BRAZING FILLER METALS OF Ti–Zr–(Fe, Mn, Co) SYSTEM FOR BRAZING OF TITANIUM ALLOYS

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Titanium alloys are perspective materials for different branches of industry. Appearance of new high-strength materials, in particular intermetallic alloys, provides for increasing interest to processes of their joining by brazing methods. Meanwhile, the most wide spread brazing filler metals (Ti–Cu–Ni and Ti–Zr–Cu–Ni systems) developed decades ago do not always correspond to current requirements, as, for example, in brazing of intermetallic alloys. Present work provides the results of complex investigations of brazing filler metals of Ti–Zr–Fe, Ti–Zr–Mn and Ti–Zr–Co systems using differential thermal analysis, light and scanning microscopy, X-ray microspectrum analysis. Data on melting ranges of pilot alloys were obtained, and liquidus surfaces of given systems using simplex-lattice method were build. Brazing filler metals covering brazing temperature range of current structural titanium materials based on solid solutions as well as intermetallics were proposed. Structure, chemical inhomogeniety and strength characteristics of brazed joints were studied. It is determined that brazing of solid solution based alloys (OT4, VT6) using indicated brazing filler metals ensures strength characteristics of joints, which are not inferior to that obtained with application of known brazing filler metals. Proposed brazing filler metals provide strength on the level of base metal at room and elevated temperature as well as in creep-rupture testing during brazing of γ-TiAl intermetallic based alloy. 13 Ref., 4 Tables, 8 Figures.

Keywords: *vacuum brazing, titanium alloys, intermetallic alloys, brazing filler metals, brazed joints, structure, strength of brazed joints*

Area of application of welded structures from titanium and its alloys constantly expands with rise of volume of its manufacture and cost reduction. It is of course promoted by favorable combination of mechanical and special properties of titanium, among which, first of all, are its low specific weight, high strength and corrosion resistance. Undoubtedly, welding takes the leading role in development of titanium structures. However, in number of cases technological processes of brazing are more appropriate and, sometimes, being the single possible, in particular, during production of multilayer thin-wall structures. Appearance of new intermetallics based high-strength titanium alloys also increases probability of application of brazing technology. This explains constant attention of high range of specialists to development of brazing filler metals (BFMs) for brazing of titanium alloys and methods of their manufacture in appropriate for application form.

It should be noted that BFMs of Ti–Cu–Ni, Ti–Zr–Cu–Ni, Zr–Ti–Ni and Cu–Zr–Ti systems in a form of plastic foils, obtained by method of ultraspeed quenching or traditional methods of metallurgical redistribution with pressure (rolling) treatment and vapor phase deposition, as well as in powder form [1–5] are mainly used in world practice for brazing of titanium alloys.

However, development of new alloy systems is continued. It is related with the tasks of reduction of brazing temperature for wrought titanium alloys, as well as expansion of area of BFM application (for example, in medicine, in brazing of intermetallic alloys etc.). It should be noted that reduction of temperature of brazing of wrought titanium alloys by BFMs of existing systems decreases, as a rule, strength characteristics of the brazed joints.

Present work proposes the braze compositions selected on the basis of complex investigation of Ti–Zr–(Fe, Mn, Co) system alloys, which can be used for brazing of wrought and intermetallic titanium alloys providing temperature-time parameters of technological process of vacuum brazing and preserving microstructure and mechanical properties of initial material to be brazed, as well as eliminating formation of brittle intemetallic phases in metal of the seams.

Studies of Ti–Zr–Fe, Ti–Zr–Mn, Ti–Zr–Co system alloys [6–8] were carried out at the E.O. Paton Electric Welding Institute as an alternative to existing ones. Constitutional diagrams of Ti–Fe, Ti–Mn and Ti–Co systems are similar. Eutectics with high content of titanium and wide area of solid solution based on titanium and eutectoid are present in high-titanium area of these

Table 1. Temperature of eutectic melting and eutectoid transformation of alloys of the various systems [9]

Temperature, °C	Ti–Mn	Zr–Mn	Ti–Fe	Zr–Fe	Ti–Co	Zr–Co
Eutectic melting	1180	1090	1085	928	1020	981
Eutectoid transformation	550	790	595	730	685	834

alloys. Ti–Mn system has the highest temperature of eutectic melting, Ti–Fe system displays significantly lower and Ti–Co has the smallest one (Table 1).

Typical characteristics described above are preserved in the alloys of Zr–Fe, Zr–Mn and Zr–Co binary systems [9]. At the same time, areas of solid solutions are narrower, and eutectoid transformation takes place at higher temperatures. Melting temperatures of eutectics follow the tendency of indicated titanium-based alloys except for Zr–Co system (see Table 1).

It can be assumed based on study of binary systems that ternary eutectics with temperature suitable for brazing of titanium wrought pseudo-α and (α + β)-alloys (not more than 935 °C) and intermetallic alloys (above 1150 °C) are present in three-component systems. It was necessary to build liquidus surfaces of these three-component systems in order to verify this hypothesis. Combination of calculation and experimental methods, in particular, method of simplex-lattice planning of experiment [10, 11], was used for realization of this task. This method is developed for reduction of number of physical experiments, decrease of time consumption as well as costs. Field of application of present method is sufficiently wide and can be used for building of «composition-property» diagrams, liquidus surfaces

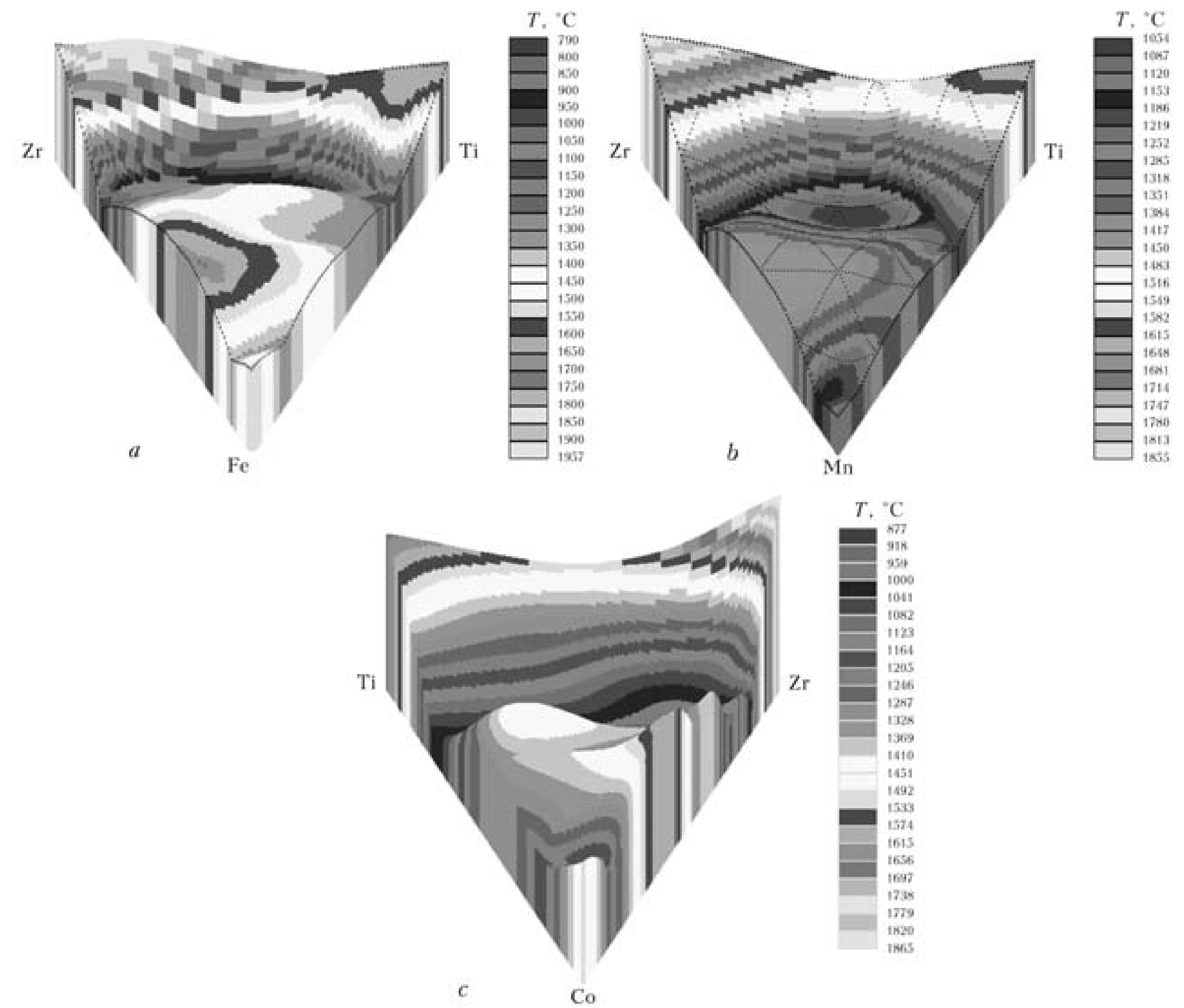

Figure 1. Liquidus surface of alloys of Ti–Zr–Fe (*a*), Ti–Zr–Mn (*b*) and Ti–Zr–Co (*c*) systems

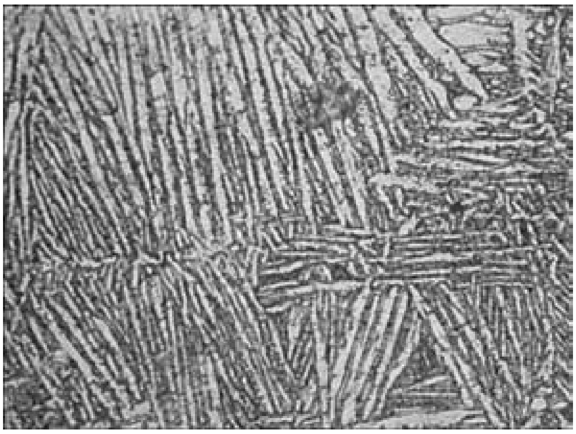

Figure 2. Microstructure (×500, light microscope) of central area of seam of brazed joint (OT4 base metal, Ti-Zr–Co BFM)

and surfaces of phase transformations in multicomponent systems etc.

From 33 to 57 alloys of each system were manufactured and their melting ranges were determined for obtaining of necessary calculation data. Results of calculations in graphical form are represented in Figure 1.

Analysis of obtained results shows that specific part of each from the three alloy systems, containing monovariant eutectics with decreased melting temperature, is the most suitable for application as BFMs in brazing of titanium and its alloys. As expected alloys of Ti–Zr–Mn system were the most refractory, and Ti-Zr–Co system had the lowest melting temperature. One BFM from each system was selected for investigation of their technological properties and strength of brazed joints in order to compare with known BFMs. BFMs of Ti–Zr–Fe and Ti–Zr–Co systems were used for brazing of structural titanium alloys (together with industrial BFM of Ti–Zr–Cu–Ni system) and Ti–Zr–Mn and Ti–Zr–Fe systems — for alloys on the basis of γ-TiAl compound.

Brazing of specimens was performed in vacuum ($7\cdot10^{-3}$ Pa) with the help of radiation heating. Temperature of brazing of wrought titanium alloys OT4 (Ti–4Al–1Mn) and VT6 (Ti–6Al–4V) using BFMs of Ti–Zr–Co and Ti-Zr-Fe systems equaled 920 and 990 °C, respectively. Brazing time made 15 min. Intermetallic titanium alloy (Ti–45Al–2Nb–2Mn + 0.8 vol.% TiB_2) was brazed at temperature close to heat treatment temperature of 1250 °C with 60 min holding.

Results of performed experiments determined that BFMs in cast form spread well over the surface of titanium alloys and form smooth full fillets.

Metallographic investigations of the brazed specimens verify that external welds, which were brazed using selected industrial and experimental BFMs, have no significant differences. Seam in some distance from the fillet represents itself common intergrown grains of the base metal. Sometimes these areas are impossible to be distinguished from the base metal and joint zone can be determined only through investigation of chemical inhomogeniety (Figure 2).

Distribution of elements in the seam metal reflects significant leveling of concentrations

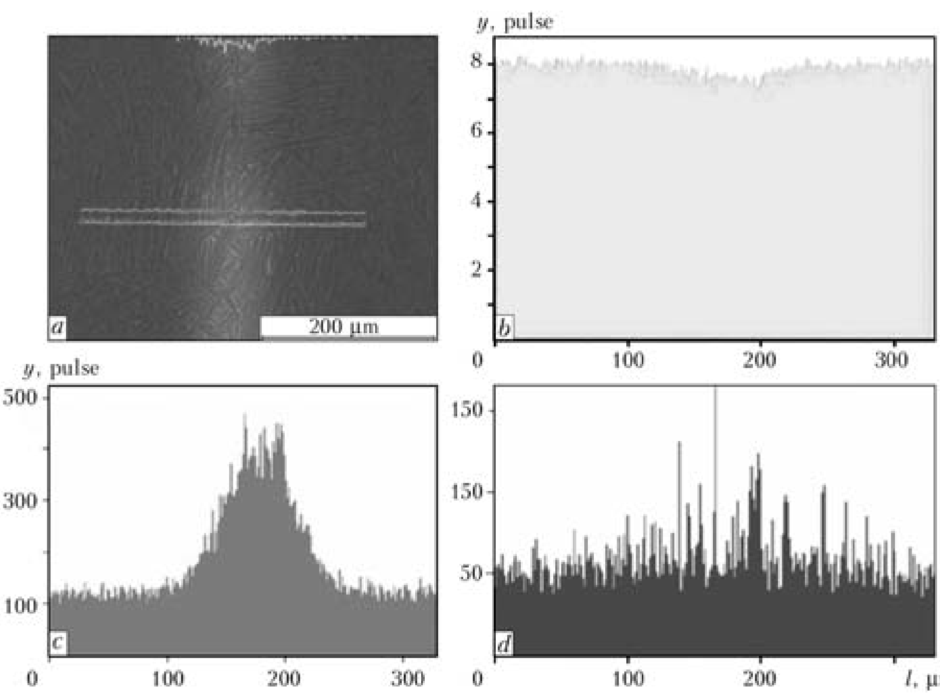

Figure 3. Microstructure of seam metal (*a*), and quantitative distribution of titanium (*b*), zirconium (*c*) and cobalt (*d*) over the width of brazed joint along scanning line (OT4 base metal, Ti–Zr–Co BFM)

Table 2. Chemical composition of brazed joint (OT4 base metal, Ti–Zr–Co BFM), wt.%

Number of spectrum	Al	Ti	Mn	Co	Zr
1	3.91	94.89	1.20	–	–
2	0.90	36.49	–	10.45	52.15
3	1	41.20	–	3.36	54.44
4	1.10	44.04	–	1.06	53.80
5	0.34	39.16	–	4.28	56.22
6	0.99	41.60	–	1.98	55.42
7	0.31	20	–	9.57	70.13
8	3.98	94.94	1.08	–	–
9	4.10	94.19	0.71	1	–
10	4.24	90.35	0.36	1.68	3.37
11	1.78	65.86	0.51	6.43	25.42
12	0.77	45.65	–	4.10	49.49
13	0.77	42.01	–	1.70	55.53
14	4.10	92.77	0.32	–	2.82
15	3.87	88.57	0.27	–	7.29
16	3.19	92.94	2.18	1.70	–

even at short indicated holding. At that weight fraction of titanium and iron does not change in the seam cross section, whereas zirconium weight fraction is somewhat increased in the seam center. This can be explained by formation of zirconium solid solution in titanium (Figure 3).

Results of X-ray microspectrum analysis of metal of seam and fillet area are represented in Table 2 and Figure 4 in more details.

First of all, it should be noted that composition of the base metal, determined for selected area, completely corresponds to the requirements of standard for OT4 alloy (Table 2, spectra 1 and 8).

Measurement results obtained in cross section of the seam in some distance from the fillet (Table 2, spectra 14 and 15) are close to these values, i.e. chemical composition of the seam is close to composition of metal being brazed even with that holding at brazing temperature. Concentration of titanium and aluminum are virtually corresponds with the same for brazed metal (see Figure 4, Table 2).

Data of chemical composition of the fillet metal (Table 2, spectra 2–7), regardless some differences, show general tendencies, namely significant reduction of titanium and aluminum content, high content of zirconium and alternating content of cobalt (1.60–9.57 %) in comparison with metal of the seam. At that spectrum 7 differs from the rest by particularly low content of ti-

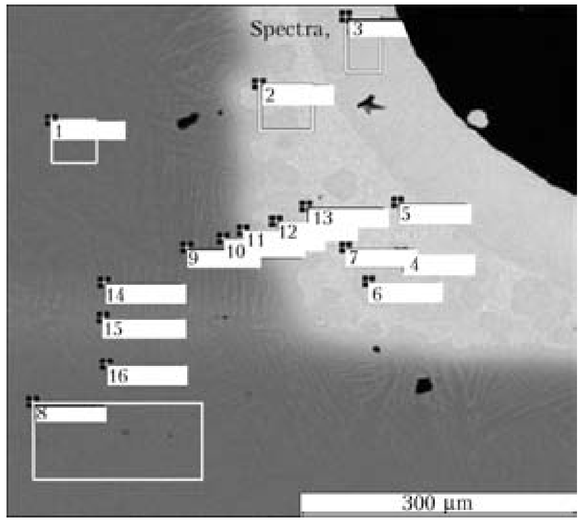

Figure 4. Microstructure and areas of X-ray microspectrum analysis of brazed joint (OT4 base metal, Ti–Zr–Co BFM)

tanium and high content of zirconium. This can be explained by the fact that the fillet has double-phase structure, and result depends on that what phases were in probe zone. It can be added that the base metal adjacent to the seam has typical plate structure consisting of two phases.

Mentioned above is confirmed by investigations of distribution of elements in base metal to fillet interface (see Table 2, spectra 9–12). Chemical composition in specified area (spectrum 11) is close to composition of the base metal, further clear appearance of tendency mentioned above is observed, i.e. reduction of titanium and aluminum content and increase of that for zirconium. Spectrum 13 corresponds to the fillet composition in full.

Distribution of elements in the seam metal has no principal differences from considered above, except for iron, concentration of which smoothly increases in the central seam area when using BFM of Ti–Zr–Fe system.

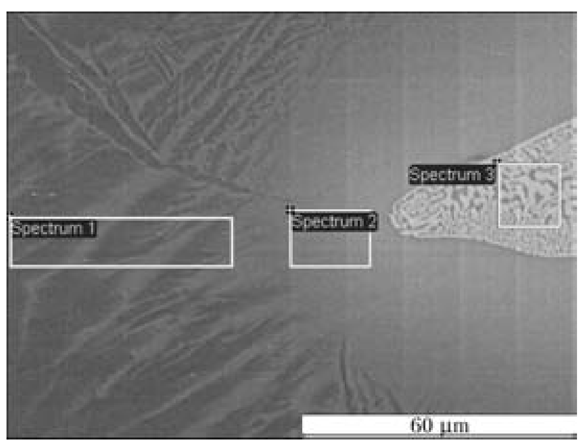

Figure 5. Microstructure and near-fillet areas of X-ray microspectrum analysis of brazed joint (OT4 base metal, Ti–Zr–Fe BFM)

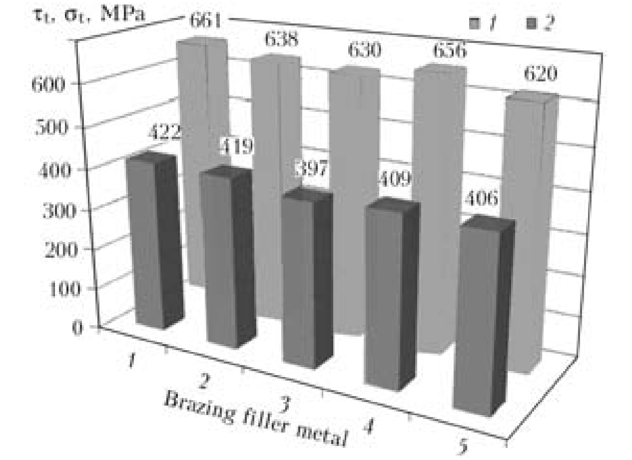

Figure 6. Tensile strength of brazed butt σ_t (*1*) and lap τ_t (*2*) specimens (base metal OT4) obtained using BFMs on the basis of systems: *1* — Ti–Zr–Co; *2* — Ti–Zr–Cu–Ni; *3* — Ti–Zr–Cu–Ni; *4* — Ti–Zr–Fe; *5* — Ti–Zr–Fe

Base metal adjacent to the fillet has double-phase structure (Figure 5), its chemical composition is close to initial composition of OT4 alloy and includes insignificant quantity of chemical elements of the BFM (Table 3, spectrum 1).

Significant reduction of content of titanium, aluminum, manganese and substantial increase of iron and zirconium are observed in the interface (see Table 3, spectrum 2). This tendency is less apparent in the fillet area (Table 3, spectrum 3).

It can be concluded considering mentioned above that 15 min holding is enough for formation in the seam of alloy close to metal being brazed during brazing using both BFMs. At that eutectic structure is preserved in the fillet.

Series of butt and lap specimens from titanium alloys OT4 and VT6 was manufactured using standard and investigated BFMs (Table 4) in order to get an idea about strength characteristics of brazed titanium alloys.

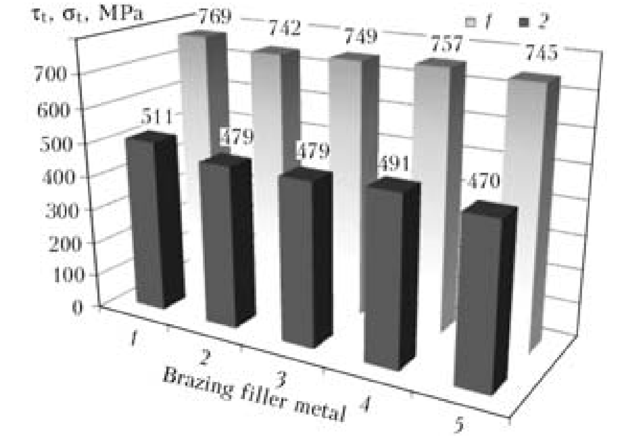

Figure 7. Tensile strength of brazed butt σ_t (*1*) and lap τ_t (*2*) specimens (base metal VT6) obtained using BFMs on the basis of systems: *1* — Ti–Zr–Co; *2* — Ti–Zr–Cu–Ni; *3* — Ti–Zr–Cu–Ni; *4* — Ti–Zr–Fe; *5* — Ti–Zr–Fe

Table 3. Chemical composition of brazed joint (OT4 base metal, Ti–Zr–Fe BFM), wt.%

Number of spectrum	Al	Ti	Mn	Fe	Zr
1	2.93	89.95	0.89	3.57	2.67
2	1.70	76.57	0.41	10.73	10.59
3	0.58	48	0.41	21.67	29.34

Table 4. BFMs and brazing modes of wrought titanium alloys OT4 and VT6

BFM system	Initial state of BFM	Brazing temperature, °C
Ti–Zr–Co	Cast	920
Ti–Zr–Cu–Ni	Amorphous strip	1000
Ti–Zr–Cu–Ni	Cast	1000
Ti–Zr–Fe	Cast	990
Ti–Zr–Fe	Amorphocrystalline strip	990

Analysis of results of mechanical test showed that proposed alloy systems provide for mechanical properties of the brazed joints at the level of that obtained during brazing using known BFM of Ti–Zr–Cu–Ni system. This is achieved at significantly lower brazing temperature applying BFM of Ti–Zr–Co system. Figures 6 and 7 show the results of tests (average of three measurements).

Application of BFM of Ti–Zr–Fe system in brazing of intemetallic alloy Ti–45Al–2Nb–2Mn + 0.8 vol.% TiB_2 provides formation of the seams of alternating width with two-phase structure (γ-TiAl and Ti_3Al) containing no eutectic constituent (Figure 8).

Width of the seams and their chemical composition are determined by capillary peculiarities of the BFM and diffusion processes taking place at liquid BFM–solid substrate interface in brazing. Formation of the seam with plate (lamellar)

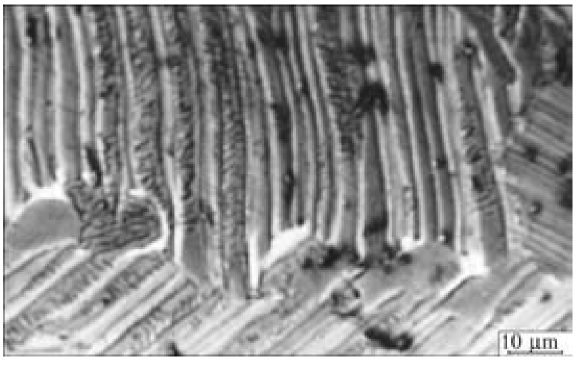

Figure 8. Microstructure of brazed joint of titanium aluminide obtained using BFM of Ti–Zr–Fe system with cast structure

structure close to the base metal structure [12] is observed. Chemical composition in these areas is virtually similar to the base metal. The latter preserves lamellar structure after brazing.

Results of the investigations obtained with the help of electron scanning microscopy and X-ray spectrum microanalysis show that chemical composition and structure of the seam metal significantly differ from such for initial BFM. This is caused by gradient of concentration of constituent elements of BFM and base material at the phase interface, capillary (0.05 mm) gaps and non-equilibrium conditions of solidification. Diffusion processes taking place at the phase interface of solid material with liquid BFM, in particular, result in leveling of aluminum concentration in the base material and seam metal and formation of phases with aluminum concentration corresponding to such for the base material.

Similar formation of the seams takes place in brazing using BFM of Ti–Zr–Mn system. There are areas where seam metal has plate (lamellar) structure close to structure of the base metal. Intergrown grains of the base material are observed in some areas, and chemical composition of the metal at the joint interface is virtually identical to the base metal.

Results of strength tests carried out at room temperature using butt specimens showed that alloys based on Ti–Zr–Fe and Ti–Zr–Mn systems provide for brazed joints of 650–700 MPa tensile strength, and this strength is at the level of short-term strength of material being brazed. Strength of the brazed joints makes around 300 MPa at 700 °C testing temperature.

Results of creep-rupture tests conforming working capacity of the joints under conditions of maximum approximation to service ones [13] are an important factor of high-temperature strength of the brazed joints. Brazed specimens did not failure in a course of 500 h during creep-rupture tests at temperature 700 °C and 140 MPa stress. Increase of stress up to 200 MPa did not cause specimen failure.

It should be noted based on test results that strength of the brazed joints obtained using BFM of Ti–Zr–Cu–Ni system is 12–18 % lower than at application of BFMs of Ti–Zr–Fe and Ti–Zr–Mn system.

Thus, BFMs, developed on the basis of performed investigations, allowed obtaining brazed joints of intemetallic alloy γ-TiAl close on structure and properties to the base metal. Received results can be a foundation for development of new critical structures of different designation from new perspective titanium materials based on intermetallics using BFMs considered above. Developed BFMs contain no copper or nickel and can be used for the parts of technical as well as medical designation.

Conclusions

1. Brazing filler metals covering temperature range of brazing of modern structural titanium materials based on solid solutions, as well as intermetallics, were proposed as a result of complex investigations of alloys of Ti–Zr–Fe, Ti–Zr–Mn and Ti–Zr–Co systems.

2. Brazing of alloys based on solid solutions using indicated BFMs showed the strength characteristics at the level of that obtained using known BFMs, even if they are received at lower brazing temperature.

3. Results of mechanical tests of the brazed joints from γ-TiAl intermetallic based alloy showed that proposed BFMs provide full-strength of the base material at room and elevated temperature, as well as at creep-rupture tests.

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