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Sh.T. Koshkarbaeva, M.S. Sataev, P.A. Abdurazova, K.B. Amanbaeva, Ye.B. Raiymbekov

M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
(E-mail: eplusr@bk.ru)

Investigation of chemical nickel plating of powdered carborundum

The technology of application of metal coatings on the surface of powder carborundum was developed. At the same time, the process of chemical nickel plating was used for this purpose. It was found that carborundum, although not included in the number of catalysts of this process, could contribute to the reduction of nickel ions. It was assumed that in the high-temperature decomposition of the hyposphyte ion, hydrogen evolution took place at the carborundum surface with a slowed-down stage by recombining hydrogen atoms into the molecule. The high reactivity of hydrogen atoms leads to the reduction of nickel ions. This makes it possible to activate the surface of carborundum and to further build up the metal under conditions typical for chemical nickel plating. Experiments in which the surface of the powder was investigated by means of a scanning electron microscope showed that such a mechanism for activating the powder surface was valid. Testing of this technology under laboratory conditions allowed obtaining a coating having the necessary adhesion to carborundum particles and containing 95 % of chemical nickel.

Keywords: carborundum, silicon carbide, chemical nickel plating, composite material, hydrogen atoms, activation, nickel-phosphorous coating.

Introduction

Carborundum (silicon carbide) is a refractory (melting point 2830 ºC), chemically permanent, second in hardness to diamond and boron nitride. Silicon carbide has high thermal, chemically and radiation permanent, stands out for its oxidation resistance among many metal-resistant alloys and chemical compounds. These properties contributed to its widespread use as a material of ceramic composite materials and coatings [1–4].

But at the same time, in order to ensure adhesion between the individual components, it becomes necessary to clad the surface of powdered carborundum with various metals. The coated particles of carborundum can be used for the manufacture of abrasive tools and composite materials such as metal-ceramics. Such materials are used for the manufacture of corrosion and erosion-resistant nozzle inserts; for the manufacture of parts of heat exchange equipment and parts of pumps for pumping acidic solutions and other corrosive liquids [1–4].

Known methods of applying metal coatings on dielectric powders can be divided into physical and chemical methods [5–7]. Physical methods, when the metal is first converted into vapor or liquid applying to the surface to be coated, where they again turn into a compact solid metal, forming a coating [8–10]. Chemical methods, when a metal is formed during a chemical reaction and, settling on the surface to be coated, create metallic coatings [6, 7]. Chemical methods are more convenient for the metallization of powders since in this case, it is easier to obtain coatings from particles uniformly distributed over the entire surface.

So for the metallization in the gas phase, the reaction of thermal decomposition of metal carbonyls can be used [11]. During the course of the reaction, they decompose, leaving the metal on the surface to be coated and release carbon monoxide, which can again be used to produce metal carbonyl. Currently, using carbonyl technology, it is possible to apply dielectric powders of iron, nickel, cobalt, tungsten, and chromium coatings. The disadvantage of this method is the use of high temperatures necessary for the decomposition of carbonyl compounds, and the high cost of carbonyls.

Plasma-chemical method [9] allows obtaining a metal coating on the surface of the powder material located in the pseudo-boiling layer. The disadvantage of this method is the need to obtain high temperatures, the complex design of the reactor, the use of the working gas, additionally purified from oxygen, the fragility of the electrodes.

The electrochemical method [12] requires preliminary deposition of a metallic sublayer on dielectric materials using other methods. The method does not have the disadvantages of the above analogues, allows obtaining higher performance, however, in the case of obtaining powders with a metal content of up to 50 %, the quality of the coating deteriorates significantly.

The chemical method of precipitation from solution involves the pretreatment of the starting powder in solutions of the palladium and tin salts in order to obtain active catalytic sites [6, 13]. Then, in solutions containing a compound of the corresponding metal, the reducing agent and the complexing agent are chemically coated with copper or Nickel coating. The disadvantages of this method are the high cost of palladium salts used to activate the surface of the powder particles and the possibility of desorption of palladium from the surface of the particles, leading to the formation of a coating metal in a solution outside the surface of the powder particles.

Palladium-free methods for powder metallization are proposed. So in [14, 15], pretreatment is carried out by creating on the surface of powdered particles a layer of copper sulphate, which is then transferred with the help of a phosphine gas to a metal-like layer of copper phosphide. This film allows to further obtaining a metallic coating by chemical or electroplating. But the use of phosphine requires a process in sealed conditions, which creates additional difficulties.

The analysis shows the relevance of the metallization of the carborundum surface and the need to develop new alternative methods for this purpose.

Experimental

In this work, it was proposed to use a process of chemical nickel plating for the application of a metallic coating. Chemical nickel plating was carried out in electrolytes containing a nickel salt, a reducing agent: sodium hypophosphite, as well as buffering additives (salts of organic acids). The process flows at a high temperature on the surface of metals that are catalysts for the decomposition of hypophosphite. Thus, the process begins spontaneously on metals such as nickel, iron, aluminum, and palladium at temperatures above 50–70 ºC. The process of chemical nickel plating was accompanied by the release of hydrogen. Moreover, there is often a relationship between the amount of the deposited nickel-phosphorus coating and the volume of hydrogen released [6].

$$NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + 2H^+ + 2e^- \tag{1}$$

$$NaH_2PO_2 + 2H_2O \rightarrow NaH_2PO_4 + H_2 + 2H^+ + 4e^- \tag{2}$$

$$3NaH_2PO_2 - 2e^- \rightarrow Na_3PO_3 + 2P + 3H_2O \tag{3}$$

$$5NaH_2PO_2 - 4e^- \rightarrow Na_3PO_4 + 4P + 2NaOH + 4H_2O \tag{4}$$

The electrons formed by reactions (1, 2) reduce the Ni^{2+} and H^+ ions in the electrolyte solution.

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{5}$$

There are other hypotheses explaining the mechanism of chemical nickel plating. So the process of deposition of coatings can be linked by the reactivity of hydrogen atoms.

$$2H + Ni^{2+} \rightarrow Ni + 2H^+ \tag{6}$$

In this case, part of the hydrogen released, always accompanying the process of chemical Nickel plating, is the result of a side reaction.

The study of the mechanism of chemical nickel plating by measuring the stationary potential of some metals in solutions containing 10 and 50 g/L of sodium hypophosphite in the temperature range of 20–100 ºC showed that the stationary potential of the nickel electrode sharply shifts to the negative nickel at temperatures above 70 ºC [16]. In addition, spontaneous chemical nickel plating on copper phosphides deposited on dielectric materials is noted, although in this case this potential is not reached. Moreover, even after the deposition of a layer of chemical nickel, the stationary potential was in a more positive area than the reduction potential of nickel ions. Therefore, the reduction of nickel ions can occur only at the expense of atomic hydrogen.

The study of chemical nickel plating was carried out on carborundum powder 93CF40. Samples of powders at various stages of the process were studied using an ISM-6490-LV scanning electron microscope (JEOL, Japan), which allowed obtaining electronic images (photographs) of individual sections (spectra) of the surface at given magnifications. The microscope made it possible at the same time to obtain elemental compositions of the spectra in the form of a table.

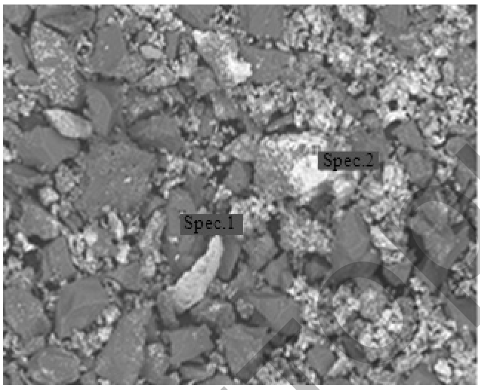
The initial powders were decreased in a 20 % solution of sodium carbonate at a temperature of 40–500 ºC until the surface of the particles was completely wetted and washed in hot running water. The powder prepared in this way was placed in a Petri dish and dried at 50 ºC to constant wt. Then 10 g of the powder was placed in a heat-resistant beaker, poured 100 ml of $NiSO_4 \cdot 7H_2O$ solution — 30 g/L. NaH_2PO_2 — 10 g/L, CH_3COONa — 10 g/L and subjected to activation. For this, the solution was heated to boiling. The heating process was carried out on a hotplate and usually took about 10 minutes. After boiling the solution, heating was stopped and the solution was allowed to cool to 70 ºC. At the same time, visual observations show that when the temperature rises, hydrogen evolution is practically absent. But after boiling it is already visually possible to observe the release of gaseous hydrogen. Consequently, silicon carbide, which has semiconducting properties, can be a catalyst for the decomposition of hypophosphite ions after such activation, and there is slow recombination of adsorbed hydrogen atoms. The temporary existence of hydrogen atoms and can lead to the process of chemical nickel plating.

Results and discussion

Figure 1 shows the electron image of the carborundum powder after such an activation cycle. This figure, it is possible to distinguish light areas characteristic of the metal phase and dark areas of carborundum. The spectral analysis presented in the table shows that the content of carborundum (Si + C) is over 94 % in dark areas, and the content of nickel phosphorus coating (Ni + P) is over 90 % in light areas.

At the same time, even in the dark area, nickel is released (3.28 %), which indicates the initial stage of activation of these areas. It also draws attention to the fact that when nickel is released, no phosphorus is released. Perhaps this is due to the fact that when activated, reaction (6) is predominant. In general, after activation, the nickel extraction process takes up about 36 % of the total carborundum.

Experiments have shown that after carrying out the activation process three times, a nickel layer is formed that is sufficient for carrying out the process at usual temperatures (80–95 ºC). This technique should be considered more preferable than prolonged boiling in the electrolyte of chemical nickel plating, in which undesirable decomposition of hypophosphite and nickel release outside the surface of carborundum is possible.

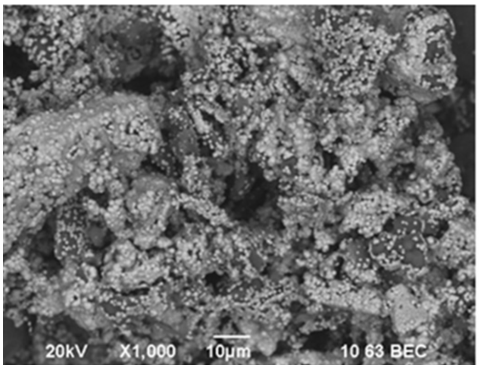


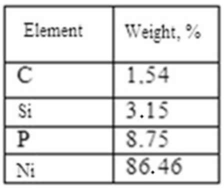
Element	Weight, %		
	Total	Spec-1	Spec-2
C	20.01	31.58	4.97
O	6.45	5.33	-
Al	0.42	-	-
Si	36.78	61.84	2.84
P	2.09	-	9.73
Fe	0.24	-	-
Ni	34.02	1.26	82.46

Figure 1. Electronic image after one activation cycle
(the Table shows the elemental composition common to the whole powder and for individual spectra)

Further growth of the metal film was carried out by chemical nickel plating in the usual solution of the following composition: $NiSO_4 \cdot 7H_2O$ — 30 g/L, NaH_2PO_2 — 10 g/L, CH_3COONa — 10 g/L, at an electrolyte temperature of 90 ºC for 30 minutes.

The data of the spectral analysis of the powder (Fig. 2) show that the carborundum particles are 95 % coated with a nickel-phosphorus coating.





Element	Weight, %
C	1.54
Si	3.15
P	8.75
Ni	86.46

Figure 2. Electronic image of carborundum powder after three cycles of activation
and chemical nickel plating at 90 ºC in ordinary acid electrolyte

A photograph of the powder, taken at a magnification of 8,000 times (Fig. 3), shows that the coating is formed in the form of spherical particles, the average diameter of which ranges from 300 to 750 nanometers. It is also seen from this figure that the individual spherical particles are collected in large agglomerates having a dense packing.

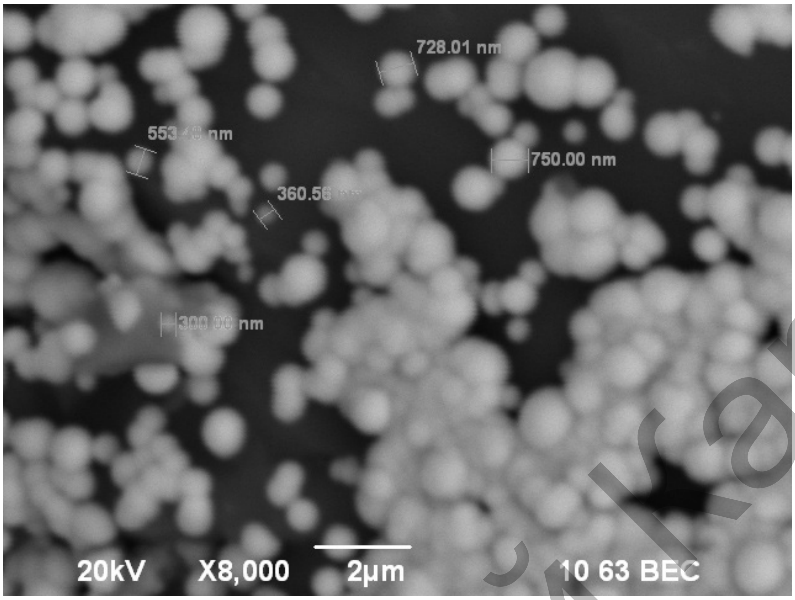


Figure 3. The structure of metallic nickel particles deposited on particles of carborundum powder after one cycle of activation in a solution of chemical nickel plating

It can also be seen from the above figures that the formation of a coating occurs only on the surface of the carborundum particles. Consequently, such a coating will provide the necessary adhesion between the particles of carborundum and the matrix in obtaining composite products or coatings.

Conclusions

Silicon carbide can be a catalyst for chemical nickel plating. However, this catalytic activity is manifested at high temperatures, which are achieved by boiling the electrolyte of chemical nickel plating. Such activation is explained by the decomposition of hypophosphite ions, leading to the release of hydrogen. The intermediate stage of the process is the formation of atomic hydrogen adsorbed on the surface of silicon carbide. As a result, the interaction of nickel ions with hydrogen atoms on the surface of carbide particles forms a metallic nickel film, which makes it possible to carry out the process at lower temperatures. In addition, for solutions for chemical nickel plating, electrolyte regeneration methods have been developed that make this process cheaper and more technologically advanced.

References

1 Ахметов Н.С. Общая и неорганическая химия / Н.С. Ахметов. — СПб.: Лань, 2014. — 495 с.

2 Патент Российской Федерации МПК C23F1/14 — № 2544319. Способ химического никелирования и раствор для его осуществления / Каблов Е.Н., Щетанов Б.В., Ефимочкин И.Ю., Севостьянов Н.В., Мурашева В.В., Вдовин С.М., Нищев К.Н. Заяв. 17.12.2013, Опубл. 20.03.2015.

3 Патент Российской Федерации МПК C23C4/12 — № 2542199. Способ получения композиционных покрытий из порошковых материалов / Григорьев С.Н., Тарасова Т.В., Попова Е.В., Смуров И.Ю. Заяв. 16.07.2013, Опубл. 20.02.2015.

4 Ferrante M. Metallization of silicon carbide with chromium powder / M. Ferrante, E. Pigoretti // Journal of Materials Science Letters. — 1992. — Vol. 11, No. 24. — P. 1687–1688.

5 Гамбург Ю.Д. Гальванические покрытия: справочник по применению / Ю.Д. Гамбург. — М.: Техносфера, 2006. — 215 с.

6 Вишенков С.А. Химические и электрохимические способы осаждения металлопокрытий / С.А. Вишенков — М.: Машиностроение, 1975. — 312 с.

7 Хокинг М. Металлические и керамические покрытия: подготовка, свойства, применение / М. Хокинг, В. Васатасри, П. Сидки. — М.: Мир, 2000. — 516 с.

8 Besov A.V. A method of manufacturing powder materials for plasma spraying retention coatings / A.V. Besov // Inventions in mechanical engineering. — 2001. — No. 2. — P. 14, 15.

9 Patent of the United States of America MPK C23C16/4417 — No. 5489449. Coated particles of inorganic or metallic materials and processes of producing the same / Kaoru U., Yukiyoshi Y., Tadashi F., Eisuke K., Satoshi A. Decl. 18.07.1994, Publ. 06.02.1996.

10 Patent of the United States of America MPK C09K3/1445 — No. 5250086. Multi-layer metal coated diamond abrasives for sintered metal bonded tools / Roger M., Edward J.C., David E.S. Decl. 25.03.1992, Publ. 05.10.1993.

11 Патент Российской Федерации МПК C23C24/04 — № 2257423. Портативное устройство для газодинамического напыления покрытий / Каширин А.И., Клюев О.Ф., Буздыгар Т.В., Шкодкин А.В. Заяв. 21.08.2003, Опубл. 10.03.2005.

12 Патент Российской Федерации МПК C23C24/04 — № 2247174. Устройство газодинамического напыления порошковых материалов / Косарев В.Ф., Лаврушин В.В., Спесивцев В.П., Сюн Т., Цзе У., Цзинь Х. Заяв. 30.04.2003, Опубл. 27.02.2005.

13 Хоперия Т.Н. Химическое никелирование неметаллических материалов / Т.Н. Хоперия. — М.: Металлургия, 1982. — 144 с.

14 Sataev M.S. A galvanic-chemical method for preparing diamond containing coatings / M.S. Sataev, S.T. Koshkarbaeva, S. Perni, S.Z. Nauryzova, P. Prokopovich // Colloids and Surfaces A: Physicochemical and Engineering Aspects. — 2015. — Vol. 480. — P. 384–389.

15 Sataev M.S. A low-temperature gold coating of the dielectric surfaces employing phosphine gas as a reducing agent / M.S. Sataev, P.A. Abdurasova, Sh.T. Koshkarbaeva, A.A. Bolisbek, N.K. Saripbekova, G.A. Kambarova, O.N. Koblanova, S. Perni, P. Prokopovich // Colloids and Surfaces A: Physicochemical and Engineering Aspects. — 2017. — Vol. 521. — P. 86–91.

16 Kozhakulov N.K. Stationary potential of metals and alloys in the process of chemical nickel plating / N.K. Kozhakulov, Sh.T. Koshkarbaeva, M.S. Sataev // Kazakhstan industry. — 2009. — Vol. 6, No. 57. — P. 56, 57.

Ш.Т. Қошқарбаева, М.С. Сатаев, П.А. Абдуразова, К.Б. Аманбаева, Е.Б. Райымбеков

Ұнтақ тәрізді карборундты химиялық никельдендіруді зерттеу

Ұнтақ тәрізді карборундтың бетіне металл жабындысын қолдану үшін технология әзірленді. Бұл мақсатта химиялық никель қаптамасы қолданылды. Бұл үрдістің катализаторлар қатарына кіре алмаса да, карборунд никель иондарының азаюына ықпал ететіндігі анықталды. Гипосфит ионының жоғары температурадағы ыдырау кезінде карборундтың бетінде молекулаға сутегі атомдарын рекомбинациялау арқылы баяулау сатысында жүреді деп болжануда. Сутегі атомдарының жоғары реактивтік қабілеттілігі никель иондарының азаюына әкеледі. Бұл карборундтың бетін белсендіруге және химиялық никель қаптамасына тән жағдайда металды одан әрі үдетуге мүмкіндік береді. Растрлы электронды микроскоп арқылы ұнтақ беті зерттелген тәжірибелерде ұнтақ бетін белсендірудің осындай механизмі жарамды екенін көрсетті. Осы технологияны зертханалық жағдайларда сынау карборундты бөлшектерге қажетті адгезиясы бар және құрамында 95 % химиялық никель бар жабынды алуға мүмкіндік берді.

Кілт сөздер: карборунд, кремний карбиді, химиялық никельдендіру, композициялық материал, сутегі атомдары, белсендіру, никель-фосфорлы қаптама.

Ш.Т. Кошкарбаева, М.С. Сатаев, П.А. Абдуразова, К.Б. Аманбаева, Е.Б. Райымбеков

Исследование химического никелирования порошкообразного карборунда

Разработана технология нанесения металлического покрытия на поверхность порошкообразного карборунда. При этом для этой цели использован процесс химического никелирования. Найдено, что карборунд, хотя и не входит в число катализаторов этого процесса, может способствовать восстановлению ионов никеля. Предполагается, что при высокотемпературном разложении гипосфит-иона выделение водорода происходит на поверхности карборунда с замедленной стадией рекомбинации атомов водорода в молекулу. Высокая реакционная способность атомов водорода приводит к восстановлению ионов никеля. Это позволяет активировать поверхность карборунда и проводить дальнейшее наращивание металла в условиях, обычных для химического никелирования. Эксперименты, в которых поверхность порошка исследовалась при помощи растрового электронного микроскопа, показали справедливость такого механизма активирования поверхности порошка. Проверка данной технологии в лабораторных условиях позволила получить покрытие, имеющее необходимое сцепление с частицами карборунда и содержащее 95 % химического никеля.

Ключевые слова: карборунд, карбид кремния, химическое никелирование, композиционный материал, атомы водорода, активация, никель-фосфорное покрытие.

References

1 Akhmetov, N.S. (2014). *Obshchaia i neorhanicheskaia khimiia [General and Inorganic chemistry]*. Saint-Petersburg: Lan [in Russian].

2 Kablov, E.N., Shchetanov, B.V., Ephimochkin, I.Y., Sevostiyanov, N.V., Murasheva, V.V., Vdovin, S.M., & Nishev, K.N. (2015). Sposob khimicheskoho nikelirovaniia i rastvor dlia eho osushchestvleniia [Method of chemical nickel-plating and solution for its realization]. *Patent of the Russian Federation MPK C23F1/14 — No. 2544319.* Decl. 17.12.2013, Publ. 20.03.2015 [in Russian].

3 Grigorev, S.N., Tarasova, T.V., Popova, E.V., & Smurov, I.Y. (2015). Sposob polucheniia kompozitsionnykh pokrytii iz poroshkovykh materialov [Method for preparing composite coatings of powder materials]. *Patent of the Russian Federation MPK C23C4/12 — No. 2542199*. Decl. 16.07.2013, Publ. 20.02.2015 [in Russian].

4 Ferrante, M., & Pigoretti, E. (1992). Metallization of silicon carbide with chromium powder. *Journal of Materials Science Letters, 11(24)*, 1687–1688.

5 Hamburg, U.D. (2006). *Halvanicheskie pokrytiia. Spravochnik po primeneniiu [Electroplated coatings. Application Guide]*. Moscow: Tekhnosfera [in Russian].

6 Vishenkov, S.A. (1975). *Khimicheskie i elektrokhimicheskie sposoby osazhdeniia metallopokrytii [Chemical and electrochemical methods of metal plating]*. Moscow: Mashinostroienie [in Russian].

7 Hawking, M., Vasatasri, V., & Sidky, P. (2000). *Metallicheskie i keramicheskie pokrytiia: podhotovka, svoistva, primenenie [Metallic and ceramic coatings: preparation, properties, application]*. Mosow: Mir [in Russian].

8 Besov, A.V. (2001). A method of manufacturing powder materials for plasma spraying retention coatings. *Inventions in mechanical engineering, 2*, 14–15.

9 Kaoru, U., Yukiyoshi, Y., Tadashi, F., Eisuke, K., & Satoshi, A. (1996). A. Coated particles of inorganic or metallic materials and processes of producing the same. *Patent of the United States of America MPK C23C16/4417 — No. 5489449*. Decl. 18.07.1994, Publ. 06.02.1996.

10 Roger, M., Edward, J.C., & David, E.S. (1993). Multi-layer metal coated diamond abrasives for sintered metal bonded tools. *Patent of the United States of America MPK C09K3/1445 — No. 5250086.* Decl. 25.03.1992, Publ. 05.10.1993.

11 Kashirin, A.I., Kliuev, O.F., Buzdygar, T.V., & Shkodkin A.V. (2005). Portativnoie ustroistvo dlia hazodinamicheskoho napyleniia pokrytii [Portable apparatus for gasodynamic deposition of coatings]. *Patent of the Russian Federation MPK C23C24/04 — No. 2257423.* Decl. 21.08.2003, Publ. 10.03.2005 [in Russian].

12 Kosarev, V.F, Lavrushin, V.V., Spesivtsev, V.P., Sjun, T., Tsze, U., Tszin, K. (2005). Ustroistvo hazodinamicheskoho napyleniia poroshkovykh materialov [Apparatus for gasodynamic deposition of powder materials]. *Patent of the Russian Federation MPK C23C24/04 — No. 2247174.* Decl. 30.04.2003, Publ. 27.02.2005 [in Russian].

13 Hoperia, T.N. (1982). *Khimicheskoe nikelirovanie nemetallicheskikh materialov [Chemical nickel plating of non-metallic materials]*. Moscow: Metallurhiia [in Russian].

14 Sataev, M.S., Koshkarbaeva, S.T., Perni, S., Nauryzova, S.Z., & Prokopovich, P. (2015). A galvanic-chemical method for preparing diamond containing coatings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 480*, 384–389.

15 Sataev, M.S., Abdurasova, P.A., Koshkarbaeva, Sh.T., Bolisbek, A.A., Saripbekova, N.K., & Kambarova, G.A., et al. (2017). A low-temperature gold coating of the dielectric surfaces employing phosphine gas as a reducing agent. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 521*, 86–91.

16 Kozhakulov, N.K., Koshkarbaeva, Sh.T., & Sataev, M.S. (2009). Stationary potential of metals and alloys in the process of chemical nickel plating. *Kazakhstan industry, 6(57),* 56–57.