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Morphology of Barrier Coatings and Formation of an Interphase Boundary by Brazing of Dissimilar Alloys

S. V. Maksymova, P. V. Kovalchuk, and V. V. Voronov

E. O. Paton Electric Welding Institute, N.A.S. of Ukraine,
11 Kazymyr Malevych Str.,
UA-03150 Kyiv, Ukraine

As established by the conducted studies of brazing dissimilar joints of Kovar with titanium alloy, applying a standard procedure of barrier nickel coating deposition on a titanium alloy by electrolytic method does not ensure its integrity during vacuum heating in the brazing mode. The structure, chemical heterogeneity of brazed joints and surface morphology of the nickel coating are studied by applying the chemical method of producing a barrier nickel coating. Proceeding from the derived investigation results, a 4-stage technology of electrolytic application for the barrier nickel coating is proposed. This coating preserves its integrity during vacuum brazing of the following dissimilar metals: BT1-0 titanium alloy with 29NK precision alloy. A detailed study of the Kovar + BT1-0 brazed joints with the application of electron microscopy and x-ray microspectral analysis confirm the formation of dense brazed seams with full penetration fillet regions with a eutectic rod-like structure, when using silver brazing filler metal.

Key words: structure, barrier coating, vacuum brazing, Kovar, titanium alloy.

Проведено дослідження з лютування різнорідних з’єднань ковару з титановим стопом. Встановлено, що застосування стандартної методики нанесення бар’єрного ніклевого покриття електролітичним шляхом на титановий стоп не забезпечує його цілісність під час нагріву за режимом високотемпературного лютування у вакуумі. Досліджено морфологію поверхні ніклевого покриття, структуру та хемічну неоднорідність паяних з’єднань із застосуванням хемічного методу одержання бар’єрного нікле-

Corresponding author: Svitlana Vasylivna Maksymova
E-mail: maksymova@paton.kiev.ua

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вого покриття. На основі одержаних результатів досліджень запропоновано 4-стадійний технологічний процес електролітичного нанесення бар'єрного ніклевого покриття, яке зберігає свою цілісність під час високотемпературного вакуумного лютування різнорідних металів: титанового стопу ВТ1-0 з прецизійним стопом ковар (29НК). Детальне дослідження лютованих з'єднань ковар (29НК) + ВТ1-0 із застосуванням електронної мікроскопії та мікрорентґеноспектральної аналізи підтвердило формування щільного лютованого шва з утворенням повних плавних галтельних ділянок з евтектичною стрижнеподібною структурою із застосуванням срібної люти.

Ключові слова: структура, бар'єрне покриття, вакуумне високотемпературне лютування, ковар, титановий стоп.

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1. INTRODUCTION

Brazed components from dissimilar metals are widely applied in the fabrication of various-purpose structures in nuclear, petrochemical, cryogenic, aerospace, shipbuilding and other industries. They include joints of titanium alloys with copper and nickel alloys, corrosion-resistant steel, and Kovar-type precision alloys. When producing this type of joints, the main objective is reducing the finished structure weight by preserving the special properties of its individual elements [1–5].

It should be noted that producing dissimilar joints of titanium alloys with Kovar is extremely poorly covered in the literature. However, the general approaches to producing dissimilar joints of this type are similar to those for titanium joints with corrosion-resistant steel.

Ensuring a reliable joint of bimetal titanium-steel (Kovar) structures is limited by two aspects: first, a considerable difference in the physical properties, such as the coefficient of thermal expansion, density and heat conductivity, which may lead to microstructural heterogeneity in the interphase region and high residual stresses [6–8]; and second, formation of intermetallic compounds at direct contact of titanium with other metals and alloys, which is due to the presence of a concentration gradient on the interface active running of the diffusion processes and seam metal saturation with base metal elements. Such structural features may lower the service properties of the combined dissimilar joints [9–11].

In order to avoid the formation of intermetallic phases, which may appear at the contact of molten brazing filler metal with titanium and Kovar (copper, corrosion-resistant steel, nickel, *etc.*), barrier coatings are used, which should prevent direct contact and their active interaction. Applying such coatings in combination with optimal temperature–time parameters of the brazing process promotes the improved performance of the produced brazed joints.

Metal, which is compatible with the brazing filler metal and forms strong bonds with the main structural material, is used for such barrier coatings. Coatings are produced using different methods: electrochemical, chemical, plasma deposition, or by vapour phase deposition on a cold substrate at electron beam heating, *etc.* [12–17]. Different elements, ensuring the required level of protection, are used as coatings. Barrier nickel coatings became widely applied at brazing. Their disadvantages include possible delamination at furnace treatment, which is attributable to hydrogenation during electrolysis with subsequent evolution of gaseous hydrogen, which impairs the physical-mechanical properties of the cathodic deposit, promotes the increase of internal stresses, leading to brittleness, the appearance of cracks, and delamination in some regions [18].

The purpose of the work is to study the structure of barrier nickel coatings on the BT1-0 titanium alloy and their behaviour, when heated according to the brazing thermal cycle, and to create a bearing technology that ensures integrity by brazing dissimilar materials and prevents chemical interaction of the molten brazing filler metal with the titanium substrate.

2. EXPERIMENTAL PROCEDURE

BT1-0 titanium alloy, Kovar precision alloy (29NK), and BAg8 brazing filler metal were used to perform the experiments (Table 1).

The barrier nickel coating was applied on BT1-0 titanium alloy using chemical and electrolytic methods.

For chemical deposition of nickel on BT1-0 titanium alloy, the following solution was used (g/l): nickel chloride—12–15, sodium hypophosphite—15–25, sodium citric acid—30–50, ammonium chloride—30–40, aqueous ammonia 25%—70–100, $pH = 8–9$. The time, during which the nickel layer was deposited, varied from 1 to 1.5 h. The solution was heated to the temperature of 80–90°C, and the temperature was monitored during the entire deposition process.

Electrolytic deposition of the barrier nickel coating was performed,

TABLE 1. Chemical composition of experimental materials.

Material/Grade	Chemical elements, wt. %					
	Fe	Ni	Co	Ti	Cu	Ag
BT1-0	up to 0.15	–	–	99.58–99.9	–	–
Kovar	51.14–54.5	28.5–29.5	17–18	up to 0.1	up to 0.2	–
BAg8	up to 0.1	–	–	–	27.29–28.4	71.5–72.5

using the following electrolyte (g/l): nickel sulfuric acid ($NiSO_4$)—250–300; nickel chloride ($NiCl_2$)—50–60; boric acid (H_3BO_3); $\tau = 25–30$ s. The schematic of the electrolytic method of barrier coating deposition is given in Fig. 1.

Further, the samples with the deposited nickel layer were heated in a

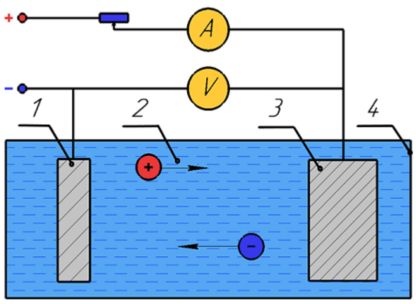


Fig. 1. Schematic of electrolytic method of barrier coating deposition: *1*—anode; *2*—electrolyte; *3*—cathode; *4*—container.

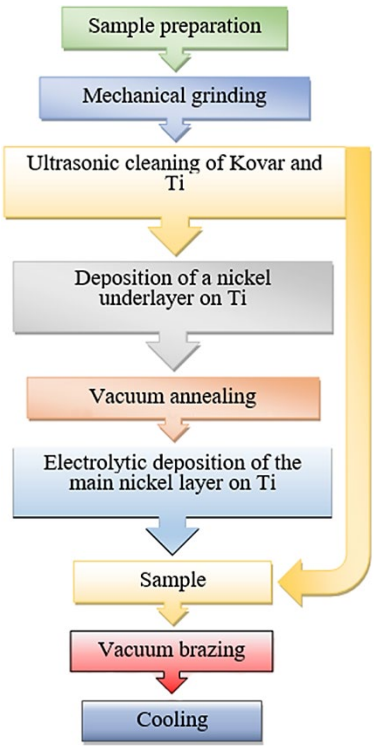


Fig. 2. Experimental procedure of brazing.

vacuum of $5 \cdot 10^{-5}$ mm Hg up to the temperature of 800°C with 3 min soaking and were brazed with the application of silver brazing filler metal (BAg8). Experimental procedure of brazing is shown in Fig. 2.

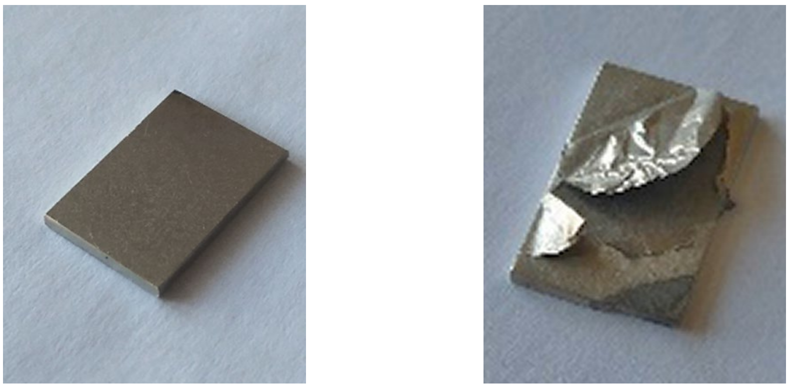
The produced samples with coating and samples of brazed dissimilar joints were used to prepare microsections by the standard procedure. They were studied (without chemical etching) by applying a scanning electron microscope Tescan Mira 3 LMU, fitted with energy-dispersive spectrometer Oxford Instruments X-max 80 mm^2 with INCA software package.

3. RESULTS AND DISCUSSION

During the investigation of titanium alloy samples with a nickel coating, which was produced by chemical method, it was established that despite the coating appearance (without any visible defects), it does not preserve its integrity at subsequent high-temperature heating in vacuum (Fig. 3, *a*, *b*).

It is related to the presence in the coating composition of a considerable amount of phosphorous, which precipitates from the electrolyte. During heating by the thermal mode of brazing, phosphorus interacts with the titanium substrate to form a brittle layer, which leads to the cracking of the coating with its further delamination (Fig. 3, *b*). The increase of phosphorus concentration in the coating along the seam–titanium alloy interface is confirmed by the results of x-ray microspectral studies, which were derived at electron beam scanning of dissimilar Kovar–titanium alloy joints (Fig. 4, *a*, *b*, *c*, *d*).

Local x-ray microspectral analysis revealed that, after brazing, the



a *b*

Fig. 3. Sample of BT1-0 alloy coated by a layer of nickel by the chemical method: before (*a*) and after heating (*b*) in vacuum at the temperature of 800°C, 3 min.

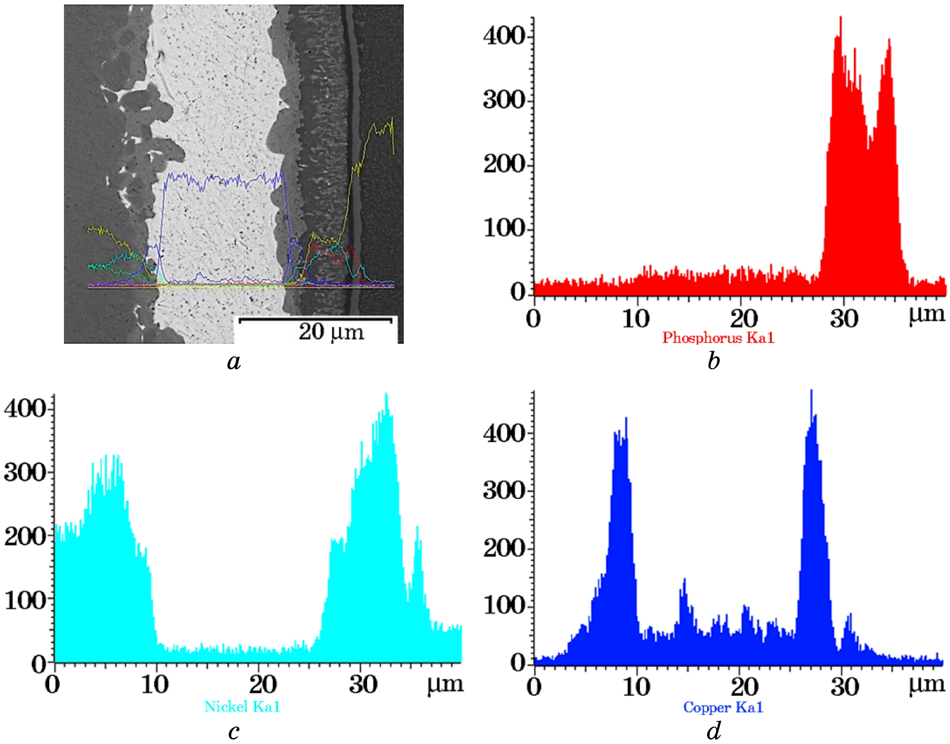


Fig. 4. Electronic image (*a*) and qualitative distribution of the following elements: phosphorus (*b*); nickel (*c*); copper (*d*); at electron beam scanning of Kovar–titanium alloy brazed joint.

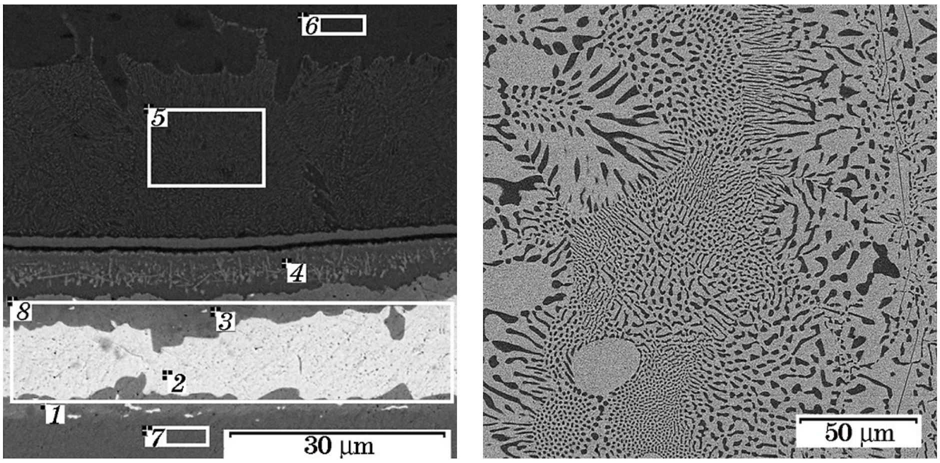
zone of the nickel coating (produced chemically) contains up to 18.34 wt. % phosphorus (Fig. 5, *a*, Table 2).

A silver-based solid solution with inclusions of copper-based solid solution in the central zone and a copper-based solid solution in the peripheral regions are predominantly crystallized in the brazed seam.

The structure of the fillet region differs from the one described above. It is characterized by a classical rod-like eutectic structure formed by two solid solutions: silver-based and copper-based (Fig. 5, *b*). A classical electrolytic method of coating deposition was used to eliminate the presence of phosphorus and improve the quality of barrier nickel coating [12].

The main advantages of this method are simplicity, relatively low cost, stability and controllability of the process, and the possibility of simultaneous deposition on the entire product surface. The scheme of this process is given in Fig. 1.

Based on the available published data, nickel plating is usually performed using electrolytes, in which nickel is present mainly in the



a *b*

Fig. 5. The studied regions (*a*) and the microstructure of the fillet (*b*) of Kovar–titanium alloy brazed joint with chemically produced barrier coating.

TABLE 2. Chemical composition of individual phases in Kovar–titanium alloy brazed joint.

No. of spectrum	Chemical elements, wt.%							
	Al	P	Ti	Fe	Co	Ni	Cu	Ag
1	0.00	0.00	0.25	2.09	0.74	7.61	86.24	3.07
2	0.00	0.00	0.48	0.24	0.35	0.34	8.40	90.19
3	0.00	0.20	2.79	2.31	0.65	29.20	64.37	0.48
4	0.00	18.34	25.63	0.64	0.26	50.08	5.04	0.00
5	0.25	0.19	92.29	0.24	0.00	7.03	0.00	0.00
6	0.37	0.00	99.39	0.00	0.00	0.24	0.00	0.00
7	0.00	0.00	0.39	52.95	18.28	28.38	0.00	0.00
8	0.10	0.00	0.58	0.76	0.22	4.37	37.28	56.69

form of two-valent cations Ni^{2+} [12, 13].

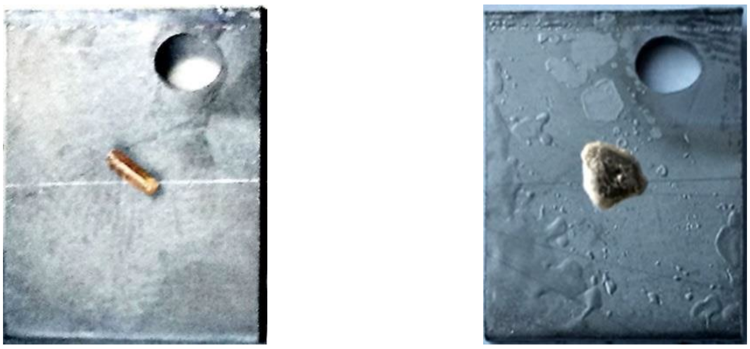
Depending on the nickel salt used, the electrolytes are divided into three main groups: sulphate, sulfamate and fluoroborate. In addition to nickel salts, various organic and inorganic additives are introduced into the composition of electrolytes, which promote an increase of the solutions' electrical conductivity and anode solubility, prevent slurry formation, allow obtaining shiny deposits on the base metal surface, increase the hardness, reduce porosity and eliminate the process of pitting formation in the coatings [12, 13].

It should be noted that the proposed in literature etching and deposition of underlayers, using a mixture of nitric and hydrofluoric acids in any concentration, leads to deterioration of the coating properties and its adhesion to the substrate, causing delamination during heating. This is related to the formation of titanium hydrate on the surface, which decomposes at heating in a vacuum with hydrogen evolution, which is exactly what results in coating delamination. As nickel precipitation on the cathode occurs with a considerable electrode polarisation and the overvoltage of hydrogen evolution on nickel is low, the amount of coating metal decreases at nickel plating. In order to increase it, the solution *pH* is maintained in the range of 4.0–4.5. Under such conditions, there is no formation of nickel hydroxides, which influence the coating's mechanical properties. In order to stabilize the solution *pH*, buffer additives are introduced into the electrolyte composition (usually boric acid H_3BO_3) [14].

During the performance of experiments on spreading of BAg8 brazing filler metal over the barrier nickel coating (on titanium alloy samples), it was found that the application of a standard procedure of electrolytic deposition of the barrier coating does not ensure its integrity during heating in vacuum (vacuum of $5\cdot10^{-5}$ mm Hg, 800°C, 3 min). In some areas, it peels off with the formation of convex regions, which is clearly shown in Fig. 6, *a*, *b*.

Detailed microstructural studies showed that when producing a nickel coating on the titanium plate by electrolytic method (without deposition of a nickel interlayer), crystallization of a dispersed crystalline structure takes place, consisting of particles of a faceted shape. Its density is very low in some regions (Fig. 7, *a*, *b*).

The formation of isolated defects in the form of pores of different geometry and dimensions is observed in individual regions of the pro-



a *b*

Fig. 6. Samples of BT1-0 alloy with barrier nickel coating and BAg8 brazing filler metal: before (*a*) and after heating (*b*) in vacuum.

duced coating surface. It should be noted that the presence of porosity in the coating at the brazing of dissimilar materials has an adverse effect on the brazed joint quality.

Proceeding from the obtained investigation results, a 4-stage tech-

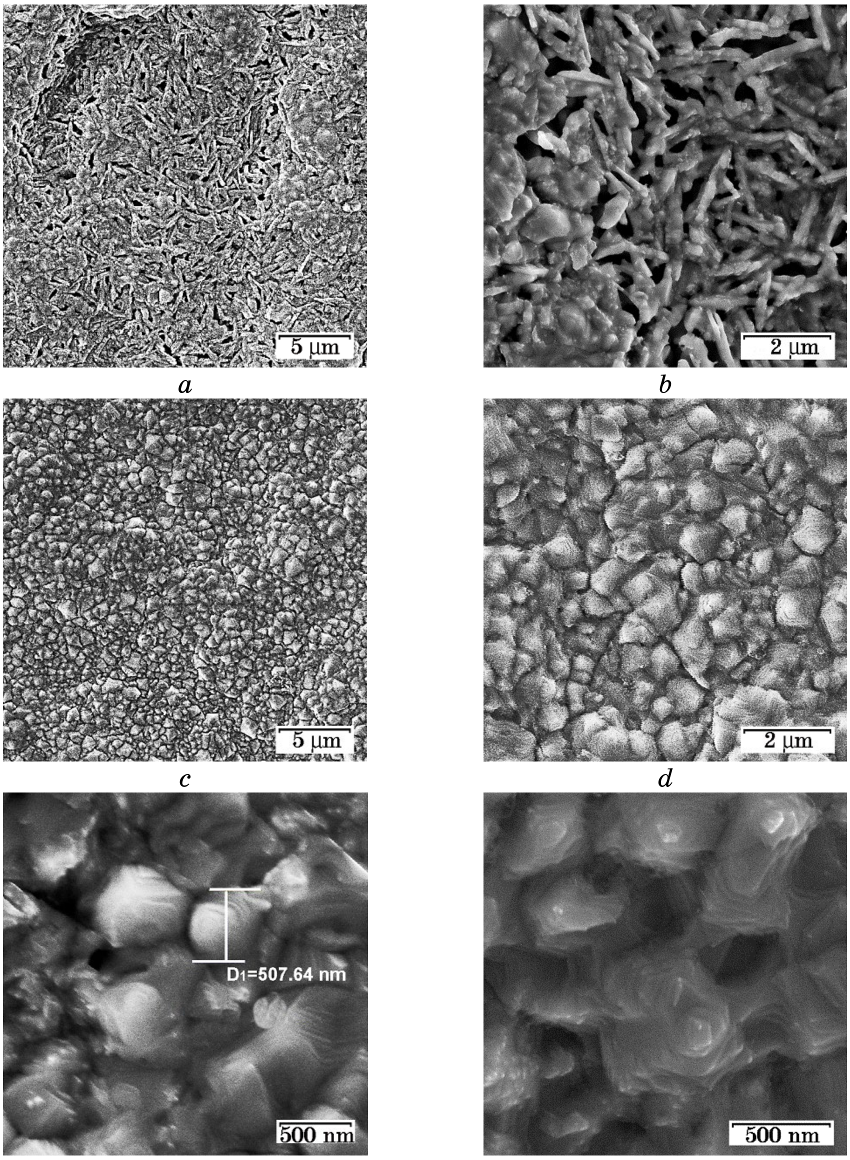


Fig. 7. The surface of the nickel coating of a low density (*a*, *b*) produced without underlayer (heat treatment) and with underlayer and heat treatment (*c*, *d*, *e*, *f*).

nological process of deposition of a barrier nickel coating on the titanium alloy was proposed and verified, which ensures its density and integrity at further vacuum heating [19]. This technology includes the following stages: mechanical grinding; chemical deposition of a nickel underlayer (solution composition (g/l): 200–220 of $NiCl_2$; 140–150 of HCl; ammonium fluoride 20–40, $T = 35–40°C$, $\tau = 3–25$ s); annealing in the following mode: $T = 500°C$, $\tau = 2.5$ h under a vacuum not worse than $5 \cdot 10^{-5}$ mm Hg.

At the electrolytic deposition of the main nickel layer, the nickel particles are formed on the already existing underlayer, their crystallization and growth occurring in different directions and, thus, they cover the entire surface of the underlayer and form the main dense coating (Fig. 7, *c*, *d*, *e*, *f*). The dispersed structure of the coating consists of particles of faceted morphology of various sizes from 507 nm to 1 µm (Fig. 7, *c*, *d*). Results of local x-ray microspectral analysis revealed the presence of titanium in the amount not exceeding 7.8 wt.%.

During the performance of experiments to produce dissimilar joints of Kovar + BT1-0 with the application of BAg8 brazing filler metal in keeping with the thermal mode of brazing, it was found that at the application of the proposed procedure of nickel coating deposition, it preserved its integrity during brazing, and delamination was absent (Fig. 8, *a*, *b*). The input (Fig. 8, *a*) and output fillets (Fig. 8, *b*) are clearly visible on the brazed samples.

A detailed study of Kovar + BT1-0 brazed joints with the application of electron microscopy and x-ray microspectral analysis confirmed the sound formation of the coating (Fig. 9, *a*) and dense brazed seams with full fillet regions (Fig. 9, *b*).

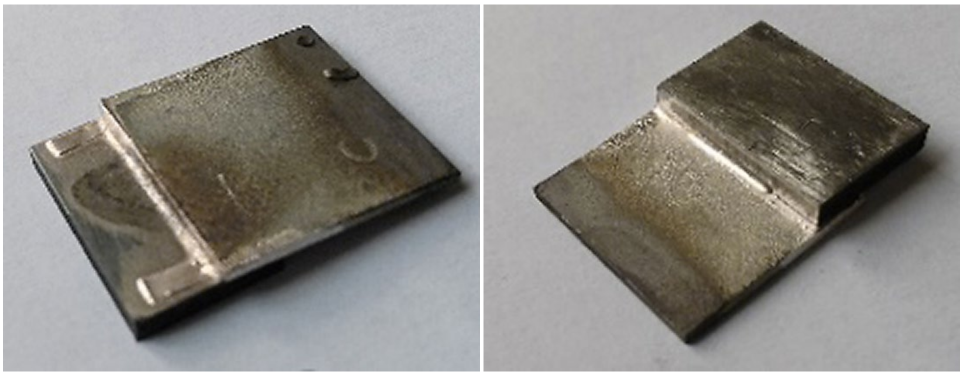
During brazing studies, it was established that the proposed procedure of barrier nickel coating deposition on a titanium alloy allows producing sound brazed joints and preventing chemical interaction of molten brazing filler metal with BT1-0 titanium alloy.

4. CONCLUSION

As determined, applying the standard procedure of chemical and electrolytic deposition of barrier nickel coating on the titanium alloy does not ensure its integrity at further heating by the mode of the technology of brazing Kovar–titanium alloy dissimilar joints (in vacuum).

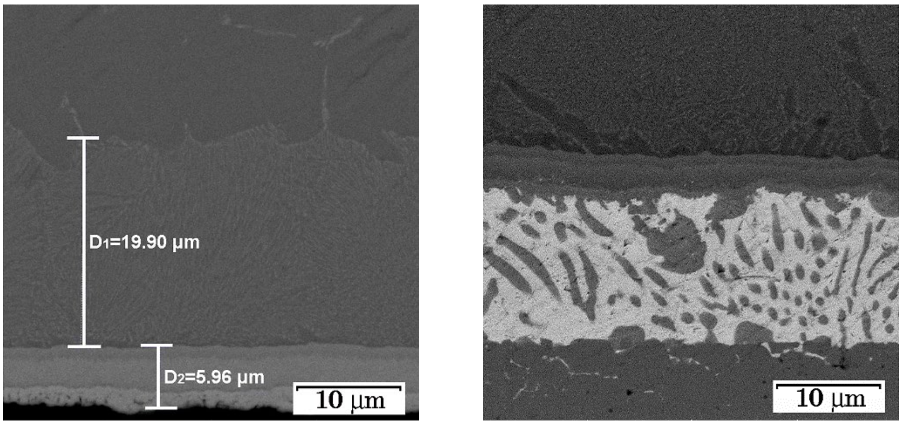
The results of local x-ray microspectral analysis confirmed that at the application of the chemical method of producing the nickel coating, a nickel layer is deposited, which contains phosphorus (up to 18 wt.%).

Proceeding from the performed research, a 4-stage technology of electrolytic deposition of a barrier nickel coating on BT1-0 titanium alloy was proposed. It includes producing a nickel interlayer and its heat treatment (before deposition of the main layer) to ensure the in-



a *b*

Fig. 8. Appearance of brazed samples with input (*a*) and output fillets (*b*) in joints of Kovar (29NK)–titanium alloy (BT1-0).



a *b*

Fig. 9. Nickel coating on a titanium plate (*a*) and seam microstructure (*b*) in Kovar + BT1-0 brazed joint.

tegrity under vacuum heating by the mode of brazing Kovar–titanium alloy dissimilar joints and to prevent the interaction of molten brazing filler metal with BT1-0 titanium alloy.

It was proved empirically, using electron microscopy, that, at vacuum brazing of Kovar + BT1-0 dissimilar joints, the proposed barrier nickel coating promotes the formation of tight sound brazed seams.

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