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CREATION OF ELECTRIC CONDUCTIVE COATINGS USING GAS-DYNAMIC SPRAYING

The article presents the results of research on the processes of creating conductive coatings based on copper and aluminum in order to determine the interaction of components on each other during cold gas-dynamic spraying (CGDS) and substantiate the method of introducing an additional component to obtain the desired composite coating. In particular, under conditions when the copper sputtering coefficient is almost zero (at a working air temperature of 300 °C), it is the search for the experimental dependence of the sputtering coefficient on the percentage of copper and aluminum powders in the sprayed mixture, determining their residual content in the coating and then calculating based on these data, the sputtering coefficients of copper and aluminum.

The CGDS method obtained samples with composite coatings from mixtures of aluminum and copper powders at different initial mass concentrations of aluminum (from 0 to 100%, in increments of 10%) Other things being equal (air pressure 0,6 MPa, air heating temperature 300 ° C) .

The spraying ratio of the mixture and the residual content of the components in the obtained composite coatings were measured. Data on the residual content of the components in the coating allows you to select the composition of the source powder required to obtain a given content of components in the coating.

The dependences of the sputtering coefficients of copper and aluminum on the mass content of aluminum in the sprayed mixture are found. At an initial concentration of aluminum less than 66%. the coefficient of copper sputtering is higher than the coefficient of sputtering of aluminum. Both increase monotonically with increasing aluminum concentration until it reaches 61%. At high concentrations of aluminum (more than 66%) the spray coefficients of copper, aluminum and their mixtures coincide. The obtained data on the residual content of the components in the coating allows you to select the composition of the source powder required to obtain a given content of components in the coating. For example, the maximum residual copper content (~ 95%) can be obtained by adding to the source powder 30-40% aluminum.

The obtained results confirm the interaction of the components on each other and justify the method of introducing an additional component to obtain a composite coating containing a component that is difficult to spray.

Key words: *gas-dynamic coatings, spraying, electrically conductive coating, spraying coefficient.*

Introduction. Cold gas-dynamic spraying (CGDS) - a method of powder coating, rapidly evolving [1], in which particles with a characteristic size of 10-150 μm are accelerated in the gas velocity to speeds of 250-1200 m/s and when hitting the substrate are fixed on it without phase transitions. The absence of high temperatures allows to significantly expand the possibilities of methods of coating with powder materials and provides the method of CGDS before the known gas-thermal methods the following advantages:

- the possibility of using for spraying powders with a size less than 30-50 μm, including ultrafine, which improves the quality of the coating - increases its density, reduces the volume of microcavities, the structure becomes more homogeneous, it is possible to reduce the thickness of the coating;

- the absence of significant heating of the particles and related processes of high-temperature oxidation, phase transitions, etc., which allows to obtain coatings with properties close to the properties of the material of the initial particles, as well as composite coatings of mechanical mixtures of powders physical and thermal properties;

- no significant thermal impact on the product, which allows you to apply a coating on substrates of non-heat-resistant materials;

- simplicity of technical implementation and improvement of work safety due to the absence of high-temperature jets, as well as flammable and explosive gases.

Based on the CGDS method technologies are created to solve energy and resource saving problems in various industries, which are introduced into the practice of non-traditional and efficient methods of production, repair, restoration, corrosion protection, obtaining electrically conductive, thermally conductive, antifriction, insulating and other coatings for machinery and equipment.

Analysis of recent research. The possibility of formation of coatings from particles in the solid (unmelted) state was unexpected for experts, because there were ideas about the need for melting (general or local) for adhesion between the particle and the substrate surface and the formation of the coating and that rebound of the sprayed particle from the obstacle.

Beginning in about 2000, centers and laboratories began to appear around the world to study the possibilities of the CGDS method. The intensity of research is clearly demonstrated by a large number of publications, a detailed review of the literature is presented in the monograph [6] (the world's first monograph on the basics of CGDS), and works [1 - 5]. As a result of the research, various technical solutions were proposed due to the optimal choice of working gas [9], size and shape of powder particles [10], spraying strategy (number of passes, scanning speed) [11], spraying angle [12], powder heating [13], the creation of sublayers [14].

It should also be noted that vacuum spraying of submicron powders [15], the use of micro nozzles (up to 50 μm in diameter) for spraying nanopowders (including nonmetals) [16], the metallization of glass and silicon by CGDS [17], various plastics [18- 21], as well as spraying of plastic powders [22, 23]. All these achievements show how wide the scope of CGDS. The great variety of materials and coatings obtained with its help is presented in detail in published scientific works [24, 25].

However, the potential of CGDS is not fully disclosed, some aspects of the process require further research to create new technologies, their optimization, as well as a deeper understanding of the physics of high-speed shock interaction of heterogeneous flows with interference.

One such task is to study the formation of composite coatings from multicomponent mixtures, in particular from two-component, which are mixtures of two different metal powders. It is especially important to detect the mutual influence of the components, for example, when the sputtering ratio of one of the components in the presence of another component differs from the sputtering ratio in the absence of another component. To study this phenomenon was chosen as an example a mixture of powders of aluminum and copper. Early experiments showed that at a temperature of 300 °C the coefficient of spraying of copper powder is almost zero. At the same time, the spraying coefficient of aluminum powder at this temperature is markedly different from zero (below are the specific values). The novelty of this study is to show that at the same operating air temperature (300 °C) it is possible to increase the coefficient of copper deposition by creating a mixture with the addition of aluminum. This will justify that in cases where it is not possible to obtain a coating from a powder due to the limited capabilities of a particular CGDS installation, the addition of a suitable component that relatively easily forms a coating, will obtain a composite coating, which will include in a certain proportion and " hard to spray "component.

The purpose of research. The purpose of the work is to prove the interaction of components on each other in CGDS and substantiation of the method of introduction of an additional component to obtain a composite coating. In particular, under conditions when the copper sputtering coefficient is almost zero (at a working air temperature of 300 °C), it is a search for the experimental dependence of the sputtering coefficient on the percentage of copper and aluminum powders in the sprayed mixture, determining their residual content in the coating and then calculating based on these data, the sputtering coefficients of copper and aluminum.

Presenting main material. To obtain composite coatings used a mechanical mixture of aluminum powder A20-11 and copper C01-11. In Fig. 1 shows the form of these powders, and in Fig. 2 - photomicrographs of their particles.

Fig. 1. Photos of sprayed powders. On the left aluminum powder A 20-11, on the right copper powder C01-11.

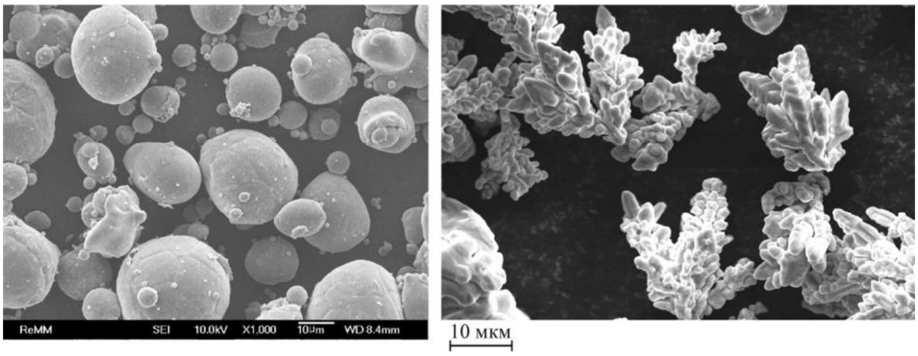


Fig. 2. Photomicrographs of sprayed powder particles. On the left aluminum powder A 20-11, on the right copper powder C01-11.

The particle size distribution of the powder is one of the most important parameters that determine the possibility of its use in CGDS and the quality of the obtained coatings [1].

Average values of particle sizes d_{cp}. and the standard deviation S_d, calculated from the photomicrographs shown in Fig. 2, are presented in table 1. The maximum share by volume (Mass) is occupied by particles of size 20-52 μm for aluminum and 42 - 78 μm for copper.

Table 1.

Powder	d_{cp}, μm	s_d, μm
A 20-11	30,3	15,8
C 01-11	46,4	26,6

To create composite coatings were prepared mechanical mixtures of two powders in the proportions shown in table 2. The total weight of each portion was 0,5 grams.

Table 2.

Powder	The mixture number										
	1	2	3	4	5	6	7	8	9	10	11
C 01-11	1	0,9	0,8	0,7	0,6	0,5	0,4	0,3	0,2	0,1	–
A 20-11	–	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1

The coating was carried out using a gas-dynamic spraying device [2] developed and manufactured at the Department of Power Engineering, Electrical Engineering and Electromechanics of Vinnytsia National Agrarian University shown in Fig. 3.

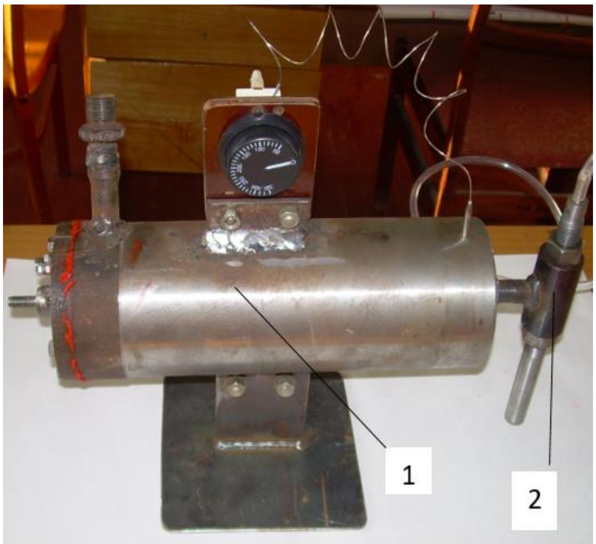


Fig. 3. Gas-dynamic spraying device. 1 - compressed air heater. 2 - nozzle accelerator of compressed air and spray powder.

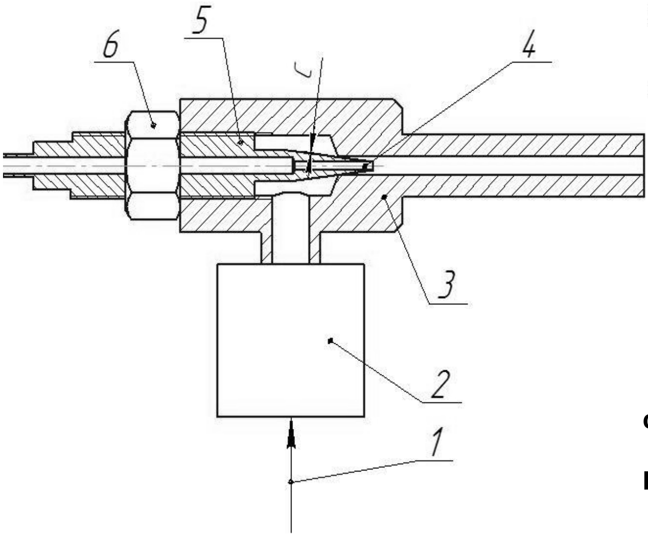


Fig. 4. The scheme of realization of CGDS by means of an ejector nozzle: 1 - supply of compressed air, 2 - an electric heater, 3 - a nozzle, 4 - a cone with the central axial aperture for giving of a dusting powder, 5 - a screw part of a cone, 6 - a locknut, C - ring critical section (gap) between the cone and the nozzle hole.

The device for CGDS works as follows. Compressed air 1 from the compressor is fed into the electric heater 2 where it is heated to the desired temperature and heated enters the nozzle through the annular gap C. Circumventing the cone 4 axial hole creates the effect of ejection. By adjusting the size of the annular gap C, due to the presence of the threaded part 5 and the locknut 6, it is possible to adjust the ejection pressure and the corresponding size and feed rate of the spray powder.

For the study, the following modes of operation of the CGDS device were set. Air pressure P_0 = 0,6 MPa, ejection pressure R_e = 0,095 MPa, heating temperature of compressed air at the inlet to the nozzle T_0 = 300 °C. Spraying distance 20 mm. The spraying ratio of the mixture was defined as the ratio of the mass of the obtained coating to the mass of spent powder (in the experiments it was 0,5 g). The mass difference of the substrate before and after spraying was determined by the mass of the obtained coating. The sputtering coefficients of copper and aluminum separately in the sputtered mixture were calculated from the measured sputtering coefficient of the mixture and the results of elemental analysis of samples on an electron microscope.

Fig. 5. Application of composite coatings on a metal substrate.
1 - metal substrate, 2 - sputtering Figure, 3 - nozzle of the CGDS device.

To determine the composition of the obtained composite coatings, the coated samples were cut and prepared for examination under a microscope in accordance with Fig. 6.

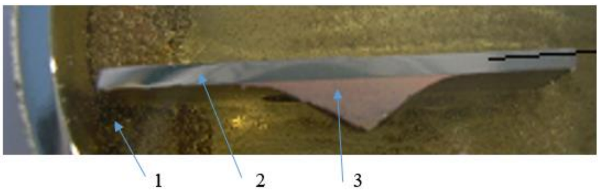


Fig. 6. Prepared section section of the spray Figure to study the composition of the obtained coating. 1 - epoxy resin, 2 - metal substrate, 3 - composite coating.

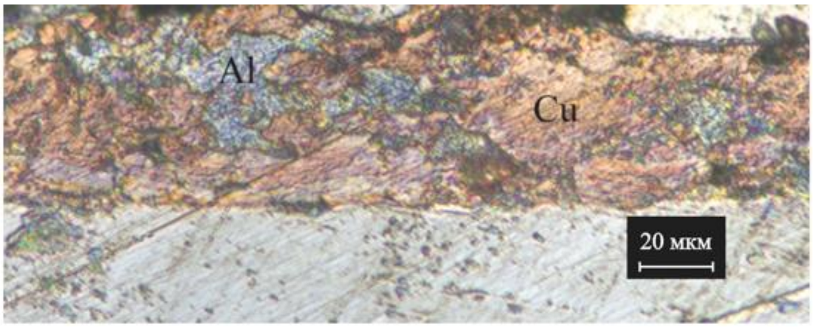


Fig. 7. Photomicrograph of the section of the substrate with a composite coating of copper - aluminum.

The micrographs were processed using PhotoM 1.21 software and the area of each of the components, ie copper and aluminum, was determined. The photograph of the processed microslice is shown in Fig. 8.

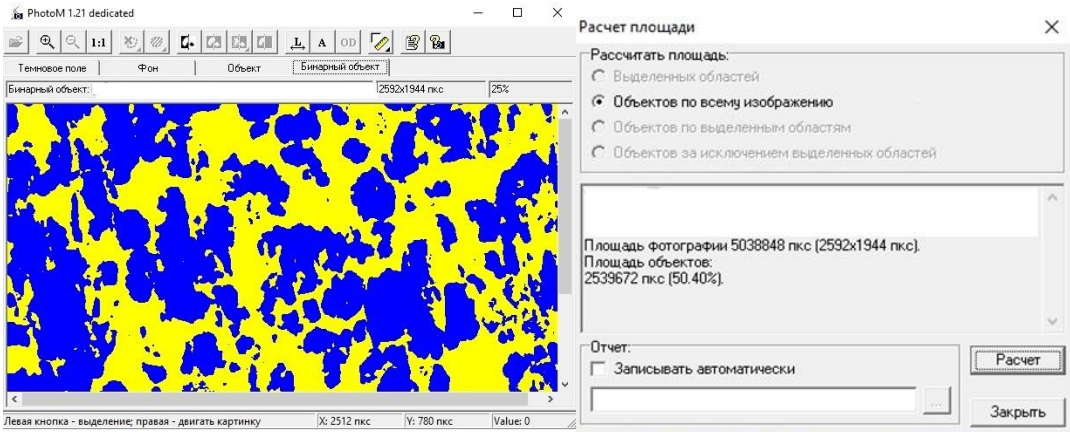
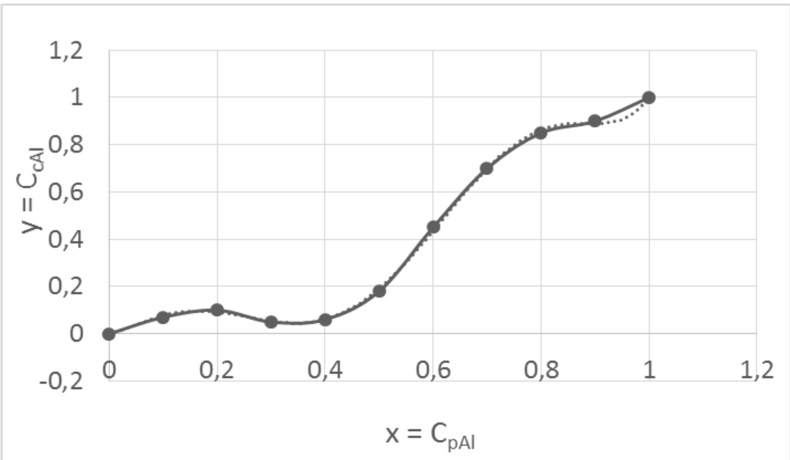


Fig. 8. The results of processing the photomicrograph of the section with a composite coating using the program PhotoM 1.21, and determining the content of copper and aluminum.

In Fig. 9, presents data on the mass content of aluminum in the coating (hereinafter referred to as C_{cAl}) depending on its mass content in the source powder (hereinafter referred to as C_{pAl}). The dependence graph which can be approximated by polynomial (1) on the graph is obtained. The approximation is shown by a dotted line.

$$y = 79{,}003x^6 - 214{,}09x^5 + 199{,}99x^4 - 71{,}815x^3 + 7{,}338x^2 + 0{,}5835x - 0{,}001 \qquad (1)$$

where x is C_{pAl}, and y is C_{cAl}.



The absolute value of the aluminum content in the C_{cAl} coating depending on its content in the original C_{pAl} powder.

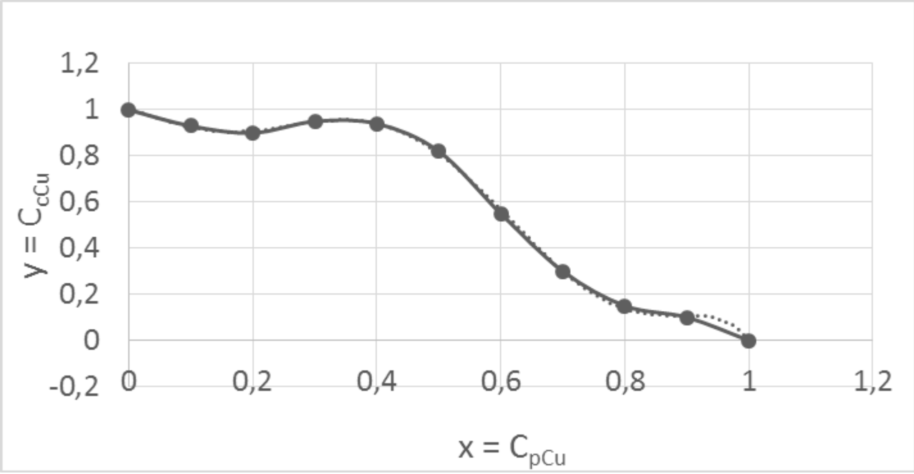


Fig. 10. The absolute value of the copper content in the C_{cCu} coating depending on its content in the original C_{pCu} powder.

In Fig. 10, presents data on the mass content of copper in the coating (hereinafter referred to as C_{cCu}) depending on its mass content in the source powder (hereinafter referred to as C_{pCu}). The dependence graph which can be approximated by polynomial (2) on the graph is obtained. In the graph of Fig. 10 the approximation is shown by a dotted line.

$$y = -79{,}003x^6 + 214{,}09x^5 - 199{,}99x^4 + 71{,}815x^3 - 7{,}338x^2 - 0{,}5835x + 1{,}0014 \qquad (2)$$

In Fig. 11 shows the dependences of the spraying coefficients of the mixture of aluminum and copper 1, only aluminum 2 and only copper 3 from the mass content of aluminum in the original mixture. The spraying coefficients are determined by the content of aluminum in the coating according to formulas (3):

$$k_{dAl} = \frac{C_{cAl}}{C_{pAl}} k_{dmix},\ k_{dCu} = \frac{C_{cCu}}{C_{pCu}} k_{dmix} \qquad (3)$$

Де k_{dmix} – Coefficients of spraying of a mixture of powders of aluminum and copper.

k_{dAl} – Coefficients of dusting of aluminum powders.

k_{dCu} – Coefficients of dusting of copper powders.

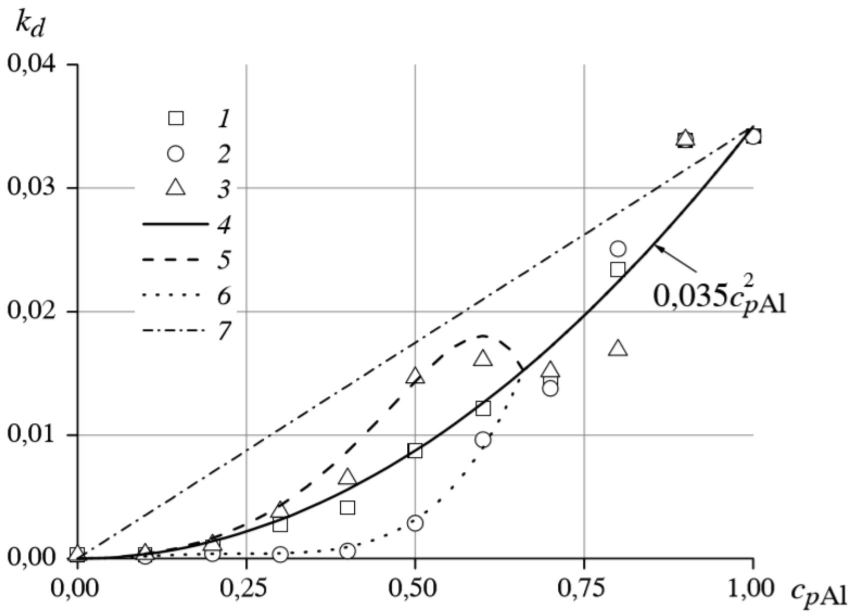


Fig. 11. Dependences of the spray coefficients of the mixture 1, aluminum 2, copper 3 on the concentration of aluminum in the original mixture; 4 - parabolic approximation of the sputtering coefficient of the mixture; 5 - approximation of the copper sputtering coefficient; 6 - approximation of the coefficient of aluminum sputtering; 7 - spray coefficient of the mixture according to linear theory (when the components do not affect each other).

The data for the sputtering coefficient of the mixture are well approximated by parabola 4 (see Fig. 11). The dashed curve 5 shows the approximation of the copper sputtering coefficient, and 6 - the aluminum sputtering coefficient. It is seen that at an initial aluminum concentration of less than 66%, the copper sputtering ratio is higher than the aluminum sputtering ratio. Both increase monotonically with increasing aluminum concentration until it reaches 61%. At high concentrations of aluminum (more than 66%) the spraying coefficients of copper and aluminum coincide with each other and with the spraying coefficient of the mixture.

According to linear theory, if the powders do not affect each other, their spray coefficients remain the same regardless of the proportion in which they are mixed. This allows you to calculate the spraying ratio of the mixture on the basis of only two measurements: the spraying ratio of only the first component (copper in the absence of aluminum) k_{dCu0} and only the second component (aluminum in the absence of copper). Then by formula (4) you can find the coefficient of spraying the mixture at a given initial content of aluminum (C).

$$k_{dmix} = Ck_{dAl0} + (1 - C)k_{dCu0} \qquad (4)$$

The obtained data on the residual content of the components in the coating allows you to select the composition of the source powder required to obtain a given content of components in the coating. For example, the maximum residual copper content (~ 95%) can be obtained by adding to the source powder 30-40% aluminum. At this initial concentration of aluminum, the sputtering ratio of copper will be 0,5%, which is still significantly higher than the sputtering ratio of pure copper (0,01%). If, for example, you want to get a residual copper content of 50%, you need to add to the original powder 61% Aluminum. In this case, the coefficient of dusting of copper will increase significantly and will be 15%, etc.

From this study we can conclude that in the process of spraying the components of the mixture affect each other. Presumably, the mechanism of interaction of the components is that the components with different probabilities are fixed on a surface consisting of different materials (ie the probability of fixing copper particles on the surface of aluminum particles is higher than the probability of fixing copper particles on steel or copper particles).

Conclusions. Samples with composite coatings from mixtures of aluminum and copper powders at different initial mass concentrations of aluminum (from 0 to 100% with a step of 10%) were obtained by the CGDS method. Other things being equal (air pressure 0,6 MPa, air heating temperature 300 °C).

The spraying ratio of the mixture and the residual content of the components in the obtained composite coatings were measured. Data on the residual content of the components in the coating allows you to select the composition of the source powder required to obtain a given content of components in the coating.

The dependences of the sputtering coefficients of copper and aluminum on the mass content of aluminum in the sprayed mixture are found. At an initial concentration of aluminum less than 66%. The coefficient of copper sputtering is higher than the coefficient of sputtering of aluminum. Both increase monotonically with increasing aluminum concentration until it reaches 61%. At high concentrations of aluminum (more than 66%) the sputtering coefficients of copper, aluminum and their mixtures coincide.

The obtained results confirm the interaction of the components on each other and justify the method of introducing an additional component to obtain a composite coating containing a component that is difficult to spray.

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СОЗДАНИЕ ЭЛЕКТРОПРОВОДЯЩИХ ПОКРЫТИЙ С ИСПОЛЬЗОВАНИЕМ ГАЗОДИНАМИЧЕСКОГО НАПЫЛЕНИЯ

В статье приведены результаты исследования процессов создания электропроводящих покрытий на основе меди и алюминия с целью выяснения взаимовлияния компонентов друг на друга при холодном газодинамическом напылении (ХГДН) и обоснование методики введения дополнительного компонента для получения желаемого композиционного покрытия. В частности, в условиях, когда коэффициент напыления меди почти равна нулю (при температуре рабочего воздуха 300 °С), это поиск экспериментальной зависимости изменения коэффициента напыления от процентного содержания порошков меди и алюминия в смеси которая напыляется, определения их остаточного содержания в покрытии и затем вычисления на основе этих данных коэффициентов напыления меди и алюминия. Методом ХГДН полученные образцы с композитными покрытиями из смесей порошков алюминия и меди при различной исходной массовой концентрации алюминия (от 0 до 100%, с шагом 10%) При прочих равных условиях (давление воздуха 0,6 МПа, температура нагрева воздуха 300 °С). Измеренные коэффициент напыления смеси и остаточное содержание компонентов в полученных композитных покрытиях. Данные по остаточному содержанию компонентов в покрытии дают вожможность выбрать состав исходного порошка, необходимый для получения покрития с заданим содержаним компонентов. Определены зависимости коэффициентов напыления меди и алюминия от массового содержания алюминия в смеси которая напыляется. При исходной концентрации алюминия менее 66% коэффициент напыления меди оказывается выше коэффициента напыления алюминия. Оба монотонно увеличиваются с ростом концентрации алюминия, пока она не достигнет величины 61%. При высоких концентрациях алюминия (более 66%)

коэффициенты напыления меди, алюминия и их смеси совпадают. Найденые данные по остаточному содержанию компонентов в покрытии дают возможность выбрать состав исходного порошка, необходимый для получения требуемого содержания компонентов в покрытии. Например, максимальное остаточное содержание меди в напыленом покрытиии (~ 94%) может быть создано при добавлении в исходный порошок 30-40% алюминия. Полученные результаты указывают на наличие влияния компонентов друг на друга и позволяют обосновано рекомендовать введения дополнительного компонента для создания композиционного покрытия, содержащего компонент, который трудно напыляется.

Ключевые слова: *газодинамическое покрытия, напыление, електропроводящее покрытие, коэфициент напыления.*

СТВОРЕННЯ ЕЛЕКТРОПРОВІДНИХ ПОКРИТТІВ З ВИКОРИСТАННЯМ ГАЗОДИНАМІЧНОГО НАПИЛЕНЯ

В статті наведено результати дослідження процесів створення електропровідних покриттів на основі міді та алюмінію з метою з'ясування взаємовпливу компонентів один на одного при холодному газодинамічному напиленні (ХГДН) і обгрунтування методики введення додаткового компонента для отримання бажаного композиційного покриття. Зокрема, в умовах, коли коефіцієнт напилення міді майже дорівнює нулю (при температурі робочого повітря 300 °С), це пошук експериментальної залежності зміни коефіцієнта напилення від процентного вмісту порошків міді та алюмінію в суміші яка напилюється, визначення їх залишкового вмісту в покритті і потім обчислення на основі цих даних коефіцієнтів напилення міді і алюмінію.

Методом ХГДН отримані зразки з композитними покриттями з сумішей порошків алюмінію і міді при різній вихідної масової концентрації алюмінію (від 0 до 100%, з кроком 10%) При інших рівних умовах (тиск повітря 0,6 МПа, температура нагріву повітря 300 °С).

Виміряні коефіцієнт напилення суміші і залишковий вміст компонентів в отриманих композитних покриттях. Дані за залишковим змістом компонентів в покритті дозволяють вибрати склад вихідного порошку, необхідний для отримання заданого вмісту компонентів в покритті.

Знайдено залежності коефіцієнтів напилення міді і алюмінію від масового вмісту алюмінію в суміші, що напиляється. При вихідній концентрації алюмінію менше 66 %. коефіцієнт напилення міді виявляється вище коефіцієнта напилення алюмінію. Обидва монотонно збільшуються зі зростанням концентрації алюмінію, поки вона не досягне величини 61 %. При високих концентраціях алюмінію (більше 66%) коефіцієнти напилення міді, алюмінію і їх суміші збігаються. Отримані дані за залишковим змістом компонентів в покритті дозволяють вибрати склад вихідного порошку, необхідний для отримання заданого вмісту компонентів в покритті. Наприклад, максимальне залишковий вміст міді (~ 95 %) може бути отримано при додаванні в вихідний порошок 30-40 % алюмінію.

Отримані результати підтверджують наявність взаємовпливу компонентів один на одного і обґрунтовують метод введення додаткового компонента для отримання композиційного покриття, що містить компонент, який важко напилюється.

Ключові слова: *газодинамічне покриття, електропровідне покриття, коефіцієнт напилення.*

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