Materials Physics and Mechanics 47 (2021) 787-795
Research article

Received: August 9, 2021
Accepted: November 15, 2021

COLD SPRAY DEPOSITION OF COMPOSITE COPPER-TUNGSTEN COATINGS

V.S. Shikalov✉, A.A. Filippov, T.M. Vidyuk

Khristianovich Institute of Theoretical and Applied Mechanics SB RAS, Novosibirsk, Russia

✉ v.shikalov@gmail.com

Abstract. The work is devoted to the experimental study of the mechanical properties of cold sprayed composite copper-tungsten coatings. Using the instrumental indentation technique, mechanical tests of coatings containing tungsten microinclusions in the content range 0-32 wt.% were carried out. It was shown that an increase in the content of tungsten in the copper matrix of the coating promotes an increase in the microhardness and elastic modulus of the coating. Adhesion strength tests of coatings were carried out, which showed that an increase in the content of tungsten in the feedstock mixture leads to a significant increase in the value of the adhesion-cohesion strength of the coating.

Keywords: cold spray, coating, composite, copper-tungsten, microhardness, elastic modulus, adhesion strength

Acknowledgements. *The research was funded by RFBR and Novosibirsk region, project number 20-48-543011. The study was conducted at the Equipment Sharing Center «Mechanics» of ITAM SB RAS.*

Citation: Shikalov V.S., Filippov A.A., Vidyuk T.M. Cold spray deposition of composite copper-tungsten coatings // Materials Physics and Mechanics. 2021, V. 47. N. 5. P. 787-795. DOI: 10.18149/MPM.4752021_12.

1. Introduction

Tungsten is one of the heaviest, hardest, and most refractory metals. Tungsten-based alloys are distinguished by high hardness, heat-, acid- and wear resistance, and the high density of tungsten makes its alloys an indispensable material for protection against ionizing radiation. Tungsten and the substances that make up its heavy alloys (Cu, Ni, Fe) have significantly different physical properties, primarily the melting point. It is impossible to get an alloy from them in the usual sense because, at the melting point of tungsten (3420ºC), most metals are in a gaseous state, therefore the so-called pseudo-alloys are produced only by powder metallurgy methods, which is described in detail in reviews [1-4].

The use of copper-tungsten composites provides high electrical and thermal conductivity at elevated temperatures in cases where the use of copper contacts is not possible. To produce such refractory conductive coatings, gas-thermal methods can be used, in particular, plasma spraying [5-8] and high-velocity oxygen fuel (HVOF) spraying [9]. From the analysis of published works, it can be concluded that these methods allow obtaining sufficiently dense and hard coatings of various thicknesses and compositions, including gradient ones, by flexibly varying the content of components in each sprayed layer. However, the resulting coatings are often characterized by high thermal stresses and a significant

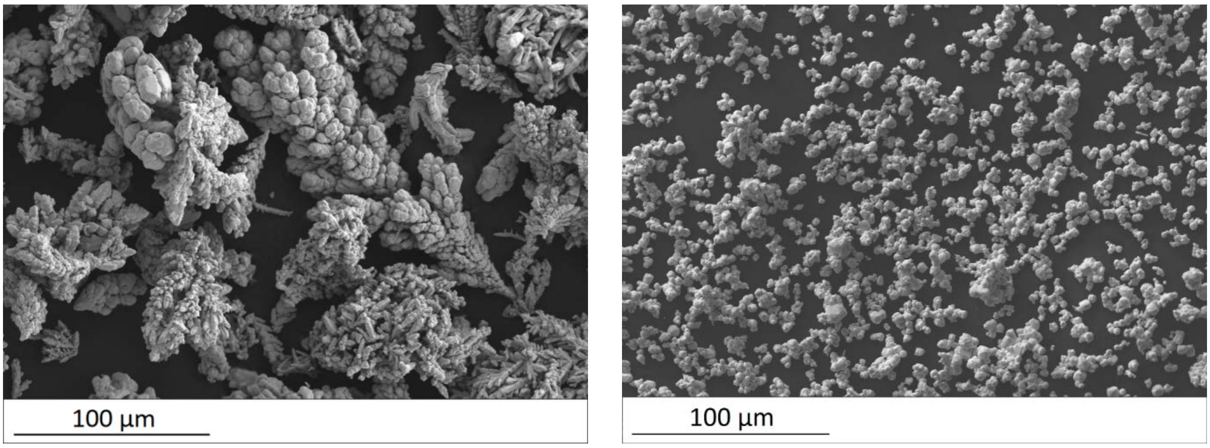
http://dx.doi.org/10.18149/MPM.4752021_12

number of oxides due to the effect of high temperatures on the sprayed material and the substrate, which in turn can adversely affect their mechanical properties.

An attractive alternative for producing tungsten-containing coatings is the cold spray method, which makes it possible to obtain coatings with low porosity, uniform distribution of components, and preservation of their phase composition [10-16]. The temperature of the working gas during cold spraying is always lower than the melting point of the sprayed material, therefore the formation of oxides and thermal stresses in cold sprayed coatings are minimized or completely eliminated in comparison with gas-thermal coatings. The kinetics of cold spraying of copper-tungsten coatings, as well as the microstructure, phase composition, and some properties, are described in sufficient detail in [13-16]. However, in spite of the fact that cold spray allows to flexibly vary the ratio of components in the resulting coating and, therefore, to control its mechanical properties, these issues have not been fully studied in the works cited. The present work is devoted to an experimental study of the effect of the tungsten microparticles content both in the feedstock mixture and in the copper matrix of the cold sprayed coating on its mechanical properties (microhardness, elastic modulus, adhesion strength).

2. Materials and methods

Copper and tungsten powders with an average size of 52 μm and 9 μm, respectively, were used for cold spraying the coatings. Microphotographs of the powders are shown in Fig. 1.



a) b)

Fig. 1. Micrographs of copper (a) and tungsten (b) powders used for cold spraying

From these powders using a V-shaped mixer were prepared mixtures with content of tungsten 0, 25, 50, and 75 wt.%. Plates made of AlMg2 alloy sized of 30×30×4 mm were used as substrates. Before spraying, the substrates were sandblasted with alumina abrasive.

The mixtures were sprayed on an experimental high-pressure cold spray facility (ITAM SB RAS, Russia) [17] using an axisymmetric de Laval nozzle. The accelerating gas was the air with a stagnation pressure of 4 MPa and a stagnation temperature of 773 K. The standoff distance was 30 mm. The nozzle was moved relative to the substrate at a speed of 200 mm/s along a zigzag trajectory with an offset step of 3 mm to obtain one coating layer over the entire substrate surface. The final thickness of all coatings was 500 ± 50 μm and was achieved by varying the number of layers.

The chemical composition of the coatings was determined by energy-dispersive X-ray spectroscopy using an X-Max 80 mm^2 spectrometer (Oxford Instruments, UK), which was mounted on a scanning electron microscope (SEM) EVO MA15 (Zeiss, Germany).

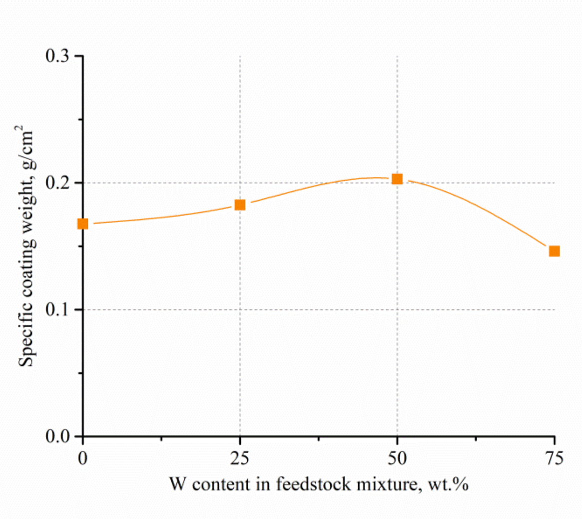
Mechanical tests to measure the microhardness and elastic modulus of coatings were carried out using a 4D+ nanoindenter (Nanoscan, Russia) with a module for instrumental indentation [18] by the method of Oliver and Pharr [19]. Berkovich tetrahedral diamond pyramid with an angle between the axis and the facet of 65° was pressed into the polished cross-section of the coating at a constant loading rate of 0.01 N/s for 10 s until the target load value of 0.1 N was reached, followed by holding for 3 s and unloading within 10 s. The load-displacement diagram was recorded, which was used to determine the hardness and elastic modulus during indentation. The resulting estimate was compared with a standard sample – fused quartz under the same indentation conditions. The recalculation of the obtained microhardness values H_V was carried out in Vickers units to compare the obtained data with the results of other authors [15,16].

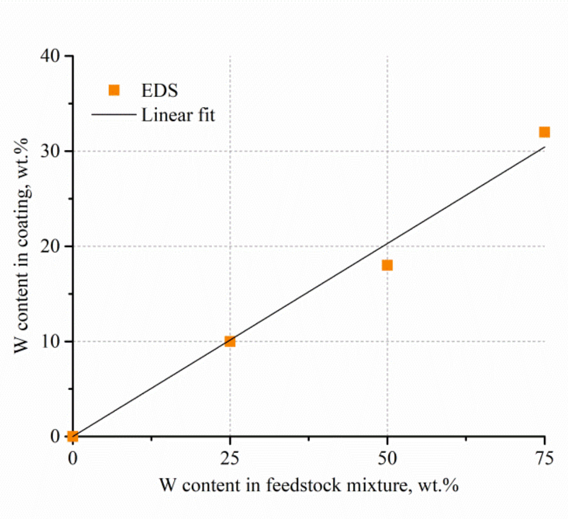
Adhesion strength tests were carried out on a Z100 testing machine (Zwick/Roell, Germany) by the glue method (Ultra Bond 100 glue (HTK Hamburg, Germany) with an adhesion strength of about 70 MPa) in accordance with the ASTM C633-01. The thickness of the coatings on the test specimens was kept equal to 500 ± 50 μm. Average values of adhesion strength were determined from 3 measurements.

3. Results and discussion

For the selected spraying parameters, a series of deposited samples were obtained for further investigation of their mechanical properties. Figure 3a shows the dependence of the specific weight of one coating layer on the content of tungsten in the feedstock. On the basis of these results, the deposition efficiency of the mixtures can be estimated.

It is known that when cold spraying coatings from powder mixtures, the ratio of the components in the coating can differ significantly from the initial ratio in the feedstock [20,21]; therefore, it was important to obtain an experimental dependence of the tungsten content in the coating on its content in the feedstock. This dependence was obtained using the method of energy-dispersive X-ray spectroscopy (Fig. 2b).





a) b)

Fig. 2. Experimental dependences of the specific coating weight (a) and the content of tungsten in the coating (b) on the content of tungsten in the feedstock

As can be seen from Fig. 2a, with an increase in the tungsten content in the feedstock, the specific weight of the coating first increases and then decreases. Under typical cold spray conditions, hard particles (in this case, tungsten) do not form a coating by themselves but only lead to erosion of the substrate. However, under certain conditions, the addition of hard particles to a more ductile powder contributes to an increase in the deposition efficiency of the entire coating [21,22]. It is most likely that the hard particles are cleaning the substrate surface from the oxide film that prevents the formation of bonds. Removal of oxides lowers the activation energy, which leads to an increase in the probability of particle bonding. A further increase in the content of hard particles (tungsten) in the feedstock leads to a decrease in the deposition efficiency of the coating since the content of the ductile component (copper) that forms the coating is significantly reduced. In this case, the tungsten content in the coating increases linearly from 0 to 32 wt.% with an increase in its content in the feedstock from 0 to 75 wt.% (Fig. 2b). Cross-sectional micrographs of deposited samples are shown in Fig. 3.

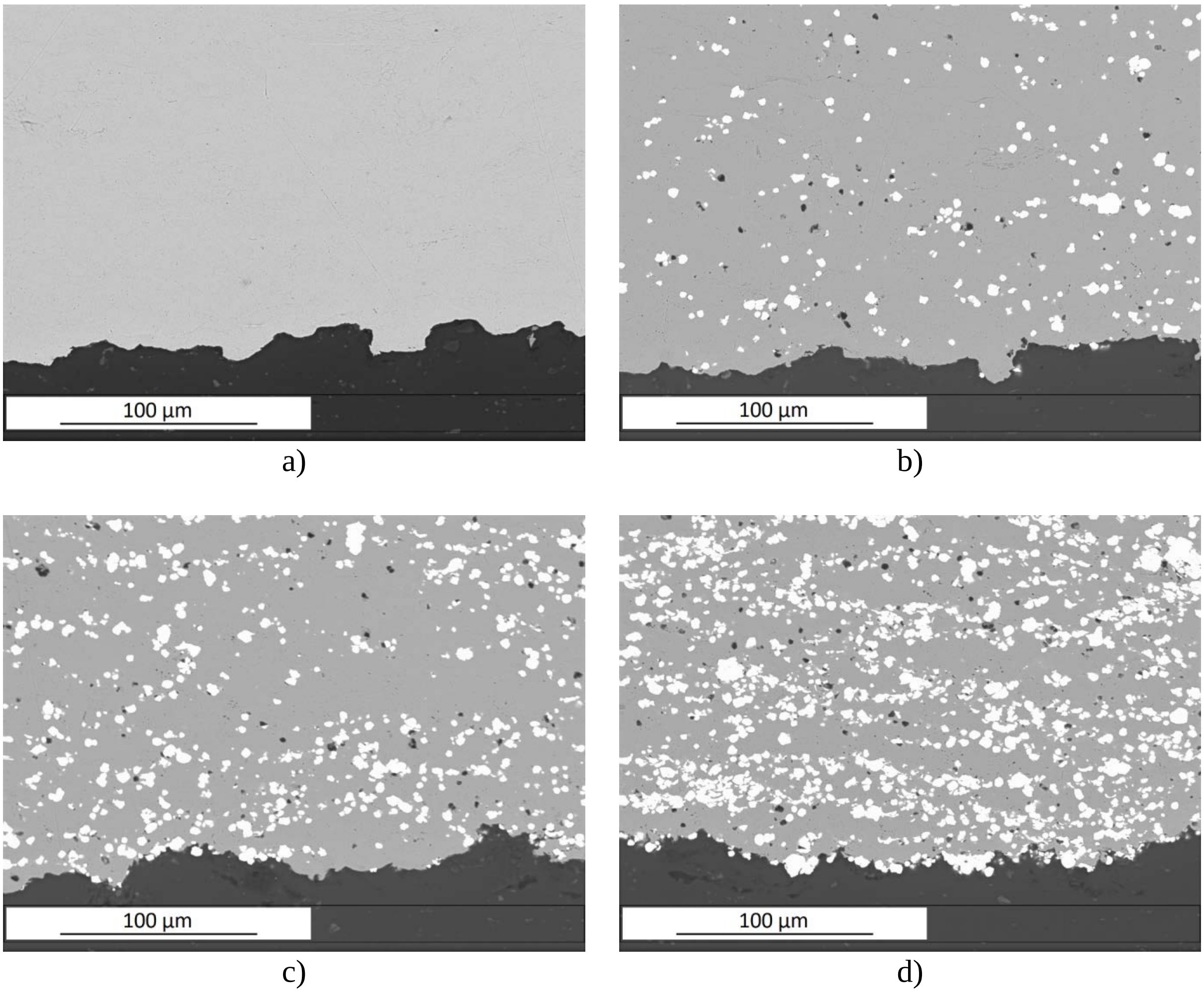


Fig. 3. Cross-sectional micrographs of deposited samples with a tungsten content of 0 (a), 10 (b), 18 (c), and 32 wt.% (d)

The study of the microhardness of the coatings was carried out in the mapping mode in the area of 210×210 μm, equidistant from the interface and the top of the coating. For each sample, 64 indents were made with a step of 30 μm between the centers of adjacent indents, the results of which were used to plot maps of microhardness and elastic modulus. Figure 4 shows micrographs of the indentation areas of coatings and the corresponding maps of microhardness and elastic modulus. It can be seen that the inhomogeneity of the distribution of mechanical properties increases with an increase in the content of the hard tungsten phase in the coating. At a given load (0.1 N), the characteristic size of the indent (≈ 15 μm) is comparable to the average size of tungsten particles (≈ 9 μm), respectively, the higher the tungsten content in the copper matrix of the coating, the higher the probability of the indenting into the tungsten particles or into the pores from particles crumbled during the sample preparation process. At the same time, the indent size is too large to determine the mechanical properties of only tungsten inclusions. Thus, the inhomogeneity of the mechanical properties over the area can be associated, on the one hand, with the presence of pores and local accumulations of tungsten particles, which is confirmed by SEM, and, on the other hand, with low indentation load.

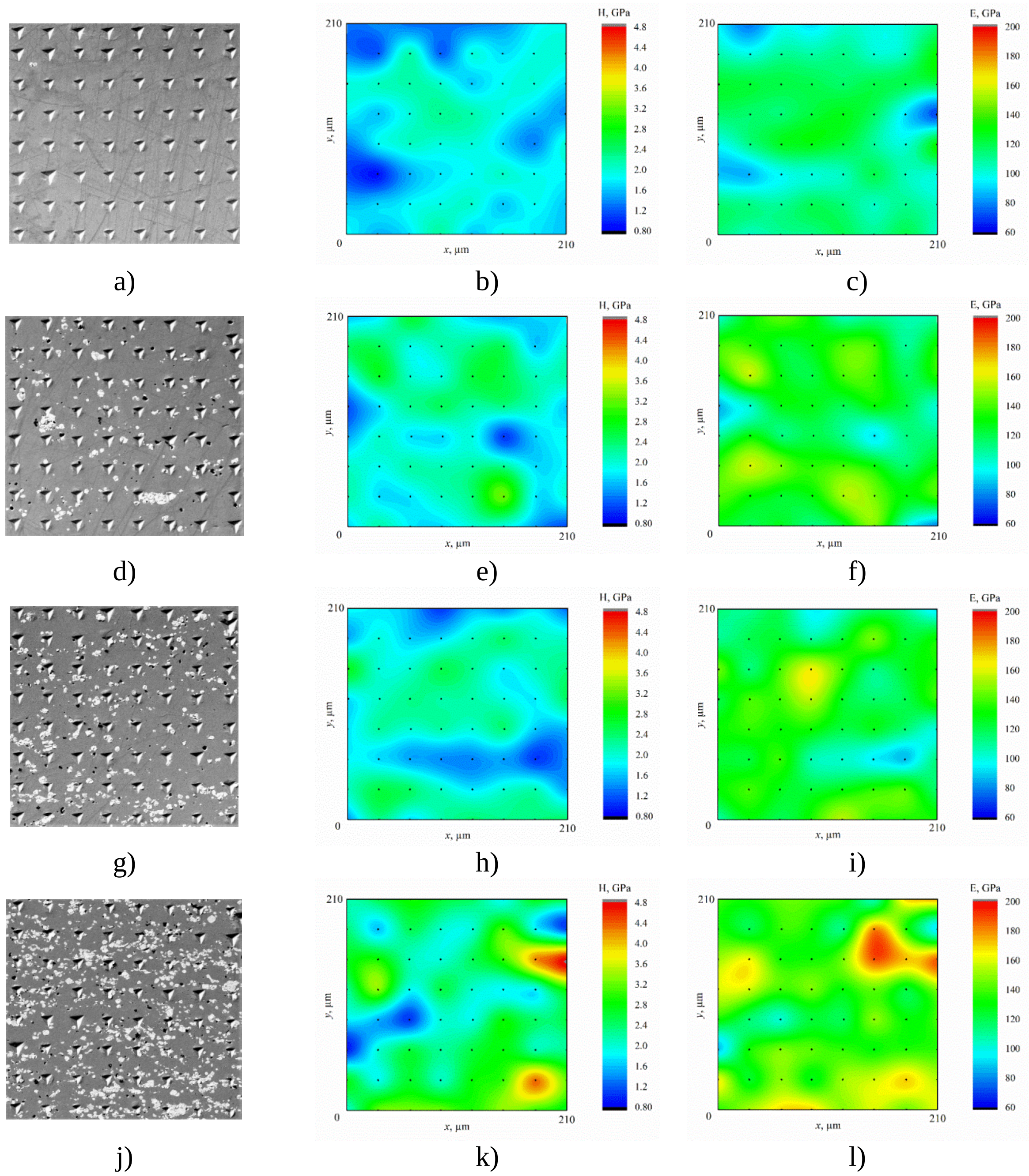


Fig. 4. SEM-micrographs of the indentation areas of coatings (a, d, g, j) and the corresponding maps of microhardness (b, e, h, k) and elastic modulus (c, f, i, l). Tungsten content in coatings: 0 (a, b, c), 10 (d, e, f), 18 (g, h, i) and 32 wt.% (j, k, l)

The averaging of the values for the elastic modulus and microhardness was carried out over the obtained 64 points and was determined as the mean value with the standard error.

The results of microhardness are also presented in Vickers units (Fig. 5) for comparison with the results from [15,16].

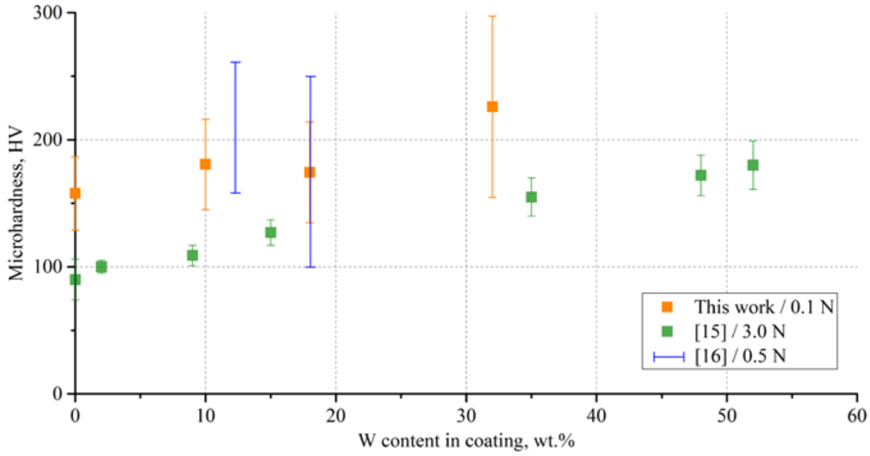
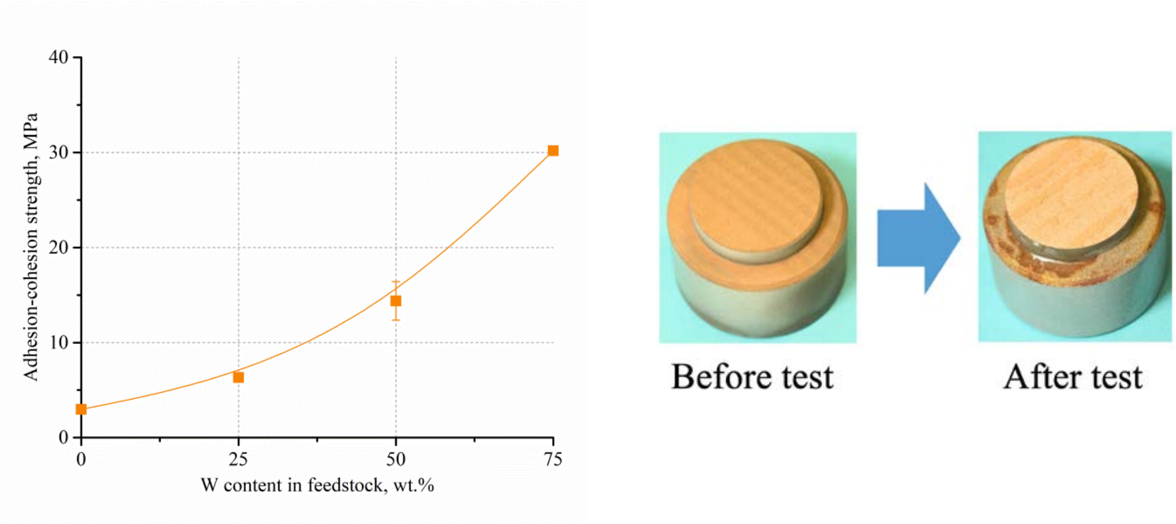


Fig. 5. Experimental dependence of microhardness on the content of tungsten in the copper matrix of the composite coating

The microhardness of the coating increases from 1.7 ± 0.3 GPa to 2.5 ± 0.7 GPa with an increase in the content of tungsten in the copper matrix from 0 to 32 wt.%. In this case, the elastic modulus of the coating increases from 108.5 ± 12.3 GPa to 142.7 ± 20.9 GPa, respectively. As can be seen from Fig. 5, the Vickers microhardness values at the same tungsten content in the coating turned out to be higher than in [15], but they are characterized by a larger standard error and are closer to the results [16]. To clarify the reasons for this behavior, additional experiments are required under different loading conditions.

It is known that the adhesion strength of cold sprayed composite coatings depends to a greater extent on the content of the hard component in the feedstock [21]. Figure 6a shows the experimental results on measuring the adhesion strength of coatings in the form of its dependence on the tungsten content in the feedstock. Note that the tests did not make it possible to measure the clear adhesion strength, because the destruction occurred not only along with the coating-substrate interface but also along with the coating (Fig. 6b). Therefore, the measured values will be called adhesion-cohesion strength.

As can be seen from Fig. 6, the pure copper coating has a rather low adhesion-cohesion strength – about 3 MPa. An increase in the content of tungsten in the feedstock leads to a significant increase in the adhesion strength of the composite coating. The addition of 75 wt.% tungsten into the feedstock mixture leads to an increase in the strength by a factor of 10 (up to 31 MPa) in comparison with the pure copper coating. This behavior can be explained by the formation of roughness on the substrate upon impacts of hard particles on its surface, which contributes to an increase in the contact area. Simultaneously with this process, the surface of the substrate is cleaned from oxides, which can also lead to an increase in the bonding strength. In addition, the effect of hardening by rebounded tungsten particles can promote densification of both the coating structure, reducing its porosity, and the substrate-coating interface, increasing the adhesion strength. To assess the effect of each of these mechanisms on the adhesion strength of coatings, additional experiments are required.



a) b)

Fig. 6. Experimental dependence of the adhesion-cohesion strength on the tungsten content in the feedstock (a) and a photograph of the sample before and after test (b)

4. Conclusions

A series of coatings based on a copper matrix and tungsten inclusions uniformly distributed in it with the content of 0, 10, 18, and 32 wt.% were obtained using the cold spray method. The estimation of the deposition efficiency is carried out and it was shown that with an increase in the tungsten content in the feedstock, the specific coating weight first increases, then decreases, which is associated with the activation effect. Using the method of instrumental indentation, mechanical tests of coatings were carried out and maps of microhardness and elastic modulus were obtained. It was shown that the inhomogeneity of the distribution of mechanical properties increases with an increase in the content of the hard phase in the coating, which can be associated, on the one hand, with the presence of pores and local accumulations of tungsten particles, and, on the other hand, with the loading conditions. The microhardness and elastic modulus of the coating increases with an increase in the tungsten content in the coating. For a correct comparison of the results obtained with the results of other authors in the future, additional experiments are required under different loading conditions. For the first time, adhesion strength tests of cold sprayed copper-tungsten coatings were carried out, which showed that the destruction of the coating occurs both along with the interface and along with the coating, and an increase in the content of tungsten in the feedstock from 0 to 75 wt.% leads to an increase in the value of adhesion-cohesion strength from 3 to 31 MPa.

Reference

[1] Senthilnathan N, Raja Annamalai A, Venkatachalam G. Sintering of tungsten and tungsten heavy alloys of W-Ni-Fe and W-Ni-Cu: A review. *Transactions of the Indian Institute of Metals*. 2017;70: 1161-1176.

[2] Dong LL, Ahangarkani M, Chen WG, Zhang YS. Recent progress in development of tungsten-copper composites: Fabrication, modification and applications. *International Journal of Refractory Metals & Hard Materials*. 2018;75: 30-42.

[3] Hou C, Song X, Tang F, Li Y, Cao L, Wang J, Nie Z. W-Cu composites with submicron- and nanostructures: progress and challenges. *NPG Asia Materials*. 2019;11: 74.

[4] Lungu MV. Synthesis and processing techniques of tungsten copper composite powders for electrical contact materials: A review. *Oriental Journal of Chemistry*. 2019;35(2): 491-515.

[5] Kang H, Kang SB. Behavior of porosity and copper oxidation in W/Cu composite produced by plasma spray. *Journal of Thermal Spray Technology*. 2004;13(2): 223-228.
[6] Pintsuk G, Smid I, Doring J, Hohenauer W, Linke J. Fabrication and characterization of vacuum plasma sprayed W/Cu-composites for extreme thermal conditions. *Journal of Materials Science*. 2007;42: 30-39.
[7] Song S, Zhou Z, Yao W, Cong W, Ge C. Layered and graded coatings as plasma facing materials for fusion in LSCPM. *Key Engineering Materials*. 2008;368-372: 1795-1798.
[8] Luzin V, Matejicek J, Gnaupel-Herold T. Through-thickness residual stress measurement by neutron diffraction in Cu+W plasma spray coatings. *Materials Science Forum*. 2010;652: 50-56.
[9] Matejicek J, Zahalka F, Bensch J, Chi W, Sedlacek J. Copper-tungsten composites sprayed by HVOF. *Journal of Thermal Spray Technology*. 2008;17(2): 177-180.
[10] Barnett B, Trexler M, Champagne V. Cold sprayed refractory metals for chrome reduction in gun barrel liners. *International Journal of Refractory Metals & Hard Materials*. 2015;53: 139-143.
[11] Xia M, Huang P, Cu R, Ge C. Cold sprayed W/Ni/Fe alloy coating: Microstructure and mechanical properties. *Surface & Coatings Technology*. 2016;291: 376-381.
[12] Cizek J, Vilemova M, Lukac F, Koller M, Kondas J, Singh R. Cold sprayed tungsten armor for tokamak first wall. *Coatings*. 2019;9(12): 836.
[13] Kang H, Kang SB. Tungsten/copper composite deposits produced by a cold spray. *Scripta Materialia*. 2003;49: 1169-1174.
[14] Shin S, Yoon S, Kim Y, Lee C. Effect of particle parameters on the deposition characteristics of a hard/soft-particles composite in kinetic spraying. *Surface & Coatings Technology*. 2006;201: 3457-3461.
[15] Petrovskiy P, Doubenskaia M, Sova A, Travyanov A. Analysis of copper-tungsten cold spray coating: Kinetics of coating formation and its thermal properties. *Surface & Coatings Technology*. 2020;385: 125376.
[16] Deng N, Tang J, Xiong T, Li J, Zhou Z. Fabrication and characterization of W-Cu composite coatings with different W contents by cold spraying. *Surface & Coatings Technology*. 2019;368: 8-14.
[17] Kiselev SP, Ryashin NS, Maksimovskii EA, Kiselev VP, Klinkov SV, Kosarev VF, Filippov AA, Shikalov VS. Creating a coating from a titanium-aluminum intermetallic compound by the cold spray technology. *Journal of Applied Mechanics and Technical Physics*. 2018;59(6): 1126-1135.
[18] Gladkikh EV, Maslenikov II, Reshetov VN, Useinov AS. Portable hardness tester for instrumental indentation. *Journal of Surface Investigation*. 2020;14(4): 846-850.
[19] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research*. 1992;7(6): 1564-1583.
[20] Kosarev VF, Polukhin AA, Ryashin NS, Fomin VM, Shikalov VS. Influence of the powder mixture composition on the deposition coefficient and the properties of Ni+B4C CGDS coatings. *Mechanics of Solids*. 2017;52(4): 457-464.
[21] Fernandez R, Jodoin B. Cold spray aluminum-alumina cermet coatings: effect of alumina content. *Journal of Thermal Spray Technology*. 2018;27: 603-623.
[22] Klinkov SV, Kosarev VF. Cold spraying activation using an abrasive admixture. *Journal of Thermal Spray Technology*. 2012;21(5): 1046-1053.

THE AUTHORS

Shikalov V.S.
e-mail: v.shikalov@gmail.com
ORCID: 0000-0002-0491-2803

Filippov A.A.
e-mail: filippov@itam.nsc.ru
ORCID: 0000-0003-1145-6356

Vidyuk T.M.
e-mail: vidyuk@itam.nsc.ru
ORCID: 0000-0002-6819-8290