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Application of Porous Tantalum for Formation of Energy Storage System

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--**ABSTRACT**--

This article describes a method for producing a porous tantalum during heat treatment of tantalum-cadmium coatings in a vacuum system with various ratios of tantalum and cadmium. Thesurface area was assessed by BET method showing that increase of specific surface area of the samples equals to 277.52 m^2/g in terms of porous tantalum. We studied the capabilities of the resulting porous structure to the charge accumulation and reviewed the processes occurring in porous tantalum during forming in the acid electrolyte.

Keywords: *tantalum, cadmium, porous structures, forming, capacity*

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I. INTRODUCTION

At present, the super-capacitors based on porous carbon electrodes [1-5] are applied more and more frequently as the storage of electrical energy. Due to the fact that the thickness of the double electric layer is extremely small, the energy stored up by the ionistor is higher compared with conventional capacitors of the same size.Therewith, the double electric layer instead of conventional dielectric greatly increases the area of the electrodesurface. Typical capacitance of ionistorequals to several farads at the rated voltage of 2-10 volts. But it is known that the highest quality electrolytic capacitors can be formed based on tantalum [6]. Therefore, creation of energy storage system that combines the advantages ofionistor(such as high-density charge storage) and capacitor (unlimited number of charge and discharge cycles, low internal resistance) is of great interest.In this regard,we studied the formation of porous tantalum structures and their ability to accumulate energy.

The papers [7,8] report about formation of thin β-Ta films bydc-magnetron sputtering. Subsequent heating to 1000 °C is accompanied by irreversible β-Ta→α-Ta transition, indicating the metastability of β-phase. In this regard, and based on previously obtained a priori data we attempted to form the porous structures from tantalumbased on tantalum-cadmium system. The potential formation of solid solutions of tantalum with metals having very different physical properties, such as cadmium, which vapor pressure can reach the atmospheric pressure (101325 Pa) at 766^oC, suggests the possibility of formation and preservation of pores in the matrix of tantalum film during evaporation of cadmium from double film system at low pressure.

II. MATERIALS AND METHODS

The studied material included the cadmium-tantalum films, prepared by thecodeposition of ultradispersed metal particles which were obtained by ion-plasma sputtering on cold substratesmade frommonocrystalline silicon Si, poli-cor and copper (due to methodical difficulties that requirebending of a sample to determine the specific surface area of porous tantalum).

Tantalum (99.96 mass.% of main element) and cadmium(99.99 mass.%) targets 40 mm in diameter and 4 mm thick were used in the experiments. Argon purified with a getter (sputtered titanium) was used as a plasma-forming gas for magnetron sputtering.

Theprocedureofalloycoatingssamplesformationimpliedtheion-plasmasputteringoftantalumandcadmiumandtheircooperativedepositiononsubstrates, that are movable with respect to plasma streams, in the form of short-period (with a low number of crystal lattice periods) sublayers that form films 0.7-3.1 μm thick. The velocity of substrate movement was $5\cdot10^{-2}m\cdot s^{-1}$. Sputtering was carried out simultaneously from two opposite magnetrons;the spacing between them was separated by the substrate moving unit.

The composition of coatingswascontrolled by varying the powerssupplied to tantalum and cadmium sputtering magnetrons. The ratio of deposited metals was checked by the weighing method according to the amounts of each sputtered and deposited metal during the formation of coatings. The film thickness was determined byRutherfordproton back-scattering spectrometry using a tandem accelerator UKP-2-1 and calculated based on the amount of deposited metals.

X-ray diffraction studies were performed using aD8 Advance (Bruker) diffractometer, copper radiation$\lambda_{k\alpha}$ = 0.154051 nmand a graphite monochromator. Thelatticeparameters were determined by averaging magnitudes obtained using all diffraction reflections of identifiable phase.Electron microscopic studies were performed using aJSM-8230 (JEOL) electron microprobe analyzer.High-temperature annealing's were performed using a vacuum high temperature furnace designed based on aURVT-2500setup.

The specific surface area of porous alpha-tantalum film was evaluated by BET (Brunauer, Emmett and Teller) methodaccording to low temperature nitrogen adsorption, which is based on the equation describing the multilayer adsorption (at pressure $>10^{-4}$ Pa). Nitrogen was usedto investigate the sorption process. We studied two film samples with equal mass quantity of tantalum: tantalum coating itself and tantalum-cadmium based film after evaporation of cadmium at 750°C in a vacuum. The samples, preliminarily degassed at 220 °C temperature,were cooled to temperature of liquid nitrogen. By measuring the pressure difference (Δp) in the system from initial (p_1)to certain equilibrium (p_p) we found the value $\Delta p = p_1 - p_p$, which determines the amount of adsorbed gas V. By measuringof$\Delta p$for severalp_1, we found the dependencies of $V=f(p_p)_{T=const}$ and determined the surface area. The AccuSorb instrument produced by US Micromeritics Company was used.

III. RESULTS AND DISCUSSION

At the stage of preliminary studies we prepared the samples of tantalum-cadmium films with0.7 - 86.3 at.%Cdconcentrationanddeterminedthecoatingsstructure.

The phase analysis of the samplesrevealedthat as the cadmium contentin Ta-Cd coatingsincreases,the following four concentration intervals can be distinguished:0-44.0 at.% Cd range, which corresponds to the existence of theβ-Ta phase; 48.8-56.6 at.% Cd range, which corresponds to the coexistence of the β-Ta and α-Ta phases; 59.6-66.2 at.% Cd range which corresponds to the α-Ta phase; 74.4-100 at.% Cd range which corresponds to the presence of cadmiumandamorphoustantalumphases.

To examine the thermal stability of the tantalum-cadmium films, the isochronous (1 h) vacuum annealing of the produced coatings at300-700°C (at a step of 100°C)was made.

SEM studies of the morphology of the coatings in the initial stateandafter annealing at 700°C at 30.4 at. % Cd concentration in the filmshowed a flat surface with fine projectedcrystallites with a lateral size of 300-400 nm. After annealing, sizes of crystallites decrease, small pores less than 100 nm in lateral size are present between some crystallites as the consequence of cadmium evaporation from solid solution.

Annealing of the coating with 59.6 at.%Cd, which, in the initial state, consists of the fine-grained mixture of α-andβ-Ta phases, showed the stability of the initial state up to the temperature 600°C, and at 700°Cthe major portion of β-Ta modification transforms intoα-tantalum. Electron-microscopic studies of the coating enabled us to determine the increase of through pores amount after annealing at 700°C comparing with the sample containing 30.4 at.%Cd.However, the expected significant development of the samples surface was not observed.

In this regard, the basic studies aimed at achieving the objectives of the study were conducted with the samples of tantalum-cadmium coatings within the concentration range 74.4-87.6 at. % Cd, which diffraction patterns of boundary compositions are presented in Fig.1.

The phase composition of coating with 74.4, 75.4 and 86.3 at.% Cd is represented by cadmium with a hexagonal lattice and amorphous phase of tantalum (Fig. 1), the amount of which (according to halo) decreases with increasing of cadmium content in the coating. The lattice parameters of cadmium slightly vary irregularly from a = 0.29769 nm and c = 0.56154 nm at 74.4 at.% Cdto$a$ = 0.29785nmand$c$= 0.56114nmat 87.6at. % Cd.

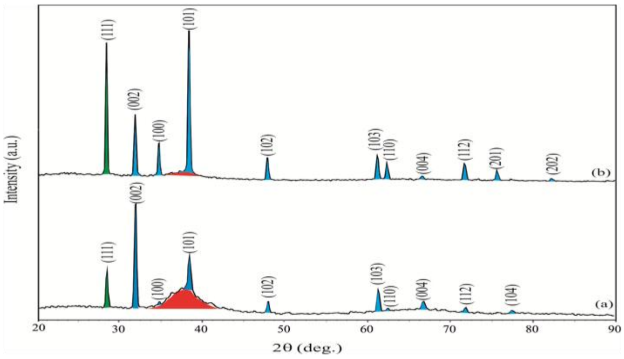


Fig. 1. X-ray diffraction patterns of Ta-Cd coatings withat. %Cd:(a) – 74.4; (b)– 86.3; 🟦 - Cd;🟥 - amorphous Ta; 🟩– Si (substrate) with the [111] orientation.

Thisfactenablesustostatethatthecoatingconsists of a solid solution of tantalum in the hexagonal lattice of cadmium.Since a portion of tantalum precipitates in the form of individual amorphous phase, it was impossible to calculate the amount of tantalum dissolved in cadmium.
Thecalculatedlatticeparametersof the phases in the film coating are shown in Table1.

Table1.The lattice parameters of the phases in the tantalum-cadmium coating

Cd concentration in the coating, at.%	Cd, hexagonal lattice, nm	
	a	*c*
74.4	0.29769	0.56154
75.4	0.29772	0.56136
87.6	0.29785	0.56114

Thefollowingwasfoundduringtheheattreatmentofthecoatingwith 74.4 at.%Cd. Intheinitialstage (Fig. 2, spectrum(a)) the X-ray diffraction pattern is characterized by a series of reflections belonging to cadmium and a wide halo belonging to amorphous tantalum. Afterannealingat300°C the reflections belonging to Cd disappear (Fig.2, spectrum(b)), and the reflection (110) belonging to α-tantalum with the lattice parameter a = 0.3315±0.0001 nm appears over the halo from amorphous Ta. As the temperature of isochronous annealing increases, the amount of amorphous tantalum decreases, and after annealing at 700°C (Fig.2, spectrum(c)) almost all tantalum of the coating becomes crystalline and represented by the α-Ta phase with the lattice parameter*a* = 0.3311±0.0001 nm. Therearenoreflections of cadmium phase observed in the spectra (b, c).

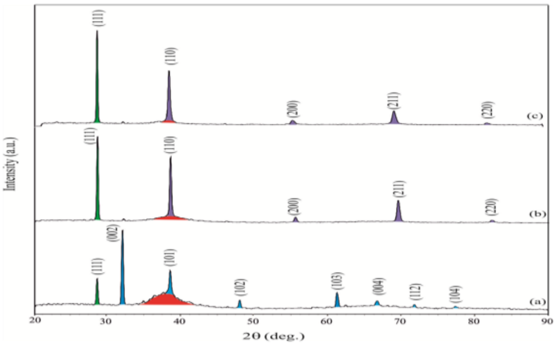
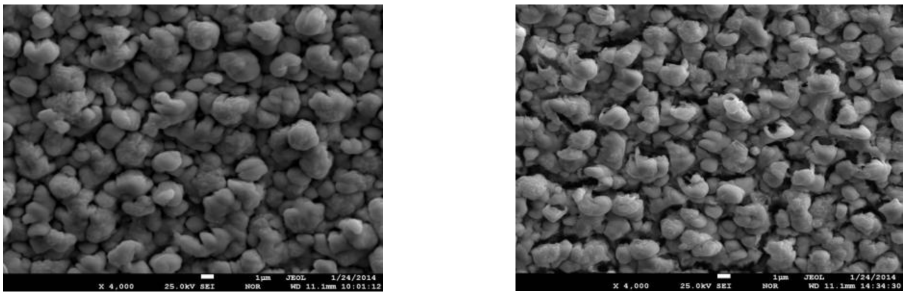


Fig.2. X-ray diffraction patterns of the sample with 74.4 at.% Cd: (a)–in the initial state; (b) - after annealing at 300°C; (c) – the same at 700°C; 🟦 - Cd; 🟪 – α-Ta; 🟩 – Si (substrate).

The morphology of the abovementioned coating is shown in Fig. 3. In the initial stage the coating is a conglomerate of closely adjoining rounded crystallites (Fig. 3a). Afterannealing, the surface of the coating is characterized by the presence of elements, the shape of which is similar to that of crystallites in the initial sample, i.e. not containing cadmium according to X-ray diffractometry data. However, accordingtomicroprobe analysis data, the film contains the traces of cadmium. In this case wecannotstatewhether through pores are present; however the probability of their presence is rather high. Theformationofthefilmstructurewiththedevelopedsurface occurs as follows, in our opinion. Thetemperatureincreaseresultsinmeltingofcadmiummesoparticles accompanied by displacement and concentration of amorphous tantalum on their surface and its following recrystallization in α-Ta. The evaporation of cadmium and crystallization of tantalum are aligned in time. Intheprocessofcadmiumevaporation,i.e.its transfer to the vapor phase, the scaly formations of alpha-tantalum of various shapes can be observed in the film coating.



a b

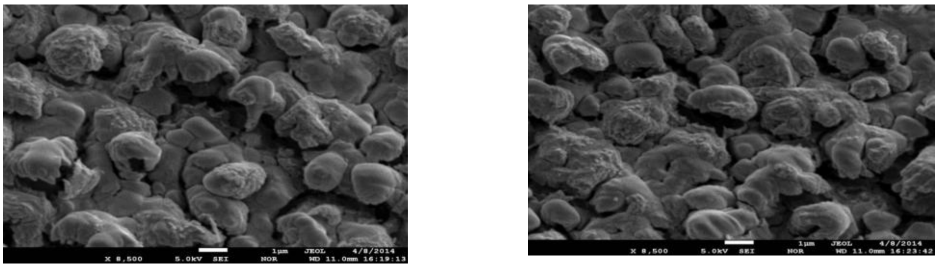

c d

Fig. 3.Electron-microscopicimagesofthecoatingwith74.4 at.%Cd with no annealing (a) and after annealing at 700^{o}Cfor 1 hour (b,c,d).

Thescalymicro-crystals, producedbythismethod, form the skeletal structure of the coating with a developed surface. The specific surface area increase was evaluated by BET method on two samples of the film coating, one is made from tantalum and the second sample was obtained by thermal treatment of tantalum-cadmium with concentration 79.3 at.% Cd, both samples are on copper foil of the same size. Application of copper foil as a substrate is required for deformation of the film samples (of maximum possible size as a result of low coating mass) to be placedin the inlet chamber of small volume. The tantalum mass after heat treatment at 750°C in a vacuum $1\cdot10^{-3}$Pafor 1 hour was identical~13 mg in both samples. Determination of specific surface area resulted in total surface area2.32 m^2/gfor copper foil with the continuous coating of tantalum and 5.95 m^2/gfor copper foil coated with porous tantalum. Since both pieces of copper foil are identical to each other and contain the same amount of tantalum on the surface, the surface increase is referred only to the porous tantalum (~13 mg). The increaseof the samples specific surface area equals to 277.52 m^2/g,in terms of porous tantalum.Considering that the BET method provides the correct results by low-temperature nitrogen adsorption for the pores in the size range (10 - 40) nm for the pore of 1-10 nm size, and the electron-microscopic images show that the coating contains theporesup to 2 μm, the real value of the porous tantalum specific surface area is much greater.

To check the ability of porous tantalum to accumulate the energy we sputtered the additionalcoatingswith68.6 at.% Cd and 64.7 at.% Cd on poly-core22×30 мм^{2}substrates,which were annealed in the vacuum at 700°C for 1 hour. Checking of porous tantalum ability to accumulate the energy was made by forming of the produced porous structures in H3PO$_4$-solutionwith 1 vol.% concentration. If we dip a metal, coated with the oxide film, as an anode in the electrolyte not dissolving metal and its oxide, the voltage applied in the oxide would cause the electric field. Under the influence of this field the film growth will occur on many metals due to migration of metal and oxygen ions through it [10].The process of oxide film formation underelectrochemical oxidation in the electrolytes is called forming. The oxide film of metals,preparedbyforming, often has a clearly expressed unilateral conductivity in the electrolyte, i.e.the valve properties: in case of anode inclusion of the oxidized metal the resistance of the film is larger in $10^3 – 10^4$than for cathode inclusion. The film, prepared byforming, is dense and thin; its thickness is proportional to the forming voltage, the proportionality coefficient is equal to 1.5-1.6 nm/V fortantalum [11].

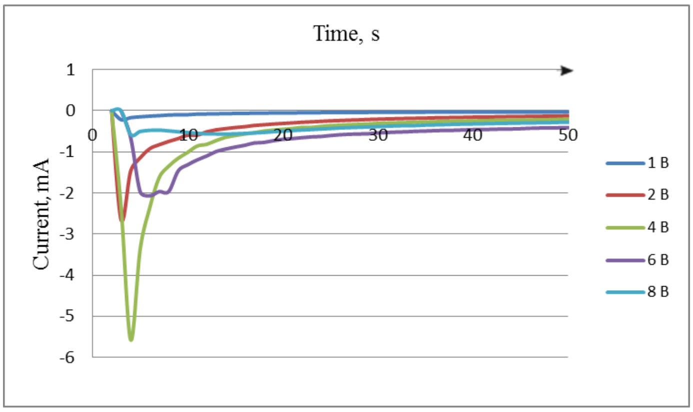


Fig. 4.Changeofformingcurrent bytimefor the porous tantalum producedfrom the coating with theinitial concentration 86.3 at.%Cd.

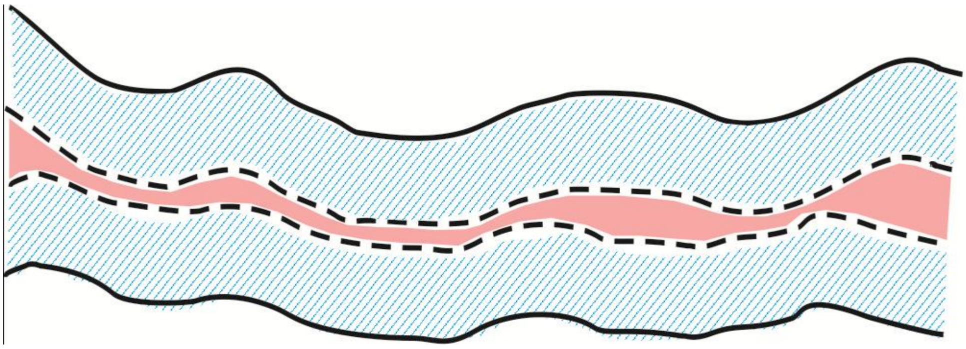


Fig. 5.The schemeofoxide layers mutual overlapping by forming of porous tantalum structure. Blue shading is a layer of tantalum oxide, pink shading is the remaining layer of tantalum.

Formingis performed at voltages of 0.5, 1, 2, 3, 4, 6 and 8 V. The capacitance of the resulting electrolytic capacitor was measured after each forming cycle. Fig. 4 shows the changes of forming current from time at various voltages of porous tantalum produced from the coatingwith the initial concentration 86.3 at.% Cd.Figure 4 shows that the forming peak current risesat the increase in voltage between 1 and 4 V, and the current monotonically decreases after the peak value. At theforming voltage 6 V the peak current is less than that at 4 V and the monotony of current fall is broken. We believe this is caused by the fact that with voltage increasing the total thickness of the tantalum oxide layers, formed on both sides of tantalum micro-scales intheelectrolytesolution, becomes equal to the thickness of micro-formations themselves (see. Fig. 5), therefore, destruction of individual elements of the formed oxide is possible, which results to fluctuations in formingcurrent.Accordingly, it can be concluded that the average thickness of tantalum flake in the coating, containing 86.3 at.% Cdafter sputtering and annealing at T = 700 °C in a vacuum,is about 12-13nm. At theformingvoltage 8 V the amplitude current is even lower, and the fluctuations increase, which, in our opinion, confirms this assumption. The dependence of forming current from time has a similar viewfor other coatings. After each completed cycleofporous tantalum forming we measured the capacity of the electrolytic capacitor.Two identical samples were prepared initially containing 68.6 at % Cd and annealed at 700 °C in a vacuum. The samples were removed to air after annealing in a vacuum, therefore one sample was immersed in the electrolyte after being in air (68.6 at.% Cd dry)and another was placed in the vacuum degassed cavity of 0.1 Pa pressure, which in vacuum was filled with electrolyte (68.6 at.% Cd wet) to check the filling of pores with electrolyte.After that the vacuum wetted sample was immediately placed in the electrolytic cell and subjected to forming. The results of capacitance measurement after each forming cycle are shown in Fig. 6.

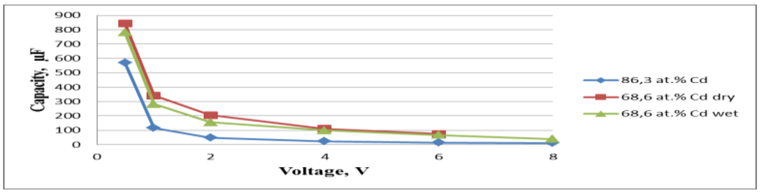


Fig. 6.Capacitance changeof electrolytic capacitors of porous tantalum from forming voltage

The tests have shown that both samples, containing 68.6 at.%Cd before heat treatment, have almost the same capacity. The sample with initial 86.3 at.% Cd has the capacity less than 68.6 at.% Cd coatings. That is, the capacity obtained after cadmium evaporation from the tantalum coating depends on the porosity degree of the resulting cellular structure, the thickness of tantalum cell walls and other parameters of the obtained structures that are largely determined by cadmium concentration and the sizes of ultra-dispersed particles during formation of the initial coatings. Based on the measurements of the deposited metal amount per the unit of area we have calculated the specific capacitance of the porous tantalum produced by this way, which is 83.4×10^3 µKl/gat1 V voltage.

IV. CONCLUSION

The cellular structures were produced by deposition of cadmium and tantalum coatings and subsequent vacuum annealing. In vacuum heat treatment (at 750^{o}C) of the tantalum-cadmium coatingswith the concentration of more than 74 at. % Cd, the last almost completely evaporateswith formation of the porous alpha-tantalum. Tantalum is presented by various scaled carcass crystals in the coating and preferably by globular shape crystals on the surface of the coating.

The measurement of the specific surface area of the porous tantalum coating revealed its increasing by at least 277.5 m^2/gTa, as compared to pure tantalum coating. The study of the produced cellular structures' ability to accumulate energy was performed. We obtained the value 83.4×10^3 µKl/g, characterizing the ability of porous tantalum to accumulate the charge. It is expected that the more detailed study of tantalum cellular structures formation and their subsequent forming will provide higher values.

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