed in order to control coating composition. The ratio of the precipitated metals was controlled by the gravimetric method according to the number of sputtered metals during the coating formation. The total film thickness was determined by the Rutherford backscattering of protons at the UKP-2-1 tandem accelerator of the Institute of Nuclear Physics and by a calculation based on the amount of deposited metals and their density, the thickness of Cadmium and Niobium sublayers by dividing the total thickness by the number of passes relative to plasma flows.

A Bruker’s D8 Advance diffractometer with copper radiation $\lambda_{k\alpha}$ = 0.154051 nm with a graphite monochromator was used to carry out X-ray diffraction studies. The value of the phase lattice parameter is calculated as an average when using all the diffraction lines from this phase.

The other coating phases than the solid solution - alloy discovered as a result of diffractometric studies, of different Niobium and Cadmium composition were considered the limits of its existence.

The coating samples with a Cadmium concentration of 13.8 to 84.2 at. % were formed in order to determine the concentration limits of the solid solutions existence in the Nb-Cd system by plasma-assisted ion sputtering taking into account the size factor. The thickness of the single layers of Niobium (dNb) and Cadmium (dCd) during the coatings sputtering, its proportion and the phases formed when sputtering are provided in Table 1.

The diffractometric study determined the concentration of Cadmium in the coating is in the range of 0 - 64.5 at. % (68.7 wt. %) of the films are represented by solid solutions of Cadmium in the Niobium with a BCCA-structure. If 32,0 at. % of the Niobium and 68 at. % of the Cadmium content in the coating, an unknown phase was detected, denoted by us as "X". The X-phase and Cadmium were presented in the coating at the concentration range of 72.5-84.5.

Two sections with a linear dependence in the range of 0 - 49.0 at. % and 49.0 - 64.5 at. % of Cadmium (the rest is Niobium), described (except for the corresponding to 46.1 at.% Cd composition and possessing a large deviation) by the equations a [nm]= $8 \cdot 10^{-5}x+0,3306$ and a [nm]=$3 \cdot 10^{-4}x+0,3218$ (respectively), where x is the Cadmium contain in the alloy, at. % were discovered when considering the parameter dependence of the body-centered cubic lattice on the Cadmium concentration in the alloy (Figure 1).

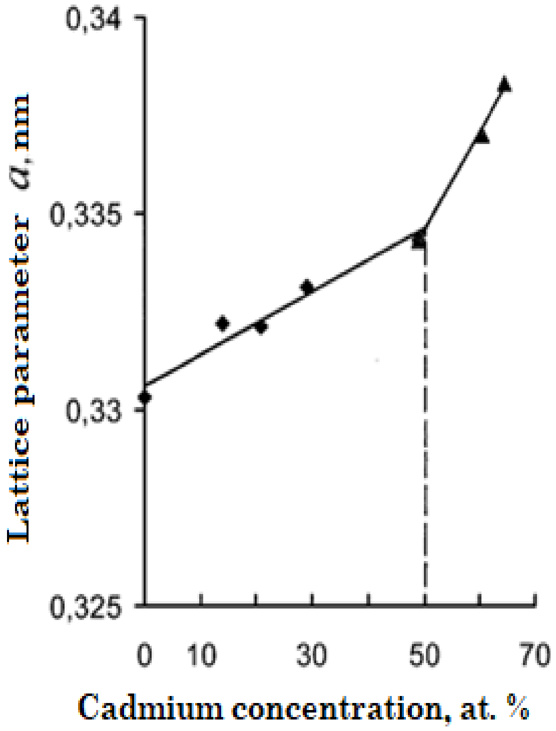


Figure 1 - The parameter dependence of the solid solution lattice on the Cadmium concentration in the Niobium

The lines intersection is observed to be corresponded to the Cadmium concentration in the alloy of 50 at. % and formally to the stoichiometry of NbCd potential compound.

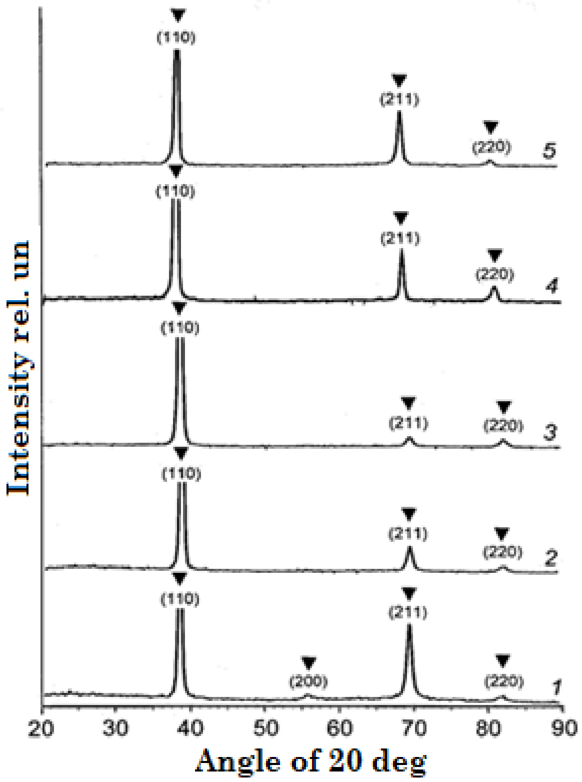
However, the diffractometric studies of the obtained alloys on a glass substrate (Figure 2) resulted in the presence of nothing but Cadmium solid solution phase in the Niobium.

The glass substrate allowed us to identify only the reflections of the phase under study. In all cases, the Cadmium solid solution is performed by a cubic body-centered lattice in the Niobium.

An increase in Cadmium concentration leads to a predictable increase in the lattice parameter, due to the fact that Cadmium atoms have a larger atomic radius than Niobium atoms: (ra) Cd = 0.1727 nm, (ra) Nb = 0.1625 nm. As well as an increase in the coating texturing in the direction [110], emerged in the reflex disappearance with Miller indices (200), observed in the solid solution from 13.8 at. % of Cadmium.

Table 1 – Coating compound, sublayers thickness of the Niobium and Cadmiun and discovered phases

Coating compound, at. %:		d_{Nb}, nm	d_{Cd}, nm	Phase compound
Nb	Cd			
86.2	13.8	2.1	0.4	solid solution Cd в Nb a = 0.3322±0.0005
79.1	20.9	1.1	0.36	solid solution Cd в Nb a = 0.3321±0.0002
71.1	28.9	1.1	0.53	solid solution Cd в Nb a = 0.3331±0.0002
54.9	46.1	0.58	0.60	solid solution Cd в Nb a = 0.3359±0.0003
51.0	49.0	1.17	1.35	solid solution Cd в Nb a = 0.3343±0.0004
39.6	60.4	0.77	1.4	solid solution Cd в Nb a = 0.3370±0.0003
35.5	64.5	0.57	1.25	solid solution Cd в Nb a = 0.3383±0.0002
32.0	68.0	0.37	1.46	X-phase
27.5	72.5	0.58	1.83	X- phase + Cd
23.2	76.8	0.57	1.25	X- phase + Cd
15.8	84.2	0.3	1.9	X- phase + Cd



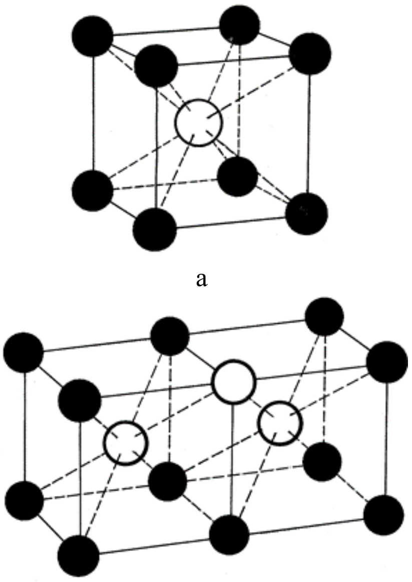
Cadmium consentration in the Niobium, at. %:
1 – 13.8; 2 – 20.9; 3 – 28.9; 4 – 60.4; 5 – 64.5.

Figure 2 – Diffractograms of alloys of different consentration of Cadmium and Niobium

The total data obtained resulted in our making the structure of the elementary cells of the Cadmium solid solution in the Niobium with a concentration of 50 at. % Cd (a) and 57.3 at. % Cd (b) (Figure 3).

The total data obtained resulted in our making the structure of the elementary cells of the Cadmium solid solution in the Niobium with a concentration of 50 at. % Cd (a) and 57.3 at. % Cd (b) (Figure 3).

As far as Cadmium accumulates in the lattice, it first replaces the Niobium atom in the center of the unit cell (Figure 3a), then as its concentration increases, another Cadmium atom is embedded in the Niobium lattice, replacing the Niobium atom in one of the cube vertices (Figure 3b).



a

b

Figure 3 – Elementary cell of Cadmium solid solution in the Niobium with a concentration of 50 at. % Cd (a) and 57.3 at. % Cd (b)

The latter, in our opinion, entails a change in the rate of the Niobium lattice parameter alteration and an “alien” Cadmium atom emerges in it and manifests itself in a dependence break of the latter on the Cadmium concentration in the Niobium more than 50 at. % (Figure 1).

Summary. The study to determine the limits existence of the Cadmium solid solutions in the Niobium, obtained by plasma-assisted ion sputtering and ultrafine particles co-precipitation has resulted in fixing the metals form an alloy with a body-centered cubic structure up to a 64.5 at. % Cd concentration. At this, the lattice parameter increases linearly in the intervals of 0-50 at. % and 50 - 64.5 at. % of Cadmium with a break in dependencies at 50 at. % Cd.

The growth of the lattice parameter is stipulated by the Cadmium atoms have a larger atomic radius than the Niobium atoms: (ra) Cd = 0.1727 nm, (ra) Nb = 0.1625 nm. The change in the growth rate of the lattice parameter in the provided intervals is explained by the fact that Cadmium first replaces the Niobium atom in the center of the unit cell, then as its concentration increases, it is further embedded in the Niobium lattice, replacing the Niobium atom in one of the cube vertices.

An opportunity to produce alloys in a wide range of concentrations as a result of the thermal-fluctuation melting and the merging of very small unlike particles that have significant differences in the physical properties of metal particles was proved by the study conducted, which is uncapable to reach by the traditional thermal production method.

The paper is accomplished owing to the financial support of the Ministry of Education and Science of the Republic of Kazakhstan (grant AP05132506 / GF).

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