The object of research is the processes of the formation of brazed joints and the stressed state. The subject of research is structure, chemical composition, long-term high-temperature strength at a temperature of 900 °C, speed of high-temperature salt corrosion. Existing brazing filler metals have a high-temperature performance of 40–50 % of the performance of the SM93-VI and SM96-VI alloys. Despite this, brazing is the main technique of joining modern heat-resistant cast alloys. Therefore, the development of new brazing filler metals that ensure the formation of joints with increased long-term high-temperature strength is relevant. Ship gas turbine blades operate at a temperature of 900 °C. The purpose of the development of the new SBM-4 brazing filler metal is to achieve long-term high-temperature strength of brazed joints at a temperature of 900 °C at the level of 85–90 % of the strength of heat-resistant alloys SM93-VI and SM96-VI.

A two-stage method was used in the development of SBM-4 brazing filler metal. At the first stage, the chemical composition of the brazing filler metal base was determined, taking into account the peculiarities of operating conditions of the blades of marine gas turbine engines and the achievements of materials science of heat-resistant alloys. At the second stage, the depressant and its necessary content were selected. Computer software was used to determine the distribution between the γ- and γ'-phases, taking into account the participation of each element in both dispersion and solid-solution strengthening. Rational limits of concentrations of alloying elements were determined. The criterion was the minimum susceptibility of brazing filler metal to the formation of brittle phases, taking into account the influence of chromium, rhenium, and tantalum concentrations on resistance to high-temperature salt corrosion and high-temperature performance. The long-term strength of SM93-VI and CM96-VI alloys brazed with SBM-4 brazing filler metal is 89–91 % of the strength of the base metal. Technologies of brazing and correction of casting defects have been introduced into production

Keywords: brazed joints, stressed state, high-temperature salt corrosion, long-term strength

UDC 621.791.3
DOI: 10.15587/1729-4061.2023.288340

DESIGNING BRAZING FILLER METAL FOR HEAT-RESISTANT NICKEL ALLOYS OF NEW GENERATION MARINE GAS TURBINES

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Received date 11.07.2023
Accepted date 22.09.2023
Published date 30.10.2023

How to Cite: *Kvasnytskyi, V., Korzhyk, V., Kvasnytskyi, V., Matviienko, M., Buturlia, Y., Lahodzinskyi, I. (2023). Designing brazing filler metal for heat-resistant nickel alloys of new generation marine gas turbines. Eastern-European Journal of Enterprise Technologies, 5 (12 (125)), 31–46. doi: https://doi.org/10.15587/1729-4061.2023.288340*

1. Introduction

The basic technique for joining heat-resistant nickel alloys (HNAs) of aviation and marine gas turbines is brazing. Heating of HNAs during fusion welding leads to the formation of crystallization and subsolidus cracks, loss of monocrystalline and directional structure, high-temperature long-term strength, and plasticity [1]. For ship turbines, it is also a problem to ensure the stability of HNAs against high-temperature salt corrosion (HSC).

Brazing also has its drawbacks. Since brazing filler metals have a lower melting and brazing temperature than HNAs, the main problem of brazing is to ensure the functionality of joints at the level of the base metal. Therefore, special brazing techniques are used, in particular, diffusion brazing, contact-reactive brazing, composite brazing filler metals, and pressure brazing. Compression ensures a brazing filler metal interlayer thickness in the joint, which makes it possible to obtain an acceptable concentration of the depressant element due to diffusion in the solid state. This process is

also called diffusion welding with a melting interlayer. The interlayer of brazing filler metal contributes to the activation of the joint surfaces, ensures the absence of microvoids in the joint and a low level of plastic deformations. The thickness of such an interlayer after compression does not exceed several micrometers. In the international literature, the term TLP-joint with the presence of a liquid phase and isothermal crystallization of the melt is used [2]. The size of the gap, temperature and time of brazing are important. They determine the chemical composition, properties, and residual thickness of the interlayer.

With capillary brazing with a gap of 0.1 mm, depending on the permissible concentration in the center of the interlayer, the time of homogenization high-temperature processing is tens of hours. It increases in proportion to the square of the interlayer thickness [3].

If the chemical composition of the interlayer differs from the composition of the base metal, then they have different physical and mechanical properties (PMPs) and react differently to external loads. But due to the discontinuity of deformation at the interface of materials, a complex stressed-strained state (SSS) is formed. For example, when an axial load is applied to a butt joint, a volumetric SSS is formed with certain equivalent stresses that determine the nature of the destruction and the serviceability of the joints [4].

The development of brazing filler metal with performance of brazed joints at the base metal level requires comprehensive research. It includes research into the formation of SSS, development of brazing filler metal taking into account the conditions and resource of work and properties of the base metal under operating conditions. An example of such an approach is the development of SBM-3 brazing filler metal for aviation HNA based on Ni_3Al [3]. But the operating conditions of aircraft and marine gas turbines are significantly different. That's why the chemical composition, PMPs, and requirements for the HNA of aviation and marine GTEs are different, and accordingly, the brazing filler metals are also different. Existing brazing filler metals for ship gas turbines have a workability of 40–50 % of the strength of the base metal. Therefore, the development of brazing filler metals that ensure operability at the level of the base metal is urgent.

2. Literature review and problem statement

The modern state of software and computer support makes it possible to study SSS under conditions of plasticity, taking into account the PMPs of materials, the nature of the load, and geometric dimensions, and their changes depending on temperature, etc. [5]. In [6], depending on the ratio of the yield strength $\sigma_{Y(intl)}$ of the interlayer and the base metal $\sigma_{Y(bm)}$, a distinction is made between "soft" ($\sigma_{Y(intl)}<\sigma_{Y(bm)}$) and "hard" ($\sigma_{Y(intl)}>\sigma_{Y(bm)}$) interlayers. In the elastic state, the criterion of "softness" is the modulus of elasticity. Interlayer with a modulus lower than that of the base metal are called "soft" and vice versa – "hard". When stretching a butt joint with a "soft" interlayer, the material of the interlayer receives more elongation along the axis and more shortening in the radial direction. Due to the non-discontinuity of deformations at the interface of materials, tensile stresses appear in the interlayer and the stressed state becomes volumetric, which reduces the equivalent stresses and plasticity of the joints. There is an effect of the so-called strengthening of the interlayer material.

In work [7] it was established that when the modulus of elasticity of the interlayer E_{intl} is lower than the modulus of elasticity of the base metal E_{bm}, the destruction of the "soft" interlayer is always fragile. It is shown that the brittle destruction of the "soft" interlayer for butt-brazed joints occurs for all values of $E_{intl}<E_{bm}$. In the "hard" interlayer, the tension of the base metal is combined with compression in the radial direction of the interlayer and the equivalent stresses increase [8]. But in these works, issues related to the study of the influence of plastic deformations of the interlayer and the base metal on the performance of the joints remained unresolved.

In [9], it was noted that a brazed joint can have greater tensile strength compared to a "soft" interlayer. It is shown that this is related to the complex SSS at different PMPs of the brazing filler metal material and the base metal. Similar results were obtained for brazed joints of nickel-based heat-resistant alloys in [10]. However, in works [9, 10] there is no qualitative analysis of the impact of the difference in the properties of the materials of brazed joints on the nature of SSS.

The influence of the difference in temperature coefficients of linear expansion (TCLE) of the brazing filler metal interlayer and the base material on SSS of brazed assemblies was studied in [11]. It is shown that when developing brazing filler metals, it is necessary to ensure that their TCLE is close to the TCLE of the base metal, that is, the brazing filler metal system must be the same or close to the system of the metal being joined. But at the same time, the influence of the stiffness parameters of the stressed state (the ratio of the modulus of elasticity, TCLE, plastic deformations of the interlayer and the base metal) on the formation and performance of the brazed joint has not been determined.

When studying the performance of a brazed joint, it is important to take into account the ability of heat-resistant alloys to break by a brittle or plastic mechanism, depending on external conditions, in particular, on the type of stressed state (SS). This very question is considered in paper [12]. The reported research results showed that the brazed joints of heat-resistant nickel alloy ZhS6U, obtained using the binary system 80 % VPr–36+20 % HC12, were brittle when stretched. The strength of 70 % of brazed joints of the VZHL12U alloy at 900 °C, obtained using brazing filler metal 20 % Ni-Co-Cr-Al-B+20 % HC12+60 % Rene-142, was 357–364 MPa. That is also close to the yield point of the alloy at this temperature. When brazing ZhS26 alloy with this brazing filler metal, after annealing at 1080 °C for two hours, the destruction also occurred below the yield point of the base metal (BM). It is known that before brittle failure, the material of the part undergoes significant plastic deformations in a narrow local area. Therefore, an increase in the plastic properties of the material, which depend on the type of SS, leads to an increase in the performance of the resulting brazed joints. In order to characterize the type of SSS, the concept of stiffness of the stressed state is used [13]. There is still no information on research that allows the use of knowledge about the stiffness of SS in order to optimize the choice of brazing filler metal material and improve the technological processes of brazing, which will ensure the increase in the performance of products obtained by brazing. This gives grounds for asserting that conducting research aimed at determining the influence of PMP ratio of the base metal and brazing filler metal during brazing on the stiffness of SS is expedient.

The operating conditions of aircraft and marine gas turbine engines (GTE) are also important. Their fundamental difference is that:

– marine gas turbines use "heavy" fuel with a high sulfur content and significant ash content (up to 2.2 % S, Na, V), and the fuel combustion products contain salt in the amount of 0.35 mg per 1 kg of gas;

– refueling by tankers and the presence of sea water during the operation of ship gas turbines leads to fuel contamination with impurities of heavy fractions of petroleum products;

– marine gas turbines operate under all permissible modes, starting from idling, ending with maximum power in the afterburner mode, and have a much longer service life.

Fuel is one of the main negative factors under the operating conditions of ship gas turbines. During combustion, sulfur forms compounds SO_2 and SO_3. The sodium contained in the fuel and coming from seawater interacts with sulfur oxides and forms sulfate Na_2SO_4, which destroys the protective oxide film Cr_2O_3. Chlorine, which is formed during the interaction of NaCl salt with sulfur oxides, initiates the processes of high-temperature salt corrosion (HSC).

The specified peculiarities of the operating conditions of marine gas turbines lead to HSC, which destroys the turbine blades. To ensure the stability of HNA against HSC, the alloys of marine gas turbines have a high concentration of chromium (18.0–24.0 % by weight), which reduces the high-temperature performance of HNAs of ship GTE.

Unlike marine gas turbines, aviation gas turbines operate on clean fuel and there is no HSC. Therefore, the chromium content in aviation fuel oil is reduced to 4.0–6.0 % by mass, which helps increase the high-temperature performance of alloys and the working temperature of gas. At the same time, during operation, an oxide film of Cr_2O_3 is preserved, sufficient to protect parts from high-temperature corrosion. The working temperature of aviation HNAs reaches more than 1100 °C. Alloys based on Ni_3Al intermetalide are also used [3, 14]. For their brazing, multicomponent brazing filler metals with a brazing temperature of 1260–1300 °C have been developed, for example, VPr36, VPr37, VPr44, BH2. However, the specified brazing filler metals for brazing vessel HNAs are unsuitable in terms of brazing temperature.

Ship GTEs have a much lower gas temperature, compared to aviation ones. It is urgent to increase the efficiency of ship GTEs. This is provided for in the design documentation for new-generation turbines, which are characterized by increased working gas temperatures, resource and power, compared to GTEs developed earlier. These indicators are determined by the characteristics of long-term high-temperature strength and resistance against the HSC of marine GTEs. The state enterprise Gas Turbine Research and Production Complex "Zorya"-"Mashproekt" (SE GTR&PC «Zorya»-»Mashproekt») and the Physical-Technological Institute of Metals and Alloys of the National Academy of Sciences of Ukraine (PTIMS) have developed new promising alloys CM93-VI and CM96-VI. These alloys make it possible to increase the working temperature of the gas by 40...60 °C [15, 16].

Alloys CM93-VI and CM96-VI are alloyed with rhenium and tantalum. These elements strengthen the solid solution and are more effective than molybdenum and tungsten and are used in aircraft turbine engines. The developed alloys are used to manufacture nozzles and working vanes of ship GTEs by precision casting using models that are melted down. The experience of using CM93-VI and CM96-VI alloys of the SE GTR&PC "Zorya"-"Mashproekt" and physical and structural stability studies at the PTIMS of the National Academy of Sciences of Ukraine showed that the temperature range of 1200–1230 °C is optimal for brazing [15]. The brazing filler metals that are used for brazing the previous generation of ship's HNAs have a brazing temperature of 1020–1160 °C (VPr11, VPr11–40N, NS12A), which does not make it possible to increase the working temperature of brazed joints and below the temperature of applying a protective coating [13]. Since the developed alloys can only be joined by brazing, the development of new brazing filler metals and brazing technology is urgent.

For alloys CM93-VI and CM96-VI it is necessary to develop a new brazing filler metal called SBM-4. Work [3] proposed a method of brazing filler metal development in two stages. At the first stage, the chemical composition of the brazing filler metal base is determined, taking into account the peculiarities of the operating conditions of the blades of ship's GTE and the achievements of the materials science of HNAs using the PHACOMP software. Alloys CM93-VI and CM96-VI have a similar chemical composition, so the program should determine the distribution of elements and the ratio between γ'/γ phases, critical temperatures (liquidus, solidus, solvus) with a comparison of the results using high-temperature differential thermal analysis. Determine the number of electronic vacancies based on the concentrations of chromium, molybdenum, rhenium, tungsten, misfit, alloy strength and creep.

At the second stage, depressants are determined experimentally. Depending on the depressants, the brazing filler metals for HNAs are divided into three groups [17]: complex brazing filler metals based on nickel with silicon and boron; brazing filler metals based on alloyed nickel with elements of groups IV and V; brazing filler metals based on alloyed nickel with palladium. Boron and silicon are most widely used as depressants. The heat resistance of alloys is provided by chromium, which is introduced for almost all brazing filler metals, as well as elements that strengthen the solid solution and provide dispersion strengthening. In the last century, brazing filler metals with a brazing temperature of up to 1160 °C were used in ship turbines. Temperatures of 1210–1230 °C are recommended for alloys CM93-VI and CM96-VI.

In work [13], vacuum brazing of ZhS6U nickel alloy with composite brazing filler metal based on VPr-36 was considered. HC12 brazing filler metal (Ni–12 % Si) is added to the brazing filler metal. It is not recommended to add silicon to VPr-36 brazing filler metal because the Ni–Si eutectic sharply lowers the melting temperature and the strength of the joints. Therefore, this composite is not suitable for alloys CM93-VI and CM96-VI.

In [18], the results of research on the effect on the heat resistance of an experimental brazing filler metal based on Ni-Cr-Co-Al-(Ti, Nb, W, Mo, Zr) and brazed joints of the heat-resistant ZhS6U alloy are considered. It was established that zirconium doping is more than 2 % by weight significantly worsens the heat resistance of both brazing filler metal and brazed joints. Partial compensation of the negative impact of zirconium is possible due to alloying with chromium. In the work, zirconium is a depressant, and its concentration is greater than 2 % by weight. As a depressant, zirconium is used in lower concentrations, so it is impossible to use these data for brazing filler metal development.

In [19], the influence of GTE fuel ash and hydrogen gas on mass loss due to long-term corrosion and mechanical properties of heat-resistant cast materials of blades CM-88U-VI, CM-90-VI and CM-104-VI was investigated. It was established that the level of sulfide-oxide corrosion resistance of the investigated alloys correlates with the chromium content. The CM-104-VI alloy has the greatest stability among alloys. The resistance of all studied alloys to high-temperature sulfide-oxide corrosion in GTE fuel ash increases in the following order: CM-88U-VI→CM-90-VI→CM-104-VI. Under the action of gaseous hydrogen under a pressure of 30 MPa, the plasticity characteristics of alloys decrease. The influence of hydrogen monotonically decreases with increasing temperature. The article does not fully disclose the procedure of researching corrosion in hydrogen.

In [20], the influence of doping with cobalt and hafnium on hydrogen embrittlement and salt corrosion of a cast nickel alloy with a content (wt.%) of 0.08 C was investigated; 21.3 Cr; 2.4 Al; 2.8 Ti; 0.5 Nb; 0.015 B; and 0.005 Zr. Resistance to high-temperature corrosion was evaluated after aging in a mixture of salts 0.25 NaCl+0.75 Na_2SO_4 at 900 °C. It was found that hafnium additives significantly increase the corrosion and hydrogen resistance of alloys. The research methodology is important because it combines strength, plasticity, low-cycle fatigue strength, hydrogen and corrosion resistance (alloy with 18.5 % cobalt and 0.7 % hafnium). The drawback is that the procedure is expensive. The work will determine the resistance of brazing filler metals against HSC by the crucible method, based on mass loss.

In [21], mathematical prediction of the properties of heat-resistant nickel alloys after directional crystallization is a promising direction for predicting the main characteristics of brazed joints. It would be interesting to compare the prediction results and calculate the strength and heat resistance due to misfeed using the PHACOMP program.

All this gives reason to assert that it is expedient to carry out a study aimed at the development of brazing filler metal for brazing promising heat-resistant nickel alloys of the new generation CM93-VI and CM96-VI.

3. The aim and objectives of the study

The purpose of this research is to obtain brazing filler metal for brazing promising heat-resistant nickel alloys CM93-VI and CM96-VI for the production of ship GTEs of a new generation with a high-temperature strength of brazed joints of HNAs not lower than 85 % of the strength of the base metal. This will provide an opportunity to increase the temperature of the working gas up to 950 °C and the efficiency of GTEs.

To achieve the goal, the following tasks are set:

– to investigate the stiffness of SSS of brazed joints by computer simulation and to formulate recommendations for choosing the optimal ratios of physical and mechanical properties of the base metal and brazing filler metal when brazing heat-resistant nickel alloys;

– to determine the limits of rational doping of the brazing filler metal base and the effective concentration of depressant elements;

– to investigate the surface interaction of brazing filler metal melts with HNAs and resistance against high-temperature salt corrosion of the developed brazing filler metal;

– to investigate the structure, chemical composition, and properties of brazing filler metal joints;

– to devise technologies for brazing and correction of surface defects of castings for perspective alloys CM93-VI and CM96-VI intended for the production of ship turbines of the new generation.

4. The study materials and methods

The object of researchis the processes of the formation of brazed joints and the stressed-strained state.

Research hypothesis assumes that it is necessary to use a joining alloy as a basis for creating a brazing filler metal, and to ensure its rational doping with a depressant element. The depressant must ensure isothermal crystallization and be diffusive to equalize the chemical composition of the brazing filler metal joint with the base material during brazing and subsequent heat treatment.

The research was carried out using the CM93-VI and CM96-VI HNAs. The chemical composition of alloys is given in Table 1. Cylindrical samples with a diameter of 12–14 mm and a height of 30 mm were used for mechanical tests. Samples with a height of 10 mm were used to study the microstructure and chemical composition of brazed joints.

The samples were delivered in a state of heat treatment after melting in a vacuum of 10^{-2} Pa. The strength limits of polycrystalline alloys are 920–1050 and 640–750 MPa at temperatures of 20 and 900 °C, respectively, for the CM93-VI alloy and 900–980 and 460–470 MPa at temperatures of 20 and 950 °C, respectively, for the CM96-VI alloy.

Smelting of experimental brazing filler metals was carried out in a water-cooled crucible made of oxygen-free copper by the electric arc method with flushing with purified argon. Before smelting, the vacuum chamber was flushed with argon and a vacuum was created with a pre-vacuum pump. Similarly, cylindrical samples were melted to study the resistance of brazing filler metals against HSC.

The influence of the difference in PMPs of the connecting materials and the interlayer metal on SSS of the brazed assembly was studied by the finite element method using the ANSYS computer software package. The research was carried out on nodes of a cylindrical shape (Fig. 1, *a*) with a diameter of d=20 mm and a height of h=20 mm with a brazing filler metal interlayer thickness of s=10...200 microns (relative thickness s/d=0.0005–0.01). When constructing the finite-element model, an axisymmetric two-dimensional finite element PLANE 183, close in shape to a square, was used. Due to the large stress gradients in the narrow zone around the brazing filler metal interlayer, a gradient grid breakdown with reduced sizes of finite elements around the brazing filler metal seam was used. Gradient breakdown was applied on the side of the base metal and in the brazing filler metal itself (Fig. 1, *b*). The dimensions of the finite elements were chosen so that there were at least 20 of them in the thickness of the brazing filler metal interlayer. Due to the symmetry of the sample with respect to the middle of the thickness of the brazing filler metal interlayer, the finite element model was built for the upper half of the sample (the upper cylinder and half the thickness of the interlayer). Nodes of the model were fixed on the *Y*-axis (cylinder axis) in the direction of the *X*-axis (radial axis) in order to avoid the "small hole" effect. Nodes on the lower edge (the middle of the thickness of the interlayer) in the direction of the *Y* axis were also fixed.

The study of SSS of brazed joints was carried out under elastic conditions and taking into account the plastic de-

formation of materials due to instantaneous plasticity and creep. The SSS was studied under force, thermal, and thermal-force loads of a brazed assembly made of materials with different modulus of elasticity, thermal coefficients of linear expansion (TCLE), yield strength, and creep resistance of the base material and the metal of the brazing filler metal interlayer.

Table 1

Chemical composition of CM93–VI and CM96–VI, alloyed with Ta and Re for new generation marine GTEs

Alloy	Chemical composition, % wt.								
	C	Cr	Mo	W	Nb	Ti	Al	Co	Fe
CM93-VI	0.08–0.12	12.3–12.8	0.8–1.2	4.3–4.7	0.1–0.3	4.6–5.0	2.8–3.2	6.7–7.3	<0.5
CM96-VI	0.04	12.5	1.1	6.35	0.3	2.3	3.4	7.25	<0.5
Alloy	Chemical composition. % wt.								
	Zr	Ta	Re	Si	B	Mn	S	P	Cu
CM93-VI	0.02–0.06	3.3–3.6	2.4–2.8	0.3	0.004–0.008	0.3	0.05	0.05	0.1
CM93-VI	–	3.45	4.05	0.3	0.004–0.008	0.3	0.05	0.05	0.1

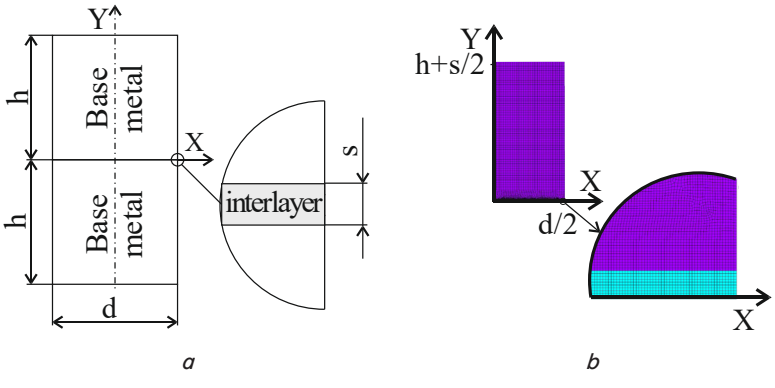


Fig. 1. brazed node: *a* – general view; *b* – finite element model

In the work, the SS stiffness coefficient was used to assess the impact of this difference on the performance of brazed joints [6]:

$$k_s=\sigma_{1(3)}/\sigma_{eq},$$

where $\sigma_{1(3)}$ are the maximum principal stresses, σ_{eq} are equivalent according to Mises.

When k_s<1.0, there is a "weakening" effect (reduction of yield strength and increase of plasticity) of the material. This reduces the probability of brittle fracture in comparison with the linear stressed state (k_s=1.0), under which standard mechanical tests of alloys are carried out. When k_s>1.0, the effect of "hardening" occurs (increasing the yield point and reducing the plasticity of the material), i.e., the threat of brittle failure increases.

For brazing and conducting research, a SNVE 1.3.1/16I1 vacuum furnace was used, which allows temperatures up to 1500 °C at a vacuum of $(2–5)\cdot10^{-3}$ Pa. The UDSV-DT installation (vacuum 10^{-2} Pa) and the ultra-high vacuum complex VVU-1D, which provides a working vacuum of 10^{-5}–10^{-6} Pa, were also used. A VIM-125 vacuum induction module was used for brazing filler metal melting, and a "Schmett" vacuum furnace was used for heat treatment.

Metallographic analysis and photographing of the metal structure was carried out on a Neofot-21 light microscope (Germany). A reaction mixture containing 80 % ethyl alcohol, 16 % HCl, 3 % $CuSO_4$, 1 % H_2SO_4, and a reagent containing 80 % glycerin, 15 % HNO_3, and 5 % HF was used to detect the microstructure.

High-temperature differential thermal analysis was performed on a VDTA-8M thermal analyzer (Ukraine). The rate of heating and cooling was 0.8 °C/s.

A raster electron microscope-microanalyzer REMMA-102-02 (Ukraine) was used to study the structure of brazing filler metal and brazed joints, as well as to carry out their chemical analysis.

Tensile tests (short-term) were carried out on P-5 and UM-20 machines at a speed of 10^{-3} mm/s. MP-1200 and AIMA-5 machines were used for long-term durability tests. Cylindrical samples with a diameter of 5 mm were tested at temperatures of 20 °C and 900 °C.

Determination of brazing filler metal resistance against HSC was carried out by the crucible method in molten salts: 25 % NaCl and 75 % Na_2SO_4 at a temperature of 900 °C for 20 hours.

5. Results of investigating the stressed state, structure, composition, and properties of brazing filler metal and brazed joints

5. 1. Research and formulation of recommendations for choosing the ratio of properties of the base metal and brazing filler metal

The analysis of the results of SSS modeling showed that when brazing nodes on most of the joint, stresses in the base metal are practically absent under thermal load and linearly distributed under force load. Only in a small area around the outer surface and in the brazing filler metal interlayer is a complex volumetric SSS formed.

When the node is compressed, there is a "weakening" of the base metal (Fig. 2, *a*) and a "strengthening" of the interlayer metal (Fig. 2, *b*) when using a "soft" interlayer (with a lower modulus of elasticity than that of the base metal). With a "hard" interlayer in the main metal, the value of k_s>1.0 (Fig. 2, *a*), in the interlayer k_s<1.0 (Fig. 2, *b*). With tensile loading, the picture will be the opposite. The change in the thickness of the brazing filler metal interlayer within the considered limits has little effect on the nature of SSS and the distribution of values of k_s, only the dimensions of the volumetric SSS zone change in direct proportion.

When cooling the brazed assembly, regardless of the ratio of TCLE and the modulus of elasticity of the base metal and the interlayer, in the base metal around the joint on a larger (85 %) length of the joint, k_s<1.0. «Hardening» of the material occurs only near the outer surface (Fig. 3, *a*). In the interlayer at 80 % of the length of the joint k_s=1, near the edge of the joint, the stiffness coefficient first slightly increases (the metal "strengthens"), and then rapidly decreases (the metal «weakens») on the outer surface of the node (Fig. 3, *b*).

During cooling of the brazed joint under pressure, with a smaller TCLE of the interlayer than that of the base metal, there is "weakening" (k_s<1.0) of the base metal (Fig. 4, *a*, 1) and "strengthening" (k_s>1.0) of the interlayer

metal (Fig. 4, *b*, 1) along the entire length of the joint. With a larger TCLE of the interlayer, the plasticity of the base metal decreases (Fig. 4, *a*, 2), and that of the interlayer metal increases (Fig. 4, *b*, 2). Cooling of a node with an interlayer of brazing filler metal, which has a lower yield strength and creep resistance than the base metal up to 15–30 %, does not significantly change the pattern of distribution of k_s in the base metal and interlayer.

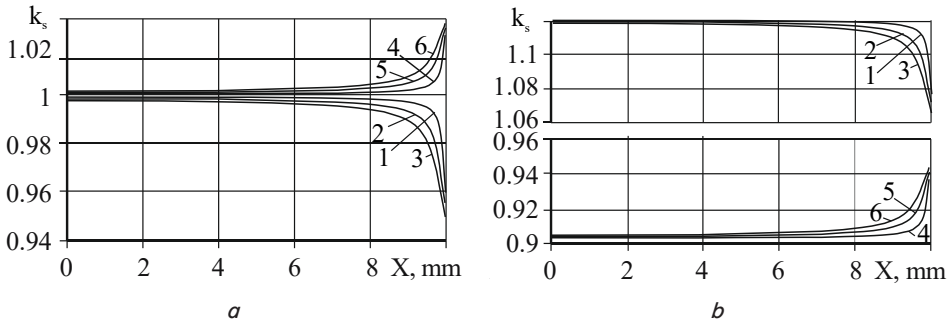


Fig. 2. Change in stiffness coefficients of the stressed state $k_s=\sigma_{1(3)}/\sigma_{eq}$ along the joint of the welded joint: 1 — with a "soft" interlayer and a relative interlayer thickness of 0.0025; 2 — with a "soft" interlayer and a relative interlayer thickness of 0.00625; 3 — with a "soft" interlayer and a relative interlayer thickness of 0.01; 4 — with a "hard" interlayer and a relative interlayer thickness of 0.0025; 5 — with a "hard" interlayer and a relative interlayer thickness of 0.00625; 6 — with a "hard" interlayer and a relative interlayer thickness of 0.01; *a* — in main metal; *b* — in the interlayer

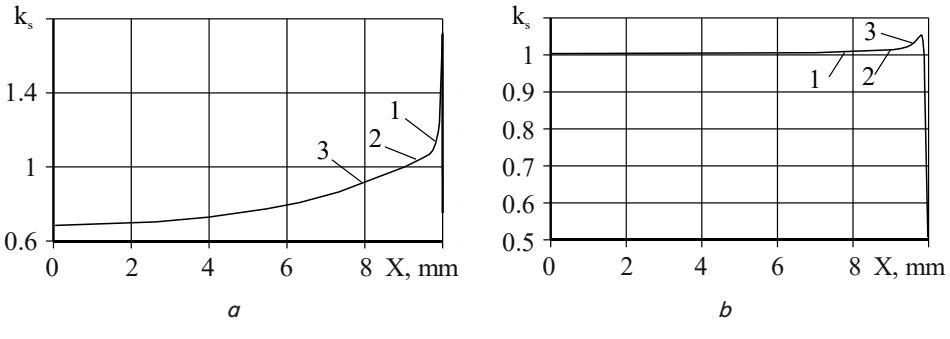


Fig. 3. Change in stiffness coefficients of the stressed state $k_s=\sigma_{1(3)}/\sigma_{eq}$ at the joint of the welded joint: 1 — with a "neutral" interlayer; 2 — with a "soft" interlayer; 3 — "hard" interlayer; *a* — in main—metal; *b* - in the interlayer

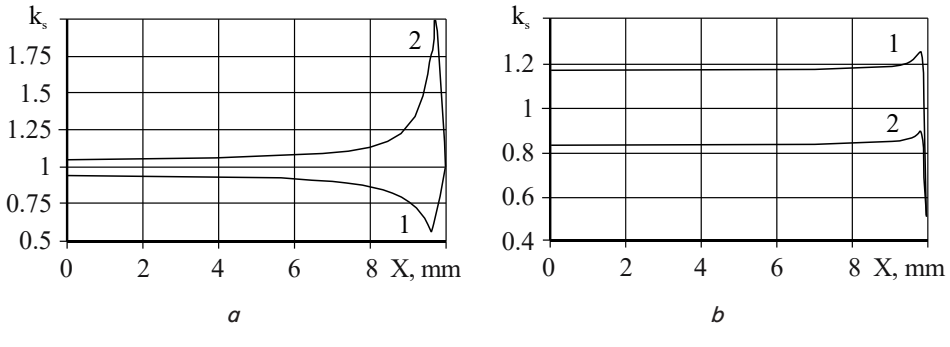


Fig. 4. Change in stiffness coefficients of the stressed state $k_s=\sigma_{1(3)}/\sigma_{eq}$ along the joint of the brazed node (thickness of the interlayer 0.08 mm): 1 — with a lower temperature coefficient of linear expansion of the interlayer; 2 — with a higher temperature coefficient of linear expansion of the interlayer: *a* — in main metal; *b* — in the interlayer

Based on our results regarding the distribution of stiffness coefficients, it can be stated that the difference of PMPs of the brazing filler metal interlayer from the properties of the base material leads to the deterioration of the plastic properties of brazed joints, reducing their performance. Therefore, it is necessary to choose a brazing filler metal with a minimal difference in properties from the base metal to ensure the chemical and structural homogeneity of the base metal and the brazing filler metal interlayer in the joint zone.

5. 2. Determination of rational doping of the brazing filler metal base and effective concentration of depressant elements

Alloys CM96-VI and CM93-VI were considered as the base of the brazing filler metal. The computer programs PHACOMP [3] and CALPHAD [22] were used to determine the distribution of elements between the γ- and γ'-phases, liquidus and solidus temperatures, and the number of electron vacancies in these alloys. The results of calculations based on the average value of element concentrations are given in Table 2.

The distribution of elements and the ratio of the concentration of elements (γ'/γ) in the phases indicates the participation of each of the elements in dispersion strengthening and solid solution strengthening. In both CM93-VI and CM96-VI alloys, Ni, Al, Ti, Ta, and Nb participate in the formation of the γ'-phase, the concentration of which in the alloys is very low, the solid solution is strengthened by Re, W, Co, Cr, and Mo, the concentration of which is also low. The calculation of the number of electronic vacancies in alloys shows that the number of electronic vacancies in the alloy is less than the critical one. The liquidus, solidus, and solvus temperatures for the CM93-VI alloy are 1330, 1169, and 1214 °C, respectively. For the CM96-VI alloy, these temperatures are 1391, 1340, and 1206 °C, respectively.

The calculated and experimentally determined temperatures of complete melting of the CM93-VI alloy practically coincide (Fig. 5). Metal melting begins at a temperature of 1255 °C and ends at 1340 °C. The CM96-VI alloy has a higher, near 1400 °C, liquidus temperature. The CM96-VI alloy also has minor thermal effects in the solid state at 1155 and 1207 °C, the onset of melting

is 1300 °C, and the beginning of crystallization is 1375 °C. According to the number of electronic vacancies, it was determined that both alloys are resistant to the formation of the σ-phase.

Table 2

Distribution of elements between phases in an alloy

Elements	CM93–VI			CM96–VI		
	Content of elements in phases, % at.		Ratio of element concentrations	Content of elements in phases, % at.		Ratio of element concentrations
	γ-phase	γ'-phase	γ'/γ	γ-phase	γ'-phase	γ'/γ
	The content of the γ'-phase is 55.2 % at., the content of carbides+borides is 2.2 % at.			The content of the γ'-phase is 47.4 % at., the content of carbides+borides is 0.57 % at.		
Ni	51.00	71.89	1.41	54.28	71.14	1.31
Cr	28.40	2.27	0.08	24.27	3.46	0.14
Co	11.67	3.56	0.30	11.08	3.56	0.32
Mo	0.64	0.10	0.16	1.06	0.26	0.25
W	2.38	0.69	0.29	3.02	1.06	0.35
Al	2.56	10.11	3.95	2.88	13.04	4.52
Ti	1.35	9.31	6.90	0.78	5.23	6.71
Nb	0.05	0.16	3.2	0.07	0.31	4.43
Ta	0.33	1.70	5.15	0.29	1.66	5.72
Re	1.63	0.21	0.13	2.27	0.28	0.12

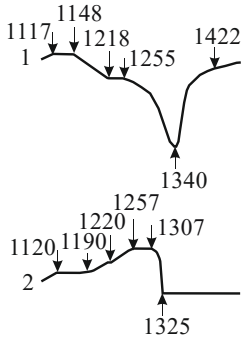


Fig. 5. The curve of high-temperature differential thermal analysis of the CM93-VI alloy: 1 — heating; 2 — cooling

The brazing filler metal, named SBM-4, is based on the polycrystalline CM93-VI alloy, which has lower liquidus, solidus, and crystallization onset temperatures.

As a depressant element, boron was chosen without alternative, taking into account its successful use in SBM-3 brazing filler metal [3]. The effective concentration of boron can only be determined experimentally by smelting alloys with different concentrations of boron.

To reduce the number of experimental melts, an alloy called 4D was melted, which consists of five elements and has a chemical composition of 14 Cr; 9.5 Co; 2.5 Al; 2.4 B % at. The chemical composition of the 4D additive alloy is chosen in such a way that the concentrations of the elements remain within the range of the selected concentrations of the brazing filler metal base. It was added to the first melting of SBM-4 brazing filler metal in the amount of 10, 20, 30 %, which made it possible to smoothly change the concentration of boron. When 10–30 % of the 4D alloy is added, the boron concentration increases from 0.915 to 1.245 %. The distribution of elements by phases was determined using the PHACOMP program. No significant changes in the distribution of elements were found.

Experimental data on the change in the area of brazing filler metal spreading with the addition of 10, 20, 30 % of the 4D alloy at temperatures of 1200, 1215, and 1230 °C are shown in Fig. 6. The exposure time at the temperature was 10 min. Changing this time from 5 to 10 min. at temperatures of 1215 °C and 1230 °C, the spread of brazing filler metal melts is not affected.

To reduce the number of experimental studies, the method of planning the experiment according to [23] was used for a complete factorial experiment of 2^2 using a first-order polynomial. The resulting general form of the regression equation takes the following form:

$$y = 124.89 + 35.83x_1 + 20.83x_2 - \\ -3.5x_{12} - 12.17x_1^2 - 4.83x_2^2. \quad (1)$$

Fig. 7 shows a graphical comparison of the results of the calculations with the experimental ones.

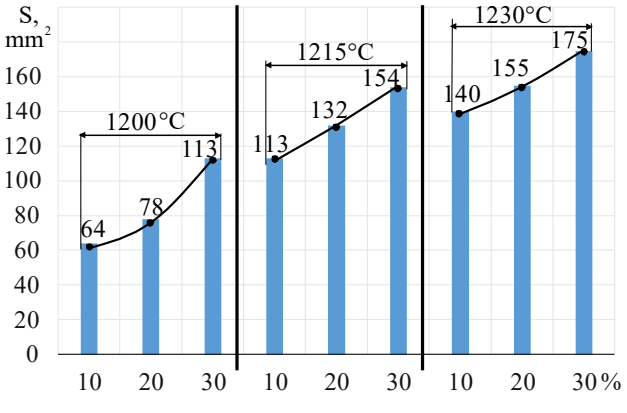


Fig. 6. Spreading areas of SBM-4 brazing filler metal at temperatures of 1200, 1215, and 1230 °C when 10, 20, and 30 % of 4D alloy is added to it

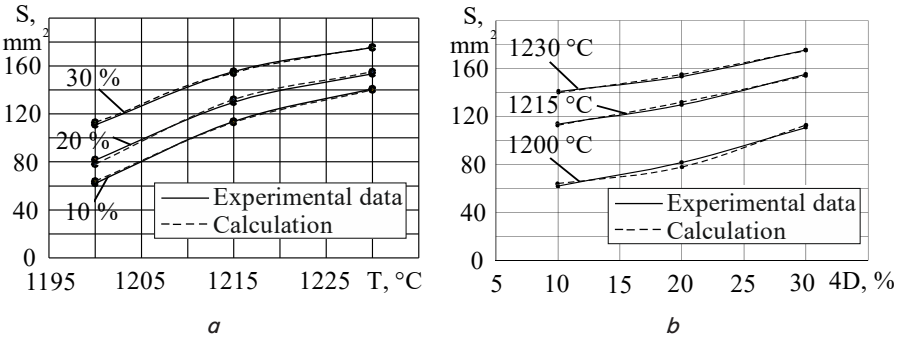


Fig. 7. Dependence of the brazing filler metal spreading area: *a* — on temperature; *b* — on the content of additive 4D

It can be seen that the calculated and experimental values in the study of the spreading area practically coincide.

According to the research results, the concentration of boron in SBM-4 brazing filler metal was taken as equal to 1.0–1.2 % by weight. According to the average values of this boron concentration and the concentration of alloying elements of the brazing filler metal base, SBM-4 brazing filler metal is for industrial use. The thermogram of SBM-4 brazing filler metal is shown in Fig. 8.

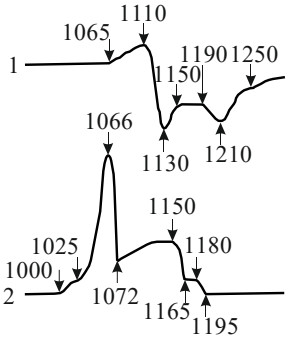


Fig. 8. Thermogram of brazing filler metal SBM-4: 1 — heating; 2 — cooling

Brazing filler metal SBM-4 contains wt%: 12.5–14.5 Cr; 6.5–7.5 Co; 3.0–5.0 Al; 3.0–6.0 Ta; 3.0–4.5 Re; 2.0–3.0 W; 1.0–2.0 Mo; 4.7–6.2 Ti; 0.2–0.3 Hf; 0.45–0.7 Zr; 0.3–0.5 Nb; 1.0–1.2 B; 0.04–0.10 C; Ni – the rest. An invention patent was obtained for brazing filler metal [24].

5. 3. Study of wetting, spreading, and resistance to high-temperature salt corrosion of SBM-4 brazing filler metal

The study of wetting and spreading of SBM-4 brazing filler metal on the surface of CM93-VI and CM96-VI alloys was carried out in a vacuum $(3...6)\cdot10^{-3}$ Pa with an inflow of no more than $3\cdot10^{-5}$ Pa·m^3·s^{-1}. The results are shown in Fig. 9, 10.

Edge wetting angles at temperatures 1210, 1215, 1220, 1225, 1230, 1235 °C are shown in Fig. 9. At temperatures of 1210–1215 °C, the edge angles were 6...4°, and at higher temperatures they did not exceed 3°. The holding time at the temperature was 15 min.

From Fig. 9, it can be seen that with increasing temperature, the depth of dissolution of the base metal brazing filler metal increases. At temperatures up to and including 1220 °C, the maximum dissolution depth does not exceed 0.1 mm, and at temperatures of 1230–1235 °C it is 0.244 mm. The depth of dissolution increases towards the center of the drop, where the thickness of the melt is greater. When the alloys are dissolved, there are no interlayers on the border between the brazing filler metal and the base metal.

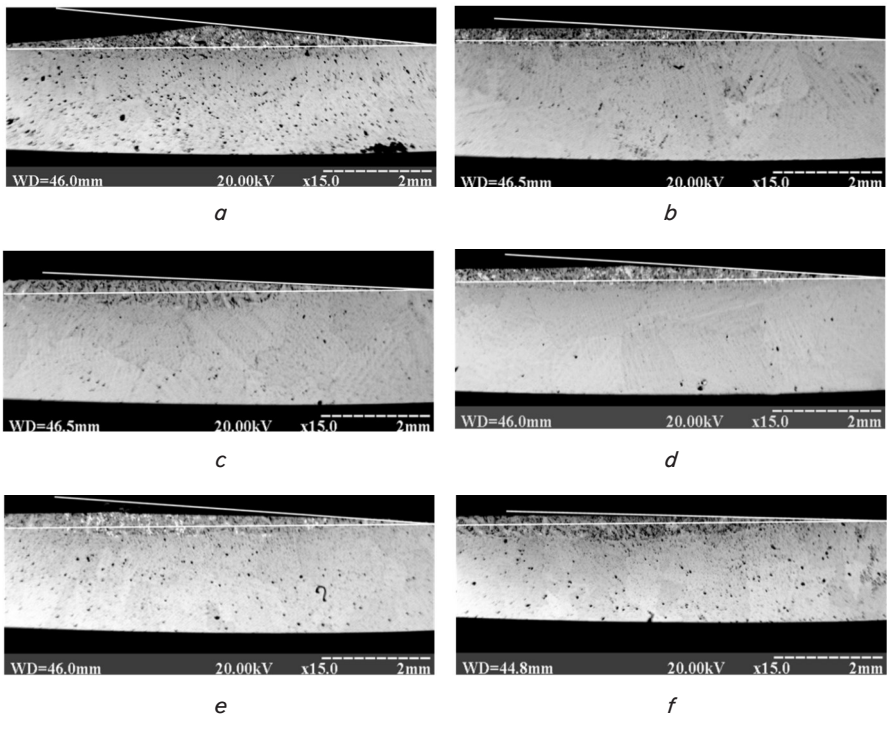


Fig. 9. Edge wetting angles of heat-resistant nickel alloys of marine GTEs: *a* — CM93—VI at a temperature of 1210 °C; *b* — CM93—VI at a temperature of 1220 °C; *c* — CM93—VI at a temperature of 1230 °C; *d* — CM96-VI at a temperature of 1215 °C; *e* — CM96-VI at a temperature of 1225 °C; *f* — CM96-VI at a temperature of 1235 °C

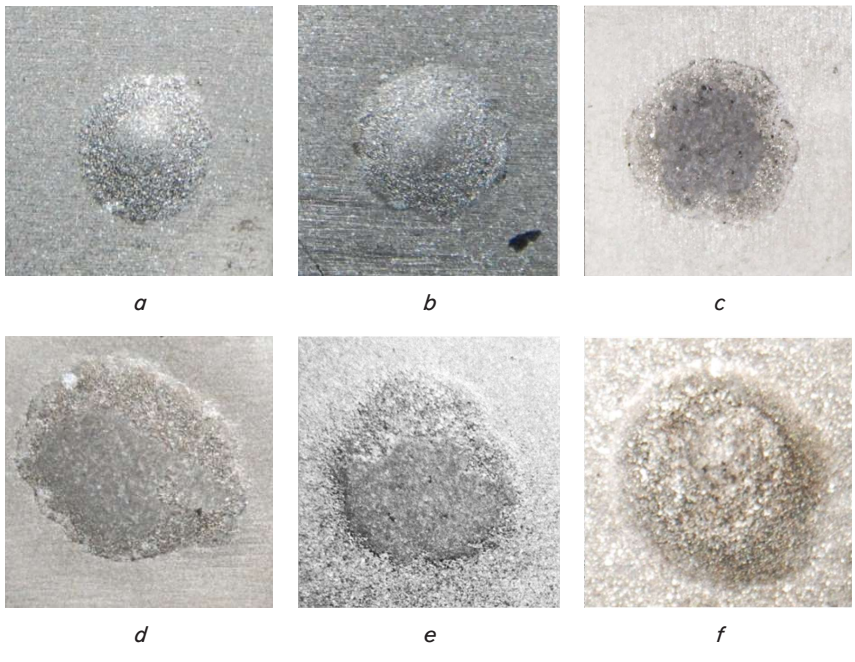


Fig. 10. Spreading of SBM-4 brazing filler metal on heat-resistant alloys: *a* — CM93-VI at a temperature of 1210 °C with a holding time of *t*=15 min.; *b* — CM93-VI at a temperature of 1220 °C with a holding time of *t*=15 min.; *c* — CM93-VI at a temperature of 1225 °C with a holding time of *t*=15 min.; *d* — CM96-VI at a temperature of 1235 °C with a holding time of *t*=15 min.; *e* — CM96-VI at a temperature of 1230 °C with a holding time of *t*=15 min.; *f* — CM96—VI at a temperature of 1230 °C with a holding time of *t*=25 min.

The spread of brazing filler metal along the HNAs is shown in Fig. 10. The spreading time was varied from 15 to 25 min. After exposure for 15 min., the spreading area is smaller. For example, in Fig. 10, *d*, the spreading time was 15 and 25 min., respectively. Subsequently, in all studies, brazing was performed with a holding time of 15 minutes. For clarity, the effect of temperature on the area of SBM-4 brazing filler metal spread for both alloys is shown on one plot (Fig. 11).

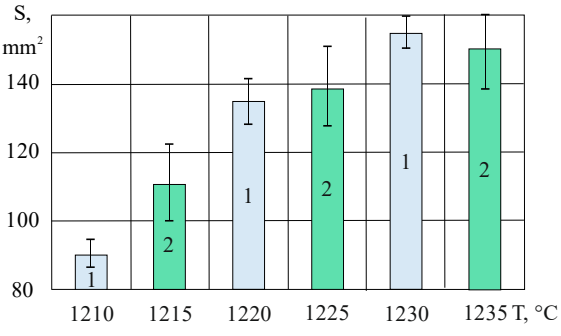


Fig. 11. The influence of temperature on the area of SBM-4 brazing filler metal spreading on the surface of alloys: 1 — CM93-VI; 2 — CM96-VI

Studies of the surface properties of SBM-4 brazing filler metal showed that it wets, spreads, and fills the gaps almost equally in the CM93-VI and CM96-VI alloys. The marginal wetting angles of both alloys are within the error of their determination.

The high resistance of CM93-VI and CM96-VI alloys against HSC was proven in [16], therefore it was important to determine the influence of boron in SBM-4 brazing filler metals on resistance against HSC. For this purpose, alloys CM93-VI and CM96-VI were smelted with boron concentrations of 1.0, 1.2, 1.5, 2.0, and 2.5 % by weight. The test was carried out at a temperature of 900 °C for 20 hours in a molten salt solution of 25 % NaCl + 75 % Na_2SO_4, as shown in Fig. 12.

It was established that at a boron concentration of 1.2 %, the resistance of alloys against HSC did not decrease. After melting the SBM-4 brazing filler metal, cylindrical samples were made, and an HSC study was carried out.

According to the research results, the HSC rate of SBM-4 brazing filler metal was 0.4–1.32 mg/cm^2·hour, such values satisfy the technical conditions of operation of the alloys. The resistance of SBM-4 brazing filler metal against HSC is ensured by selected concentrations of both alloying elements and the depressant element.

a *b*

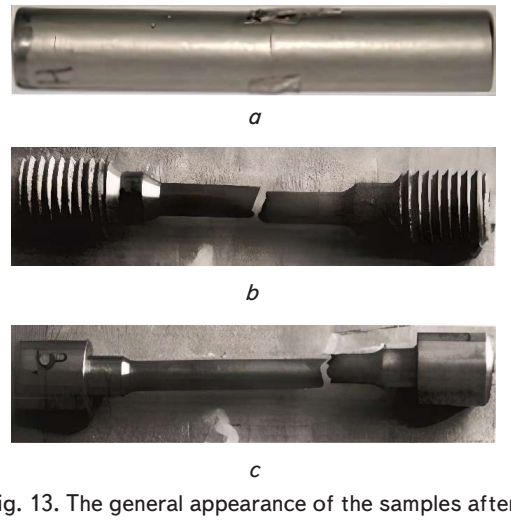
Fig. 12. Study of high-temperature salt corrosion of alloys CM93-VI and CM96-VI with boron concentration: *a* — 1.0 % by weight; *b* — 1.2 % by weight

5. 4. Investigation of the structure, chemical composition, and properties of brazed joints

Research into the structure and chemical composition of brazed joints was carried out on samples that were brazed together with samples for mechanical tests or on the same samples. Fig. 13 shows cylindrical samples after brazing (*a*) and after tests for short-term and long-term strength at a temperature of 900 °C (*b*, *c*).

For mechanical tests, the samples were brazed at a temperature of 1210–1220 °C with a holding time of up to 15 min. followed by cooling to 1070 °C and holding for 60 min. Samples were assembled without a gap and with a gap of 0.08 mm, brazed without external compression force. Brazing of the samples was performed in a vertical position, that is, the joint was in a horizontal plane. Brazing was carried out in a vacuum $(3–6)\cdot10^{-3}$ Pa. The inflow into the working chamber did not exceed $3\cdot10^{-5}$ Pa·m^2·s^{-1}. After brazing, the samples were subjected to external inspection, macro- and microstructure studies. The sequence of work with experimental samples is shown in Fig. 14. No pores, non-metallic inclusions, cracks, or gaps were found. If during the tests the samples were destroyed outside the joint, then sections were made from the joint area to analyze the structure and chemical composition of the metal.

Analysis of the structure and chemical composition of the metal of brazed joints made of the CM93-VI alloy revealed that the brazing filler metal interlayer and the base metal after heat treatment are identical in structure and composition. The microstructure and spectrum of the metal of the soldered joint are shown in Fig. 15; the chemical composition of points 2 and 3 – in Table 3.

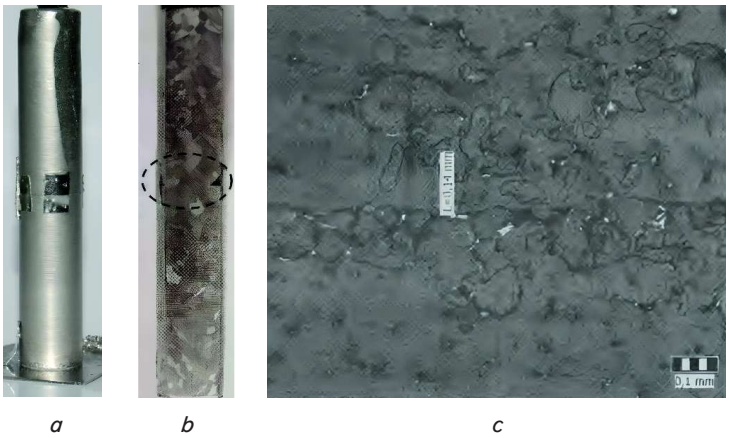


a

b

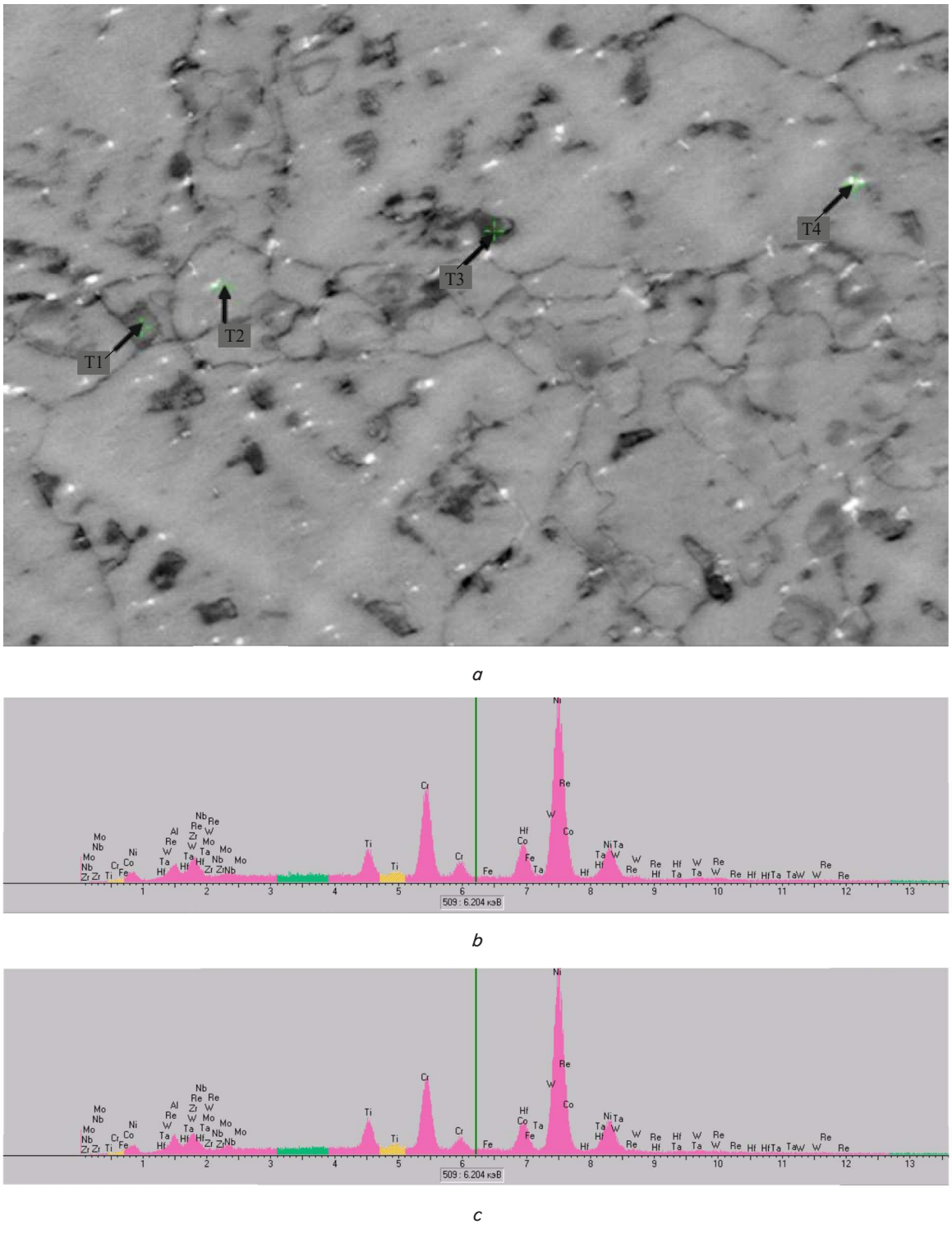
c

Fig. 13. The general appearance of the samples after: *a* — brazing; *b* — tests at a temperature of 900 °C for long-term strength; *c* — determination of strength limit



a *b* *c*

Fig. 14. The sequence of working with experimental samples: *a* — brazing of the sample; *b* — macrostructure analysis; *c* — microstructure analysis



a

b

c

Fig. 15. Analysis of the structure and chemical composition of the metal of the brazing filler metal joint of the CM93-VI alloy: *a* — microstructure (x120); *b* — spectrum at point 2; *c* — spectrum at point 3

The structures of brazed joints of the CM93-VI and CM96-VI alloys shown in Fig. 16 demonstrated the homogeneity of the metal. After brazing and heat treatment, there is no boride eutectic in the joint. The high diffusion mobility of boron atoms contributes to the isothermal crystallization of brazing filler metals, as well as the separation of dispersed borides in the transition zone. Carbide and boride inclusions have a significant concentration of elements with a high affinity for carbon and boron (Table 3).

Brazing filler metal SBM-4 provides mechanical properties of joints close to the base metal. It was established that the tensile strength σ_{TS} of brazed joints corresponds to the level of the base metal. The results of studies on determining the tensile strength of the base metal and brazed joints are given in Table 4.

The long-term strength of the base metal of the CM93-VI and CM96-VI alloys and SBM-4 brazed joints during tensile tests of samples at a temperature of 900 °C for 100 h with an interlayer thickness of 0.08 mm is given in Table 5.

Table 3

Chemical composition of the metal of the brazing filler metal joint of the CM93-VI alloy at points 2 and 3

Analysis area	Elemental content, % wt.											
	Al	Ti	Cr	Fe	Co	Ni	Zr	Mo	Hf	Ta	W	Re
Point 2	2.55	5.47	15.55	0.15	8.51	55.18	0.1	1.81	0.1	3.58	4.5	2.58
Point 3	2.98	6.17	13.75	0.52	8.38	58.52	0.04	1.77	0.1	1.96	3.74	2.18

Table 4

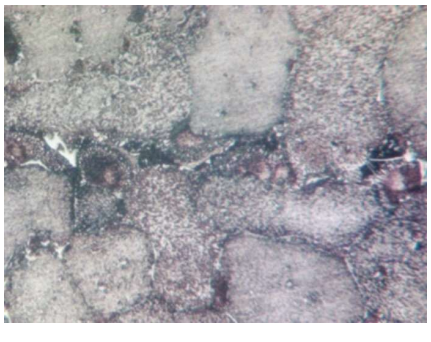
Tensile strength of CM93-VI and CM96-VI alloys and brazed joints

Alloy	Tensile strength of alloys, MPa			Tensile strength of joints, MPa	
	at 20 °C	at 900 °C	at 950 °C	at 900 °C	at 950 °C
CM93-VI	920–1050	640–750	–	697	–
CM96-VI	900–980	–	460–470	–	463

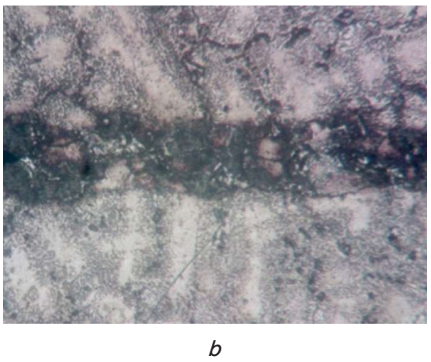
Table 5

Long-term strength of the base metal of the CM93-VI and CM96-VI alloys and SBM-4 brazed joints during tensile tests of samples at a temperature of 900 °C for 100 h with an interlayer thickness of 0.08 mm

No. of entry	Material	Long-lasting durability σ_{100}^{900}		
		Base metal $\sigma_{100\ (bm)}^{900}$, MPa	Brazed joint $\sigma_{100\ (bj)}^{900}$, MPa	Ratio $\sigma_{100\ (bj)}^{900} / \sigma_{100\ (bm)}^{900}$
1	CM93-VI polycrystalline	314	285	0.91
2	CM96-VI, polycrystalline	321	285	0.89



a



b

Fig. 16. Microstructures of brazed joints when brazing with SBM-4 brazing filler metal with a constant gap of 0.08 mm after heat treatment: *a* — CM93-VI alloy (x250); *b* — alloy CM96-VI

Tests of brazed joints for long-term strength were performed under the influence of tensile stresses of 285 MPa and removed after 100 h. The long-term strength of the joints of the CM93-VI and CM96-VI alloys is at the level of 91 and 89 % of the strength of the base metal, respectively.

5. 5. Development of brazing technology and correction of surface casting defects of CM93-VI and CM96-VI alloys

Brazing filler metal SBM-4 is intended for brazing of CM93-VI and CM96-VI alloys at temperatures of 1200...1230 °C in a vacuum of $6{\cdot}10^{-3}...10^{-2}$ Pa. Brazing filler metal can be used for brazing other marine GTE engines. It well wets the surface of HNAs, spreads over it, and fills the gaps. The marginal wetting angles do not exceed 5–7°, while the specific spreading area is 1.4–1.5 mm^2/mg. Brazing filler metal has high permeability and fills micron gaps. As with many other brazing filler metals, it is used in the form of a powder. Brazing filler metal melting is carried out in a vacuum induction furnace VIM-125. Brazing filler metal granulation is carried out by the method of cold metal processing. Next, the brazing filler metal is ground on a press and a interlayer vibrating mill in an environment of high-purity argon. The mill uses interlayers of heat-resistant nickel alloy. By sieving, the obtained brazing filler metal powder is divided into three fractions, of which the most used fraction is 0.08 mm.

Brazing technology consists of a sequence of operations at the stages of preparation of joint surfaces and technological materials, assembly, brazing, cooling, and final processing of the product. Technological materials include brazing filler metal in the form of powder and a 5 % solution of BMK-5 acrylic resin in acetone, which is used to fix the brazing filler metal near the edge of the gap or in a specially prepared «pocket».

Before assembly, the surfaces of the joint are treated by grinding in the direction of the spread of the brazing filler metal. Before assembly, the joint surface is wiped with alcohol. Other means of additional cleaning or activation are not used.

When brazing blades into a package, the preparation also includes cleaning the blades to a metallic shine at a distance of at least 5 mm from the joint, followed by degreasing with alcohol.

Brazing of blades into blocks is performed in vacuum furnaces of the SEV, SNBE, etc. type, which ensure the creation of a vacuum no worse than 10^{-2} Pa and the size of the working space no less than 200×200×400 mm. In the furnace, a package of blades is placed and fixed in a special device. Before applying the brazing filler metal, it is kneaded to a paste-like state using a 5 % solution of BMK-5 acrylic resin in acetone. The volume of applied powder is approximately 1.4 of the volume filled with brazing filler metal. Brazing is performed after complete drying of the paste in a vacuum not worse than 10^{-2} Pa. Modes of vacuum brazing with SBM-4 brazing filler metal blades made of CM93-VI alloy: temperature 1210–1215 °C, time 15±5 min. Made from the CM96-VI alloy: temperature 1220–1230 °C, time 15±5 min. After brazing, the blades are cooled to a temperature of 1070 °C and held for 60 min., then free cooling in a vacuum is continued to a temperature of 200 °C. Quality control of

brazed packages includes external inspection and measurement. Brazing filler metal melting should be uniform with complete melting of the joints between the blades.

Brazing filler metal SBM-4 showed high technological properties, as well as high permeability into microcracks and microgaps. This makes it promising for the correction of surface defects of castings and parts with defects acquired during operation, made of alloys CM93-VI and CM96-VI.

Depending on the size of the defect, its correction is carried out without filler or with filler. Small defects are corrected with SBM-4 brazing filler metal without filler. High-temperature brazing filler metal SBM-3 [3] or SM88U-VI alloy powder is used as a filler. Filler and SBM-4 brazing filler metal are a 1:1 mixture. The powder mixture is fixed on the surface of the blade with a 5 % solution of BMK-5 resin in acetone. The amount of composite powder should be greater than the volume of the developed defect by 40–50 %. The surface of the blade around the defect must be free of oxides at a distance of at least 5 mm. The places to be corrected must be designed at an angle of $90°\leq\beta\leq120°$ until the defect is completely removed, according to Fig. 17.

The correction of casting defects is regulated by the Technological Instruction (TI) of the SE GTR&PC «Zorya»-»Mashproekt». Fig. 18 shows a microstructure with corrected surface defects, and a brazed sign hole.

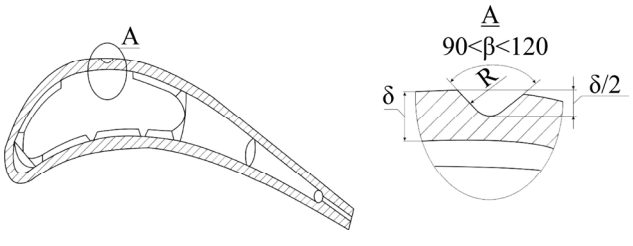
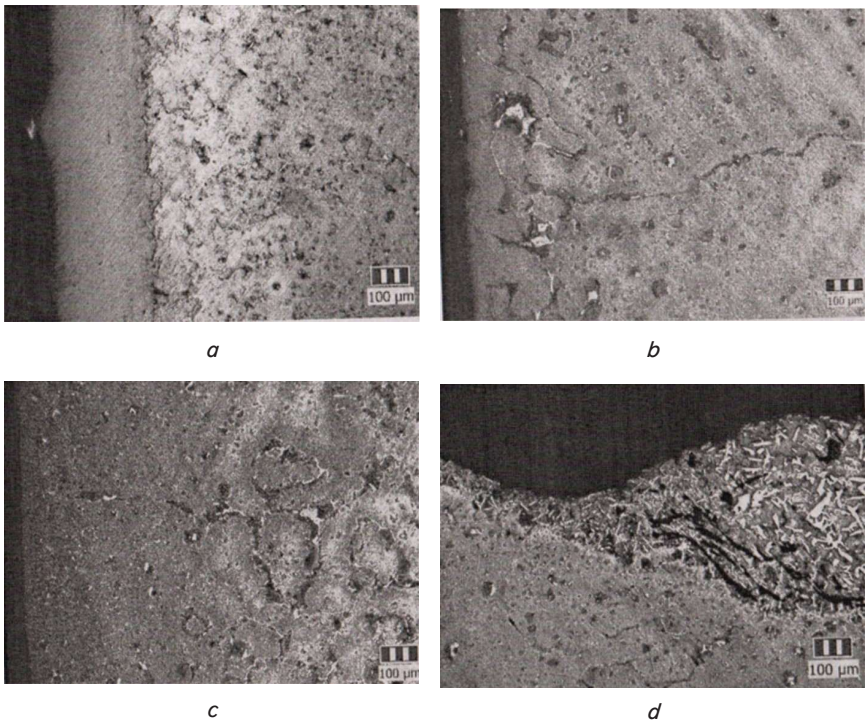


Fig. 17. Development of a shell-type surface defect



a *b*

c *d*

Fig. 18. Correction of defects of the CM93-VI alloy blade with SBM-4 brazing filler metal: *a*, *b* — microstructure with corrected surface defects; *c* — microstructure with corrected base metal defects; *d* — microstructure of the brazed sign hole

Defect correction is performed according to the same parameters of modes as brazing.

6. Discussion of results of investigating the stressed state, structure, composition, and properties of brazing filler metal and brazed joints

The peculiarity of modern heat-resistant alloys is the problem of their welding. Therefore, for their connection, brazing is used, in particular, techniques of diffusion brazing, brazing with composite brazing filler metals, and, if possible, brazing with pressure. When developing brazing filler metals for marine GTEs, it is necessary to ensure the resistance of brazed joints against HSC and high operating temperatures and the strength of the joints at the level of the base metal.

Since the brazing filler metal joint is essentially a joint with an interlayer, its performance depends on many factors, in particular, on the difference in mechanical and physical properties of the brazing filler metal materials and the base metal, the geometric shape of the joint, which determine the stressed-strained state. The influence of the difference in modulus of elasticity, thermal coefficients of linear expansion (TCLE), yield strength, and creep resistance of the base material and the metal of the brazing filler metal interlayer on the SSS of the brazed joint was investigated using the computer simulation method, applying the ANSYS software package. It was established that the difference between the properties of the interlayer and the properties of the main material leads to the formation of stresses when temperatures change. Zones of "strengthening" and "weakening" of the metal in the brazed joint are formed (Fig. 2–4). The impact on the performance of the inhomogeneity of the brazed joint on the mechanical properties is also considered in [25]. Therefore, it is recommended to choose a brazing filler metal with a minimal difference in properties from the base metal. The material to be joined should be chosen as the basis of the brazing filler metal if there is such an opportunity.

Two alloys CM93-VI and CM96-VI, which are intended for the manufacture of new generation turbines, were developed and put into production at the SE GTR&PC "Zorya"-"Mashproekt" and PTIMS of the National Academy of Sciences of Ukraine, which are characterized by a working gas temperature increased by 40–60 °C [16]. Accordingly, it is necessary to raise the brazing temperature. Existing brazing filler metals have a brazing temperature of up to 1150 °C, they melt when a protective coating is applied to the blades. For new alloys, brazing filler metals with a melting temperature of 1210–1230 °C are needed. The purpose of the current work was to obtain a brazing filler metal that ensures the performance of brazed joints at the level of 85...90 % of the base metal.

The goal of the work was achieved owing to the application of a two-stage approach to the development of brazing filler metal. In the development of SBM-4 brazing filler metal, the same method

was used, which is discussed in detail in work [3]. The essence of the first stage is to determine the most effective alloying elements that provide solid solution and dispersion strengthening, phase formation, and properties of alloys. They use computer programs and differential thermal analysis with comparison of their results. One of the main criteria for choosing rational doping limits is the calculation of the number of electron vacancies in the alloy. When calculating the number of electronic vacancies, the PHACOMP software determines the degree of danger of embrittlement or its absence at a given chemical composition. The embrittlement of HNAs is caused by the formation of topologically densely packed phases (TDP). They bind a significant amount of the main alloying refractory metals. The separation of TDP-phases occurs in the range of 1150...1200 °C during heat treatment or during operation. The distribution of elements (Table 2) reflects the participation of each element in both dispersion and solid solution strengthening, but in different proportions. The solid solution is strengthened mainly by Re, W, Co, Cr, Mo, and Al, Ni, Ti, Ta, Nb, Hf, Zr participate in the formation of ɣ' phases (dispersion strengthening). Zirconium ensures permeability of the brazing filler metal along cracks, microcracks, and grain boundaries, and hafnium promotes isothermal crystallization. Alloys CM93-VI and CM96-VI have a cubic face-centered lattice, which contains a coherent ɣ' phase and intermetallics. Carbides form Cr, Mo, W, Ti, Ta, Re. A complex combination of Al, Ti, Nb, Mo, Re, and Cr ensures workability at high temperatures, but excessive alloying and the formation of intermetallics can lead to embrittlement of alloys. According to the number of electronic vacancies, both alloys are resistant to the formation of the σ-phase.

The basis of the brazing filler metal, named SBM-4, is the polycrystalline CM93-VI alloy. It has lower liquidus, solidus, and crystallization onset temperatures when cooling than the CM96-VI alloy. Boron was chosen as a depressant element, taking into account its successful use in the development of SBM-3 brazing filler metal [3].

To reduce the number of experimental studies, we used the method of planning the experiment, according to [23], for a complete factorial experiment of 2^2 using a first-order polynomial. The regression equation (1) is obtained, the calculated and experimental values in the study of the spreading area practically coincide.

The calculated and experimental values obtained during studies of the spreading area practically coincide. According to the research results, the concentration of boron in SBM-4 brazing filler metal was taken to be equal to 1.0–1.2 % by weight. Brazing filler metal received a Ukrainian patent for an invention [24].

SBM-4 brazing filler metal contains wt%: (3.0–5.0) Al; (4.6–6.2) Ti; (12.5–14.5) Cr; (6.5–7.5) Co; (0.45–0.7) Zr; (0.3–0.5) Nb; (1.2–2.0) Mo; (0.2–0.3) Hf; (3.0–6.0) Ta; (2.0–3.0) W; (3.0–4.5) Re; (1.0–1.2) B; (0.05–0.1) C; the rest is Ni.

According to the average values of the content of alloying elements given in the patent, molten brazing filler metal SBM-4 is for industrial use. The brazing filler metal thermogram is shown in Fig. 8. The results of research on wetting and spreading of SBM-4 brazing filler metal on the surface of CM93-VI and CM96-VI alloys are shown in Fig. 9–11. Wetting edge angles and brazing filler metal spreading areas on both alloys are practically the same.

The resistance of SBM-4 brazing filler metal against HSC was determined by the crucible method [19]. It was established that at a boron concentration of up to 1.2 % by weight, the stability of SBM-4 brazing filler metal against HSC meets the requirements of regulatory documents for the manufacture of products. The HSC rate is 0.4–1.32 mg/cm^2·hour, which corresponds to the SM88U alloy with a chromium content of 18 % by weight. The calculation of the Gibbs energy of the reaction between tantalum and chromium carbide showed that the affinity of tantalum for carbon is greater than that of chromium, and tantalum partially compensates for chromium.

Analysis of the structure and chemical composition of the metal of brazed joints made of the CM93-VI alloy showed that the brazing filler metal interlayer and the base metal after heat treatment are identical in structure and composition. The microstructure and spectrum of the metal of the brazed joint are shown in Fig. 15, the chemical composition of points 2 and 3 – in Table 3.

The structures of brazed joints of the CM93-VI and CM96-VI alloys shown in Fig. 16 demonstrated the homogeneity of the metal. After brazing, there is no boride eutectic in the joints. The high diffusion mobility of boron atoms promotes isothermal crystallization, as well as the separation of dispersed borides in the transition zone.

The developed brazing filler metal SBM-4 provides mechanical properties of joints close to the base metal. The long-term strength of the base metal of the CM93-VI and CM96-VI alloys and the joints brazed with SBM-4 brazing filler metal during tensile tests of samples at a temperature of 900 °C for 100 hours with a interlayer thickness of 0.08 mm is given in Table 5.

The long-term strength of brazed joints was determined at a tensile stress of 285 MPa based on 100 hours. The long-term strength of the joints of the CM93-VI and CM96-VI alloys is at the level of 91 and 89 % of the strength of the base metal, respectively.

Brazing filler metal SBM-4 is used for brazing blades in a package, correcting surface defects of castings, sealing in cooling blades, holes for attaching ceramic rods. The advantage of SBM-4 brazing filler metal is the provision of high joint strength, close to the strength of the base metal and high resistance to HSC.

Increasing the performance of brazed joints to the level of the main alloy of ship GTEs is necessary for connecting two or three nozzle blades on the upper and lower shelves into a block. This is especially important for the first stage of a high-pressure turbine. For the current generation of ship turbines, brazing filler metals VPr11 – 40H or HC12 with brazing temperatures up to 1150 °C are used. Fusion welding of cast alloys is impossible. It is also important to correct blade defects by brazing in castings and during operation. Despite the constant improvement of refractory mixtures for the manufacture of ceramic casting forms, rods, crucibles, filters, and casting technology, the yield of suitable blades is less than 100 %. More defects occur in the manufacture of single-crystal blades from the CM96-VI alloy. Casting defects are more common in the form of slag inclusions, "beads", there are much fewer underfills, cracks, and other discontinuities. All defects are divided into those, the correction of which is not allowed, and surface defects, the correction of which is carried out depending on the location area on the blade, the size of the defects, and the distance from them. Defects on the surface of the power sides of the vanes and the radii of the transitions of the vane feather into the shank are not corrected. Other defects are limited by depth, size, number, and category of construction. The correction of casting defects is regulated by the Technological Instruction (TI) of the SE GTR&PC "Zorya"-"Mashproekt". As brazing develops, ap-

propriate additions are made to technological documents (latest in 2019). Fig. 18 shows a microcut of a blade, a microstructure with corrected surface defects, and a brazed iconic hole.

When performing brazing and correcting defects, taking into account the presence of elements in the brazing filler metal (zirconium, hafnium) with a high affinity for oxygen, it is necessary to limit the massive inflow into the working chamber (no more than $3{\cdot}10^{-5}$ Pa·m^3·s^{-1}).

In order to permanently ensure high quality characteristics of the obtained brazed joints during the implementation of brazing technologies and correction of foundry defects, highly qualified personnel and appropriate equipment must be involved in the performance of the work.

For the further development of our work, it is advisable to determine the surface energy of the processes of wetting and spreading of the melt of the proposed brazing filler metal when interacting with HNAs.

7. Conclusions

1. A further development of ideas regarding the formation of a stressed state of brazed joints with a brazing filler metal interlayer, which has physical and mechanical properties different from the base metal, was obtained. According to the research results, it was established that in the brazed assembly, with a relative thickness of the brazing filler metal interlayer s/d=0.0005–0.01, a volumetric stressed-strained state is formed in the main metal near the outer surface of the joint and in the interlayer itself. This condition leads to strengthening or weakening of the base metal and interlayer. It is recommended to choose an alloy with a minimal difference in physical and mechanical properties from the material to be joined as the basis of the brazing filler metal.

2. A two-stage method of brazing filler metal development has been improved by alloying it with 0.45–0.7 % by weight Zr, 0.2–0.3 wt % Hf, which ensures the correction of defects such as cracks that occurred during the operation of the blades. Zirconium ensures permeability of the brazing filler metal along cracks, microcracks and grain boundaries, and hafnium promotes isothermal crystallization. Calculation of the Gibbs energy showed that the affinity of tantalum for oxygen is greater than that of chromium, which favors the interaction of tantalum with the carbon of chromium carbide and releases chromium. Therefore, the increased concentration of tantalum in the brazing filler metal helps increase the resistance of the brazing filler metal to HSC. A method for calculating the brazing filler metal base with the optimal content of tantalum and rhenium is proposed. At the first stage, with the help of the computer program PHACOMP, the limits of rational alloying of brazing filler metal with elements that provide solid-soluble and dispersion strengthening are determined. The distribution of elements between the phase components, the main physical and mechanical properties of the alloy, the danger of the formation of phases and compounds that embrittle the joints have been established. The polycrystalline alloy CM93-VI was used as the basis of the brazing filler metal, and boron is chosen as the depressant element. At the second stage, using the method of high-temperature differential thermal analysis, taking into account the temperatures of phase transformations, as well as the liquidus and solidus temperatures, the rational content of the depressant element boron, which is accepted in the SBM-4 brazing filler metal in the range from 1.0 to 1.2 % by weight, was determined. Brazing filler metal SBM-4 contains % by weight: (3.0–5.0) Al; (4.6–6.2) Ti; (12.5–14.5) Cr; (6.5–7.5) Co; (0.45–0.7) Zr; (0.3–0.5) Nb; (1.2–2.0) Mo; (0.2–0.3) Hf; (3.0–6.0) Ta; (2.0–3.0) W; (3.0–4.5) Re; (1.0–1.2) B; (0.05–0.1) C; the rest is Ni.

3. It was established that the edge wetting angles of the base metal CM93-VI and CM96-VI with the developed brazing filler metal are up to 6°. The specific spreading area is up to 1.4–1.5 mm^2/mg at a temperature of 1200–1230 °C, which allows correction of surface defects of castings. The rate of high-temperature salt corrosion of the developed SBM-4 brazing filler metal was 0.4–1.32 mg/cm^2·hour, which satisfies the technical conditions of operation of the CM93-VI and CM96-VI alloys.

4. Analysis of the structure and chemical composition of the metal of brazed joints made of the CM93-VI alloy showed that the brazing filler metal joints after heat treatment correspond to the base metal in terms of their structure and chemical composition, there is no boride eutectic in the joint. Due to the significant diffusion mobility of boron atoms, isothermal crystallization of the brazing filler metal is observed. Brazing filler metal has high permeability and fills micron gaps. It was established that multicomponent brazing filler metals with rhenium and tantalum of the system Ni-Cr-Co-Al-Ta-Re-W-Mo-Ti-Nb-B-Hf-Zr-C provide the formation of brazed joints with short-term strength at a temperature of 900 °C with equal strength of the base metal. The long-term strength of the joints of the CM93-VI and CM96-VI alloys is at the level of 90 % of the strength of the base metal.

5. For the promising CM93-VI and CM96-VI alloys, which are intended for the production of new generation marine GTEs, technologies for brazing nozzle blade packages into blocks and correcting surface defects of castings, in particular cracks, have been developed. The recommended parameters of the vacuum brazing modes with SBM-4 brazing filler metal of blades made of CM93-VI and CM96-VI alloys were defined: brazing temperature 1210–1215 °C and 1220–1230 °C, respectively, brazing time 15±5 min, vacuum depth $6{\cdot}10^{-3}$ –10^{-2} Pa, the amount of inflow into the working chamber is no more than $3{\cdot}10^{-5}$ Pa·m^3·s^{-1}.

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.

Funding

The study was conducted without financial support.

Data availability

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

Acknowledgments

The authors sincerely thank the employees of SE Gas Turbine Research and Production Complex "Zorya"-"Mashproekt" who took part in brazing filler metal smelting, its mechanical grinding, and correction of defects.

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