Microstructure formation and mechanical properties of isothermally-solidified titanium alloy joints brazed by a Ti – Zr – Cu – Ni – Be amorphous alloy foil*

P. V. Morokhov, Engineer Department No. 9 "Physical Problems of Materials Science"¹, e-mail: morokhov@mail.ru

A. A. Ivannikov, Senior Lecturer, Department No. 9 "Physical Problems of Materials Science"¹, e-mail: ivannikov7@rambler.ru

N. S. Popov, Masters Student, Department No. 9 "Physical Problems of Materials Science"¹, e-mail: NSPopov@mephi.ru

O. N. Sevrjukov, Associate Professor Department No. 9 "Physical Problems of Materials Science"¹, e-mail: Sevr54@mail.ru

¹National Research Nuclear University "MEPhI", Moscow, Russia.

Two titanium alloys, OT4 and VT6-c, with a pseudo- α and $\alpha + \beta$ structure, respectively, were brazed using transient liquid phase (TLP) bonding. To obtain high strength joints an amorphous foil (Ti – 12Zr – 22Cu – 12Ni – 1.5 Be – 0.8V wt. %) was used.

Based on microstructural studies and analysis of two- and three-component phase diagrams, the mechanism of the microstructural evolution of the brazed seams of titanium alloys OT4 and VT6-c is described. Brazing at 800 °C with exposure for 0.5 h leads to the formation of a heterogeneous structure consisting of Widmanstätten, eutectoid, and eutectic. Brazed OT4 and VT6-c joints with the presence of a eutectic layer in the centre show low mechanical properties; their ultimate strength lies in a range from 200 to 550 MPa. Increasing the brazing temperature to 840 °C and the exposure time to 2 h, leads to the disappearance of the brittle eutectic component from the seam. This structure typically consists of Widmanstätten with a small number of eutectoid fractions. Joints with the absence of a eutectic layer in the brazed seam demonstrate a strength equal to the base titanium alloys. In this case, failure occurs in the base metal. For brazed samples from the OT4 alloy, the tensile strength value is $\sigma_b = 750 \pm 3$ MPa, and for samples from VT6-c, $\sigma_b = 905 \pm 3$ MPa.

Key words: titanium, TLP bonding, diffusion brazing, microstructure, tensile strength, amorphous alloy, micro-hardness.

DOI: 10.17580/nfm.2020.02.08

Introduction

Creating complex geometric structures from titanium alloys for heavily loaded equipment uses welding and brazing technologies. Welding cannot be applied to create thin-walled structures, especially in the case of joining titanium with other materials. High-temperature diffusion brazing (TLP bonding) is much more desirable because of some unique features [1–2]. This technology has numerous advantages. Firstly, the formation of the brazed joint occurs at a temperature below the melting temperature of the base material (or temperature of phase transformation). Secondly, brazing allows you to choose the temperature to maintain the properties of the brazed materials to a high level. Besides that, an accurate selection of brazing filler metals provides thermal stability and high-temperature mechanical properties at the level of the base material.

Brazing alloys based on Ag – Cu – Sn – Mn, Ag – Cu – Ti, Al – Si, and Al – Mg systems are widely used for brazing titanium and its alloys. However, the joints obtained using these systems display low mechanical characteristics at high temperatures [2–3]. Titanium and zirconium-based filler metals demonstrate the capability of creating

high-strength and heat-resistant joints between two similar titanium alloys, or between titanium alloys and other metals [4–11]. Application of existing Ti – Zr – Ni – Cu and Zr – Ti – Ni filler metals [12–13], usually with Be additives, causes the formation of brittle intermetallics (Ti,Zr)₂Cu, (Ti,Zr)₂Ni, and (Ti,Zr)Be₂ in the brazed joint [14–15]. It is possible to avoid the formation of brittle phases by ensuring the diffusion of undesirable depressant elements (Cu, Ni, Be) from the seam zone into the base material. Therefore, the use of diffusion brazing, under certain conditions, allows you to get homogeneous plastic structures based on solid solutions in the brazed joint [16–17].

For diffusion brazing of $\alpha + \beta$ titanium alloys, it is recommended to use temperatures below the polymorphic transformation point, which lie in the range of 950–1000 °C [4]. Exceeding the polymorphic transformation temperature leads to grain growth and a significant reduction of the mechanical properties [18–19].

Wrought titanium alloys OT4 and VT6-c (TC4 analogue) are widely used in the aviation industry. The OT4 alloy is classified by its structure as a pseudo- α alloy. Details of a complex configuration, which work for a long time at a temperature of 300–350 °C, and for a short time at a temperature of 500–600 °C, can be easily manufactured from OT4 alloy. VT6-c alloy is classified by structure as $\alpha + \beta$, and it can be applied for manufacturing of large-sized modular aircraft structures [20].

*The article was attended by the staff of the Department No. 9 "Physical Problems of Materials Science" NRNU MEPhI — **Sidorenko A. A.**

Brazing alloys in the form of rapidly-quenched amorphous foils are prospective for diffusion brazing due to their high chemical and microstructural homogeneity [21–22]. The small thickness (30–70 μm) of amorphous foils ensures uniform filling of the brazed gap with a small amount of liquid. In this case, the diffusive outflow of depressant elements from the melted brazing alloy to the base material can be finished in an acceptable, for industrial applications, time. The diffusive outflow of elements into the base material and, as a result, the homogenisation of the joint, increases the strength and corrosion resistance of the compounds [23–24].

This study aimed to obtain brazed joints of titanium alloys OT-4 and VT6-c with a strength equal to the base material, and to identify the dependence of mechanical properties on the microstructure of the joint seam and the brazing mode.

Materials and Methods

1. Materials

Titanium alloys OT4, VT6-c and amorphous rapidly-quenched foil “STEMET®” 1202 were used in this work. Their chemical composition is presented in Table 1. According to differential thermal analysis with a SDTQ600 thermal analyser, the STEMET 1202 liquidus temperature is 794 °C.

2. Investigation of physical and chemical interaction of filler metal melt with basic materials

To study the physical and chemical interaction of the filler metal melt with the basic materials, samples with a wedge-shaped gap were used. The scheme of the samples is shown in Fig. 1. The plates of the chosen alloys were attached to each other using tungsten wire. A gap of 100 μm was fixed on one side only, so obtaining a wedge shape. Filler metal was placed next to the gap. The amount exceeded the required volume to completely fill the wedge-shaped gap with the melt. The foil was fixed on the surface of the sample using condenser spot welding.

Fig. 1. Wedge-shape sample scheme
1 — titanium alloy plates; 2 — tungsten wire; 3 — brazing seam;
4 — eutectic zone

Table 1
The chemical composition of the used materials

Alloy names	Chemical composition wt. %								
	Ti	Al	Mn	Fe	V	Cu	Zr	Ni	Be
OT4	bal.	3.5–5	0.8–2	0.3	–	–	–	–	–
VT6-c	bal.	5.3–6.5	–	–	3.5–4.5	–	–	–	–
STEMET 1202	bal.	–	–	–	0.8	22	12	12	1.5

*STEMET is an official trademark of MEPhI-AMETO company.

By using samples with a wedge-shaped gap, you can determine the maximum brazing clearance (MBC) at which there will be no eutectic layer in the brazing seam and estimate the required time of isothermal exposure to obtain a uniform structure.

Brazing of the wedge-shaped samples was performed in a SSHVE–25 vacuum furnace at a residual gas pressure of $1 \cdot 10^{-2}$ Pa and a temperature of 800 °C, with an exposure time of 0.5 and 2 h, and a temperature of 840 °C for 4 h. For all modes, an additional exposure was performed at 700 °C for 15 minutes for equalising the temperature gradient between the vacuum furnace and the equipment.

Dotted lines indicate the initial gap. In the structure of the brazed joint; three areas can be distinguished: the base material, the diffusion zone, and the eutectic component of the seam.

3. Preparation of thin sections

The samples were polished using sandpaper with a grit size from 120 to 1200 units, followed by polishing using diamond pastes with a particle size of 9, 3, and 1 μm on cloth. For optical microscopy, the samples were chemically etched for 3 seconds with a mixture of hydrofluoric acid, nitric acid, and water in a ratio of 1:1:1.

4. Investigation of the microstructure and properties of the brazed joints

The microstructure of the samples was studied after brazing, as well as before mechanical testing, using the METAM PB–21–1 optical microscope and the EVO 50 (Carl Zeiss) scanning electron microscope. The elemental composition of the brazed joints was studied using an INCA 350 x-act energy dispersive spectrometer (Oxford Instruments).

Due to the small atomic number and limited sensitivity of the spectrometer, the beryllium content in the various phases is difficult to detect with high accuracy. Therefore, we have not considered its impact when discussing the results. Based on Phase diagram of Ti – Be alloys, it can be argued that the influence of beryllium in this study is comparable to the influence of Cu and Ni. In this case, Be, in contrast to Cu and Ni, has a significantly higher diffusion coefficient and solubility in the main material, so it has a uniform distribution over the joint and will not affect the microstructure.

For tensile strength tests, brazed cylindrical samples, with a diameter of 14 and 16 mm, were used. Immediately before brazing, their end faces were cleaned with 320-unit grit sanding paper and washed with ethyl alcohol. For brazing, a single layer of filler metal with a thickness of 50 μm was used and placed directly in the gap between the connected samples. Brazing was performed in a SSHVE–25 vacuum furnace at temperatures: 800 °C for 2 h – 3 samples, and 840 °C with an exposure time of 2 h – 3 samples. Specific holders were used to

Fig. 2. Tensile test sample

create a uniform pressure on the samples during brazing. To equalise the temperature gradient between the vacuum furnace and the equipment, an additional exposure was performed at 700 °C for 15 minutes.

Brazed samples for tensile testing were prepared according to GOST 17349–79, as shown in Fig. 2. Tensile tests were carried out on an Instron test machine at a temperature of 22–24 °C with a traverse speed of 1 mm/min.

To study the microstructural properties in the brazed joint, Vickers microhardness measurements were carried out using a HVS–1000 hardness tester. During the measurement, a load of 100 g was applied for 20 seconds. Each print was measured at least three times (using the TE Vickers hardness testing microhardness programme).

Results and discussion

1. Structure and its dependence on brazing gap OT4/1202

To analyse the microstructural features, let us consider the diffusion brazing process, which includes several stages:

Dissolution stage:

During the initial stage, the connected parts are heated to a temperature higher than the melting point of the filler metal. After that, interaction of the melted filler metal with the base material occurs which causes the dissolution of the base material. The dissolution process then ceases.

Diffusion and isothermal solidification stage:

During the isothermal exposure, the alloying elements actively diffuse from the liquid to the base material and back under the influence of a concentration gradient. The concentration of depressants in the liquid phase decreases resulting in the solidification process at a constant temperature (isothermal solidification). This process proceeds until the complete exhaustion of the liquid phase.

Homogenisation stage:

At the final stage, under the influence of the residual concentration gradient, a solid-phase diffusion process occurs which leads to further equalisation of the concentrations of alloying elements in the area of the brazed joint. Homogenisation improves the mechanical characteristics of the joint.

If cooling starts before the isothermal solidification process is fully completed, a fragile eutectic structure will form in the seam.

To analyse the microstructure of the brazed joints depending on the size of the initial gap between the joined materials, the wedge-shaped samples were studied. A typical microstructure of a wedge-shaped sample is shown in Fig. 3 which illustrates an example of an OT4 alloy brazed joint obtained using STEMET 1202 brazing alloy at 800 °C and exposure for 2 h.

The microstructure of the wedge-shaped joint clearly shows a thin layer of the eutectic component (the white structure in the centre), which only begins at a certain gap size. The MBC is measured from the border to border of the base material. The MBC values for other modes are shown in Table 2.

This data allows us to estimate the gap size and the exposure time at 800 °C which is necessary to obtain a brazed joint without a eutectic layer. The wedge-shaped samples cannot give us the precise value of the initial gap between the base material plates since it is impossible to determine the thickness of the dissolved layer in the melt base material. Besides, the MBC is affected by the diffusion of elements from the melted filler metal at the second brazing stage. The MBC values only allow us to estimate the thickness of the filler metal foil required to obtain a seam without a eutectic layer for a specific brazing mode.

The typical microstructure of an OT4 alloy brazed joint obtained on a wedge-shaped sample at a large gap can be divided into several zones, as shown in Fig. 4. Green zone I is the area where the Widmanstätten structure is formed, consisting of the α -Ti and the (ex- β)-Ti phases (ex- β phase is the β -phase that decomposes during cooling by a eutectoid reaction to α -phase and intermetallics). According to previous studies [6–7], this structure type possesses high mechanical properties. It is only formed during long exposures at high temperatures, sufficient for the diffusion outflow of copper and nickel from the seam, which is responsible for the formation of intermetallic compounds with titanium.

Zone II marked in blue, consists of a eutectoid structure. The microstructural features are clearly visible at

Fig. 3. Microstructure of the OT4/1202 wedge-shape joint obtained at 800 °C – 2 h. The figures show different magnifications

Table 2

MBC, measured after brazing samples from OT4 and VT6-c at various modes using the filler alloy STEMET 1202

Alloys	OT4		VT6-c	
Modes	800 °C – 0.5 h	800 °C – 2 h	800 °C – 0.5 h	800 °C – 2 h
Gap, μm	34	75	36	85

Fig. 4. Microstructure of a wedge-shaped brazed joint OT4/1202 obtained at 800 °C — 2 h

high magnification, as shown in Fig. 4. This zone consists of α -Ti and a complex Ni- and Cu-rich chemical compound [25]. According to the binary Ti — Cu and Ti — Ni systems, the phase transformation temperature decreases greatly with the increase of Cu/Ni content. The eutectoid transformation temperatures in these binary systems are 790 °C and 765 °C, respectively. At the brazing temperature of 800 °C, zone II includes the β -Ti structure with a high content of copper and nickel. During slow cooling, the β -Ti decomposes into two solid phases by a eutectoid mechanism [26–27]. The presence of intermetallics in such a structure leads to a degradation of the mechanical characteristics [27–28].

Red zone III in the centre of the seam has a eutectic structure. Zone III, as well as zone II, contains a large amount of elements from the brazing alloy composition. However, in contrast to zone II, this eutectic structure is formed athermally during cooling from the liquid state.

2. Microstructure evolution mechanism

Diffusion brazing is based on the process of isothermal solidification where the phase transition from liquid to solid state occurs at a constant temperature. Crystallisation of the liquid phase is caused by a change in its chemical composition due to the diffusion of depressant elements into the base material. The main depressant elements of STEMET 1202 filler metal, such as Be, Ni, and Cu, have a similar effect on the base material. Ti — Be, Ti — Ni, and Ti — Cu binary systems contain low-temperature eutectics based on the β -titanium and intermetallics. Be, Ni, and Cu have significant solubility in the β -Ti, but during cooling, the β -phase decomposes by a eutectoid mechanism into α -Ti and intermetallics. The influence of vanadium (β -stabiliser) on the microstructure is negligible; as we show later the vanadium content is extremely small (approximately 1 wt.% or less).

To describe the microstructure evolution mechanism, it is necessary to consider the imaginary phase diagrams of the binary system, which are presented in Fig. 5.

After melting, the brazing alloy melt actively interacts with the solid base material, dissolving its boundaries. During the dissolution process, the composition of the

melt changes. According to the phase diagram, the composition will change from a higher content of element X (depressant element) to a lower one at a constant temperature. The equilibrium between the liquid phase and the solid phase occurs when the composition of the liquid phase corresponds to point 1, marked in Fig. 5. Fig. 6 illustrates all stages of the microstructural evolution during the brazing process. Figs. 6, *a* and 6, *b* show the initial stage — the moment when the melt appears, followed by the subsequent dissolution of the base material in the melt. The joint width increases significantly due to the melting (dissolution) of the base material in the melt.

Fig. 6, *c* illustrates the next stage — the growth of the β -phase. Crystallisation begins on the base material surface, with nucleation occurring over the entire area of this surface. Then the growth of the nucleus occurs, which forms a continuous crystallisation front of the β -phase. The chemical composition of the liquid does not change and corresponds to point 1 on the phase diagram, but the amount of liquid continuously decreases. The chemical composition of the β -phase nuclei corresponds to point 2 in Fig. 5. The diffusion rate in the solid phase is several orders of magnitude lower than in the liquid phase. Depressant elements (Be, Ni, Cu) diffuse from the β -phase into the base material.

The distribution of depressant elements in the β -phase is non-uniform, their composition can vary from point 2 to point 3. At the liquid/ β -phase boundary, the front of the growing β -phase has the composition of point 2, and the β -phase/base material boundary composition is between points 2 and 3.

At a certain point in time, the outflow of β -stabilisers (Be, Ni, and Cu) into the base material causes the formation of the α -phase nuclei of the composition of point 4. This evolution stage is schematically shown in Fig. 6, *d*.

Fig. 5. Imaginary phase diagram of binary system Ti — X (where X is Be, Ni or Cu)

Fig. 6. Microstructure evolution of a brazed seam

In this case, the composition of this two-phase structure varies between points 3 and 4. The chemical composition of the β -phase in this two-phase zone is enriched by Ti and corresponds to point 3. Unlike the β -phase, which grows through the liquid phase, the α -phase colonies emerge inside the solid β -phase. In two-phase titanium alloys, the α -phase colonies form in the shape of lamellae along certain crystallographic directions. Growth occurs both inside the grains and from the boundaries. The α -phase colonies grow from the β -phase/base material boundary towards the liquid/ β -phase boundary. Thus, this proeutectoid (Widmanstätten) structure is formed in the form of α -phase lamellae inside the β -phase [29]. The Widmanstätten structure develops from the proeutectoid structure after cooling with eutectoid transformation. This process can occur because of the diffusion of elements (Ni, Cu) with the shift of the composition to the $\alpha + \beta$ region, and also during cooling from the β region with the $\beta \rightarrow \alpha$ transformation after crossing the solvus line.

All these stages result in the formation of the structure shown in Fig. 6, e. The number of structural components (zones) and their chemical composition depends on the composition of the base material, the used filler metal, and the time-temperature brazing mode.

The final stage that determines the final microstructure is the cooling stage. As shown above, the brazed seam at a specific temperature includes three zones: liquid (the composition of point 1), β -phase (with composition between point 2 and 3) and $\alpha + \beta$ proeutectoid (Widmanstätten) structure consisting of the α -phase composition of point 4 and the β -phase composition of point 3. Furthermore, upon cooling, the composition

of the phases within these structural components changes according to the curves of the solidus, liquidus and solvus. When the temperature decreases, transformation reactions occur. During the eutectic transformation $L \rightarrow \beta + \text{Int}$ (here Int is an intermetallic compound), the β -phase inside the eutectic decomposes into $\alpha + \text{Int}$ by the eutectoid mechanism. As a result, a brittle structure with a low deformation capacity forms in the centre of the seam. The pure β -phase undergoes the same eutectoid transformation as the β -phase in the eutectic. Inside the Widmanstätten structure, the α -lamellae are stable with the β -phase between the lamellae also decomposing by a eutectoid reaction. The final microstructure is shown in Fig. 6, f.

Other variants of the final structure type are also possible. If the growth of the proeutectoid is not limited by the exposure time at high temperature, then it is possible to obtain a seam

structure consisting only of Widmanstätten. An intermediate variant is a structure without eutectic in the centre of the seam, formed when the exposure time is insufficient for complete overgrowth of the seam with Widmanstätten.

3. Microstructure evolution of brazed joint OT4/1202

Let us take a closer look at the OT4 alloy joints obtained using STEMET 1202 filler metal by the mode: 800 °C – 0.5 h and by the mode with an increased temperature and exposure time: 840 °C – 4 h.

Fig. 7 shows the microstructure of the OT4 joint obtained by the first mode. Energy dispersive spectroscope (EDS) chemical analysis was performed for the 10 marked areas. The results are presented as a graph in Fig. 8.

Fig. 7. Microstructure of brazed joint OT4/1202 obtained by mode 800 °C – 0.5 h

The Widmanstätten structure has not formed in this brazed joint. The temperature and exposure time are insufficient for diffusion. Under such conditions, a large amount of Cu and Ni remains in the seam, which causes the formation

Fig. 8. Elemental distribution in the brazed joint OT4/1202 obtained at 800 °C – 0.5 h:
1 – Al; 2 – Ni; 3 – Cu; 4 – Zr; 5 – Ti

Fig. 9. Microstructure of brazed joint OT4/1202 obtained by mode 840 °C – 4 h

Fig. 10. Elemental distribution in the brazed joint OT4/1202 obtained at 840 °C – 4 h:
1 – Al; 2 – Ni; 3 – Cu; 4 – Zr; 5 – Ti

of eutectic and eutectoid structures. This structure clearly shows that during isothermal crystallisation, the β -phase of titanium is formed first, followed by the formation of the α -phase. The authors [25, 30] incorrectly described the microstructural evolution mechanism in similar systems, assuming that at first, the α -phase crystallises from the liquid at the boundary of the base material/liquid and displaces Cu and Ni into the intergranular space where the β -phase is formed.

The graph shows that the eutectic (spectra 1–3) is close in chemical composition to the original STEMET 1202 filler metal (50.8 Ti – 12Zr – 22Cu – 12Ni – 1.5Be – 0.8V wt.%). When crossing the eutectic-eutectoid boundary, the content of Zr, Ni, and Cu markedly decreases. There is also a smooth increase in the content of Al and Ti, from the eutectic up to the main material. Depressant elements barely penetrate the base metal. At a distance of 20 μm from the seam, a small amount of Cu, Ni, and Zr from the filler metal are observed in the main material.

With an increase in temperature and exposure time, the structure evolves significantly. Figs. 9 and 10 show the microstructure of the joint obtained at 840 °C – 4 h and the distribution of the elements over the width of the joint, respectively. The microstructure shows 20 zones where the chemical composition was measured. Only Widmanstätten is present in the seam structure, in contrast to the previously considered seam structure obtained at 800 °C, where eutectoid and eutectic were observed.

The graphs of chemical elements distribution show an average twofold decrease in the content of Ni and Cu depressants, as well as Zr, compared to the previously considered eutectoid structure of OT4/1202 800 °C – 0.5 h joint. With increasing temperature and exposure time, accelerated diffusion of Al from the base material causes an increase of its concentration by 1.5 times.

At a distance of 100 μm from the seam in the base material, a small amount of Ni from the filler metal was detected. Thus, with an increase in temperature and exposure time to 840 °C – 4 h, the depth of diffusion of nickel increased by 5 times compared to 800 °C – 0.5 h.

4. Microstructure evolution of brazed joint VT6–c/1202

Let us consider in detail the brazed joint of the VT6–c alloy obtained using the STEMET 1202 filler metal, the microstructure of which is shown in Fig. 11. As earlier, the zones are marked on the microstructure and the dimensions are given in μm .

Green zone I is the area of formation of a needle-like (or plate-like) two-phase Widmanstätten structure made of α and ex- β (former β -Ti after eutectoid decomposition) titanium. The size of this zone is 10–15 μm . Even with a long exposure time, its formation is at the initial stage. Blue zone II is a eutectoid structure based on α -Ti and the intermetallic compounds $(\text{Ti}, \text{Zr})_n(\text{Ni}, \text{Cu})_m$, the formation of which is described by the study [25]. The eutectoid structure is noticeable at high magnification in the right-hand

Fig. 11. Microstructure of brazed joint VT6-c/1202, obtained by mode 800 °C – 2 h

Fig. 14. Microstructure of eutectic structure formed within joint VT6-c/1202 obtained by mode 800 °C – 2 h

Fig. 12. Microstructure of VT6-c/1202 joint, obtained by mode 800 °C – 2 h

Fig. 13. Elemental distribution in the brazed joint VT6-c/1202, obtained at 800 °C – 2 h:
1 – Al; 2 – V; 3 – Ni; 4 – Cu; 5 – Ti; 6 – Zr

part of Fig. 11. At high magnifications, it can be seen that the eutectic (red zone III) consists of a grainy mixture of dark phases, which have undergone a eutectoid transformation, and a light phase apparently enriched with heavy elements. This structure will be studied in more detail later.

Joints of VT6-c/1202 obtained at 800 °C – 2 h were studied using EDS analysis. As can be seen in Fig. 12, the seam has a eutectic layer in the centre. Fig. 12 shows 11 areas where the chemical composition was measured. The results are presented as a graph in Fig. 13.

The central eutectic layer contains a large amount of Zr, Cu, and Ni. The chemical composition measured in the eutectic region: Ti – 19Cu – 1Al – 1V – 15Zr – 13Ni wt.% is close to the composition of the initial brazing alloy STEMET 1202: Ti – 12Zr – 22Cu – 12Ni – 1.5Be – 0.8V wt.%. Apparently, the temperature of 800 °C is not enough for intensive diffusion of the elements from the centre of the seam to the base material. Most of the Al, Ni, Cu and Zr are distributed within the eutectic and eutectoid structures. In comparison with the eutectoid structure, the Widmanstätten has a lower Cu and Ni content.

Fig. 14 shows the microstructure of the central eutectic zone III with the results of the chemical composition of the phases. The eutectic consists of three structural components. Spectrum 1 is an α -Ti solid solution. Spectrum 2 is a eutectoid structure formed after decomposition of the β -phase, which consist of α -Ti and a chemical compound enriched with Cu and Ni. Spectrum 3 is an intermetallic compound $(\text{Ti, Zr})_2(\text{Cu, Ni})$ [25]. These compounds have a high hardness. For titanium intermetallics of the Ti_2Cu type, the hardness is 4.5 GPa. For zirconium intermetallics of the Zr_2Cu type, the hardness is 6.8 GPa, which is significantly higher compared to the main material [31–32].

It is important to note that the chemical composition of the phases in the brazed joints obtained at 800 °C – 0.5 h and 2 h, with a large gap, is the same, despite the fact that they were obtained at different time exposures. This is because in both thermodynamic systems, the liquid and solid phases are in equilibrium. Until the liquid phase completely disappears there will be no change in the composition of the solid phases in the system. The main difference between the structures obtained by different modes is the different number of zones in the system.

At small gaps, when the isothermal solidification of the brazed joint and the formation of the Widmanstätten

structure is complete, the exposure time is one of the important parameters since it leads to the homogenisation of the chemical composition of the joint due to the redistribution of alloying elements between the phases.

5. Microhardness measurements

To study the properties of the structural zones formed in the brazed joint, the microhardness was measured. The results of the microhardness measurements of OT4/1202 and VT6-c/1202 joints are shown in Table 3. Since it was difficult to separate type I and II zones during the microhardness measurements, the results were averaged over these two zones. The microhardness of the eutectic layer (zone III) in the brazed joint is significantly higher than the microhardness of the base metal and zones I-II, which is due to the presence of a large number of intermetallics in the eutectic. Thus, the eutectic layer, which has a high hardness, is more brittle compared to zones I-II and the base material. Increasing the exposure time from 0.5 to 2 h does not change the microhardness of zone III. However, there is a decrease in the microhardness of zones I-II caused by growth of the α -phase (growth of plate-like zone I through zone II, containing intermetallic).

Table 3
Microhardness of brazed joints OT4/1202 and VT6-c/1202 obtained by different modes

Sample No.	Alloy	Brazing mode	Microhardness HV10 ⁻¹ , MPa	
1	OT4	800 °C, 0.5 h	Base material	330 ± 20
			Zone III	720 ± 80
			Zone I,II	580 ± 20
2	OT4	800 °C, 2 h	Base material	310 ± 30
			Zone III	730 ± 80
			Zone I,II	500 ± 50
3	VT6-c	800 °C, 0.5 h	Base material	340 ± 10
			Zone III	740 ± 40
			Zone I,II	570 ± 40
4	VT6-c	800 °C, 2 h	Base material	330 ± 20
			Zone III	760 ± 70
			Zone I,II	430 ± 40

6. Tensile strength tests

As shown below, the tensile strength strongly depends on the microstructure of the brazed joint. The brazed joints were examined along the seam circumference at 4 points in 90° increments, which allows for a more accurate analysis of the microstructure of the entire joint. The microstructures of all samples from both OT4 and VT6-c alloys can be divided into three types:

1. Samples in which zone III, i.e. the eutectic layer, is present over the entire area of the brazing seam.
2. Samples in which part of the seam area contains zone III, the rest consists of zones I and II.
3. Samples with a homogeneous structure consisting of zones I and II (eutectoid + Widmanstätten structure).

The structures of samples of the first type, illustrated in Fig. 15, *a*, showed poor results: the ultimate strength of the OT-4 brazed joint at 800 °C for 2 h was 294 MPa, which is only 40% of the strength of the titanium alloy OT4 annealed at 800 °C for 2 h – 730 ± 3 MPa. Table values of the ultimate strength for the initial OT4 are in the range of 635–885 MPa. A brittle eutectic layer with a thickness of 3 to 7 µm passes through the entire seam. The eutectic layer is the most favourable place for crack propagation which can cause the destruction of the entire brazed joint, even at low stress. Testing the tensile strength of this type of joints shows that the failure occurs along the weakest and most fragile structure at the elastic deformation stage.

The second type of joints mainly consist of zones I and II with minor eutectic inclusions of zone III, as is shown in Fig. 15, *b*. In this case, the ultimate strength of such a joint strongly depends on the ratio of the areas of structural components in the cross-section of the joint. The ultimate strength for OT4/1202 varies from 420 to 549 MPa. The failure of such samples occurs at the seam.

In order to increase the strength of the joints and obtain a structure without a eutectic component in the seam, it was decided to increase the brazing temperature to 870 °C [33]. OT4 joints brazed by this mode showed results not lower than the strength of the base material. Their structure belongs to the third type, there was a complete growth of Widmanstätten structure. The microstructure of these joints is shown in Fig. 15, *c*. The true strength of this structure is higher than that of the base titanium alloy and during tensile tests, failure occurred at the base material.

Fig. 15. Microstructure of brazed joint OT4/1202 obtained at 800 °C – 2 h (*a*, *b*) and 870 °C – 2 h (*c*)

Table 4
Tensile strength OT4/1202 и VT6-c/1202 joints, brazing at 840 °C – 2 h

Sample No.	Alloy	Ultimate strength, MPa
1	OT4	754
2	OT4	750
3	OT4	747
4	VT6-c	902
5	VT6-c	909
6	VT6-c	906

Brazing at 870 °C showed the best results, but at this temperature, the thin-walled structures made of titanium alloys, deform. Therefore, it was decided to reduce the temperature to 840 °C, leaving the exposure time the same at 2 h. The results of strength tests are shown in Table 4.

The microstructure of joints brazed according to the proposed mode consists of zones I and II. This is a microstructure of the third type, hence the strength of such compounds should be at the level of the main material [34–35], which was confirmed by the experiments. Joints of OT4/1202 showed a high strength of 747–754 MPa, and that of VT6-c/1202 was 902–909 MPa. This is equal to the strength of the base material. All of the above once again confirms the fact that samples with a wide eutectic layer in the centre of the seam, or small inclusions of eutectic component, have low strength properties due to the presence of brittle intermetallics. This layer can be removed during the brazing process by increasing the temperature or exposure time.

Note that the results of brazing might depend on the external pressure since the filler metal could run out of the gap. Therefore, the final clearance for these filler metals depends not only on the thickness of the used amorphous foil, but also on the pressure applied during brazing.

The research described in this paper, related to the mechanism of formation of the structure of brazed joints, helps to predict the final properties of the product. The use of high-temperature brazing technology to develop heavily loaded equipment opens up new opportunities for designers. Today, common technologies, such as welding, are more popular in industry. However, in some cases, for joining parts of thin-walled structures, they are not applicable. Some uncertainty is present in the current development trends of mechanical engineering, and the lack of wide application of diffusion brazing technology in mass production makes it difficult to estimate the economic effect.

Conclusion

This paper studies the dependence of the mechanical properties of titanium alloys OT4 and VT6-c joints obtained by brazing with rapidly-quenched amorphous filler metal STEMET 1202, on their microstructure and brazing mode.

Based on the results of metallographic and spectral chemical analysis of brazed wedge-shaped samples made

of titanium alloys, a microstructural formation mechanism is proposed. Depending on the parameters of the brazing process and the gap size, the formation of several structural components (zones) is demonstrated (eutectic, eutectoid and Widmanstätten).

Brazed joints from OT4 and VT6-c, with a eutectic component in the structure, are characterised by low mechanical properties – the ultimate strength lies in a range from 200 to 550 MPa. Increasing the temperature to 840 °C and the exposure time to 2 h, leads to the disappearance of the brittle eutectic component from the seam due to the accelerated diffusion of the depressant elements Be, Cu and Ni, into the base material. The structure, consisting of Widmanstätten with some degree of eutectoid, demonstrates a strength at the level of the base material: for OT4 750 ± 3 MPa, for VT6-c 905 ± 3 MPa. At the same time, despite a significant increase in the exposure time, there is no degradation of the properties of the brazed materials. Thus, based on a large number of results, the relationship between the microstructure of brazed joints and their ultimate strength is revealed and described.

Acknowledgements

This work was supported by Competitiveness Growth Programme of the Federal Autonomous Educational Institution of Higher Education National Research Nuclear University MEPhI (Moscow Engineering Physics Institute).

The authors express a gratitude to the staff of "MEPhI-ANETO" for providing brazing foils".

References

1. Bertossa R. C., Hikido T. Brazing And Diffusion Bonding of Titanium Alloys to Similar and Dissimilar Materials. *SAE Technical Paper Series*. 1965. DOI: 10.4271/650752
2. Liu C. C., Ou C. L., Shiue R. K. The Microstructural Observation and Wettability Study of Brazing Ti–6Al–4V and 304 Stainless Steel Using Three Braze Alloys. *Journal of Materials Science*. 2002. Vol. 37, Iss. 11. pp. 2225–2235.
3. Shapiro A., Flom Y. Brazing of Titanium at Temperatures below 800°C: Review and Prospective Applications. *DVS-Berichte*. 2007. Vol. 243.
4. Shapiro A., Rabinkin A. State-of-the-Art of Titanium-based Brazing Filler Metals. *Welding Journal*. 2003. Vol. 82, Iss. 10. pp. 36–43.
5. Khorunov V. F., Maksymova S. V., Voronov V. V. New Filler Metal Systems for the Brazing of Titanium Alloys. *China Welding (English Edition)*. 2015. Vol. 24, Iss. 3. pp. 1–5.
6. Ganjeh E., Sarkhosh H. Microstructural, Mechanical and Fractographical Study of Titanium-CP and Ti – 6Al – 4V Similar Brazing with Ti-based Filler. *Materials Science and Engineering: A*. 2013. Vol. 559. pp. 119–129.
7. Ganjeh E., Sarkhosh H., Bajgholi M.E., Khorsand H., Ghaffari M. Increasing Ti–6Al–4V Brazed Joint Strength Equal to the Base Metal by Ti and Zr Amorphous Filler Alloys. *Materials Characterization*. 2012. Vol. 71. pp. 31–40.

8. Song X. G., Tian X., Zhao H. Y., Si X. Q., Han G. H., Feng J. C. Interfacial Microstructure and Joining Properties of Titanium-Zirconium-Molybdenum Alloy Joints Brazed Using Ti-28Ni Eutectic Brazing Alloy. *Materials Science and Engineering: A*. 2016. Vol. 653. pp. 115–121.
9. Afshar F. N., Ambat R., Kwakernaak C., de Wit J. H. W., Mol J. M. C., Terryn H. Electrochemical Depth Profiling of Multilayer Metallic Structures: An Aluminum Brazing Sheet. *Electrochimica Acta*. 2012. Vol. 77. pp. 285–293.
10. Lee M. K., Lee J. G. Mechanical and Corrosion Properties of Ti-6Al-4V Alloy Joints Brazed with a Low-Melting-Point 62.7Zr – 11.0Ti – 13.2Cu – 9.8Ni – 3.3Be Amorphous Filler Metal. *Materials Characterization*. 2013. Vol. 81. pp. 19–27.
11. Jing Y., Xiong H., Shang Y., Wang J., Cheng Y., Jiang J. Design TiZrCuNi Filler Materials for Vacuum Brazing TA15 Alloy. *Journal of Manufacturing Processes*. 2020. Vol. 53. pp. 328–335.
12. Rabinkin A., Wenski E., Ribaud A. Brazing Stainless Steel Using a New MBF Series of Ni – Cr – Si – B Amorphous Brazing Foil. New Brazing Alloys Withstand High-Temperature and Corrosive Environments. *Welding Research Supplement*. February 1998. pp. 66-s–75-s.
13. Jing Y., Su D., Yue X., Britton T. B., Jiang J. The Development of High Strength Brazing Technique for Ti – 6Al – 4V Using TiZrCuNi Amorphous Filler. *Materials Characterization*. 2017. Vol. 131. pp. 526–531.
14. Pang S., Sun L., Xiong H., Chen C., Liu Y., Li H., Zhang T. A Multicomponent TiZr-based Amorphous Brazing Filler Metal for High-Strength Joining of Titanium Alloy. *Scripta Materialia*. 2016. Vol. 117. pp. 55–59.
15. Galindo-Nava E. I., Jing Y. J., Jiang J. Predicting the Hardness and Solute Distribution During Brazing of Ti – 6Al – 4V with TiZrCuNi Filler Metals. *Materials Science and Engineering: A*. 2018. Vol. 712. pp. 122–126.
16. Cook G. O., Sorensen C. D. Overview of Transient Liquid Phase and Partial Transient Liquid Phase Bonding. *Journal of Materials Science*. 2011. Vol. 46, Iss. 16. pp. 5305–5323.
17. Way M., Willingham J., Goodall R. Brazing Filler Metals. *International Materials Reviews*. 2019. Vol. 65, Iss. 5. pp. 1–29.
18. Yang Z., Chen Y., Niu S., Wang Y., Han Y., Cai X., Wang D. Phase Transition, Microstructural Evolution and Mechanical Properties of Ti – 6Al – 4V and Ti – 6.5Al – 3.5Mo – 1.5Zr – 0.3Si Joints Brazed with Ti – Zr – Ni – Cu Filler Metal. *Archives of Civil and Mechanical Engineering*. 2020. Vol. 20, Iss. 3. pp. 1–15.
19. Banerjee S., Mukhopadhyay P. Phase Transformations. Examples from Titanium and Zirconium Alloys. Mumbai: Bhabha Atomic Research Centre, 2007. 813 p.
20. Solntsev U. P. Metals and Alloys Handbook. St. Petersburg: NPO “Professional”, 2003. 1000 p.
21. Fedotov V. T., Suchkov A. N., Kalin B. A., Sevryukov O. N., Ivannikov A. A. Rapidly Quenched Filler Metal STEMET for Brazing of Materials of Modern Technology. *Tsvetnye Metally*. 2014. No. 12. pp. 32–37.
22. Zhang J., Zhang T., Cheng Y. Laminated Forming of TC4 Titanium Alloy by High Frequency Induction Brazing. *Xiyou Jinshu Cailiao Yu Gongcheng (Rare Metal Materials and Engineering)*. 2017. Vol. 46, No. 11. pp. 3440–3445.
23. Rabinkin A. New Applications for Rapidly Solidified Brazing Foils. *Welding Journal*. 1989. Vol. 10. pp. 39–46.
24. Kalin B. A., Sevryukov O. N., Fedotov V. T., Plyushchev A. N., Yaykin A. P. New Amorphous Solders for Brazing of Titanium and its Alloys. *Svarochnoe Proizvodstvo*. 2001. No. 3. pp. 37–39.
25. Kim K.H., Lim C. H., Lee J. G., Lee M. K., Rhee C. K. Growth and Microstructure Formation of Isothermally-Solidified Zircaloy-4 Joints Brazed by a Zr – Ti – Cu – Ni Amorphous Alloy Ribbon. *Journal of Nuclear Materials*. 2013. Vol. 441, Iss. 1-3. pp. 59–66.
26. Donthula H., Vishwanadh B., Alam T., Borkar T., Contieri R. J., Caram R., Banerjee R., Tewari R., Dey G. K., Banerjee S. Morphological Evolution of Transformation Products and Eutectoid Transformation(s) in a Hyper-Eutectoid Ti-12 at% Cu Alloy. *Acta Materialia*. 2019. Vol. 168. pp. 63–75.
27. Contieri R. J., Lopes E. S. N., Caram R., Devaraj A., Nag S., Banerjee R. Effects of Cooling Rate on the Microstructure and Solute Partitioning in Near Eutectoid Ti – Cu Alloys. *Philosophical Magazine*. 2014. Vol. 94, Iss. 21. pp. 2350–2371.
28. Alshammari Y., Alqattan F., Yang F., Bolzoni L. Vacuum Sintering and Solution Plus Aging Heat Treatment of β Eutectoid Bearing Binary Ti Alloy. *International Journal of Refractory Metals and Hard Materials*. 2020. Vol. 91. 105267. DOI: 10.1016/j.jrmhm.2020.105267
29. Sun Z., Guo S., Yang H. Nucleation and Growth Mechanism of α -Lamellae of Ti Alloy TA15 Cooling from an $\alpha + \beta$ Phase Field. *Acta Materialia*. 2013. Vol. 61, Iss. 6. pp. 2057–2064.
30. Lee M. K., Kim K. H., Lee J. G., Rhee C. K. Growth of Isothermally-Solidified Titanium Joints Using a Multi-Component Zr – Ti – Cu – Ni – Be Amorphous Alloy as a Brazing Filler. *Materials Characterization*. 2013. Vol. 80. pp. 98–104.
31. Kikuchi M., Takahashi M., Okuno O. Machinability of Experimental Ti – Cu Alloys. *Materials Transactions*. 2008. Vol. 49, Iss. 4. pp. 800–804.
32. Evstuykhin A. I., Korobkov I. I., Osipov V. V. Intermetallic Compounds of Zirconium and Their Influence on the Corrosion Properties of Zirconium Alloys. *Soviet Atomic Energy*. 1970. Vol. 28, Iss. 3. pp. 262–267.
33. Liu S., Miao J., Zhang W., Wei R., Chen C., Wang T., Zhao W., Jiang Z., Li F. Interfacial Microstructure and Shear Strength of TC4 Alloy Joints Vacuum Brazed with Ti – Zr – Ni – Cu Filler Metal. *Materials Science and Engineering: A*. 2020. Vol. 775. 138990. DOI: 10.1016/j.msea.2020.138990
34. Ljüjering G. Influence of Processing on Microstructure and Mechanical Properties of ($\alpha + \beta$) Titanium Alloys. *Materials Science and Engineering: A*. 1998. Vol. 243, Iss. 1–2. pp. 32–45.
35. Jing Y., Xiong H., Shang Y., Cheng Y. Simulation on Ti-based Filler and Vacuum Brazing for TA15 Alloy. *Welding in the World*. 2020. Vol. 64, Iss. 7. pp. 1261–1268.