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BRAZING FILLER METAL WITHOUT BORON AND SILICON FOR BRAZING OF HEAT-RESISTANT NICKEL ALLOY

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The use of nickel brazing filler metals, containing boron and silicon as depressants, provides a good wetting of material brazed, allows a significant reduction in brazing temperature, but leads to formation of brittle phases and low-melting eutectics in the brazed welds. This work shows the possibility of forming brazed joints of cast heat-resistant nickel alloy ZhS6U applying brazing in vacuum with use of multicomponent nickel brazing filler metals which do not contain boron and silicon as depressants. Applying the method of high-temperature differential thermal analysis in atmosphere of high-purity helium, the temperatures of liquidus and solidus of brazing filler metals were determined. The results of metallographic and micro-X-ray spectral examinations on studying the features of structure formation of brazed welds are presented. The long-term strength of the brazed joints was evaluated. It is shown that nickel brazing filler metals, containing a large concentration of zirconium, are characterized by a lower melting point, however, in the brazed welds the precipitations of the phase $Ni(Me)_xZr$ are formed. It was determined that decrease in the concentration of zirconium in the nickel brazing filler metal allows avoiding the formation of intermetallic phase enriched in zirconium and obtaining a solid nickel-based solution as the predominant phase in the weld. The results of tests of flat brazed (butt) specimens on long-term strength, carried out at the elevated temperature of 975 °C and the stress of 140 MPa, showed that the joints preserve integrity and do not fracture after 41–60 h of testing. It is shown that zirconium can act as an alternative depressant (instead of mutual adding of boron and zirconium). 13 Ref., 3 Tables, 8 Figures.

Keywords: *vacuum brazing, heat-resistant nickel cast alloy, liquidus temperature, solidus, microstructure, multicomponent brazing filler metal, brazed joint, long-term strength*

Among the numerous heat-resistant materials applied in industry, the greatest attention is drawn to the alloys used for manufacture of parts of the hot tract of gas turbine engines, in particular, turbine blades. At the present time, in the overwhelming majority of cases, these are the high-alloy nickel alloys, in which solid-solution, carbide and intermetallic hardening are realized [1, 2]. During service, the parts of the hot tract of turbines, in the first turn guide and working blades, are subjected to corrosion, erosion and thermal fatigue fracture under the conditions of cyclically changing temperatures, centrifugal loads and the effect of combustion products of the gas turbine fuel. To extend the service life of these expensive parts, the repair technologies are used, for example, brazing [3–7]. In many cases, the brazing is the only possible way of joining.

The dispersion-hardened heat-resistant nickel alloys contain a large amount of alloying elements, respectively, and brazing filler metals, as a rule, also represent the complexly-alloyed systems on nickel base. They contain the components which provide the necessary high-temperature strength, heat resistance, resistance to high-temperature corrosion and oxidation and other characteristics of brazed joints. To decrease the melting point, the brazing filler metals are alloyed with the depressants.

Analysis of systems of existing high-temperature nickel brazing filler metals (Ni–Cr–Si, Ni–Cr–B, Ni–Cr–Si–B, Ni–Mn–Si, Ni–Mn–Cr–Si, Ni–Cr–Pd–Si, etc.) shows that they contain boron, silicon, manganese, palladium, zirconium and gafnium as depressants [5, 8, 9]. Thus, in the system Ni–Cr–Si, the reduction of liquidus temperature is achieved due to silicon, and in the system Ni–Cr–B, the liquidus is significantly influenced by boron. Applying the mentioned brazing filler metals, in the brazed welds the brittle intermetallic compounds and easily-melted eutectic phases, enriched in boron and silicon are formed in addition to the solid solution, which makes it difficult to obtain the high values of heat resistance [8–11]. It is possible to reduce the number of these phases applying a long-term heat treatment, which complicates the technological process of producing permanent joints.

The aim of this work is to create a composition of brazing filler metal for brazing heat-resistant nickel alloys with an acceptable interval of melting, which allows reducing or avoiding the formation of intermetallic phases, easily-melting eutectics and obtaining a chemical composition of the brazed weld close to the base material.

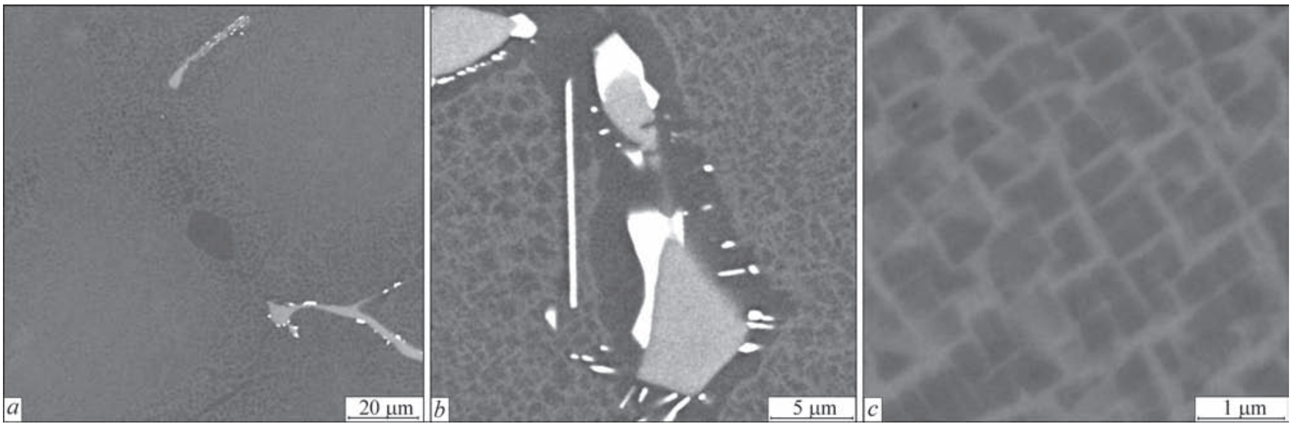

Figure 1. Microstructure of alloy ZhS6U: *a* — general view; *b* — carbide phases; *c* — (γ´ + γ)-structure

By analyzing a number of state diagrams of nickel with elements of IV–V groups of the periodic system, it can be noted that in this case it is impossible to distinguish a definite double base system for developing a brazing filler metal either due to the absence of a high-nickel eutectic with an acceptable melting temperature (the systems Ni–Ti, Ni–Nb), or in view of the extremely low solubility of the depressant element in nickel (the system Ni–Zr, Ni–Hf) [12].

The put task can be solved by applying complex multicomponent alloying, combining such elements as aluminum, zirconium and hafnium as depressants. To achieve a high fraction of solid solution in the brazed weld, it is necessary to minimize the content of elements having a low solubility in nickel.

As a base metal the cast plates of the high-alloyed heat-resistant nickel cast alloy ZhS6U (Ni–(8.0–9.5) Cr–(9.0–10.5)Co–(9.5–11.0)W–(5.1–6.0)Al–(2.0–2.9)Ti–(1.2–2.4)Mo–(0.8–1.2)Nb–1Fe–(0.13–0.02 C) were used. The total amount of elements (Al + Ti), which determine the high heat resistance of the alloy, is 7.1–8.9 wt.%. This alloy is referred to hard-to-weld one due to initiating of hot cracks in the heat-affected zone (HAZ) and weld during crystallization or subsequent heat treatment [9, 13]. The ZhS6U alloy is characterized by a coarse-grained heterophase structure, consisting of γ-solid solution, hardening γ´-phase, which is precipitated in the grain volume, carbide and boride phases (Figure 1, *a*, *b*). The amount of particles of γ´-phase in alloy matrix in the initial state (before service) is about 60 vol.% and is characterized by a cubic morphology (Figure 1, *c*). For investigations, the multicomponent brazing filler metals based on nickel, containing chromium, cobalt, tungsten and other elements, were melted by arc method on a cold substrate in argon. By applying the method of high-temperature differential thermal analysis (DTA) the temperatures of liquidus and solidus, as well as intermediate phase transformations of experimental alloys during heating were determined by using the thermal analyzer VDTA-8M3 in the atmosphere of high-purity helium at the heating rate of 40 °C/min.

Using the produced brazing filler metals, the brazing of specimens (at the liquidus temperature of each brazing filler metal) of the alloy ZhS6U was carried out in vacuum furnace SGV 2.4-2/15-I3 (rarefaction of working space was 1.33–10^{-3} Pa). The heating rate was about 12 °C/min, the holding time at the brazing temperature was 5 min.

The produced brazed specimens were cut perpendicularly to the brazed weld and according to standard procedure the microsections were manufactured. The microstructure of brazed joints and chemical composition of separate phases were investigated using the scanning electron microscope TescanMira 3 LMU, equipped with the energy dispersive spectrometer Oxford Instruments X-max 80 mm^2 (software package of INCA). The distribution of elements and shooting of microstructures were carried out in the back-scattered electrons (BSE), which allow examining the microsections without chemical etching. The micro-X-ray spectral method provides a high locality of examinations (up to 1 μm).

To carry out tests for long-term strength, the butt flat plates were brazed, which were subjected to heat treatment by the mode T = 1220 °C, τ = 4 h in order to homogenize the structure of brazed welds. Further, the special specimens of 80 mm length were cut from the brazed plates for testing on long-term strength at the elevated temperature. The width of test zone in the brazing area was 5 mm at the specimen thickness of

Table 1. Basic systems and intervals of melting brazing filler metals

Alloy number	Basic alloying system	Temperature, °C	
		T_S	T_L
1	Ni–Co–Cr–Ti–Nb–Al–(Me)–2Zr	1101	1231
2	Ni–Co–Cr–Ti–Nb–Al–(Me)–1Zr	1141	1259

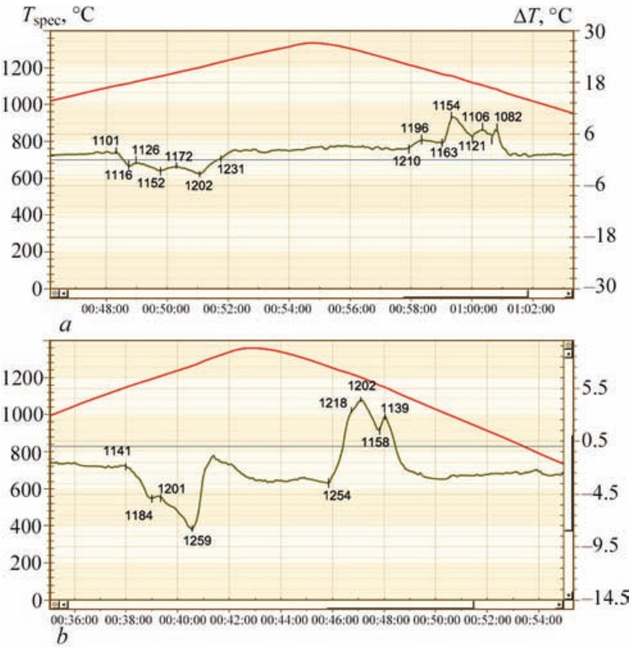

Figure 2. Curves of differential thermal analysis of brazing filler metals; No.1 (*a*) and No.2 (*b*)

4.5 mm. The tests were carried out at the temperature of 975 °C and the constant stress of 140 MPa.

As a result of carried out investigations, two promising brazing filler metals were selected based on the system Ni–Co–Cr–Me (Al, Ti, Nb, Zr) with different zirconium content (Table 1).

The results of high-temperature differential thermal analysis showed that alloy No.1, having an increased concentration of zirconium, is characterized by a wide interval (130 ° C) and a minimum melting temperature (Figure 2, *a*). The thermal effects obtained on the thermal curve indicate the presence of four phases in the initial alloy. The decrease in the concentration of zirconium (in alloy No.2) leads to decrease in a number of phases in the brazing filler metal and to increase in the temperature of solidus and liquidus (Figure 2, *b*). The temperature interval is narrowed to 118 °C.

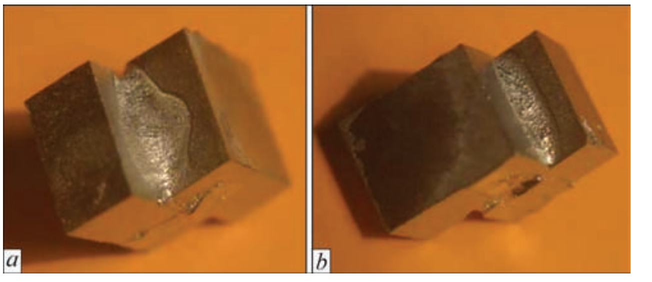

Figure 3. Appearance of overlapped joint, brazed applying brazing filler metal No.1: *a* — straight fillet; *b* — reverse fillet

The visual inspection of brazed joints of the heat-resistant alloy ZhS6U showed that when applying the brazing filler metal No.1 containing 2 % of zirconium, a good spreading and wetting of base metal is observed (Figures 3, *a*, *b*). The formation of complete fillet areas is provided, the defects on the specimens are absent, which confirms the results of further metallographic examinations (Figure 4).

The local micro-X-ray spectral analysis determined that brazed weld is characterized by a multiphase structure. The weld matrix is represented by grains of a solid solution based on nickel with a variable concentration of constituent elements, which is explained by liquation processes during crystallization. Along the grain boundaries of solid solution the separate single particles of a light phase based on tungsten (carbides), a nickel-based phase enriched in zirconium (21.78 %), a boundary eutectic γ´-phase on the basis of nickel with an increased concentration of aluminum and a nickel-based phase enriched in molybdenum, niobium and tungsten (Figure 5, *a*, *b*, Table 2) are observed.

In accordance with the state diagram of the binary system Ni–Zr, it can be assumed that the phase, enriched in zirconium, refers to intermetallic compound Ni_5Zr [12]. Due to the fact that the nickel brazing filler metal is multicomponent, it is most probable, that a complex intermetalic compound $Ni(Me)_xZr$ is formed in the brazed weld. It should be noted, that the volume fraction of this phase is insignificant.

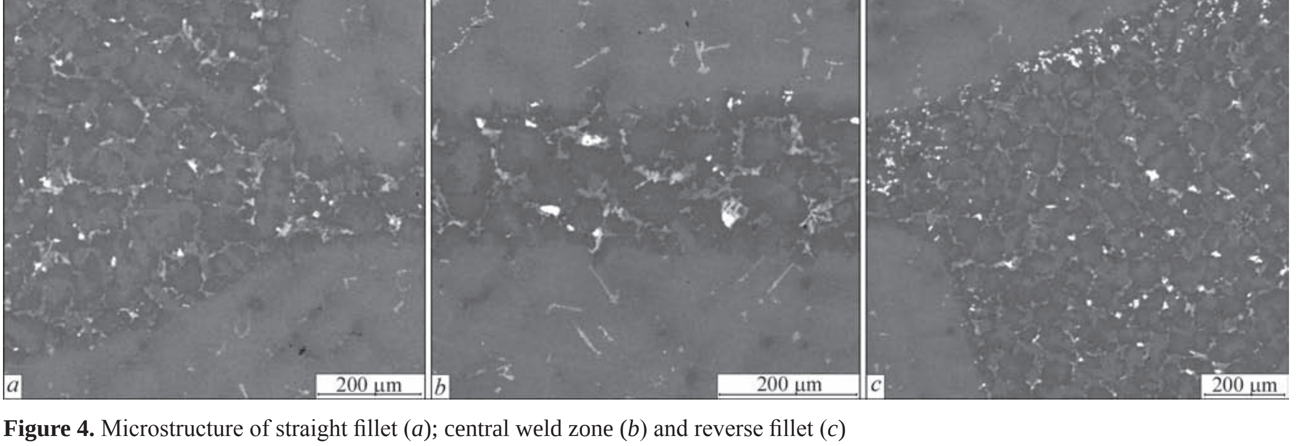

Figure 4. Microstructure of straight fillet (*a*); central weld zone (*b*) and reverse fillet (*c*)

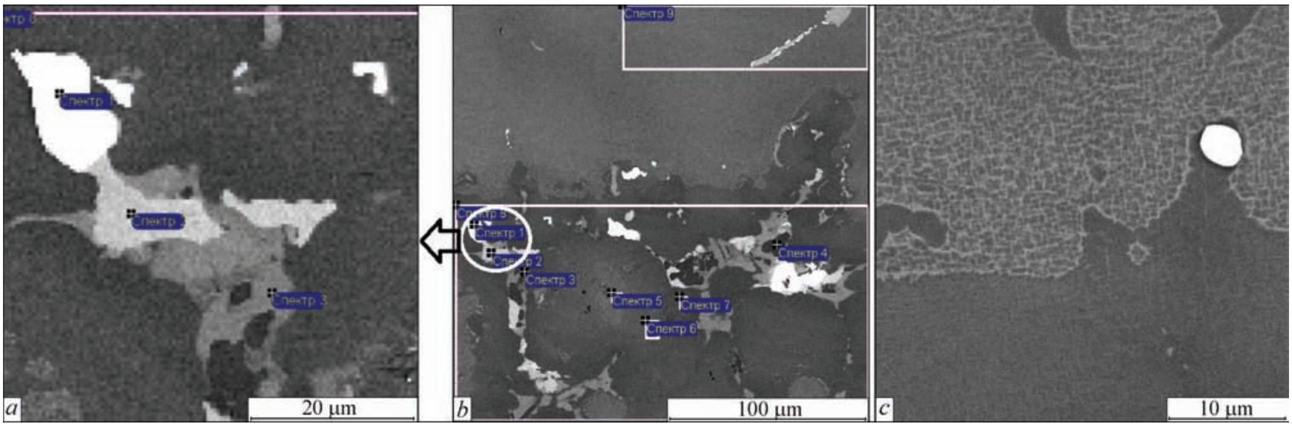

Figure 5. Microstructure of investigat of phases (*a*, *b*) and grain of (γ + γ´)-structure in weld of joint of alloy ZhS6U, brazing filler metal No.1

The dark precipitations of a nickel-based phase with an increased aluminum concentration (12.44 %) correspond to the boundary phase Ni_3 (Al, Ti, Zr, Nb), in which the aluminum atoms are replaced by γ´-forming elements. The investigations of a fine structure of the brazed weld (at a high resolution) showed the presence of γ´-hardening phase in a solid solution based on nickel, which is characterized by a cuboidal morphology and provides a heat resistance to the brazed weld (Figure 5, *c*).

In the fillet area the same structural components were revealed as in the brazed weld. The difference is that the phase enriched in tungsten is precipitated mainly along the brazing filler metal — base metal interface (Figure 4, *a*, *c*).

The reduced concentration of zirconium to 1 % in brazing filler metal No.2 allows avoiding the formation of a zirconium intermetallic compound in the brazed weld and in the fillet area. The formation of a dense, defect-free brazed weld with a thickness of about 100 μm and complete fillet areas is observed (Figure 6, *a*, *b*, *c*).

The structure of a brazed weld is similar to the structure of a fillet area (Figure 6, *b*, *c*). The matrix of a brazed weld is represented by a solid solution based on nickel with a variable concentration of constituent elements by the grain (Table 3).

The areas of (γ + γ´)-structure in weld metal are also observed (Figure 6, *d*). The formation of dispersed carbide phases based on tungsten is typical for both systems of the applied brazing filler metals. The elevated

Table 2. Concentration of elements in brazed joint using brazing filler metal No.1, wt.%

Number of spectrum	Al	Ti	Cr	Co	Ni	Zr	Nb	Mo	W
1	0.25	0.19	2.52	0.36	3.23	0.00	0.00	8.32	85.14
2	0.70	1.52	19.24	12.90	17.02	0.00	10.84	10.52	27.26
3	2.03	1.50	3.95	10.12	48.37	21.78	10.14	0.00	2.11
4	12.44	7.63	8.18	10.88	53.81	1.43	4.05	0.46	1.13
5	5.45	4.58	7.60	10.49	58.43	0.00	1.38	1.56	10.52
6	6.12	6.09	4.39	9.01	64.65	0.00	1.52	1.32	6.91
7	6.64	7.31	3.76	9.42	65.68	0.00	2.62	0.48	4.08
8	4.96	6.45	7.42	9.55	55.56	0.71	3.72	1.39	10.25
9	5.08	3.09	8.51	9.44	56.11	0.00	1.77	1.94	14.06

Table 3. Content of chemical elements in brazed weld of joint of alloy ZhS6U, produced using brazing filler metal No.2

Number of spectrum	Al	Ti	Cr	Fe	Co	Ni	Nb	Mo	W
1	0.19	0.19	3.41	0.00	0.64	3.08	0.00	13.57	78.92
2	0.98	1.31	17.88	0.20	12.95	18.02	14.36	11.68	22.62
3	14.04	5.18	8.82	0.00	9.96	56.62	3.07	0.61	1.70
4	7.16	4.89	3.73	0.00	8.23	67.23	2.57	1.38	4.81
5	7.21	4.99	7.97	0.34	9.57	56.72	5.74	1.80	5.65
6	5.33	3.75	11.04	0.00	10.50	54.70	3.75	2.90	8.03
7	5.49	3.42	8.92	0.19	9.51	58.45	2.46	1.51	10.06
8	5.43	2.27	9.57	0.16	10.41	58.93	0.00	1.30	11.93

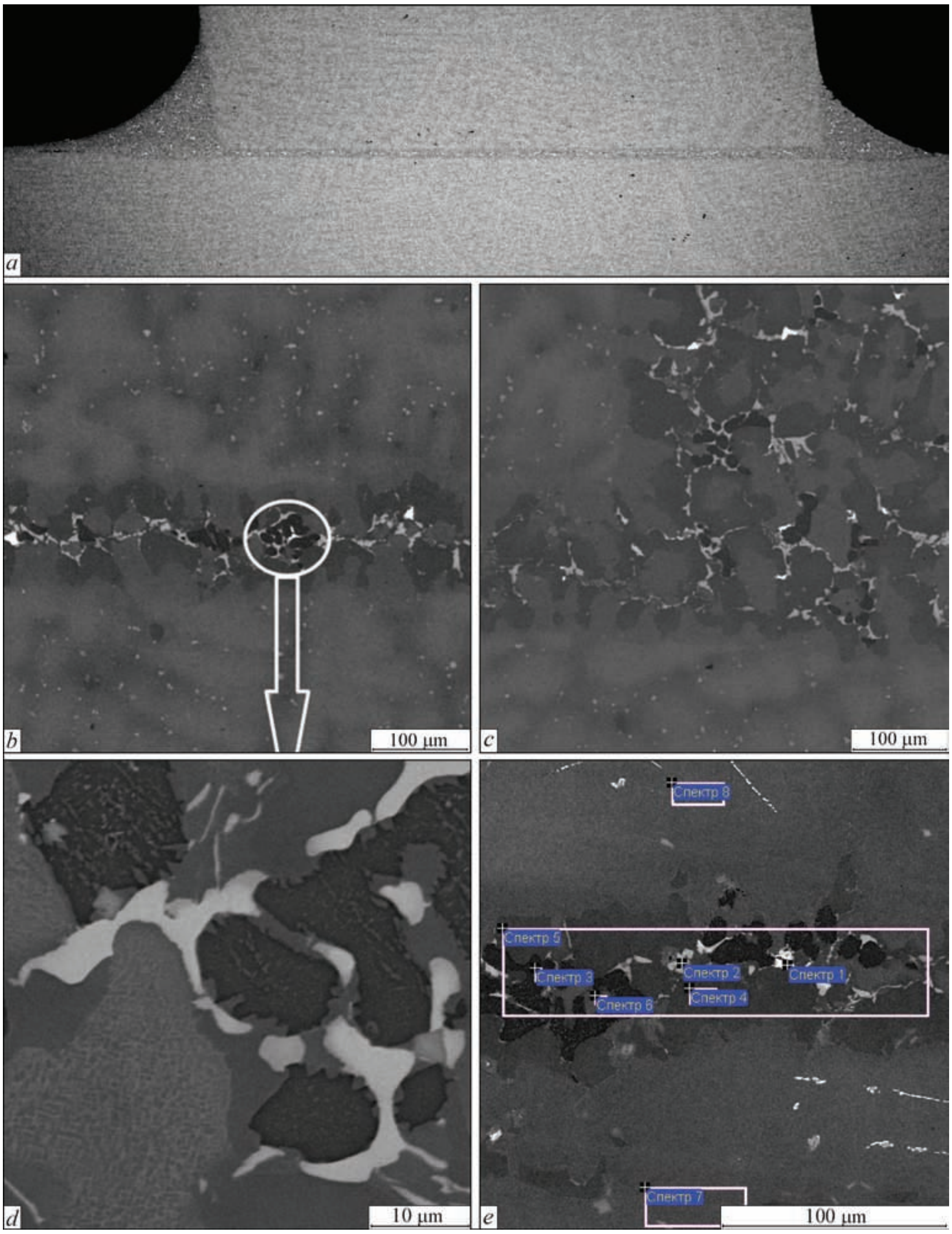

Figure 6. Microstructure of brazed T-joint produced using brazing filler metal No.2: *a* — general view; *b* — brazed weld; *c* — fillet area; *d* — phase in the interdendritic region; *e* — investigated phases in the brazed weld

temperature of brazing by the given filler metal promotes a partial dissolution of these phases in a solid solution, which leads to decrease in their number.

Figure 7. Appearance of flat butt specimens for tests on long-term strength

In the interdendritic regions of the brazed weld, a dark phase is observed, representing the boundary phase Ni_3 (Al, Ti, Zr, Nb), as in the previous case (Figure 6, *e*, spectrum 3, Table 3). In addition, a complex phase is formed on the base of system Ni–Nb, enriched in chromium, cobalt, molybdenum, tungsten (Figure 6, *e*, Table 3).

The obtained results of micro-X-ray spectral examinations showed that by applying the brazing filler metal No.2 the brazed welds contain a minimum amount of carbide phases, which positively affects the results of mechanical tests.

The butt brazed specimens (Figure 7), produced by applying brazing filler metal No.1, were characterized by minimal values of long-term strength and were fractured after 18–19 h at the test temperature $T = 975$ °C and the stress of 140 MPa (Figure 8). The specimens produced by applying brazing filler metal No.2 showed the better results: they preserved structural integrity and did not fracture after 41–60 h of tests (Figure 8). Based on the results of structural investigations and mechanical tests, a correlation between the microstructure of welds and the level of long-term strength of brazed joints is observed.

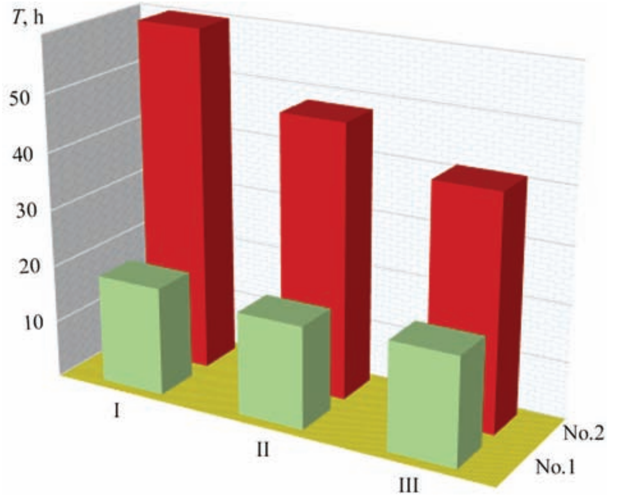

Figure 8. Results of tests on long-term strength of brazed joints produced using brazing filler metals No.1 and No.2 (I–III — test specimens)

Conclusions

The carried out micro-X-ray spectral examinations of brazed joints of ZhS6U alloy produced applying a brazing in vacuum using multicomponent nickel brazing filler metals, not containing boron and silicon, showed the formation of quality, defect-free welds with predominance of a significant volume fraction of a solid nickel-based solution in the brazed weld.

It was found that the decrease in concentration of zirconium in nickel brazing filler metal (up to 1 %) provides a significant increase in the long-term strength of brazed joints at elevated temperature. Thus, at the test temperature of 975 °C and stress of 140 MPa, the specimens preserved structural integrity and did not fracture after 41, 48 and 60 h of testing.

Thus, the application of brazing filler metal with a minimum amount of zirconium provided 2–3 times increase in the duration of tests without fracture of brazed joints.

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