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INVESTIGATION OF BRAZING FILLER FOR BRAZING HIGH-TEMPERATURE NICKEL ALLOYS OF MARINE GAS TURBINES

ДОСЛІДЖЕННЯ ПРИПОЮ ДЛЯ ПАЯННЯ ЖАРОМІЦНИХ НІКЕЛЕВИХ СПЛАВІВ МОРСЬКИХ ГАЗОВИХ ТУРБІН

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Abstract. Aim. The creation of a brazing filler for brazing high-temperature nickel alloys of new generation marine gas turbine engines, which will increase the temperature of the working gas by 40 ... 60°C. **Methodology.** To achieve this goal, high-temperature differential thermal analysis and crucible methods were used to study high-temperature salt corrosion of brazing filler. **Results.** The method of high-temperature differential analysis was used to study critical temperatures of the alloys CM93-VI and CM96-VI. Zirconium, hafnium, and boron were taken as depressants. After studying the interaction of the brazing filler with the base metal, the most effective depressant boron was selected for further use, which allows to

control the brazing and melting temperatures of the brazing fillers by changing its concentration. Brazing filler were melted for experimental investigation of surface properties. For illustrative purposes, VPr36 brazing filler was used to compare the results. As an assessment of the flow of solders into the gaps, wedge samples were used, where gaps variability has fluctuated from 0 to 0.6 mm. In the work, the main factor of influence on contact angles and the effect of surface preparation on the spreading of the brazing filler was established. In parallel, calculations of the stability of alloys against sigmatization, critical points, composition and content of γ and γ' -phases, carbides, borides, etc. were carried out. The study of the resistance of brazing filler against high-temperature salt corrosion was carried out in a molten salt of 75% Na₂SO₄ + 25% NaCl at a temperature of 900 °C in 24 hours. The developed brazing filler can be used not only for joining heat-resistant alloys, but also for correcting surface defects in castings. The modes of brazing with SBM-4 brazing filler for polycrystalline and single-crystal alloy are given. **Scientific novelty.** The usage of the principle of alloying of alloys of marine gas turbines doped with tantalum and rhenium in the development of brazing filler for alloys of marine turbines is investigated. **Practical significance.** The SBM-4 brazing filler has been developed for brazing high-temperature nickel alloys with both directional solidification and monocrystalline ones. The long-term strength of the welded joints is not inferior to the world level.

Key words: heat-resistant alloys, brazing, wetting, structure, high- temperature corrosion, technological properties of the solders.

Анотація. Мета. Створення припою для паяння жароміцних нікелевих сплавів морських газотурбінних двигунів нового покоління, що дозволить підняти температуру робочого газу на 40...60°C. **Методика.** Для досягнення мети, було використані високотемпературний диференціальний термічний аналіз та тигельний методи дослідження високотемпературної сольової корозії припою. **Результати.** Методом високотемпературного диференціального аналізу досліджувались критичні температури сплавів CM93-BI і CM96-BI. В якості депресантів бралися цирконій, гафній і бор. Після дослідження взаємодії припою з основним металом було вибрано депресант найбільш ефективний депресант бор для подальшого використання, який дозволяє регулювати температуру паяння і плавлення припої шляхом зміни його концентрації. Було виплавлено припої для експериментального дослідження поверхневих властивостей. Для порівняння Припій ВПр36 використовувався для порівняння результатів. В якості оцінювання затікання припоїв у зазори використані клинові зразки, в яких зазор змінювався від 0 до 0,6 мм. В роботі було встановлено основний фактор впливу на крайові кути та вплив підготовки поверхні на розтікання припою. Паралельно проведено розрахунки стійкості сплавів проти сігматизації, критичних точок, складу і вмісту γ і γ' -фаз, карбідів, боридів тощо. Дослідження стійкості припою проти високотемпературної сольової корозії проводили у розплаві солей 75 % Na₂SO₄ + 25 % NaCl при температурі 900 °C протягом 24 годин. Розроблений припій може використовуватись не тільки для з'єднання жароміцних сплавів, а і для виправлення поверхневих дефектів відливок. Наведено режими паяння припоєм SBM-4 для полікристалічного і монокристалічного сплаву. **Наукова новизна.** Досліджено використання принципу легування сплавів морських газових турбін легованих танталом і ренієм при розробці припою для сплавів морських турбін. **Практична значимість.** Розроблено припій SBM-4 для паяння жароміцних нікелевих сплавів як із спрямованої кристалізації так і для монокристалічних. Тривала міцність спаяних з'єднань не поступається світовому рівню.

Ключові слова: жароміцні сплави, паяння, змочування, структура, високотемпературна корозія, технологічні властивості припоїв.

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Problem statement. Heat-resistant nickel alloys (HNA) are the main structural material in current gas turbine construction. Increasing the temperature of the working fluid, raising the resource and efficiency of power plants requires the development of new heat-resistant alloys capable of withstanding the entire range of influencing factors that exist in the real conditions of their operation. Aviation turbines operate on pure aviation kerosene with a low content of harmful impurities, in particular sulfur, and traditionally they have higher gas temperatures in comparison with sea ones. Marine turbine fuel contains sulfur, sodium, etc., while the combustion products contain salts that enter with seawater vapor. Therefore, the blades of offshore gas turbines undergo intense corrosion, the rate of which can be hundreds of times higher than the rate of corrosion in air or in an oxygen atmosphere [1]. This type of corrosion is called high temperature salt corrosion (HSC). HSC is associated with the condensation of alkali metal salts, of which sodium sulfate is the most aggressive. Heat-resistant nickel alloys are complexly alloyed [2, 3]. Alloying elements are divided into several classes according to their purpose. The heat resistance of the alloys is provided by chromium, which forms a dense thermodynamically stable oxide film, but during the combustion of fuel, which contain sulfur and sodium as a result of the interaction of sodium with SO_2 and SO_3 the salt Na_2SO_4 is formed, which destroys the protective oxide film of Cr_2O_3 . Chlorine, which is formed when the NaCl salt interacts with sulfur oxides, contributes to HSC. To ensure the high resistance of marine turbine alloys against HSC, it is necessary to increase the chromium concentration in them, but the long-term high-temperature strength decreases. Since the corrosion rate of alloys of aircraft turbines operating on clean fuel is much lower than marine ones, this allows the concentration of chromium in them to be reduced, which increases their heat resistance, gas temperature and efficiency, using the same strengthening methods (solid-soluble and dispersive). This is the big difference between the high-temperature nickel alloys (materials) of aircraft and marine turbines. Despite the difficult operating conditions of marine gas

turbine engines (GTE), according to the requirements of design documentation for modern power and marine GTEs, it is necessary to ensure their reliable operation at a gas temperature at the turbine inlet up to $1150 \dots 1200^\circ\text{C}$, which will increase their power and efficiency in compressing with previously developed gas turbine engines. For this new alloying systems have already been created [4, 5]. Since brazing is the main way of connecting them and correcting surface defects in castings, the relevance of the development of new solders is beyond doubt. Common features of aviation and marine GTE alloys are the problem of their fusion welding and the widespread use of brazing, in particular, methods of diffusion brazing, brazing with composite brazing fillers, and, if possible, brazing with pressure, which are better known in foreign literature as TLP-bonding (Transient liquid phase bonding) [6-8].

Analysis of recent research and publications. The most heat-loaded parts made of heat-resistant nickel alloys are straightening and rotor blades of aircraft GTEs, which are now made from ZhS32, ZhS36 alloys, etc. [9]. Therefore, their chemical composition, manufacturing technology, heat treatment are constantly being improved [10]. The strategic direction for the development of materials and technologies until 2030 is described in [11], but as noted above, alloys of aircraft turbines cannot be used for marine ones, since aircraft alloys in marine conditions are subject to catastrophic HSC. Therefore, alloys with high resistance to HSC have been developed for parts of marine turbines [4, 5]. In this case, alloying of alloys with tantalum and rhenium was used [4, 5], which is used in alloys of aircraft turbines [10, 11]. At the same time, the usage of rhenium reduces the rate of diffusion processes and increases long-term strength [12]. In works [13-15], the efficiency of using the indicated alloying elements was proved.

Investigation of the brazing of heat-resistant nickel alloys of marine turbines is focused on promising materials for new generation turbines with increased parameters of the working fluid. In new high-temperature nickel alloys of marine turbines a high concentration of chromium is traditionally used to ensure resistance

against HSC, and to increase the high-temperature strength, they are used by regulating the structure, optimizing the chemical composition, alloying with tantalum and rhenium, etc. [4,5]. Considering the results of detailed studies of new alloys, the same alloying complex was chosen in the development of brazing fillers.

When choosing depressants, we took into account the solidus and liquidus temperatures of alloys, brazing temperatures, technological properties of brazing fillers and their effect on resistance to HSC and mechanical properties of joints.

It is known [16, 17] that brazing fillers, depending on the depressants (elements that reduce the melting point of the alloy), are divided into three groups:

1) brazing fillers based on nickel with silicon and boron, which are usually introduced together to reduce the concentration of each of them;

2) brazing fillers based on alloyed nickel with elements of IV and V groups, are introduced as depressants;

3) Palladium-based nickel-based brazing fillers for lower melting and brazing temperatures.

Brazing fillers of the third group were not used because their resistance to HSC has not been studied in the literature, and given the high value of palladium. Depressants from the first and second groups were used in the investigated brazing fillers [16].

Separation of previously unresolved parts of the general problem. The analysis of publications did not reveal the use of marine alloys resistant to HSC alloyed tantalum and rhenium for the development of brazing fillers.

The aim of the study. Creation of a brazing filler for brazing heat-resistant nickel alloys for the manufacture of new generation marine gas turbine engines, which will increase the gas temperature by 40 ... 60°C.

Methods, object and subject of research. The research methods were high-temperature differential thermal analysis and the crucible method for studying the HSC brazing filler.

The object of the study is the formation of a soldered joint of heat-resistant nickel alloys CM93 and CM96.

The subject of research is the structure, chemical composition of the soldered joint and the speed of the HSC brazing filler.

Basic material. At the first stage of the study, the research was carried out by the method of high-temperature differential thermal analysis (HDTA) of the liquidus and solidus temperatures of the base metal CM93 and CM96. Zirconium, hafnium and boron, which are used in VPr36, VPr37 and VPr44 brazing fillers, were chosen as depressants [17-20]. Boron was selected as a depressant based on the results of HDTA and a study of the interaction of brazing fillers with the base metal. It allows, by changing its concentration in the brazing fillers, to regulate the melting and brazing temperature. The results of the HDTA base metal and brazing filler, which contains 1% of the mass. boron is shown in Fig. one.

The melted brazing fillers were investigated experimentally for wetting, gap filling and dissolution of the base metal. For comparison, VPr36 brazing filler was also used in the experiments. To assess the flow of brazing filler into the gaps, samples with a wedge-shaped gap were used, in which the gap varied from 0 to 0.6 or 0.3 mm. Such samples are shown in Fig. 2.

It should be noted that temperature is the main factor influencing the contact angles. Above 1220 °C for the developed SBM-3 brazing filler and 1240 °C for VPr36 brazing filler, the contact angles sharply decrease regardless of the surface preparation method (mechanical or chemical method). Both sol brazing fillers wet the casting surfaces almost equally after mechanical cleaning. When heating the casting to a temperature above 1200°C for 6 min. in a vacuum of $6 \cdot 10^{-3}$ Pa with a leakage of $3 \cdot 10^{-5}$ m²·s⁻¹, the surface becomes light. Under these conditions, even after preliminary oxidation of the sample, its surface is cleaned.

Such studies were carried out at temperatures of 1200, 1220, 1230, 1240, 1250, and 1265°C, depending on the purpose of the brazing filler. The brazing temperature was chosen when the contact angles of wetting did not exceed 10° and flowed into the gaps from 0 to 0.2 ... 0.3 mm.

The microstructure of a brazed based on the CM93-VI heat-resistant nickel alloy is shown in Fig. 3

X-ray spectral analysis of the welded joints shown in Fig. 3 did not detect eutectic phases, pores, cracks, non-solders or non-metallic inclusions.

Fig. 1. Thermograms of alloy CM93-VI (a) and brazing filler, which contains 1.0 % of the mass. in (b): 1 – heating; 2 – cooling

Fig. 2. Appearance the surfaces of the heat-resistant alloy after spreading (a) and flowing of the brazing filler into the gap (b)

Fig. 3. Microstructure of the brazed connection of HNA CM93-VI at assembly with a backlash of 0,1 mm (a) and with a backlash of 0,07-0,08 mm (b)

At the same time, research was carried out on the resistance of brazing fillers against HSC by the crucible method and the calculation of the resistance of alloys against sigmatization,

critical points, composition and content of γ and γ' phases, carbides, borides, etc.

Experimental studies of resistance to HSC were carried out simultaneously for new alloys and brazing fillers in a molten salt of 75% Na₂SO₄ + 25% NaCl. Crucibles with cylindrical samples and salts were loaded into a furnace, then they were kept for a certain time at a temperature of 900 °C. After the tests, the samples were cleaned of salt and scale, the loss of their weigh, the corrosion rate (mg/cm²·h) and the depth of corrosion destruction were determined. The general view of the samples after testing is shown in Fig. 4.

Processing of the test results showed that the rate of HSC brazing filler SBM-4 at 900 °C is in the range of 0.4-3.32 mg/cm²·h, which indicates a high resistance to high temperature corrosion.

Due to its surface properties, SBM-4 solder can be used not only for soldering HNA CM93-VI

and CM96-VI, but also for correcting surface defects.

As a mode of vacuum brazing with SBM-4 brazing filler for alloy CM93-VI indicates the soldering temperature of 1200-1215°C for 15 ± 5 min, and for alloy CM96-VI with a single-crystal or directional structure soldering temperature of 1220-1230 °C for 15 ± 5 min.

Discussion of the results. Based on the research results, SBM-4 brazing filler was developed for brazing high-temperature alloys of marine turbines, including those with directional crystallization and single-crystal ones. The long-term strength of the welded joints with SBM-4 brazing filler at a temperature of 900 °C on the basis of 100 hours is 285 MPa, which is 90% of the strength of the base metal. This indicator is not inferior to the world level.

Conclusions. 1. Heat-resistant alloys of marine gas turbines, unlike aviation ones, operate in an aggressive environment, which leads to high-temperature corrosion, which determines a significant difference in the alloying system of alloys.

2. To ensure the stability of alloys against HSC, alloys of marine gas turbines have a high concentration of chromium, which

Fig. 4. General view of specimens after testing for resistance to HSC

reduces their long-term high-temperature strength. To reduce the chromium concentration with a high stability of HSC and increase the long-term strength, the alloys of marine turbines are alloyed with tantalum and rhenium.

3. Studies have shown that a similar principle of alloying is effective in the development of brazing alloys for high-temperature alloys of marine turbines, which is confirmed by the results of experimental and industrial testing of the SBM-4 brazing alloy developed at NUS.

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