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New MoCd₂ phase in film coatings of molybdenum-cadmium system

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Ion-plasma sputtering and code position of Mo and Cd ultrafine particles have been used for the first time to prepare solid solutions that are alloys with a concentration up to 57.3 at. % Cd in the film; this confirms the thermal-fluctuation and coalescence of small particles. When coatings are formed by molybdenum and cadmium nanolayers less than 2 nm in the concentrations range of 60-66 at. % Cd, a new phase was found that was prepared directly in the course of film coating formation; it was identified as the MoCd₂ compound with a tetragonal face-centered lattice, with the parameters $a = 0.78231$ nm and $c = 0.77039$ nm. X-ray diffraction data for the identification of the intermetallic compound were determined. The unit cell of MoCd₂ has been constructed. Upon accumulation in the lattice, cadmium first replaces the molybdenum atom in the center of the unit cell, then another cadmium atom is embedded in the molybdenum lattice, replacing the atom at one of the cube corners and accompanied by a cubic-to-tetragonal cell transformation where the cadmium atoms are embedded in pairs on the side faces of the cell in the MoCd₂ compound. Thermal stability of the intermetallic compound is limited by 200 °C. Synthesized phase of MoCd₂ has a metallic type of conductivity.

Keywords: ion-plasma sputtering, alloys, coatings, nanolayers.

Introduction

Modern technological progress provides higher demands for structural and functional metallic materials [1]. The key requirement among them is multi functionality, i.e. combinations of high and often difficult to combine mechanical,

physical and chemical properties in the same material. Standard materials science principles for formation of structure and properties, based on the traditional thermal and deformation effects on solids, are no longer able to meet these requirements. One way to impart new properties to materials is to create previously unknown structural states in them, which is facilitated by extreme effects on solids. One of these types of effects is a mechano melting, significantly expanding the zone of mutual solubility of metals [2]. Another method of producing new phases is the technology of ion-plasma deposition of metals alternating layers by ultra-fine particles [3-6]. Options for choosing the incompatible metals are molybdenum and cadmium.

Up to now, no diagram of the molybdenum-cadmium system is available [7]. No data on the structure of any phases and compounds besides molybdenum and cadmium are available in the ICPSD tables and other reference books.

The aim of the present study is to determine the possibility of the formation of molybdenum-cadmium alloys with allowance for the size factor and concentration limits of solid solution existence, to prepare and identify the intermetallic compound, and to determine the structure of prepared alloys film coatings.

Experimental

As the material for the investigation, we used molybdenum-cadmium films, which were prepared by the codeposition of ultrafine particles (prepared by ion-plasma sputtering) of the metals on cold substrates made from polycrystalline silicon (polycor), single-crystal silicon Si and glass.

In experiments we used molybdenum 99.9 mas. % purity and cadmium (99.99 mas. %) in the form of targets for sputtering 40 mm in diameter and 4 mm thick. During magnetron sputtering, argon purified with a sputtered-titanium getter was applied as a plasma-forming gas.

The procedure for formation of alloy-coating samples consists in the ion-plasma sputtering of molybdenum and cadmium and subsequent co-deposition of them on substrates moving relatively to plasma beams in the form of sublayers about 1 nm thick, to a total thickness of film of (1.5-2) μm . The rate of substrate movement is from 2 to $(30 \cdot 10^{-2}) \text{ m} \cdot \text{s}^{-1}$. The deposition was achieved with the simultaneous use of two oppositely located magnetrons separated by a unit for the displacement of substrates.

The composition of coating was controlled in varying the relationship of powers supplied to magnetrons that sputter molybdenum and cadmium. The relationship of deposited metals was determined using the weights of each of the metals sputtered in the course of coatings formation. The thickness of films was determined by Rutherford proton back scattering spectrometry using a UKP-2-1 tandem accelerator and by calculations using amounts of deposited metals and their density.

X-ray diffraction analysis was performed using a D8 Advance (Bruker) diffractometer, copper radiation ($\lambda_{\text{CuK}\alpha} = 0.154051 \text{ nm}$) and a graphite monochromator. The lattice parameter was determined using all diffraction reflections or identified

phase and taken as the average magnitude.

Mo-Cd films (50-60) nm thick, which were used for transmission electron microscopy (TEM), were deposited on NaCl single-crystal plates and subsequently removed from the substrate in distilled water and placed on standard carbon grids with nickel coating. The study of the fine structure of the coating was performed using a JEM-2100 (JEOL) electron microscope at an accelerating voltage of 200 kV.

Results and discussion

To determine the concentration, range of the existence of solid solutions in the Mo-Cd system, coating samples with cadmium concentrations from 0.45 to 97.6 at. % were prepared by ion-plasma deposition taking into account the size factor. Thickness of single layers of molybdenum (d_{Mo}) and cadmium (d_{Cd}) during coatings deposition, coating composition and phases formed during sputtering are presented in Table. 1.

Table 1.

Composition of coatings, thickness of molybdenum and cadmium sublayers and identified phases.

Coating composition, at. %:		d_{Mo} , nm	d_{Cd} , nm	Phase composition
Mo	Cd			
99.55	0.45	1.28	0.01	Cd solid solution in Mo a = 0.3147±0.0001
86.9	13.1	1.72	0.3	Cd solid solution in Mo a = 0.3156±0.0002
82.0	18.0	1.31	0.4	Cd solid solution in Mo a = 0.3173±0.0001
69.0	31.0	1.32	0.82	Cd solid solution in Mo a = 0.3214±0.0002
60.7	39.3	1.39	1.24	Cd solid solution in Mo a = 0.3233±0.0002
53.8	46.2	1.33	1.58	Cd solid solution in Mo a = 0.3241±0.0002
50.7	49.3	1.40	1.88	Cd solid solution in Mo a = 0.3256±0.0002
47.6	52.4	1.45	2.21	Cd solid solution in Mo a = 0.3247±0.0002
42.7	57.3	3.5	6.5	Cd solid solution in Mo a = 3275±0.0003+Cd
39.3	60.7	3.5	7.6	Cd solid solution in Mo a = 0.3231±0.0002 + Cd + X-phase
39.4	60.6	0.48	1.02	X-phase
34.6	65.4	0.44	1.15	X- phase

Continuation of the Table 1.

Coating composition, at. %:		d_{Mo} , nm	d_{Cd} , nm	Phase composition
Mo	Cd			
31.3	68.7	0.39	1.17	X- phase + Cd
30.1	69.9	0.34	1.11	X- phase + Cd
26.6	73.4	0.37	1.32	X- phase + Cd
20.9	79.1	0.34	1.78	X- phase + Cd
11.4	88.6	0.34	3.63	X- phase + Cd
2.4	97.6	0.09	5.24	Cd

Diffraction study has showed that the film coatings are solid solutions of cadmium in molybdenum with a body centered cubic bcc-lattice (body centered cubic) and linear variation of lattice parameter depending on cadmium concentration (Figure 1) at cadmium concentration from 0.45 to 57.3 at. % in the coating.

The presented dependence is described by the linear equation a (nm) = $(0.0002C_{Cd} + 0.3137)$, where C_{Cd} is cadmium concentration (at. %). The phase, previously never observed (we identified it as X phase), appears in the coating at cadmium concentration of 60.6 at. %.

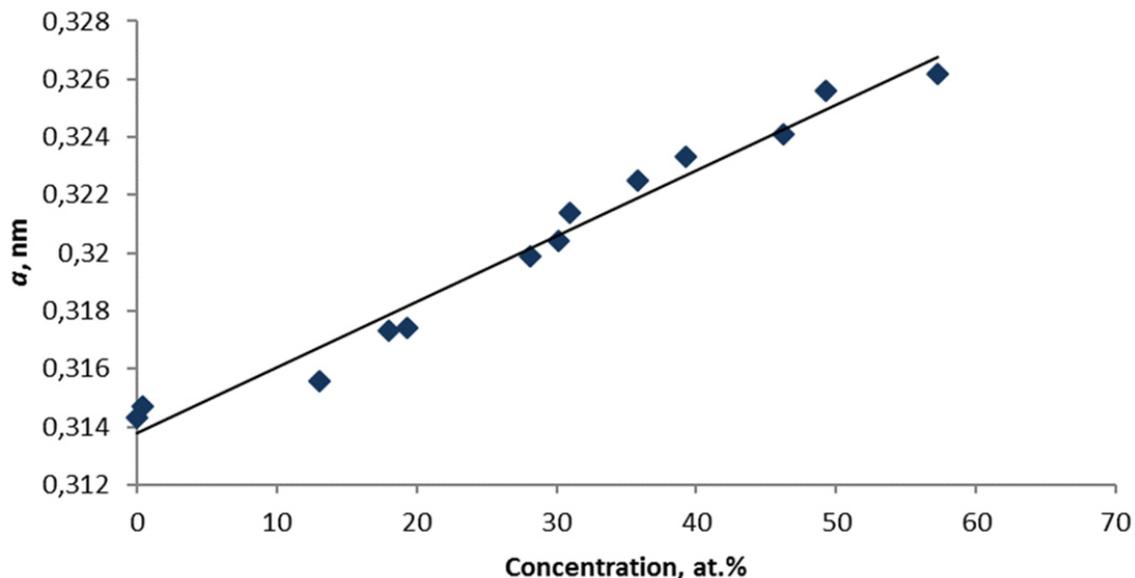


Figure 1. Dependence of solid solution lattice parameter of cadmium in molybdenum from cadmium concentration.

The most distinct reflections from this phase are observed at cadmium concentration of 65.4 at. %. When cadmium content increases to 68.7 at. %, the reflections from cadmium are added to the reflections from X-phase, which become dominant with cadmium concentrations increase.

Figure 2 represents the coatings diffraction patterns in the concentration range (60.6, 65.4 and 69.9 at. % Cd), confirming the appearance of unknown phase.

To identify the conditions for appearance of the unknown phase in the coating we defined the influence of the size factor (size of particles) in our case metals sublayers thickness during formation of the film.

The diffraction patterns of almost identical coatings (60.7 and 60.6 at. %), formed by sublayers 3.5 nm Mo, 7.6 nm Cd thick in one case, 0.48 nm Mo and 1.02

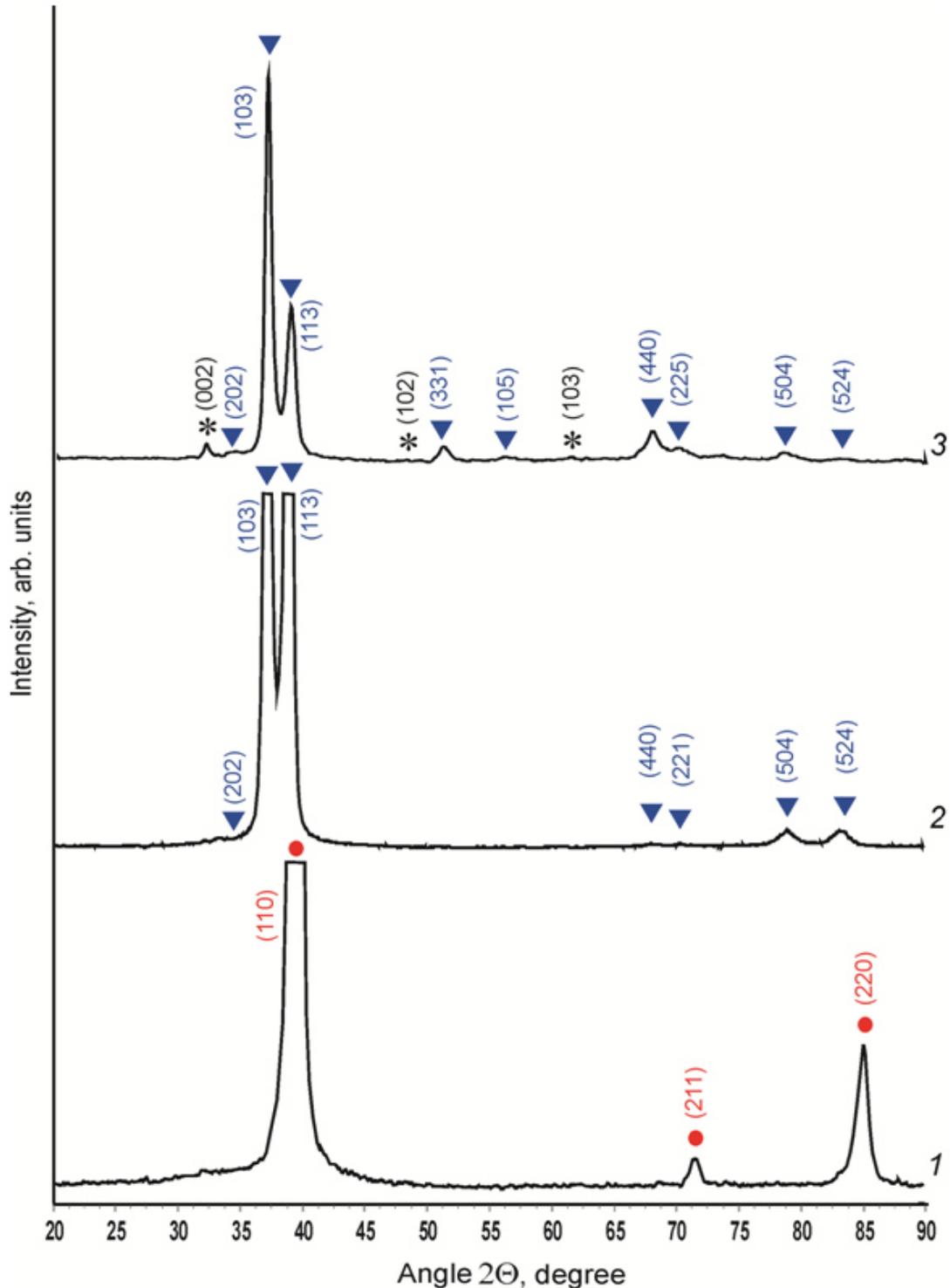


Figure 2. Diffraction pattern of molybdenum-cadmium coatings with cadmium content: 1 - 60.6 at. %, 2 - 65.4 at. %, 3 - 69.9 at. %. • - Cd solid solution in Mo; ▽ - x-phase; * - Cd.

nm Cd in another case, are shown in Figure 3.

Diffraction pattern (1) on Figure 3 indicates the reflexes from cadmium solid solution in molybdenum with the lattice parameter $a = 0.3274 \pm 0.0004$ nm, cadmium and X phase beginning to form, Figure 2 (2) shows the reflexes from formed X-phase, epitaxially related to cadmium solid solution in molybdenum with $a = 0.3281$ nm. Comparison of the spectra shows that the size factor plays the

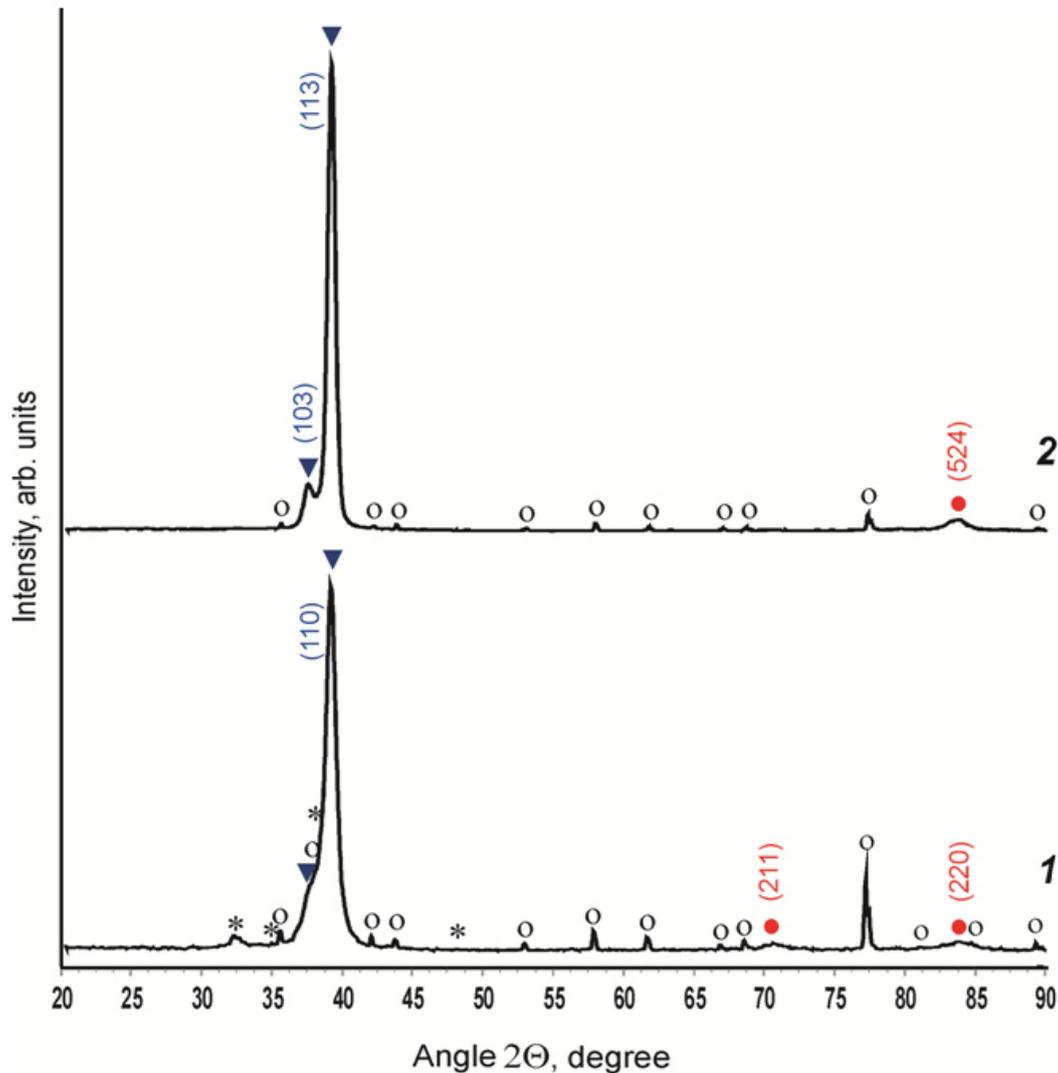


Figure 3. Diffraction patterns of coatings with cadmium 60.6 at.% (1) and 60.7 at.% (2): ● - Cd solid solution in Mo; ▽ - X-phase; * - Cd; ○ - polycor (α - Al_2O_3).

main role in formation of a new phase [8]. The well-formed X phase is obtained under cadmium content increase in the coating to 65.4 at. % and sublayers thickness of molybdenum 0.48 nm and cadmium 1.15 nm, as shown in Figure 2 (spectrum 2). Thus, we found that the film coating is represented by X phase in the concentration range of (60.6-65.4) at. % Cd and during formation of sublayers less than 2 nm. With the cadmium concentration increase in the coating to 68.7 at. % the latter is represented by a separate phase.

Interplanar spacings (d_{hkl}) of the newly discovered phase and the Miller indexes of these reflexes calculated according to program "Tabular processor for X-ray diffractometry RTP (rtp32.cab, RTP 4.2 for Win32, English version dated 1.02.2014)" are given in Table 2. The found phase can be described by tetragonal unit cell with the parameters $a = 0.78231$ nm and $c = 0.77039$ nm.

Table 2.

Interplanar spacings d_{hkl} and associated Miller indexes hkl of the found phase.

d_{hkl} , nm	0.2742	0.2437	0.2328	0.1791	0.1514
hkl	(202)	(103)	(113)	(331)	(105)
d_{hkl} , nm	0.1383	0.1344	0.1215	0.1160	
hkl	(440)	(225)	(504)	(524)	

Since the texturization effect is possible during coating formation, the relative lines intensities are not given in Table 2.

Electron microscopic study of Mo-Cd coating surface (69.9 at. % Cd) (Figure 4) showed that the coating consists of variously rounded crystallites with the pores observed between them in some places.

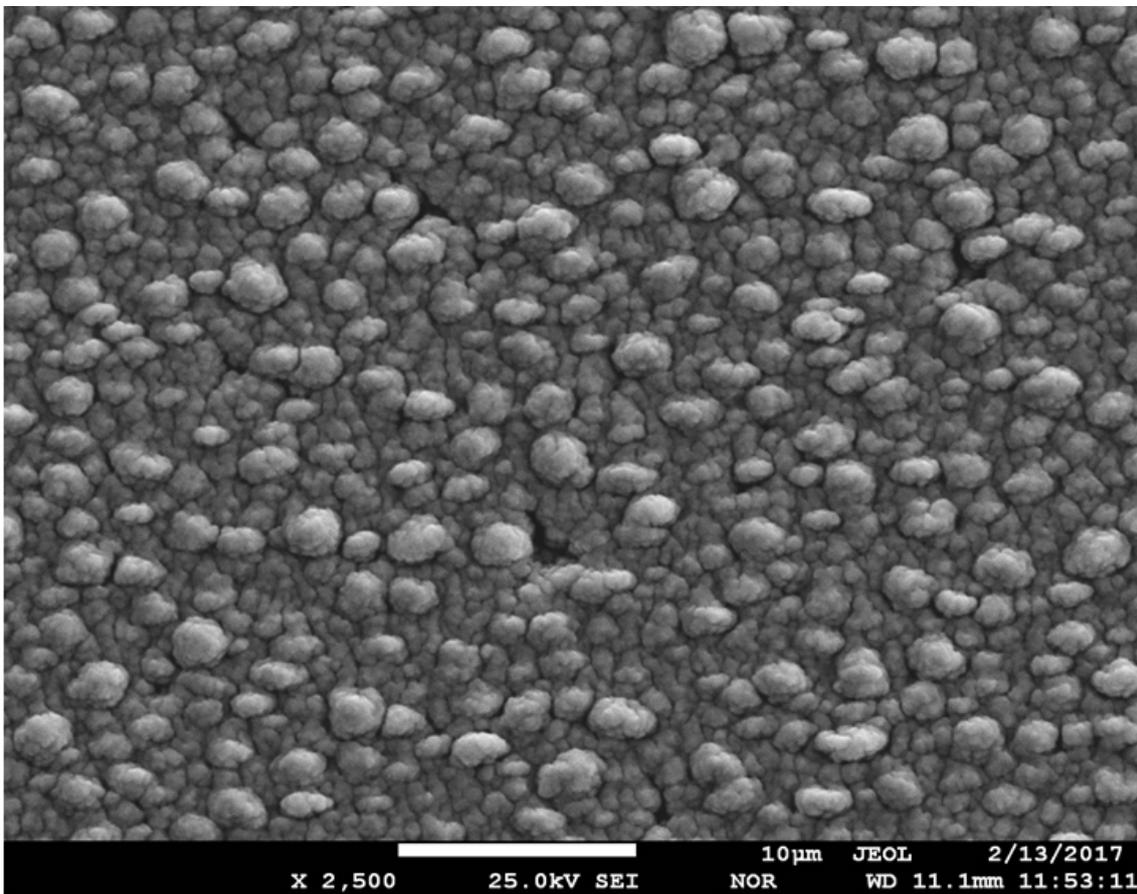


Figure 4. Electron microscopic images of molybdenum-cadmium film coating with Cd 69.9 at. %. (a) comparison mode; (b) scattering electron mode. Magnification $\times 2500$.

TEM studies (electron microscope JEM-2100 (JEOL)) were performed to determine the composition of the found phase using the sample with cadmium concentration of 68.0 at. % (Figure 5).

The sample is a film with the grown particles different in size and shape. The film itself is fragmented and consists of many fine particles. The large particles on the sample have the sizes $d =$ from 0.2 μm to 0.5 μm , and are characterized by an island shape with a non-uniform thickness and torn uneven edges. The particles of medium size have a predominantly globular shape, and their dimensions vary in the range of (40-180) nm. The particles with the sizes less than 40 nm, which

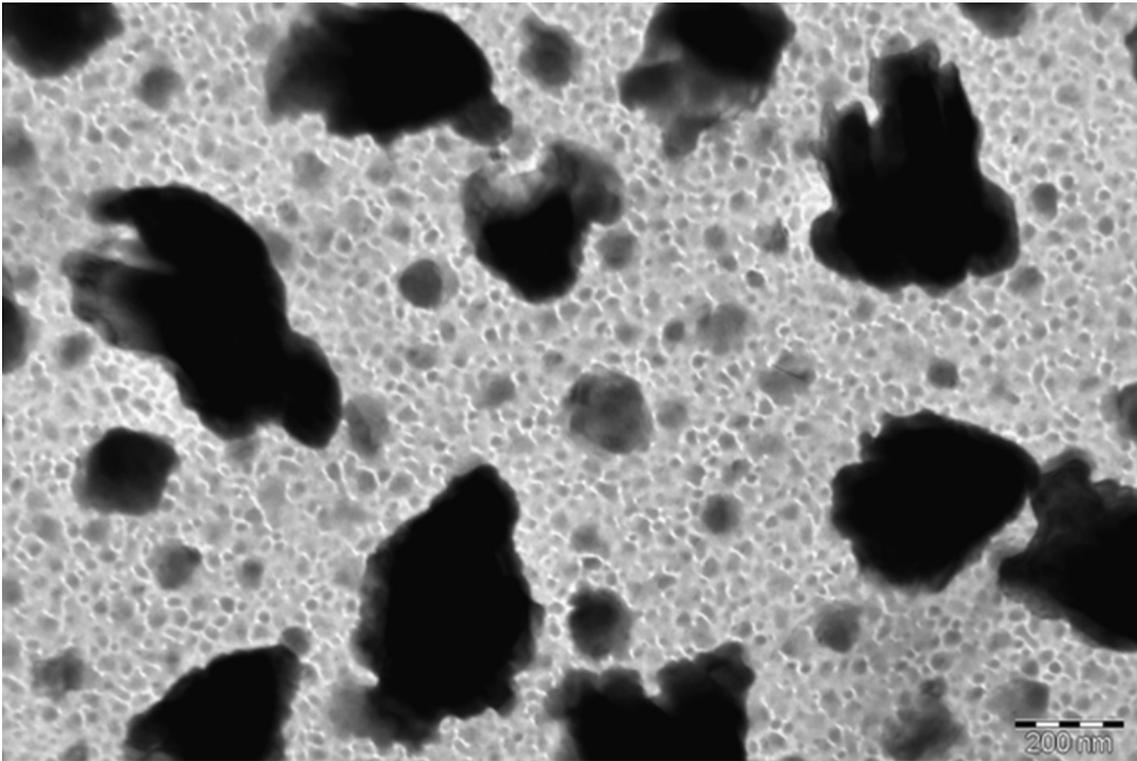


Figure 5. Microstructure of coating sample (68.0 at. % Cd).

can be conditionally classified as fine-grained, form the basis of the film. In the image, the large particles have a dark contrast as a result of greater thickness, the smaller particles are more transparent, indicating their smaller thickness.

Decoding of the electron diffraction pattern of the coating with cadmium concentration of 68.0 at. % (point of spectrum 2 removal and associated EDS-spectrum (energy dispersive spectroscopy) in Figure 6) showed that all lines, listed in Table 2, have the images in the form of rings with corresponding sizes.

General mapping, performed according to EDS-analysis results, shows that molybdenum is uniformly distributed over the entire surface of the sample and is part of the particles, cadmium is localized in large particles. The result of numerical processing by the method of quantitative analysis of EDS-spectrum is given in Table. 3

Table 3.

Result of numerical processing of the spectrum 2.

Element	Weight, %	Atomic, %
Mo K	33.92	37.55
Cd L	66.08	62.45
Total	100.00	

According to results of EDS -analysis of the fine-dispersed formations in the film and the concentration interval for X phase appearance, we can state that the atomic ratio of cadmium to molybdenum is 2:1 in the new phase, and the formula corresponds to MoCd_2 .

Based on the obtained data, we constructed the unit cells of cadmium solid solution in molybdenum with the concentration 50 at. % Cd (a) and 57.3 at. %

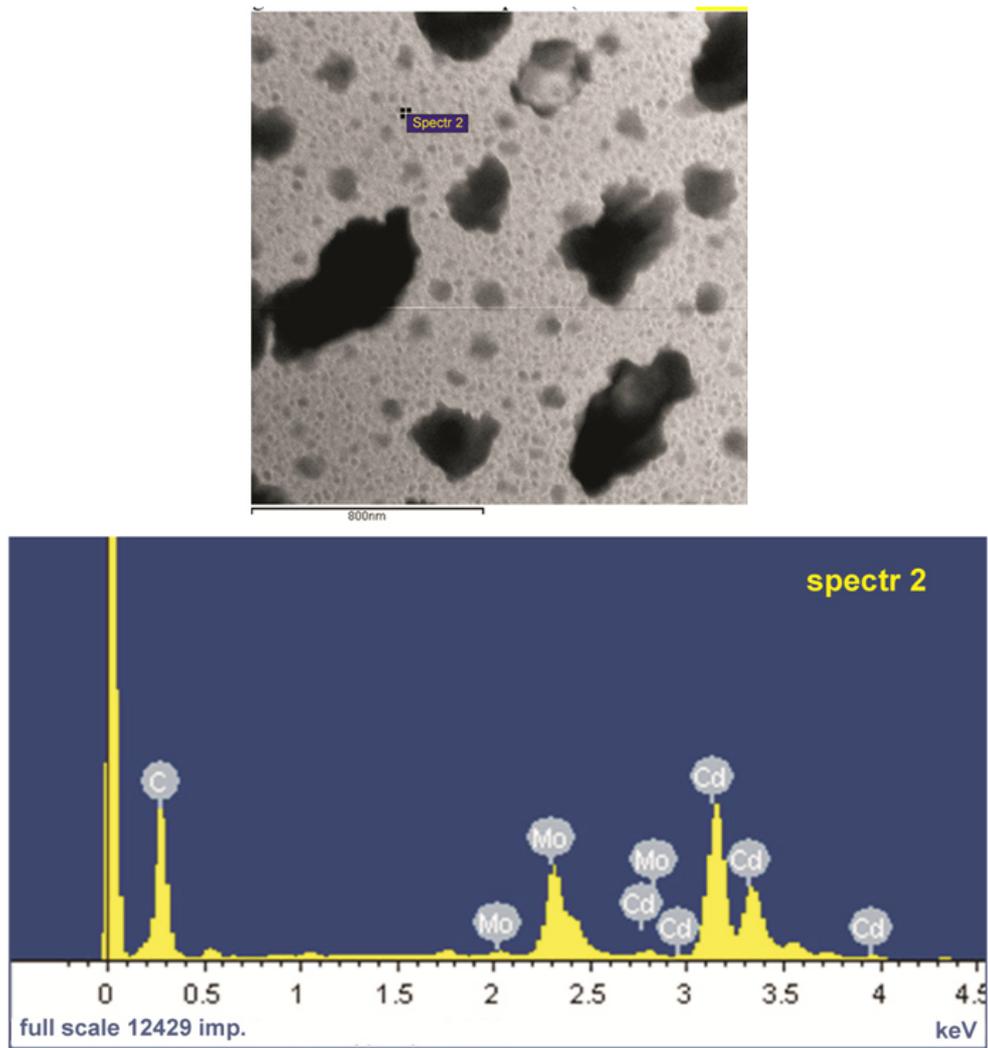


Figure 6. Point of spectrum 2 removal and associated EDS-spectrum.

Cd (b) and the supposed type of the intermetallic MoCd_2 compound unit cell (Figure 7c).

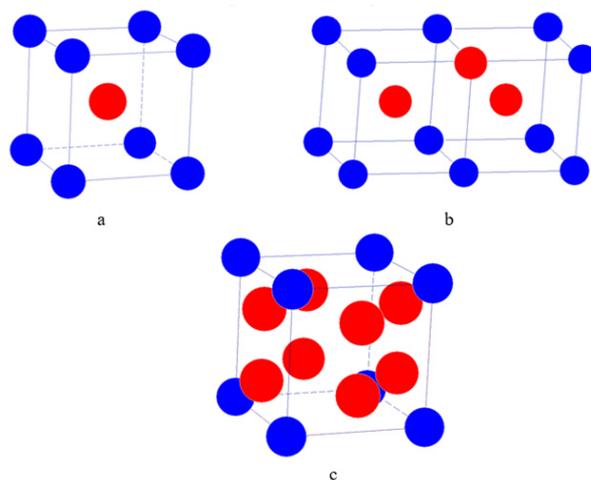


Figure 7. Unit cell of cadmium solid solution in molybdenum with concentrations 50 at. % Cd (a), 57.3 at. % Cd (b) and intermetallic MoCd_2 compound (c).

Upon accumulation in the lattice, cadmium first replaces the molybdenum atom in the center of the unit cell (50 at. % Cd) (figure 7a), then as its concentration increases another cadmium atom is embedded in the molybdenum lattice, replacing molybdenum atom at one of the cube corners (Figure 7b, 57.2 at. % Cd). Further growth of cadmium concentration is accompanied by a cubic-to-tetragonal unit cell transformation where cadmium atoms are embedded in pairs on side faces of the cell (Figure 7c, 66.6 at.% Cd).

Vacuum annealings were performed at the temperatures of 200 and 300 ° C to study thermal stability of the prepared phase of intermetallic MoCd_2 compound. Annealing at the temperature of 200 ° C showed no changes in the annealed samples, and at 300 ° C the compound loses cadmium due to evaporation with appearance of the molybdenum phase, and the coating itself is scattered into ultrafine powder which particles are not bound with each other (Figure 8). The sizes of individual grains range from 2 μm to 100 nm.

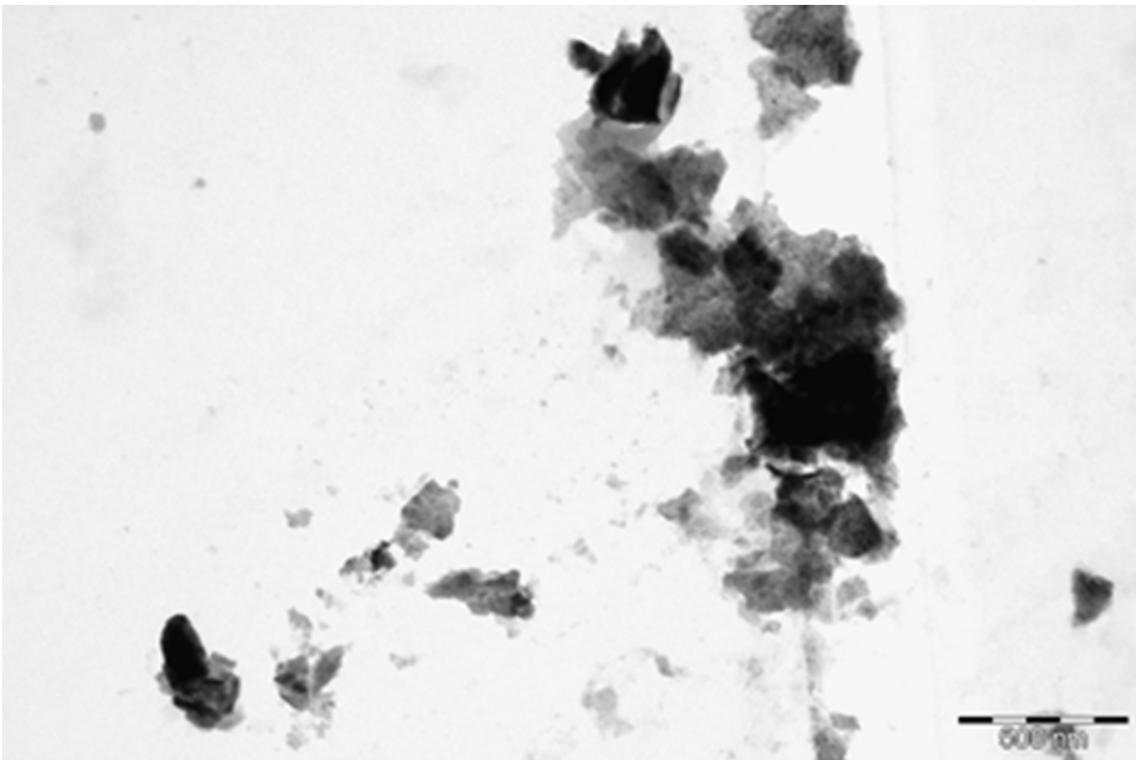


Figure 8. Electron microscopic image of the particles after cadmium evaporation.

They are shown on the T-x diagram (Figure 9) to visualize the position of fields of phases existence found in the initial film coatings prepared by ion-plasma formation.

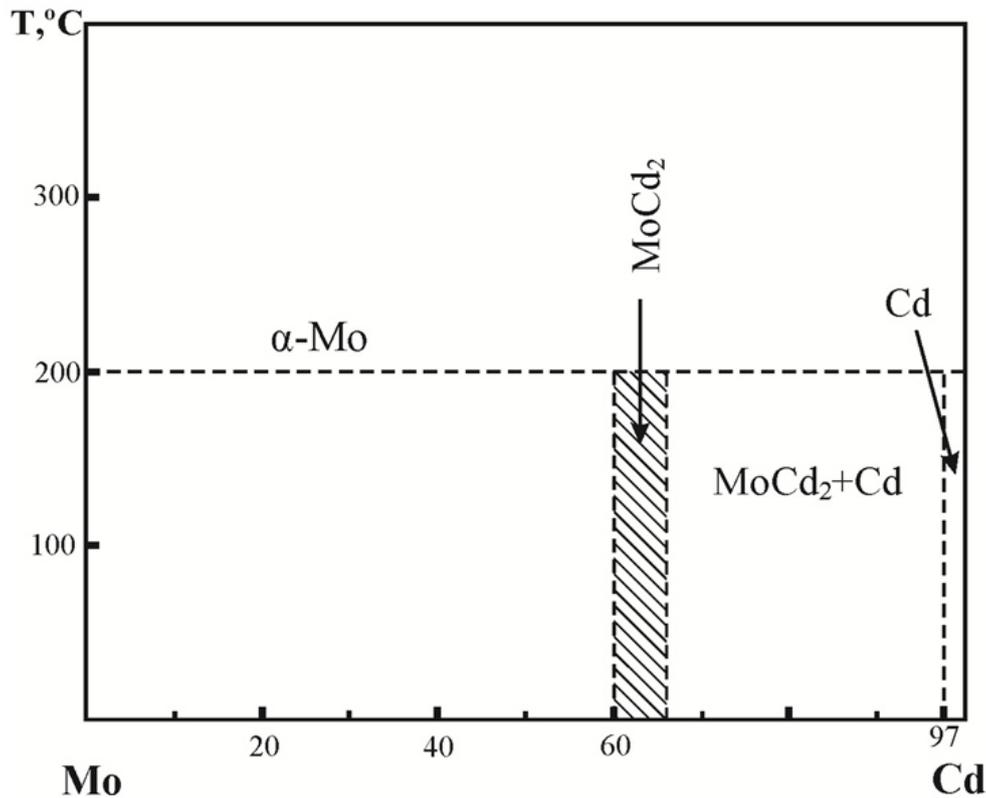


Figure 9. Position of the fields of phases existence in initial film coatings.

The metallic type of electrical conductivity (resistance decreases from 0.2 to 0.118 Ohm) was established in measurement of electrical resistance of MoCd₂ compound in a film with a temperature decrease from room temperature to 11 K (Figure 10).

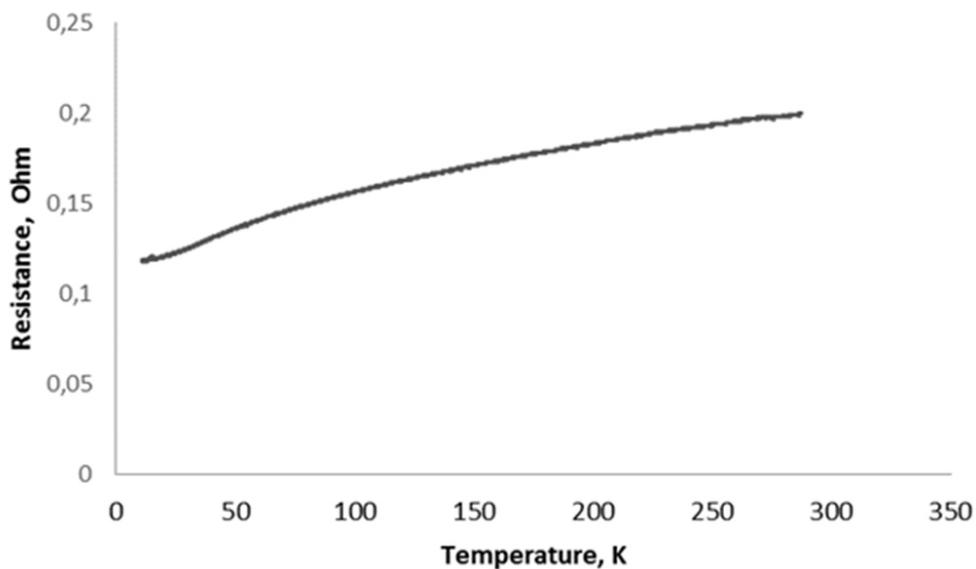


Figure 10. Dependence of MoCd₂ phase sample resistance on temperature.

Conclusion

Solid solutions or alloys of metals, which are immiscible under traditional preparation conditions up to concentration of 57.3 at. % Cd, were prepared for the first time using the sputtering in low-pressure plasma and the codeposition of the ultra-fine molybdenum and cadmium particles on moving substrates. Thus, the theory of thermal fluctuation melting and coalescence of small particles, which results in the formation of molybdenum and cadmium based alloy, has been confirmed.

We found a new phase, identified as MoCd₂ compound, at the concentration of (60-66) at. % Cd, prepared directly in formation of film coating with a tetragonal face-centered lattice with the parameters $a = 0.78231$ nm and $c = 0.77039$ nm. X-ray diffraction data to identify the intermetallic have been determined. Thermal stability of new intermetallic is limited by 200 °C.

The synthesized phase of MoCd₂ has a metallic type of conductivity.

This method of preparing alloys and synthesizing compounds can be used for other metallic systems, the components of which are immiscible under traditional preparation conditions.

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