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POSSIBILITY OF THE METHOD OF EXPLOSIVE ELECTRON-BEAM EVAPORATION-CONDENSATION IN VACUUM TO OBTAIN THE REFRACTORY AND COMPLEXLY DOPED COMPOUNDS FOR VARIOUS PURPOSES

Background. The method of explosive electron-beam evaporation-condensation of materials in vacuum opens up new possibilities for obtaining materials containing components, with a significant difference in the elasticity of the vapor, as well as complex alloyed compounds. This technology is promising for the production of various types of materials of controlled chemical composition in the form of powder products.

Objective. The purpose of the paper is to study the possibilities of the method of electron-beam explosive evaporation-condensation of materials in vacuum to obtain in granular and film form refractory and composite materials based on tungsten and copper, and complex alloyed materials based on titanium.

Methods. The method of explosive evaporation-condensation was used to obtain vapor-phase refractory, composite and complex alloyed materials based on the WC–W₂C, Cu–W and Ti–Si–Zr–Nb systems. The experiments were carried out on the L-4 electron-beam installation, which was developed by the Scientific and Production Company “ELTECHMASH” (Vinnytsia, Ukraine) in cooperation with the Frantsevich Institute for Problems of Materials Science, NAS of Ukraine. The changes in the chemical composition and morphology of obtained products depending on the deposition conditions in vacuum were studied.

Results. For the first time, refractory alloys and composite materials based on tungsten and copper and complex alloyed compounds based on titanium were obtained in granular form by explosive evaporation-condensation in vacuum. Using this technology makes it possible to control the chemical composition and morphology of the produced powder products, widely used in various fields of science and technology.

Conclusions. The technological conditions for the production of materials containing components with a significant difference in vapor pressure by the method of explosive evaporation-condensation in vacuum are determined. The method allows obtaining granular and film deposition products with refining of materials with respect to oxygen and some metal impurities.

Keywords: electron-beam technology; method of explosive evaporation-condensation in vacuum; tungsten and copper based refractory and composite materials; complex alloyed materials based on titanium.

Introduction

Dispersed powders of metals and alloys play an important role in solving problems of creating material and products with controlled complex of properties. Material based on eutectic mixture of tungsten carbides WC and W₂C is widely used as a component of wear-resistant surfacing material, working under conditions of intense abrasive wear under moderate impact loads, for example, in roller bits, drill pipe locks, and other applications [1]. Materials of the Cu–W system are traditionally manufactured by powder metallurgy and are widely used in the electrical industry. Traditional technology of producing electrocontact materials include multi-stage process for obtaining a mixture of powders of the required chemical composition, compressing them and conducting high-temperature processing in

controlled gas media (restorative, neutral) or in vacuum. Until recently, the manufacturing technology of these materials were based on powder metallurgy high-cycle methods, including such technological operations as the production of powders, their subsequent compaction (cold or hot pressing); high temperature treatment; and/or deformation processing of obtained materials and products [2]. Investigation of the conditions for obtaining Ti-based complex-alloys is dictated by a unique complex of properties, which makes them an indispensable component for medical purposes [3]. Recent studies have shown that a compromise between the required set of mechanical properties and biomedical constraints can be obtained by doping Ti with the most biocompatible elements such as Si, Nb, Zr, and Mo, which are stabilizers of the α -phase of Ti [4].

Electron-beam technology of evaporation-condensation of materials in vacuum promotes new opportunities for obtaining composite powders (from nanoscale to several hundred micrometers) in a wide range of quantity components, phases, dispersed inclusions, and other parameters [5]. Since the dependence of vapor pressure and evaporation rate on temperature for various metals can be quite large, fractionation in composition is one of the main problems of evaporation-condensation in vacuum for obtaining materials which have components with a significant difference in vapor pressure. It is known that during evaporation of alloys consisting of components with different vapor elasticity, the degree of their fractionation in composition decreases with increasing temperature and this regularity was used by Harris and Siegel when developing the high-speed method of evaporation of alloys [6]. The method consists in the fact that particles of finely ground material (alloy of the required composition or mixture of components) are uniformly fed to the evaporator, and heated to the temperature of intensive evaporation of the most difficult volatile components of the alloy. Due to the ultra-fast heating of the alloy, its explosive evaporation occurs, which is characterized by matching the composition of the starting material, vapor over the evaporator and condensate. The research in this direction was started at

the Frantsevich Institute for Problems of Materials Science (NASU) in collaboration with the Scientific and Production Company "ELTECHMASH" (Ukraine).

Problem statement

The main purpose of these studies is to discover the possibilities of obtaining powder products of different chemical composition, including components with a significant difference in vapor elasticity by the method of explosive evaporation-condensation in vacuum.

Results and discussion

SPC "ELTECHMASH" developed a new electron-beam installation modification L-8 (Fig. 1), which allows solving a wide range of tasks, in particular, to simulate various versions of structures in order to test modern concepts of physics, chemistry and solid mechanics and create materials with a given structure and properties for solving a variety of applied problems. For the first time, a successful attempt was made at this installation to obtain, by explosive evaporation-condensation in vacuum, powdered composite materials consisting of components with a significant difference in vapor pressure,

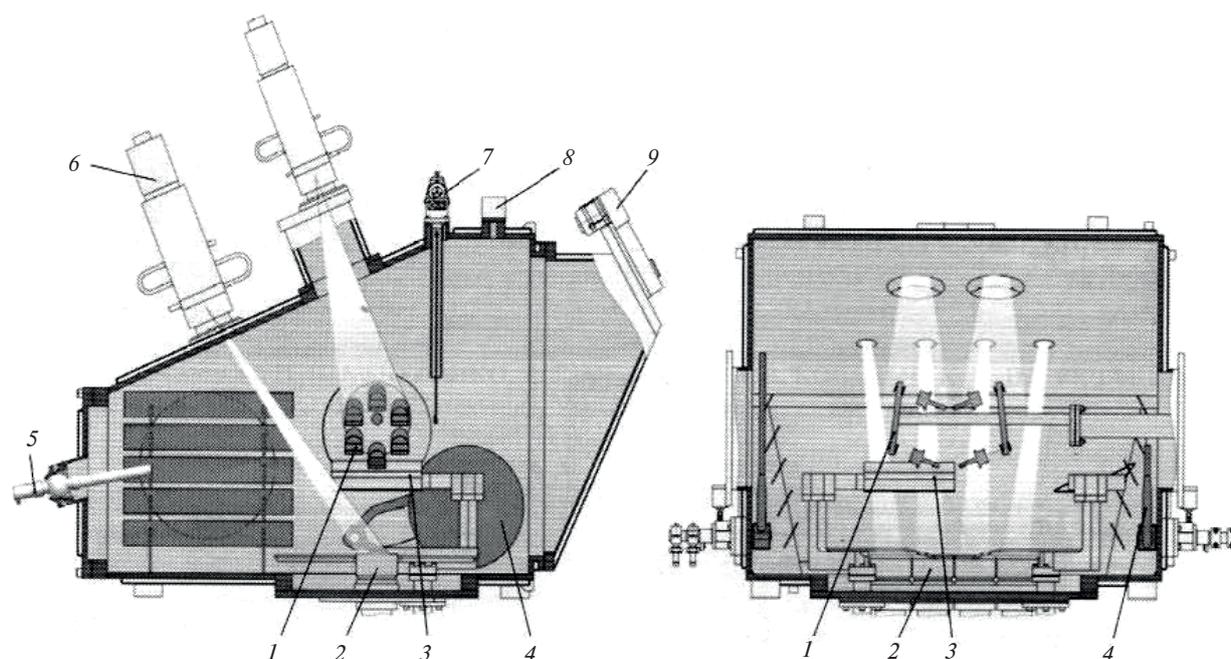


Fig. 1. Scheme of the electron-beam installation L-8: 1 – cassette with vanes; 2 – crucibles; 3 – evaporator dampers; 4 – gate valves; 5 – ball inlet to install the pyrometer; 6 – electronic gun; 7 – weight sensor; 8 – process gas closing valve; 9 – viewing system

in particular, materials based on tungsten, copper, and titanium.

In the process (working) chamber of the installation, the vacuum is maintained at the level of $5 \cdot (10^{-2} - 10^{-3})$ Pa, and the vapor flow is deposited on the substrate or finished parts requiring coating. Loading of blanks for evaporation into the mechanisms is carried out from above through crucibles. Electronic guns are installed on the top cover of the working chamber. The valves are designed for shielding blanks during heating to establish a stable technological mode of evaporation and to protect the valves, which separate the sluice and working chambers from dust and high temperatures during the process [7].

Temperature measurement of products in the installation is carried out using a high-tech infrared pyrometer and is controlled by special software. Entering a small amount of gas (argon) in the process of evaporation leads to dispersion of the vapor stream, which allows a more uniform deposition of the material on the substrate [5]. The installation also provides for the possibility of partial ionization of the process gas and metal vapor by supplying a negative potential to the workpieces (up to 2 kV). Ionization helps to obtain a precipitate with a favorable structure, devoid of crystallographic defects that occur in the condensed layer during gas inlet. The full technological process of material obtaining occurs without depressurization of the process chamber. For heating products there are two electron guns with a capacity of 60 kW. The unit used gas discharge electron beam guns; Use of a cold cathode of low-alloyed aluminum alloy eliminates any distortion, which makes it possible to obtain a stable electron beam. The total cathode life is about 1000 hours. The use of an electromagnetic focusing system in cold cathode guns makes it possible to obtain a high-quality beam with a minimum focal spot diameter of about 10 mm.

In the first time, a successful attempt was made at the installation to obtain powder composite products, which include components with a significant difference in vapor pressure. In particular, conditions for production of composite powders of such refractory materials widely used in industry based on system of tungsten carbides and tungsten-copper, as well as titanium-based complex alloyed systems were studied. The placement of the main nodes in the working chamber of the installation was carried out in accordance with the scheme given in Fig. 2.

The following materials were used as source materials: cast tungsten carbide grade TUU 24.6-33876998-001-2006 (OOO SpetsPromSplav, Russia)

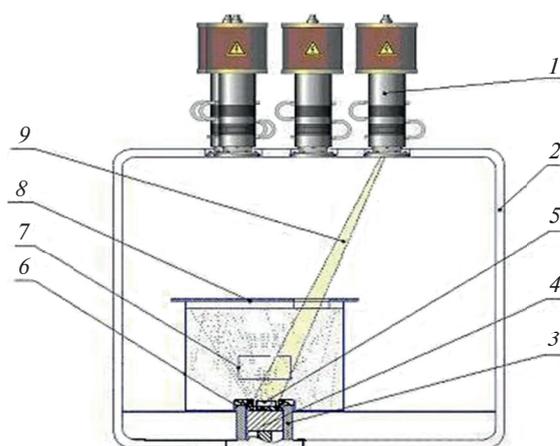


Fig. 2. Schematic placement of main units in the working chamber of the L-8 installation: 1 – electron beam guns; 2 – technological camera; 3 – crystallizer; 4 – device for supplying the raw material to the evaporation zone; 5 – evaporating material; 6 – water-cooled crucible; 7 – viewing window for observation; 8 – sarcophagus with a water-cooled lid and an opening for passage of an electron beam; 9 – trajectory of the path of an electron beam

after crushing; copper-tungsten vapor-phase condensate production waste and crushed alloy ingots based on composition Ti–Si–Zr–Nb, developed by the Frantsevich Institute for Problems of Materials Science, and obtained by electron beam evaporation-condensation in vacuum. The materials were used in the form of ingots or pressed pieces, if the raw material was in powder form. The disposable loading of the preforms into the copper crystallizer, for evaporation of the starting materials, ranged from 1.9 to 3 kg. To collect evaporation products on top of the crystallizer, a steel cylinder-shaped sarcophagus was installed with uncooled walls, which was covered with a water-cooled lid, with an opening for passage of an electron beam.

In the course of experiments, the possibility of obtaining film and granular deposition products of refractory and alloyed materials was established by using a sarcophagus with cooled and non-cooled walls. Determination of the granules' shape was carried out by quantitative metallography methods on thin sections [8]. Sections were prepared by standard methods from pressurized mixtures of granules with epoxy. The obtained samples were pressed and hardened, grinded and polished on an aqueous suspension of chromium oxide. Quantitative micro-

structure analysis and microhardness of granules' cross-section (after etching thin sections) were carried out with an "AMIS" image analyzer [9].

In our experiments, it was possible to obtain film and granulated precipitation products (Fig. 3) for one technological cycle, which have a chemical composition close to the original (Table 1). It should be noted that due to conducting experiments in vacuum, the oxygen content in the deposition products decreases by almost three times (from 0.30–0.35 and 0.15–0.1 % mass. accordingly).

Film and granulated products of deposition of the material based on eutectic mixture of tungsten carbides WC and W₂C were obtained. It has been established that the use of powder materials with a spherical shape particle increases the flowability of the powder and, accordingly, increases the stability of the metering devices, and in addition, contributes to improving the wear resistance of the coating. Grading analysis of the composition of the granular product showed that more than 80 % of the total mass of particles have sizes from 500 μm and above (up to a maximum of 3 mm); fractions of 500/350 and 350/100 microns occupy 3.8 and 13.5 % of mass accordingly, the rest is smaller fractions.

In the cross-section, the granules have a structure typical of the cast alloy of this composition [1] (Fig. 3, *b*). The main part of the granules has dimensions from 3 mm to 500 μm and more than 80% is characterized by a sphere factor of 0.98–1 (calculated using the formula for the Saltykov form [8]). Microhardness in particle cross-sections of the granulated material varies within 25 to 30 GPa, reaching up to 40 GPa at individual sites of structure, which is higher, than the microhardness of tungsten carbides of industrial production (TUU 24.6-33876998-001-2006).

Composite materials based on Cu and W also participated in the experiments, and the difficulty of obtaining them being determined by the substantial difference in the elasticity of the vapors of the main

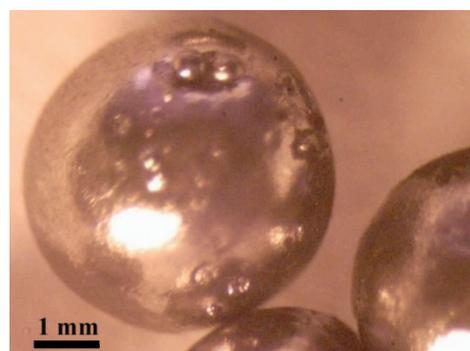
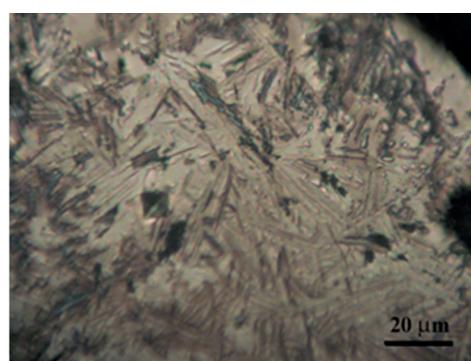
*a**b*

Fig. 3. General form (*a*) and microstructure (*b*) of granulated deposition products obtained by evaporation-condensation of the material based on the eutectic WC and W₂C mixture

components. In our experiments only a film product has been formed, the superficial of which has a transverse porosity (Fig. 4).

The chemical composition of the film is close to the original (Table 2). The increased fragility of the product of evaporation of copper and tungsten composites obtained in our experiments gives us the opportunity for its further easy dispersion to obtain composite powders of a given chemical composition.

Table 1. Elemental composition of the initial material and final products obtained by evaporation-condensation of the material based on the eutectic WC and W₂C mixture

Material	Composition, % mass.												
	W	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Y	Zr	Mo	
Initial	Basis	0.40	0.21	0.30	0.01	0.15	0.09	0.62	0.54	≤10 ⁻³	10 ⁻³	0.08	
Deposition products:	film	Basis	0.96	0.09	1.92	0.06	1.09	0.27	5.3	15.2	≤10 ⁻³	0.03	–
	granular	Basis	0.76	0.20	0.90	≤10 ⁻³	0.09	≤10 ⁻³	≤10 ⁻³	–	–	–	0.06

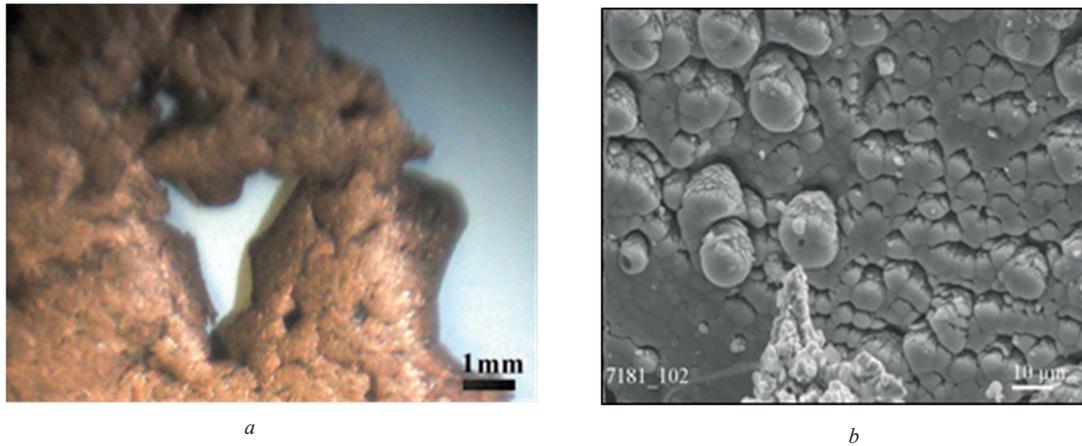


Fig. 4. General view (a) and surface relief of deposition products (b) obtained by evaporation-condensation of composites Cu-W

Dispersed product was tested at experiments for laser deposition using laboratory laser installation developed by IPMS of NASU, in which a mixture of argon and hydrogen appears as a plasma transporting powder on a rotating disk. The power of the laser installation in various tests ranged from 23 to 38.5 kW. The results of experiments show that the resulting spray powder takes a round shape with a spherical coefficient of particles at a level of 0.6–0.7. But this process of powder spraying in plasma is

characterized by rather significant mass loss (up to 30%), and requires further research to improve.

In our experiments, the complex alloy Ti–Si–Zr–Nb used, which belongs to the group of alloys for medical purpose, developed in IPMS of NASU [3] (Table 3).

The deposition products obtained by condensing the material on the non-cooled surfaces of the chamber got the form of the film product, whereas

Table 2. Elemental composition of the initial material and final products obtained by evaporation-condensation of the composites Cu–W

Material	Composition % mass.								
	Cu	Al	Fe	Cr	Co	Ni	Nb	Ag	W
Initial	70	0.85	0.47	0.38	0.13	0.06	0.06	0.85	Remain
Deposition products	76	0.89	0.38	0.12	0.1	0.06	0.2	0.28	Remain
Candle-end	12.97	–	0.09	–	–	–	–	–	Remain

Table 3. Composition of initial materials and deposition products obtained by evaporation-condensation of Ti–Si–Zr–Nb alloy

Material	Composition %, mass.									
	Ti	Al	Si	Fe	Cu	Y	Zr	Nb	Mo	
Initial	Basis	0.18	1.07	0.15	0.11	0.01	3.29	15.53	0.35	
Deposition products: film granular with dimensions, mkm	Basis	0.23	0.16	1.52	0.15	–	0.74	3.99	0.09	
	≥200	Basis	0.14	0.50	0.10	0.08	0.01	4.01	20.79	0.41
	<200	Basis	0.06	1.00	0.05	0.20	0.02	2.70	14.10	0.40

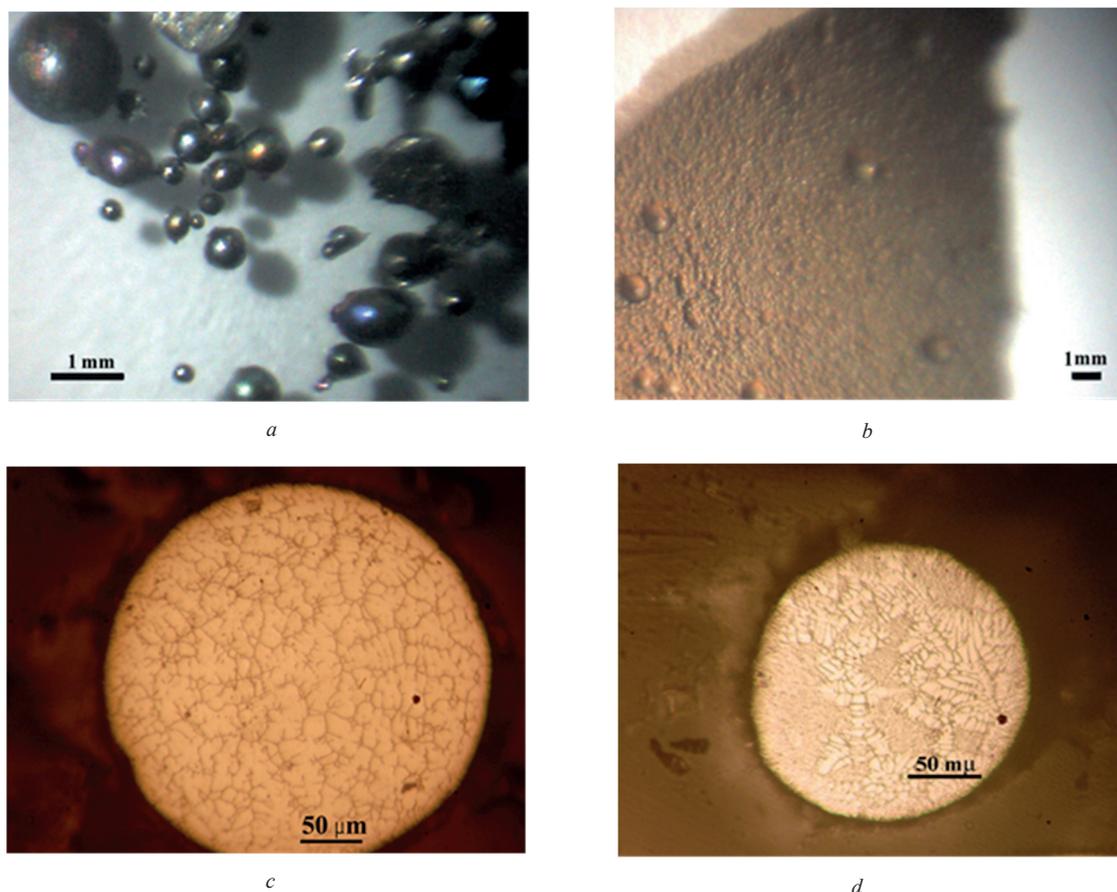


Fig. 5. General view of granulated (*a*) and film (*b*) deposition products obtained by evaporation-condensation of an alloy of the Ti–Si–Zr–Nb system in vacuum and the main types of microstructure in the cross section of granules (*c*, *d*)

products deposited on the cooled surface of the sarcophagus – form of a granular product with a particle shape, preferably close to the spherical (Fig. 5).

The granules have a shape close to spherical in the size range from 1–3 mm to several 10 μm. Chemical composition of the obtained products (see Table 3), showed that in the conditions of explosive evaporation-condensation there is a tendency to preserve the main refractory components in the composition of the granules formed in conditions of rapid crystallization. Inspection of the microstructure in cross section of the granules showed that large number of granules was found with a dispersed polygranular disoriented microstructure (Fig. 5, *c*). Relatively large grain sizes (20–30 μm) and their equilibrium shape indicate that the granule formation was carried out under lower cooling conditions than the critical ones. Many granules have a dendritic structure and length along the main axis of dendrites varies from submicron to tens of microns, which indicates non-equilibrium crystallization

conditions (Fig. 5, *d*). In general, the microstructure of the granules is similar to the structure of cast materials of this composition, which is characterized by the presence of a mixture of α and β solid solutions based on titanium [4].

Conclusions

Refractory and composite materials based on tungsten (WC–W₂C), copper (Cu–W) and titanium (Ti–Si–Zr–Nb) were obtained by the method of explosive evaporation-condensation in vacuum. The technological conditions of the evaporation-condensation in the vacuum of materials with components with significantly different vapor elasticity, in which the film and granular product of deposition with the restored basic chemical composition is formed, are determined.

It has been established that by forcing evaporation and material due to the increase of the power of the electron beam and the temperature lowering

of the substrate, it is possible to create conditions for obtaining the granular product with the simultaneous refining of the material with oxygen and some metallic impurities.

Further research should be developed towards study of the influence of technological factors on the

rate of evaporation and deposition of various components under conditions of superfast heating in vacuum in order to develop technologies for producing materials of complex composition with a predefined composition and morphology.

References

- [1] G.V. Samsonov *et al.*, *Tungsten Carbides*. Kyiv, SU: Naukova Dumka, 1974.
- [2] *Sintered Materials for Electrical Engineering and Electronic*, G.G. Gnesin, Ed. Moscow, SU: Metallurgy, 1981.
- [3] Fisk *et al.*, "Titanium based ceramic reinforced alloy for use in medical implants", U.S. Patent 2014/0105781 A1, 17 Apr. 2014.
- [4] *Titanium Alloys for Biomedical Applications* [Online]. Available: <http://www.dierk-raabe.com/titanium-alloys/biomedical-titanium-alloys>
- [5] B.A. Movchan and I.S. Malashenko, *Heat-Resistant Coatings Deposited in Vacuum*. Kyiv, SU: Naukova Dumka, 1983.
- [6] L.V. Harris and B.A. Siegel, "A method for evaporation of alloys", *J. Appl. Phys.*, vol. 19, no. 8, pp.739–741, 1948.
- [7] N.I. Grechanyuk *et al.*, "Industrial electron-beam installation L-8 for deposition of heat-protective coating on turbine blades", *Paton Welding Journal*, vol. 10, pp. 45–50, 2014. doi: 10.15407/tpwj2014.10.09
- [8] *Stereology in Material Science*, K.S. Cherniavskii, Ed. Moscow, SU: Metallurgy, 1977.
- [9] O.I. Khomenko and O.V. Khomenko, "Microstructural analysis software package", *Powder Metallurgy and Metal Ceramics*, vol. 46, no. 1-2, pp. 100–104, 2007. doi: 10.1007/s11106-007-0016-6

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ЗАСТОСУВАННЯ МЕТОДУ ВИБУХОВОГО ЕЛЕКТРОННО-ПРОМЕНЕВОГО ВИПАРОВУВАННЯ-КОНДЕНСАЦІЇ У ВАКУУМІ ДЛЯ ОТРИМАННЯ ТУГОПЛАВКИХ І СКЛАДНОЛЕГОВАНИХ СПЛАВІВ РІЗНОГО ПРИЗНАЧЕННЯ

Вступ. Метод вибухового електронно-променевого випаровування-конденсації матеріалів у вакуумі відкриває нові можливості для отримання матеріалів, що містять компоненти, з істотною різницею в пружності пару, а також складнолегованих сплавів. Ця технологія перспективна для виробництва різних видів матеріалів заданого хімічного складу у вигляді порошкових продуктів.

Мета дослідження. Вивчити можливості методу електронно-променевого вибухового випаровування-конденсації матеріалів у вакуумі для отримання в гранульованому і плівковому вигляді тугоплавких і композиційних матеріалів на основі вольфраму і міді, а також складнолегованих матеріалів на основі титану.

Методика реалізації. Метод вибухового випаровування-конденсації застосували для отримання парофазових тугоплавких, композиційних і складнолегованих матеріалів на основі систем WC–W₂C, Cu–W і Ti–Si–Zr–Nb. Експерименти проводили на електронно-променевої установці L-4, яка розроблена науково-виробничим підприємством "ЕЛТЕХМАШ" (м. Вінниця, Україна) спільно з Інститутом проблем матеріалознавства ім. І.М. Францевича НАН України. Вивчено зміни хімічного складу і морфології отриманих продуктів залежно від умов осадження у вакуумі.

Результати дослідження. Вперше методом вибухового випаровування-конденсації у вакуумі отримано в гранульованому вигляді тугоплавкі сплави і композиційні матеріали на основі вольфраму та міді, а також складнолеговані сплави на основі титану. Використання цієї технології дає можливість регулювати хімічний склад і морфологію вироблених порошкових продуктів, які мають широке застосування в різних галузях науки і техніки.

Висновки. Визначено технологічні умови отримання методом вибухового випаровування-конденсації у вакуумі матеріалів, що включають компоненти з істотною різницею в пружності пару. Метод дає змогу отримувати гранульовані та плівкові продукти осадження з рафінуванням матеріалів по кисню і деяких металевих домішках.

Ключові слова: електронно-променева технологія; метод вибухового випаровування-конденсації у вакуумі; тугоплавкі й композиційні матеріали на основі вольфраму і міді; складнолеговані сплави на основі титану.

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ПРИМЕНЕНИЕ МЕТОДА ВЗРЫВНОГО ЭЛЕКТРОННО-ЛУЧЕВОГО ИСПАРЕНИЯ-КОНДЕНСАЦИИ В ВАКУУМЕ ДЛЯ ПОЛУЧЕНИЯ ТУГОПЛАВКИХ И СЛОЖНОЛЕГИРОВАННЫХ СПЛАВОВ РАЗЛИЧНОГО НАЗНАЧЕНИЯ

Введение. Метод взрывного электронно-лучевого испарения-конденсации материалов в вакууме открывает новые возможности для получения материалов, содержащих компоненты, с существенной разницей в упругости пара, а также сложнолегированных сплавов. Данная технология перспективна для производства различных видов материалов заданного химического состава в виде порошковых продуктов.

Цель исследования. Изучить возможности метода электронно-лучевого взрывного испарения-конденсации материалов в вакууме для получения в гранулированном и пленочном виде тугоплавких и композиционных материалов на основе вольфрама и меди, а также сложнолегированных материалов на основе титана.

Методика реализации. Метод взрывного испарения-конденсации применили для получения парофазных тугоплавких, композиционных и сложнолегированных материалов на основе систем WC–W₂C, Cu–W и Ti–Si–Zr–Nb. Эксперименты проводили на электронно-лучевой установке L-4, разработанной научно-производственным предприятием "ЕЛТЕХМАШ" (г. Винница,

Україна) спільно з Інститутом проблем матеріалознавства ім. І.Н. Францевича НАН України. Вивчені зміни хімічного складу та морфології отриманих продуктів залежно від умов осадження в вакуумі.

Результати дослідження. Вперше методом вибухового випаровування-конденсації в вакуумі отримані гранульовані тугоплавкі сплави та композиційні матеріали на основі вольфраму та міді, а також складнолегіровані сплави на основі титану. Використання даної технології дає можливість регулювати хімічний склад та морфологію вироблених порошкових продуктів, які мають широке застосування в різних галузях науки та техніки.

Висновки. Визначено технологічні умови отримання методом вибухового випаровування-конденсації в вакуумі матеріалів, що містять компоненти з суттєвою різницею в еластичності пара. Метод дозволяє отримувати гранульовані та плівочні продукти осадження з рафінуванням матеріалів по кисню та деяким металічним домішкам.

Ключові слова: електронно-лучева технологія; метод вибухового випаровування-конденсації в вакуумі; тугоплавкі та композиційні матеріали на основі вольфраму та міді; складнолегіровані сплави на основі титану.

Рекомендована Радою
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