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DETERMINING PHYSICAL-CHEMICAL PATTERNS DURING THE FORMATION OF BRAZED JOINTS BETWEEN TUNGSTEN AND CARBON-CARBON COMPOSITE MATERIAL

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This study investigates experimentally produced brazed joints between carbon-carbon composite material (CCCM) and tungsten in a vacuum.

The task addressed is to obtain high-temperature brazed joints capable of operating at temperatures of 1400–1600°C in a vacuum under conditions of high thermal cycling loads. Existing methods for joining CCCM with tungsten testify for a virtual lack of experience in brazing such materials, especially for structures of thermal emission equipment.

In this work, a method was used to produce a metallized layer zone with partial melting using a mixture of Ti-Nb-Zr powders on the inner surface of an CCCM sample. Subsequently, the CCCM and tungsten samples were brazed with a Ti-Nb filler metal at a temperature of 1840°C in a vacuum.

The results of microstructural analysis revealed that the brazed joint exhibits a zonal structure. Zone I – a reaction carbide layer (width 10–12 µm), zone II – diffusion layer (width up to 70 µm), zone III – reaction layer adjacent to tungsten (width up to 30 µm). The results of phase formation modeling conducted at a temperature of 1840°C indicate the predominant formation of TiC, NbC, Nb6C5, and Nb2C. Additionally, the distribution of C, Ti, Nb, and W in the brazed joint was determined. The results of the microhardness study confirmed the accuracy of the simulation and showed that microhardness values decrease from Zone I (2300 HV) to Zone III (500–600 HV).

The proposed solutions demonstrate that the metallized layer helps retain filler in the joint gap; reduces thermomechanical stresses; and promotes the formation of a gradual hardness gradient. Together, these characteristics improve the ductile properties of the brazed joint.

The results of this study could be applied in the field of instrument engineering, specifically in the manufacture of cathode components whose emitters are made from ultrafine powders of rare-earth borides or their alloys

Keywords: carbon-carbon composite material, vacuum brazing, tungsten, phase formation, cathode

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1. Introduction

Carbon-carbon composite material (CCCM) can be used in the parts of thermionic equipment, namely the parts of resistive heaters, current conductors, and in the design of cathodes. Such parts operate at temperatures of 1400–1600°C under conditions of high thermocyclic loads in a vacuum environment [1]. The term of reliable operation of such joints, first of all, determines the operating time of the entire paper; therefore, prolonging this term is an important task to ensure the reliability and durability of the cathode.

A significant issue in the use of CCCM is obtaining a high-quality connection with refractory metals that will be operational at temperatures of 1400–1600°C. For cathode parts made of CCCM, the use of such types of fixation as threaded or riveted is not recommended due to the fragile nature of CCCM and the need to obtain sufficiently hermetic joints. The high operating temperature of joints prevents the use of adhesive compositions [2, 3]. Thus, brazing becomes one of the most promising methods for connecting parts from CCCM to each other and to refractory metals.

Techniques of joining carbon materials with metals are based on the formation of the joint zone in the liquid or solid phases, taking into account the physicochemical processes occurring in this process. It has been established that the strength of the brazed joint depends on the depth of penetration of the melt into the pores of the CCCM, as well as the technological parameters of brazing: compression force, temperature, holding time, and rate of temperature change [4]. One of the main difficulties that arise when brazing thin-walled cylindrical parts made of CCCM and tungsten is the high and uneven structural porosity of CCCM. During brazing, a branched capillary system contributes to the drawing of filler into the pores of CCCM and filling the voids of the part at high speed, forming defects in the brazing joint in the form of cavities. Capillaries have different geometry and dimensions: 10…70 μm in the longitudinal direction of the fibers and up to 0.5 mm in the transverse direction.

To solve this problem, the application of an intermediate zone of a metallized layer and promising filler metals for high-temperature brazing in a vacuum using carbide-forming metals Ti, Nb, Zr are used. The use of these metals contributes to obtaining a strong bond, reduces thermomechanical loads, and contributes to the formation of a more gradual gradient of carbon concentration during brazing from the carbide phase to the metal [5, 6].

The limitations of existing technologies for obtaining reliable high-temperature joints between CCCM and tungsten stress the relevance of determining the physicochemical regularities in the formation of brazed joints in a vacuum environment.

2. Literature review and problem statement

The most widely used techniques for joining refractory metals to carbon-based materials are the ones given in [7]:

– diffusion welding in a vacuum through a non-melting metal layer;

– welding using an electron beam and a gas-electric arc;

– high-temperature brazing in furnaces with a controlled atmosphere.

There are known methods for diffusion welding of graphite in the solid phase. Patent [8] describes the gas-phase deposition of nickel and platinum, which is carried out on the joined surfaces heated to 500°C. It is shown that nickel is deposited by deposition from an atmosphere containing nickel carbonyl (a mixture of carbonyl and hydrogen vapors). It is possible to deposit intermediate metal layers of nickel and platinum by electrolytic method. After metallization, the joined surfaces are compressed together under pressure and at a temperature sufficient to obtain a strong weld. However, the adhesion strength of electrolytic coatings with graphite is low and does not exceed 20 kgf/cm^2. The cited study mainly concerns the connection of graphite and titanium, which limits its application for CCCM. The heterogeneous surface of CCCM, which has irregularities and high porosity, requires the application of a larger amount of metals for deposition. Such a mechanism leads to the formation of irregularities in the metallized layer and, as a result, thickening of the carbide layer, which reduces the mechanical properties of the joint. In addition, the use of equipment for deposition, as well as the use of platinum, significantly increases the cost of the final product.

An option for overcoming these shortcomings is the technology of high-temperature brazing of graphite materials with metals involving a liquid phase. Thus, patent [9] provides a method of high-temperature brazing of graphite and corrosion-resistant refractory metal, which is used for parts of electrovacuum devices and nuclear reactor assemblies. The following filler metals were used to implement the technology: 20…50% Au; 20…50% Ni; 15…45% Mo; 30…45% Graphite-metal products brazed with these filler metals have high corrosion resistance in molten salt systems of the LiF-ReF$_2$-UF$_2$ or LiF-BeF$_2$-ZrF$_4$-UF$_4$ type. The brazing temperature was 1200–1400°C. Such compounds withstood ten-fold thermal cycling at temperatures from 20 to 700°C. The disadvantage of this method is the low duration of operation under thermocyclic loads, which the brazed joint can withstand at temperatures up to 700°C. The most likely reason is high thermomechanical loads and excessive diffusion of carbon into the brazing zone, which contributes to embrittlement of the brazed joint.

In work [1], laboratory tests of heaters made of CCCM and conductors made of titanium alloy VT1-00 were conducted. The temperature range of operation of the brazed joint is from minus 100 to plus 400°C. TIG (Tungsten Inert Gas) surface arc welding in an argon environment was used for the joint, which was supplied between the welding site and a non-consumable tungsten electrode. It was shown that during mechanical tests of the welded joint, the wire separation from the heater occurs with the remains of CCCM and the transition layer of titanium carbide formed during welding. The disadvantage of this method is the impossibility of its use at temperatures above plus 400°C. In addition, the use of TIG (Tungsten Inert Gas) welding for parts with CCCM titanium alloy VT1-00 leads to active saturation with liquid titanium of the entire volume of the thin-walled CCCM part. Due to the capillary effect, liquid metal leaks to the outside and defects in the brazed joint in the form of cavities are formed. In addition, the use of filler materials for welding is limited to the use of standardized grades, which complicates the process of optimizing the joint technology.

An option to eliminate the drawbacks is brazing in vacuum, using zones of a metallized layer. In work [10], a comprehensive review of the problems of joining CCCM and metals was conducted, technologies and brazing of CCCM and titanium alloys with filler metals using a wide range of materials were analyzed. In [11] it was shown that when brazing CCCM with titanium alloy TC4, a metallized layer of materials of the Cu-Mo system was used. Brazing was carried out with Ag-26,7Cu-4,6Ti filler at a temperature of 910°C and a holding time of 10 minutes. The obtained joints had a shear strength of 25 MPa. In [12], when brazing CCCM with titanium alloy TC4, a metallized layer of materials of the Cu-Mo system was used. Brazing was carried out with TiZrNiCu filler at a temperature of 900°C. The resulting joints had a shear strength of 21 MPa. In [13], the brazing of CCCM with titanium alloy Ti-46Al-2Cr-2Nb was carried out using Ag-26.7Cu-4.6Ti filler with an applied pressure of 5 kPa at a temperature of 900°C. The resulting joints had a shear strength of 25 MPa. The disadvantage of the technologies in [11–13] is the formation of unstable brittle intermetallics Ti(Cu,Ni)$_2$ at temperatures of about 1000°C. One of the reasons is the dissolution of Cu in the filler metal. In addition, the disadvantage is the impossibility of using the fillers specified in [11–13] at temperatures above 1000°C due to the high degree of evaporation of the filler components in a vacuum.

In [10], a comprehensive review of the problems of joining CCCM with heat-resistant alloys based on nickel is given. It is shown in [14] that the brazing of CCCM and heat-resistant nickel alloy GH3044 was carried out using an intermediate layer, which is represented in the form of a multilayer foil Ti/Ni/Cu/Ni by a two-stage method. Brazing was carried out at a temperature of 1030°C and a holding time of 30 minutes. The resulting joints had a shear strength of 32 MPa. In [15], the brazing of CCCM and heat-resistant nickel alloy was carried out with the participation of a metallized layer with materials of the Ni-Ti system. Brazing was carried out with Ag26Cu2Ti filler at a temperature of 880°C and a holding time of 10 minutes. The resulting joints had a shear strength of 16 MPa. In [16], the brazing of CCCM and heat-resistant nickel alloy GH3044 was carried out using a metallized layer with materials of the Ni-Ti system. Brazing was performed with Ag (10, 20, 30, 40) Ti fillers at temperatures of 990–1080°C and holding time from 10 to 90 minutes. The resulting joints had a shear strength of about 45 MPa. The disadvantage of the technologies given in [14–16] is the formation of brittle intermetallic phases Ti_2Ni, as well as the impossibility of their use above a temperature of 1080°C due to the high degree of evaporation of the filler components in vacuum.

The above methods indicate the practically absent experience of joining thin-walled tubular parts of CCCM with tungsten in a vacuum environment for thermionic equipment structures operating at temperatures of 1400–1600°C. In addition, it should be noted that in all the above-mentioned methods, the selection of filler metal is provided for each specific case separately, depending on the type of materials being joined, the joining technology, operating conditions, as well as the medium.

An option for overcoming these shortcomings is to obtain an intermediate metallized zone, with plastic metals, on the surface of CCCM with subsequent high-temperature brazing in a vacuum environment. Additionally, the use of materials that do not form brittle intermetallics with titanium but form a solid substitution solution. Therefore, the use of CCCM and tungsten compounds for parts of thermionic equipment, operable at temperatures of 1400–1600°C under thermocyclic modes in vacuum, creates an urgent problem of the need for individual development of brazing technology.

All this allows us to state that it is advisable to conduct a study aimed at determining the physicochemical regularities in the formation of brazed CCCM compounds with tungsten in vacuum with a Ti-Nb system filler.

3. The aim and objectives of the study

The aim of our work is to determine the physicochemical regularities in the formation of brazed joints between carbon-carbon composite material and tungsten in vacuum with Ti-Nb system filler. This will allow us to improve the stability of the cathode operation and improve its characteristics by expanding the operating temperature range to 1600°C.

To achieve this goal, the following tasks were set:

– to investigate the microstructure and chemical composition of the brazed joint;

– to model the phase formation of the brazed joint;

– to determine the microhardness of the brazed joint to confirm the results from the phase formation modeling.

4. The study materials and methods

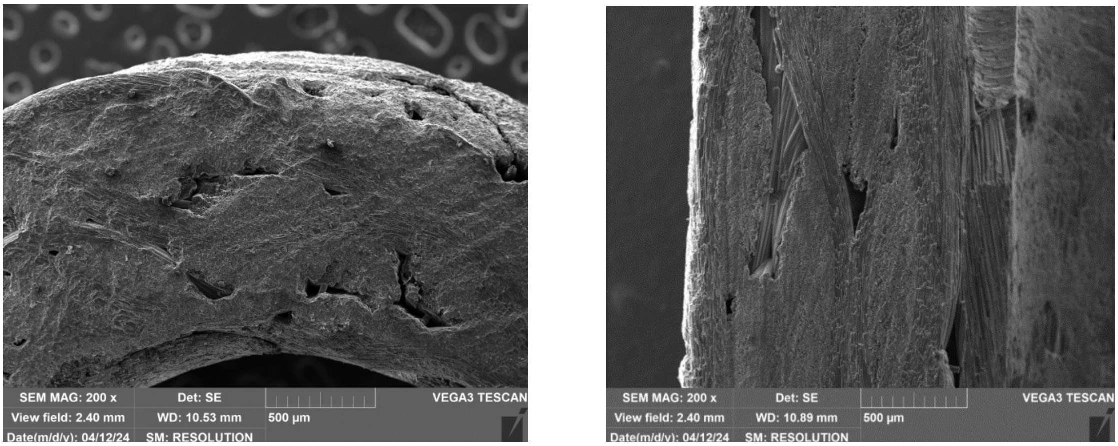
The object of our study is experimentally obtained brazed joints between carbon-carbon composite material and tungsten in vacuum.

The principal hypothesis assumes that the use of a metallized layer of the Ti-Nb-Zr system and high-temperature filler of the Ti-Nb system could make it possible to obtain strong brazed joints, operable at temperatures of 1400–1500°C and briefly up to 1600°C.

In this work, the assumptions are adopted that the phase formations obtained as a result of modeling phase formation at 1840°C are largely confirmed by the given phase diagrams at similar temperatures.

To simplify the modeling of phase formation, phases whose content was less than $1 \cdot 10^{-9}$ kmol were not taken into account.

For the study, CCCM was used in the form of tubular samples with dimensions: diameter 5.7 mm and length 8 mm. The CCCM used has a 3D structure of carbon fiber reinforcement, which is compacted with pyrocarbon during gas phase deposition. This configuration makes it possible to obtain density indicators of 1.12…1.36 g/cm^3, open porosity of 12.2…24.1% [17]. The macrostructure of CCCM includes a branched system of capillaries located between the fibers and having different geometry and dimensions: 10…70 μm in the longitudinal direction of the fibers and up to 0.5 mm in the transverse direction (Fig. 1). A cylindrical sample of tungsten of the VA grade (W-99.95%) was used as a refractory metal.



a *b*

Fig. 1. Macrostructure of a sample of carbon-carbon composite material: *a* – in the transverse direction of the fibers; *b* – in the longitudinal direction of the fibers

A metallized layer zone on the inner surface of the CCCM tube was created with a mixture of Ti-Nb-Zr system powders. The powders were ground in a ball mill to a fraction size of 10–15 μm. Before application, the CCCM samples were degreased and ultrasonically cleaned. The powder mixture layer was applied by immersion in a solution consisting of a thickener and a mixture of Ti-Nb-Zr system powders. The creation of a metallized layer zone was carried out by partial melting in a vacuum environment (pressure not more than $2 \cdot 10^{-3}$ Pa) at a temperature of 1900°C.

We obtained a brazed CCCM joint with tungsten in vacuum (pressure not more than $2 \cdot 10^{-3}$ Pa) using a heater shown in Fig. 2. The parts for brazing were placed at the bottom of a graphite crucible. A tungsten-rhenium thermocouple was used to record the temperature, which was located directly above the sample. The mixture of Ti-Nb filler powders was ground and degreased. Brazing was carried out at a temperature of 1840°C in vacuum.

Microstructure analysis was performed by scanning electron microscopy on a Tescan Vega 3 microscope (Czech Republic) using a secondary electron detector at a cathode voltage of 20 kV, under a resolution mode.

Determination of the chemical composition and mapping of the distribution of chemical elements were performed by energy dispersive X-ray spectroscopy using an Inca X-Act spectrometer and AZtecOne software (Oxford Instruments), combined with Tescan Vega 3, using line and plane scanning modes.

Phase formation modeling was performed using the HSC Chemistry software. The equilibrium composition of the heterogeneous system was simulated using the Gibbs free energy minimization method. The microhardness of the brazed joint was measured in cross-section with a PMT-3 microhardness tester by the Vickers method at loads from 10 to 200 grams on different parallel lines in width. The loading and unloading time was 15 seconds, the holding time under load was 30 seconds. The measurement step was from 5 to 20 microns, which was determined depending on the constancy of the hardness indicators and the sizes of neighboring impressions. For greater accuracy, the number of measurements in individual areas was increased.

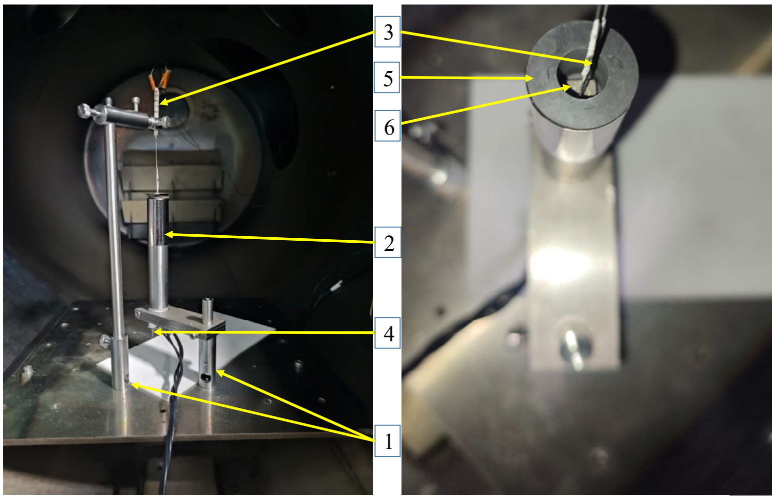


Fig. 2. Laboratory heater: 1 — brackets; 2 — carbon-carbon composite heater and heat shields; 3 — tungsten-rhenium thermocouple; 4 — current conductors; 5 — graphite crucible; 6 — carbon-carbon composite sample

5. Results of investigating the physicochemical regularities in the formation of brazed joints between carbon-carbon composite material and tungsten

5. 1. Microstructure and chemical composition

5. 1. 1. Microstructure and chemical composition of the metallized layer zone

The acquired images of the distribution maps of chemical elements, which were superimposed on the microstructure image, indicate that the thickness of the metallized layer zone varies from 20 to 75 μm along the entire length of the sample. According to Fig. 3, the layer thickness in the direction of the conditional line data 7 is 60 μm, and along line data 9–70 μm.

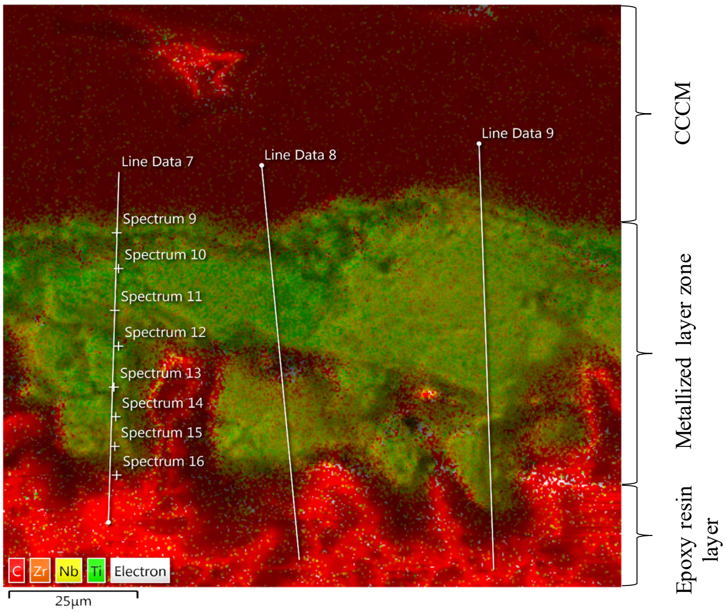


Fig. 3. Microstructure and distribution of chemical elements in the metallized layer zone of a carbon-carbon composite material

It has been established [4] that during the interaction of liquid titanium and zirconium with graphite, complete wetting occurs – the contact angle is close to or equal to zero. The wetting criterion in such systems is the spreading rate or the final radius of the liquid drop. It is known [4] that niobium does not form equilibrium contact angles on graphite and spreads worse than titanium. The contact angle of graphite wetting by niobium is 20–40 degrees.

The chemical composition of the metallized layer zone is given in Table 1.

The microstructure of the metallized layer zone of the tubular sample of the CCCM shown in Fig. 3 is characterized by the presence of sintered and fused agglomerations of Ti, Nb, and Zr metal powders. In zones where the deposition was uneven, as a result of the complex morphology of the CCCM, agglomerations of sintered particles with sizes of 7–15 μm are observed, which form a porous structure. The most uniform distribution of chemical elements of the metallized layer zone is shown in Fig. 4 in the direction of the conditional line data 7. The chemical composition of the metallized layer zone is mainly characterized by the C-Nb-Ti and C-Zr-Nb phase diagrams.

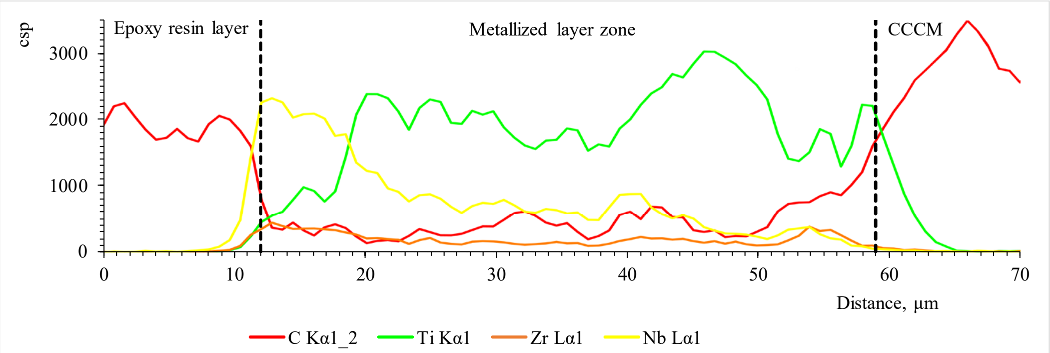


Fig. 4. Distribution of chemical elements in the zone of the metallized layer of the carbon-carbon composite material in the direction of the conditional Line Data 7 (Fig. 3)

Table 1

Chemical composition of the metallized layer zone in the direction from the carbon-carbon composite material (according to Fig. 3)

Study zone	Chemical composition, %			
	C	Ti	Nb	Zr
Spectrum 9	94.91	4.61	–	–
Spectrum 10	72.52	26.20	–	0.52
Spectrum 11	52.19	42.45	2.15	1.23
Spectrum 12	52.97	24.45	18.8	2.0
Spectrum 13	32.08	41.65	23.42	2.85

The state diagram of the C-Nb-Ti system (isothermal section at a temperature of 1700°C) is known, which indicates the formation in the zone of the metallized layer of the (Nb, Ti)C phase, which has an fcc lattice and free carbon precipitates (Spectrum 9...12); the formation of a continuous series of solid solutions (Ti, Nb), which has a bcc lattice and a carbide phase (Nb, Ti)C – fcc lattice (Spectrum 13) [18]. The C-Zr-Nb system (isothermal section at a temperature of 1700°C) may include a mixture of extremely saturated monocarbide (Nb, Zr)C, which has an fcc lattice and free carbon precipitates [19].

5. 1. 2. Microstructure and chemical composition of the brazed joint

The brazed joint between CCCM and tungsten under study consists of one diffusion layer and two reaction layers, which are shown in Fig. 5, 6: reaction zone III, adjacent to tungsten; zone II – brazed joint (diffusion layer); zone I – reaction layer adjacent to CCCM. The obtained distribution of elements during brazing of CCCM and refractory metals is similar to that given in [2]. The chemical composition of the brazed joint is given in Table 2.

Zone I is a reaction layer adjacent to the CCCM. The presence of certain elements in zone I, according to the data in Table 2, makes it possible to estimate the phase composition using the C-Nb-Ti phase diagram (isothermal section at a temperature of 1700°C) [18]. Therefore, zone I consists of the (Nb, Ti)C phase, which has an fcc lattice and free carbon inclusions. The width of zone I is about 10–12 μm.

Table 2

Chemical composition of the brazed joint

Study zone	Name and number of the study area	Chemical composition, %			
		C	Ti	Nb	W
Zone I (Reaction layer)	Carbidization zone CCCM-Ti	50.04	48.36	1.60	–
Zone II (Diffusion layer)	Map Data 31	20.50	57.00	17.00	5.80
	Map Data 30	19.00	52.30	24.90	3.80
	Map Data 29	16.30	59.70	19.30	4.80
Zone I (Reaction layer)	Map Data 27	–	1.44	–	98.56
	Map Data 26	–	1.17	–	98.83
	Map Data 25	6.5	9.80	9.52	74.18

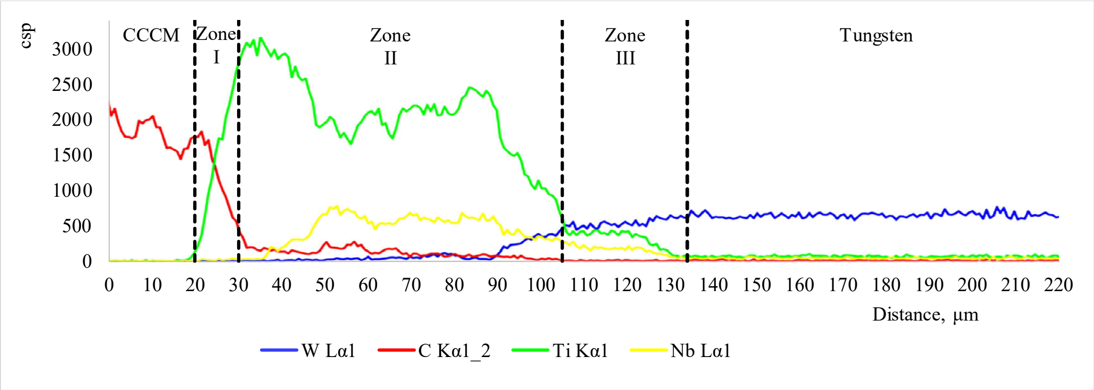


Fig. 5. Distribution of chemical elements of the carbon-carbon composite material-tungsten brazed joint in the direction of the conditional Line Data 13 (Fig. 6)

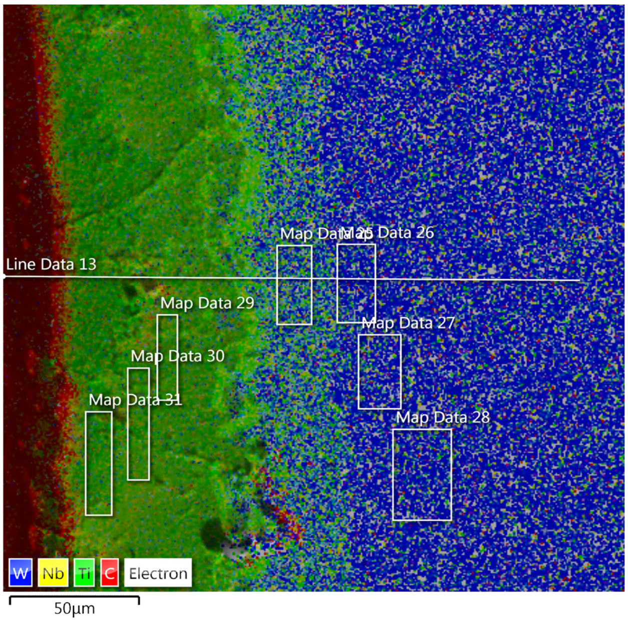


Fig. 6. Microstructure and chemical element distribution of a brazed joint between carbon-carbon composite material and tungsten

Zone II consists of three study areas: map data 31, map data 30, and map data 29 (Fig. 6). The presence of certain elements in zone II, according to the data in Table 2, makes it possible to estimate the phase composition using the C-Nb-Ti phase diagram (isothermal section at a temperature of 1700°C) [18]. Therefore, the areas map data 31, map data 30, and map data 29 consist of a solid solution (Nb, Ti) – bcc lattice and a solid solution (Nb, Ti) C – fcc lattice [18]. The width of zone II is about 70 µm.

Zone III consists of three areas: map data 25; map data 26; and map data 27 (Fig. 6). The presence of certain elements of zone III, according to the data in Table 2, allows us to estimate the phase composition using the Ti-W-C and Nb-W-C phase diagrams.

Therefore, according to the Ti-W-C diagram [20] (isothermal section at a temperature of 1500°C), the chemical composition of the area map data 25 is characterized by the formation of phases (Ti, W)C_{1-x} + (W_2C) + (Ti, W). According to the Nb-W-C phase diagram (isothermal section at 2000°C), the map data 25 region is characterized by the formation of (W_2C) + (W, Nb, C) phases [21]. The map data 27 and map data 26 regions are characterized by the formation of a continuous series of solid solutions between β-Ti and tungsten in the W-Ti system [20]. The melting point of titanium increases from 1670 to 1800–1900°C. The alloy may have a bcc lattice. The width of zone III is about 30 µm.

5. 2. Simulating the phase formation of the brazed joint

Using the HSC Chemistry software [22], the phase composition for zones I...III of the brazed joint was simulated. The simulation was performed using the Equilibrium Compositions module. The input data for the simulation were the types of reaction systems C-Nb-Ti, Ti-W-C, Nb-W-C, C-Zr-Nb and the determined chemical composition (Table 2). The simulation was performed at a temperature of 1840 °C at a partial pressure of argon in the system of $2{\cdot}10^{-3}$ Pa.

The results of our simulation of the phase composition in zone I are shown in Fig. 7. Zone I is characterized by a predominant content of titanium carbide TiC – $2.4{\cdot}10^{-3}$ kmol. As a result of carbidization of niobium, phases are formed in the following quantities: NbC – $1.34{\cdot}10^{-9}$ kmol, Nb_6C_5 – $1.95{\cdot}10^{-4}$ kmol, Nb_2C – $1.25{\cdot}10^{-5}$ kmol. Carbidization of zirconium occurs with the release of the ZrC_4 phase – $2.0{\cdot}10^{-5}$ kmol. The presence of free carbon C – $9.36{\cdot}10^{-4}$ kmol is observed. The width of the zone of active carbide formation is 10–12 µm.

The results of simulating the phase composition in zone II (areas map data 31, map data 30, map data 29) are shown in Fig. 8–10. Zone II is characterized by a decrease in the TiC content to $7.21{\cdot}10^{-4}$ kmol (map data 31), $3.39{\cdot}10^{-4}$ kmol (map data 30), and $5.13{\cdot}10^{-4}$ (map data 29). The carbon content decreases to $2.8{\cdot}10^{-7}$ kmol (map data 31), $1.6{\cdot}10^{-6}$ kmol (map data 30), $1.6{\cdot}10^{-7}$ kmol (map data 29). The Ti content increases to $7.21{\cdot}10^{-3}$ kmol (map data 31), $2.06{\cdot}10^{-3}$ kmol (map data 30), $3.29{\cdot}10^{-3}$ kmol (map data 29).

In zone II, the concentration of carbides Nb_6C_5, Nb_2C in the areas map data 31, map data 30, and map data 2 increases compared to zone I. The content of carbide Nb_2C is: $1.5{\cdot}10^{-4}$ kmol (map data 31), $1.46{\cdot}10^{-4}$ kmol (map data 30), $1.63{\cdot}10^{-4}$ kmol (map data 29). The content of carbide Nb_6C_5 is $1.56{\cdot}10^{-4}$ kmol (map data 31), $1.36{\cdot}10^{-4}$ kmol (map data 30), $1.57{\cdot}10^{-4}$ kmol (map data 29).

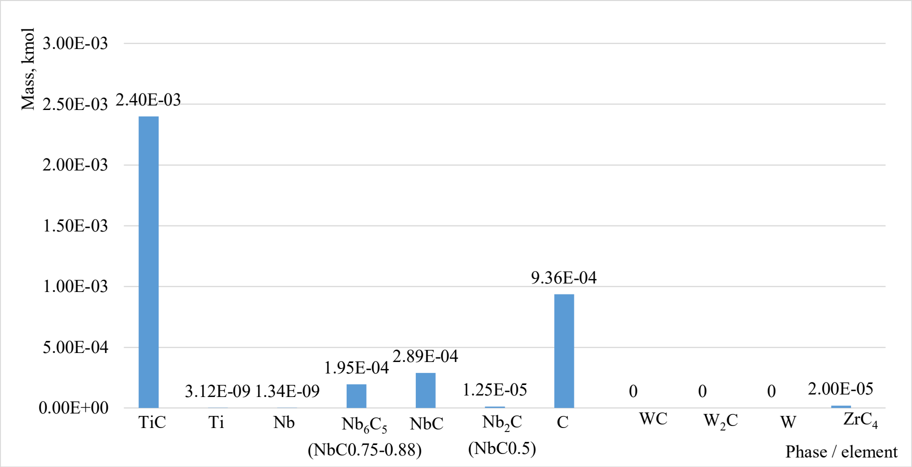


Fig. 7. Result of simulating the phase composition of a brazed joint: zone I reaction layer

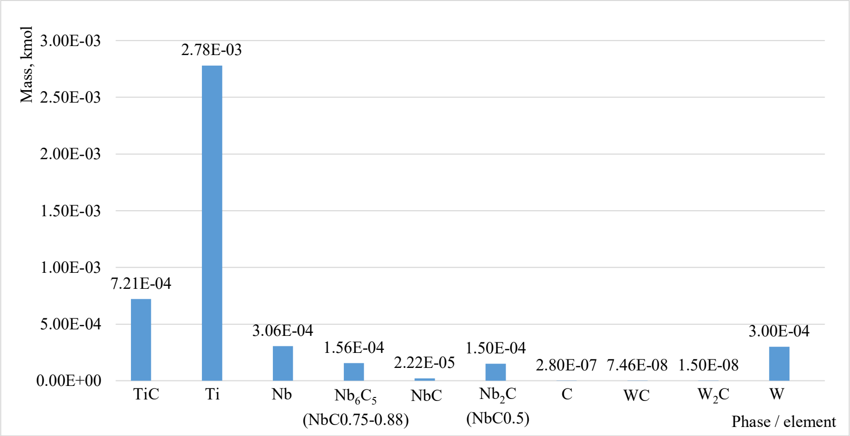


Fig. 8. Result of simulating the phase composition of a brazed joint: zone II (section map data 31)

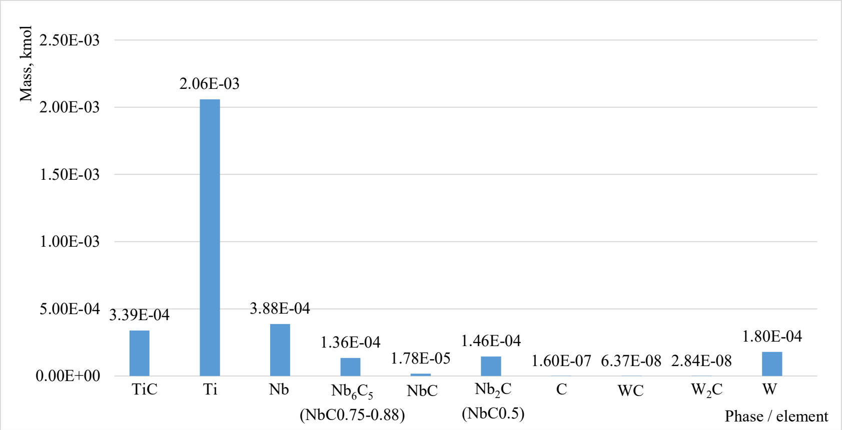


Fig. 9. Result of simulating the phase composition of a brazed joint: zone II (section map data 30)

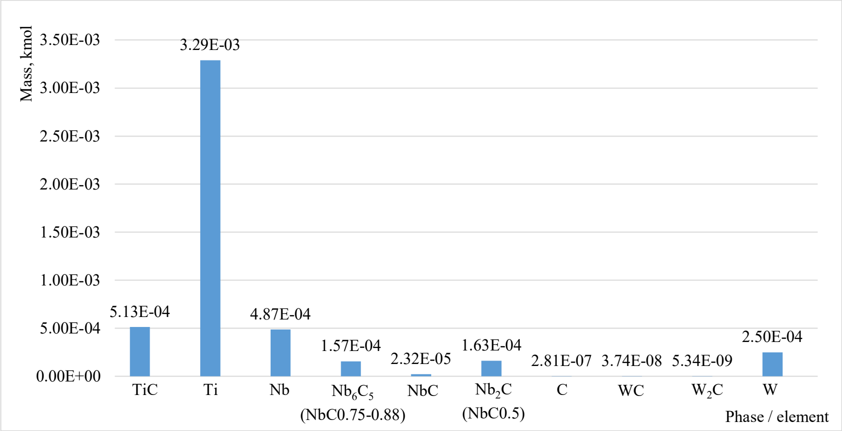


Fig. 10. Result of simulating the phase composition of brazed joint: zone II (section map data 29)

The concentration of NbC carbide in areas map data 31, map data 30, and map data 29 decreases compared to zone I. The content of NbC carbide is $2.22 \cdot 10^{-5}$ kmol (map data 31), $1.78 \cdot 10^{-5}$ kmol (map data 30), $2.32 \cdot 10^{-5}$ kmol (map data 29). The presence of tungsten content in zone II in the amount of 1.8 – $3.0 \cdot 10^{-4}$ kmol is due to its saturation with the reaction layer of zone III. The width of zone II is up to 70 μm, according to Fig. 5.

The results of simulating the phase composition of zone III (areas map data 25, map data 26, map data 27) are shown in Fig. 11, 12. Zone III is characterized by the following composition: the map data 25 section consists of W – $2.8 \cdot 10^{-3}$ kmol; Ti – $2.75 \cdot 10^{-4}$ kmol; Nb – $1.25 \cdot 10^{-4}$ kmol; Nb_6C_5 – $4.46 \cdot 10^{-5}$ kmol, Nb_2C – $2.95 \cdot 10^{-5}$ kmol; NbC – $9.44 \cdot 10^{-6}$ kmol; TiC – $7.46 \cdot 10^{-5}$ kmol; W_2C – $1.46 \cdot 10^{-6}$ kmol; WC – $7.27 \cdot 10^{-7}$ kmol; C – $1.34 \cdot 10^{-6}$ kmol. The chemical composition of the map data 27 and map data 26 sections is similar; therefore, they are combined in Fig. 11. Map data areas 26 and 27 consist of W – $3.0 \cdot 10^{-3}$ kmol, Ti – $4.0 \cdot 10^{-4}$ kmol.

The result of simulating the phase composition of a brazed joint is shown in Fig. 13.

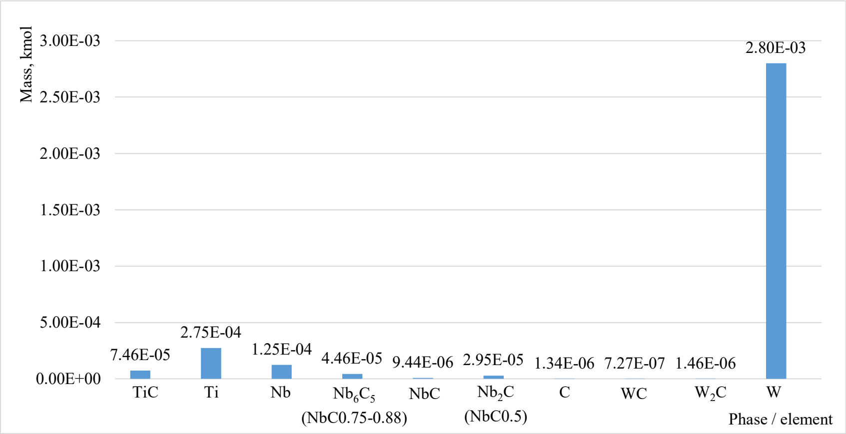


Fig. 11. Result of simulating the phase composition of a brazed joint: zone III (section map data 25)

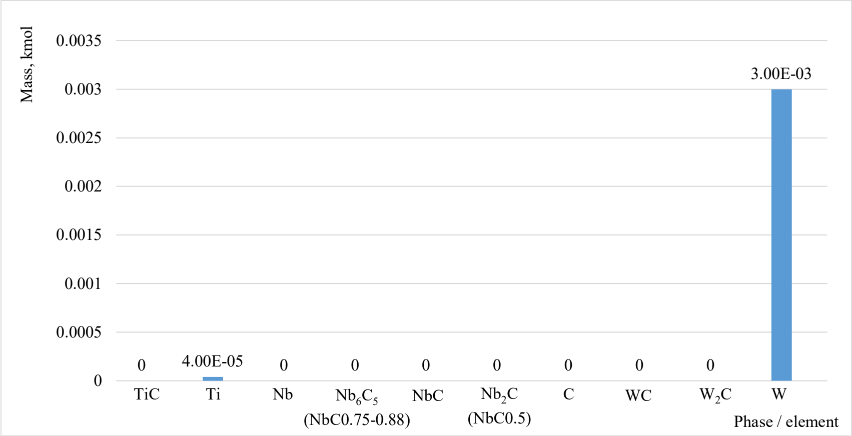


Fig. 12. Result of simulating the phase composition of a brazed joint: zone III (sections map data 26, 27)

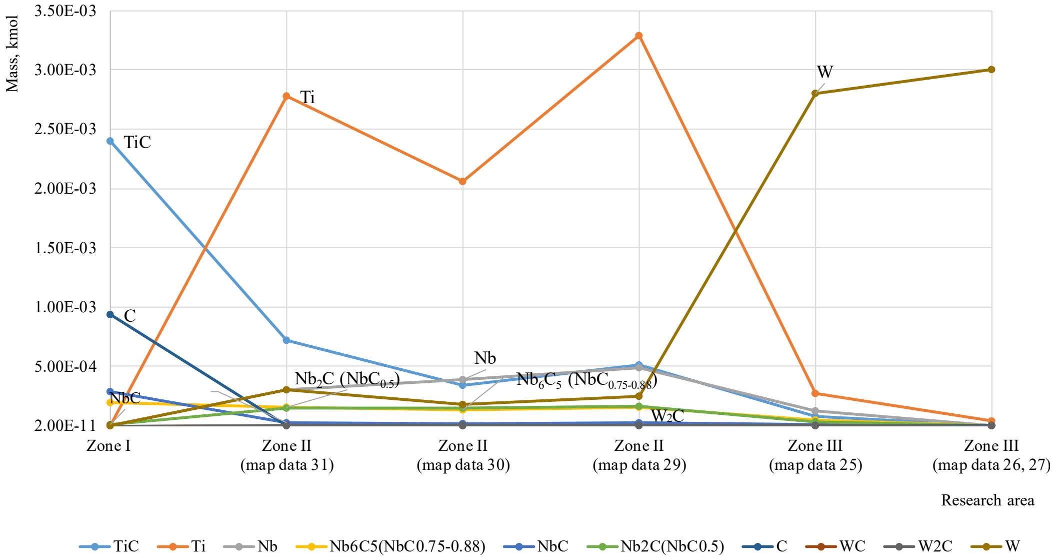


Fig. 13. Result of simulating the phase composition of a brazed joint in the direction of line data 13 (Fig. 6)

The obtained phase composition, at a temperature of 1840°C, shown in Fig. 13, allows for a comprehensive assessment of the dynamics of phase formation changes in the brazed joint.

5. 3. Microhardness of the brazed joint

As a result of our measurements of the Vickers microhardness of the brazed joint between CCCM and tungsten, shown in Fig. 14, it can be stated that the maximum hardness values are recorded in zone I and at the beginning of zone II and are about 2300 HV.

Such indicators correspond to the formation of a continuous series of stoichiometric titanium carbides. Areas map data 30 and map data 29 are characterized by a decrease in hardness of 2000...600 HV. The lowest hardness indicators are recorded in zone III and are 500–600 HV.

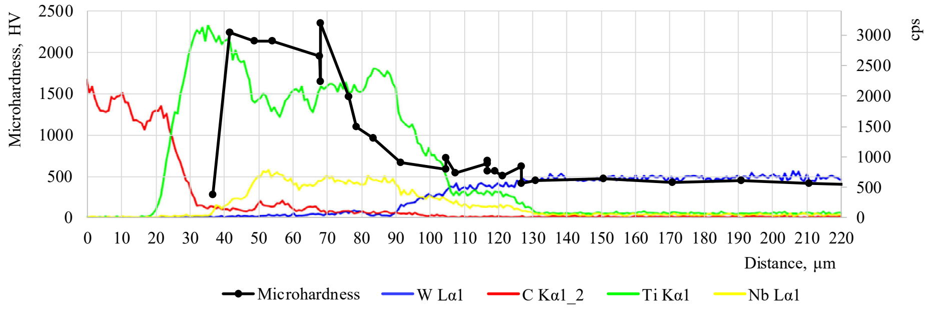


Fig. 14. Hardness (HV) values compared to the chemical element distribution of the brazed joint (Fig. 5)

6. Discussion of results based on the study of physicochemical patterns in the brazing of carbon-carbon composite material and tungsten

The proposed technology for brazing CCCM with tungsten allowed us to obtain high-quality joints by using the metallized layer zone with materials of the Ti-Nb-Zr system in a vacuum environment at a temperature of 1900°C.

Obtaining the metallized layer zone is explained by the partial melting of the applied layer of the powder mixture of metals of the Ti-Nb-Zr system, and its interaction with carbon in the liquid and solid phases. Liquid titanium penetrates the pores of CCCM due to the capillary effect, but its main mass is concentrated on the surface of CCCM. This process contributes to the formation of a strong framework with a depth of 200–400 μm in the walls of CCCM. The strength properties of the solidified metal framework, as a rule, determine the strength of the brazed joint [4]. During the interaction of liquid Ti with CCCM at temperatures close to the melting point, an initial and rather intense carbon saturation of the laminar layer occurs. Subsequently, the carbon content in it reaches a value close to the equilibrium concentration at the liquid – liquid + MeC phase boundary. Near this concentration, but somewhat earlier than it is reached, a carbide layer begins to form on the CCCM surface throughout the metal volume [7].

Based on the results from investigating the microstructure shown in Fig. 3, 4, the width of the metallized layer zone is from 20 to 70 μm. The heterogeneous and porous surface structure of the CCCM makes it difficult to uniformly apply powder materials to its surface. As a result, in Fig. 3, both denser melted areas adjacent to the CCCM and agglomerations of sintered particles with sizes of 7–15 μm are observed. The distribution of chemical elements of the metallized layer zone, shown in Fig. 4, clearly demonstrates the active interaction of carbon with titanium, and its subsequent diffusion into the metallized layer zone. It is known from [23] that the thickness of the previously applied metal layer significantly affects the adhesion between the metal carbide layer and the CCCM. Thus, it is desirable that the thickness of the metallized layer zone be in the range from 25 to 300 μm.

Experimentally obtained brazed samples of CCCM with tungsten prove that the zone of the metallized layer helps retain the filler in the seam gap. In addition, it helps reduce thermomechanical loads and reduce the diffusion of carbon from CCCM into the brazing zone. The combination of these factors minimizes the formation of unstable tungsten carbides W_2C, which embrittle the brazed joint as a whole. As a result of our analysis of the microstructure and distribution of chemical elements of the brazed joint, which is shown in Fig. 5, 6, it can be stated that the brazed joint is formed due to three main zones.

Zone I is a reaction carbide layer adjacent to the CCCM and characterized by the C-Nb-Ti phase diagrams. The width of zone I is about 10–12 μm. Zone II is a diffusion layer characterized by the C-Nb-Ti system and has a width of up to 70 μm. Zone III is a reaction layer adjacent to tungsten, characterized by the Ti-W-C and Nb-W-C phase diagrams, has a width of up to 30 μm.

The distribution of chemical elements of the brazed joint, shown in Fig. 5, demonstrates a decrease in the carbon saturation of the soldered metal melt due to the formation of a reaction carbide layer (zone I). On the other hand, in zone III, a high mutual diffusion of tungsten with Ti and Nb through vacancies in the crystal lattice is observed. In addition, the tungsten content is fixed in zone II in the amount of 3–5%.

The analyzed literature data indicate that the ternary phase diagrams mentioned in this work have been studied only at certain temperatures. Thus, the current issue is to conduct phase formation simulations using Ti, Zr, W, C at a brazing temperature of 1840°C in a vacuum environment.

The phase formation simulation was performed using the HSC Chemistry software and its Equilibrium Compositions module. The equilibrium composition of the heterogeneous system was simulated using the Gibbs free energy minimization method.

The sequence and intensity of the formation of carbides Ti, Zr, Nb, and W are determined by the magnitude of their chemical affinity for carbon, which is clearly confirmed by the mutual location of the corresponding temperature dependences on the Ellingham diagram [24].

The results of simulating the phase composition of zone I, at temperatures of 1840°C (Fig. 7), indicate that to a greater extent, TiC is formed, since titanium is partially in a liquid state and has a higher thermodynamic activity and mass content. Carbidization of niobium occurs with the participation of the phases Nb_6C_5, Nb_2C, NbC, zirconium – ZrC_4. It is also determined that in zone I a high concentration of free carbon is observed. The results of the phase formation simulation correlate well with the data on the C-Nb-Ti and C-Zr-Nb phase diagrams at a temperature of 1700°C [18, 19], which confirms the correctness of the simulation.

The results of the phase composition simulation of zone II at a temperature of 1840°C (Fig. 8–10, 13) indicate a decrease in the concentration of TiC, NbC, C, and an increase in the concentration of Ti, Nb, Nb_6C_5, Nb_2C in the diffusion layer, compared to zone I. In general, it can be stated that the phase composition of zone II consists of a Ti-Nb alloy reinforced with carbides of these elements. In addition, a significant share is occupied by the content of tungsten, the diffusion of which occurs from zone III. The results of the phase formation simulation correlate well with the C-Nb-Ti phase diagram at a temperature of 1700°C [18], which confirms the correctness of our simulation.

The results of simulating the phase composition of zone III at a temperature of 1840°C (Fig. 11–13) indicate a predominant content of W, and significantly lower concentrations of Ti and Nb than in other zones. The carbide phases TiC, Nb_6C_5, Nb_2C, NbC have the lowest values. There is a small amount of the W_2C

phase – $1.46 \cdot 10^{-6}$ kmol and WC – $7.27 \cdot 10^{-7}$ kmol. The results of simulating the phase formation correlate well with the data on the Ti-W-C phase diagrams at a temperature of 1500°C and Nb-W-C at a temperature of 2000°C [20, 21]. Despite the fact that the analyzed phase diagrams [20, 21] differ from the modeling temperature, they correlate well and can be used to verify the modeling results.

Determination of microhardness with reference to the measurement location along the width of the brazed joint made it possible to assess the correctness of the phase formation modeling. Analyzing Fig. 14, it can be stated that the hardness of the brazed joint decreases from zone I to zone III. Taking into account the data in Fig. 14, it can be noted that the highest microhardness indicators are inherent in zone I and the beginning of zone II, which are 2300…2000 HV due to the high degree of carbidization of the elements of the metallized layer zone. A decrease in hardness is observed across the entire width of zone II, especially after the map data 30 section (Fig. 6), at the end of zone II the hardness is 500–600 HV, which may indicate a decrease in the concentration of carbide phases of titanium and niobium, and as a result, a decrease in the carbon concentration. In zone III, the lowest hardness indicators are recorded, which are 500–600 HV.

The described mechanism of hardness distribution helps minimize the production of brittle W_2C carbides. Thus, our microhardness indicators confirm the correctness of the obtained data values when modeling phase formation, the results of which are shown in Fig. 13. The selected brazing technology makes it possible to obtain a hardness gradient of the brazed joint due to the use of carbide-forming elements and a zone of a metallized layer.

The proposed joint technology, unlike [8], is carried out by the method of high-temperature brazing in vacuum with refractory metals that wet the CCCM well during brazing, forming a larger contact area with its surface. In addition, the technology specified in our work does not require the use of precious metals and additional equipment. Unlike [9], the given technology uses a zone of a metallized layer, which prevents intensive diffusion of carbon into the filler and its embrittlement. The proposed technology, unlike [1], makes it possible to precisely regulate the temperature regimes during brazing, control the rate of temperature change, which affects the quality of the brazed joint. In addition, the use of powder filler materials makes it possible to create fillers, the properties of which maximally correspond to the operating conditions of the joint. Unlike [10–16], the proposed technology does not form brittle intermetallic phases $Ti(Cu,Ni)_2$, or Cr_xTi_y in the filler. The metals used in the zone of the metallized layer and in the solder Ti, Nb, Zr form solid solutions of substitution between themselves, or high-temperature carbide phases. In addition, unlike all the sources listed, the proposed technology has a significantly higher operating temperature of 1400–1500°C, briefly up to 1600°C.

Our research results could be applied in the field of instrument making, namely in the parts of cathodes, the emitter of which is made of ultra-disperse powders of borides of rare earth materials or their alloys. Thus, the use of the developed technology of high-temperature brazing in vacuum makes it possible to improve the parameters of the cathode operation, reduce energy consumption for emission, and increase its operating characteristics by expanding the operating temperature range to 1600°C. When using cathodes, it is necessary to control the pressure indicators, the value of which is usually no more than $2 \cdot 10^{-3}$ Pa. An increase in pressure in the working space of the cathode leads to a decrease in its service life. The limitation of this technology is the impossibility of operating CCCM and tungsten compounds above a temperature of 1600°C and a vacuum level of more than $2 \cdot 10^{-3}$ Pa.

The disadvantage of this work is that the maximum number of thermocyclic loads of brazed joints between CCCM and tungsten in the operating temperature range of 1400–1600°C has not been determined.

It is advisable to conduct further research into the operational properties of cathodes using the developed technology of joining CCCM and tungsten and to determine the critical factors affecting performance.

7. Conclusions

1. Our study on the microstructure of a brazed joint allowed us to determine that the structure is characterized by a zonal type and consists of two reaction zones I, III, and diffusion zone II. The distribution of chemical elements clearly demonstrates the intensity of the saturation of the brazed joint with carbon and the interaction of the filler elements with each other.
2. The results of our phase formation modeling are based on the values of the Gibbs free energy and the investigated actual values of the chemical composition of the brazed joint. The results from the phase formation simulation, carried out at a temperature of 1840°C, indicate the predominant formation of TiC, NbC, Nb_6C_5, Nb_2C in the brazed joint. The content of free elements C, Ti, Nb, W was also determined. The results allowed us to determine the pattern of phase distribution, their number and content in each zone of the study and the physicochemical nature of the joint.
3. The results of the microhardness study allowed us to determine that the hardness indicators decrease from zone I (2300 HV) to zone III (500–600 HV). It was established that the selected technology makes it possible to obtain a hardness gradient of the brazed joint due to the use of carbide-forming elements and the formation of a metallized layer zone. The obtained microhardness values confirm the correctness of simulating the phase formation of the brazed joint.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Authors' contributions

Roman Huba: Conceptualization, Methodology, Investigation, Writing – original draft; **Liudmyla Kamkina**: Conceptualization, Validation, Writing – review and editing; **Serhii Bushtruk**: Investigation, Writing – review and editing; **Andrii Troian:** Conceptualization, Supervision, Writing – review and editing; **Serhii Asmolovskyi**: Methodology, Formal analysis, Writing – review and editing; **Serhii Oslavskyi**: Resources, Validation.

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