DOI: https://doi.org/10.37434/tpwj2025.01.01

DIFFUSION BONDING OF Ti6-4 ALLOY THROUGH MULTILAYER INTERLAYERS OF AN EUTECTIC COMPOSITION BASED ON Ti–Cu SYSTEM

T.V. Melnychenko, A.I. Ustinov, O.Yu. Klepko, O.V. Samofalov

E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine

ABSTRACT

The regularities of diffusion bonding of the titanium alloy Ti6-4 through multilayer interlayers of eutectic composition based on Ti–Cu system, produced by electron beam deposition under vacuum, were investigated in this work. The microstructure and mechanical properties of the joints were analyzed using scanning electron microscopy and by determining their shear strength. It is shown that multilayer interlayers provide defect-free joints without degradation of titanium alloy properties at a temperature of 920–950 °C, corresponding to the melting range of the interlayer. It is established that the nature of the reaction interaction of the components of the interlayer and Ti6-4 alloy during heating depends on the temperature and melting range of the multilayer interlayer and determines the microstructure and phase composition of the joint. Absence of continuous layers of intermetallics (TiCu, Ti_2Cu) in the joint and formation of a dispersed Widmanstätten structure with copper and nickel content of < 7 at.% provide the joint strength at the level of the Ti6-4 alloy.

KEYWORDS: multilayer foil, EB-PVD, Ti6-4 alloy, diffusion bonding, microstructure, shear strength

INTRODUCTION

Ti6-4 titanium alloy belongs to α+β type that ensures its high values of room temperature impact toughness and high temperature creep strength. Owing to its low specific weight, high corrosion resistance and specific strength, the alloy is widely used in the aerospace, automotive, ship-building industries, nuclear power engineering, medicine, etc. [1, 2]. According to statistics, more than 50 % of titanium applied in the aerospace industry is Ti6-4 alloy, used to produce large-sized welded and prefabricated structures of flying vehicles, high-pressure cylinders operating in the temperature range of 196–450 °C, and other structural elements. However, manufacturing modern products, in particular complex-shaped and thick-walled ones, requires the technology of joining their individual elements, which, on the one hand, will prevent degradation of the structural and mechanical characteristics of the alloy, and, on the other hand, is reliable and low-cost. Ti6-4 alloy joining is performed by different methods: arc, electron beam, laser, diffusion welding and brazing [3, 4]. Welding of Ti6-4 titanium alloy by the traditional methods is conducted at a high temperature and it is accompanied by structural transformations in the material, grain growth, formation of brittle intermetallics, metastable phases, defects and pores that leads to lowering of the alloy strength values and formation of residual stresses in the joint [5, 6]. The most acceptable method for formation of the alloy joint is vacuum brazing, as the process runs in vacuum that prevents the alloy oxidation and does not require application of flux with further cleaning of the joint surface from contamination and corrosion products. Absence of considerable compressive forces allows joining thin-walled and complex-shaped parts. Considering the high temperature of α↔β transformation in Ti6-4 alloy (970–1010 °C [7]), brazing is performed with application of braze alloys, the most common of which are those based on Ti–Cu–Ni an Ti–Zr–Cu–Ni systems, at the temperature of 980–1040 °C close to the temperature of phase transformation. These braze alloys are the most acceptable to produce joints used at the temperature of ~ 600 °C in an aggressive medium, and they have the shear strength of ~ 50–70 % of that of the base material [8]. Application of braze alloys at certain technological parameters, ensures high values of joint strength [9], and additional heat treatment is performed to form a duplex structure and to recover the mechanical properties of the titanium alloy [10]. However, it is desirable to conduct brazing of thin-walled structural elements and those made from strain-hardened alloys at a lower temperature, because of the possible degradation of the titanium alloy structure. Lowering of the brazing temperature is also required during the fabrication of structures, consisting of elements of different chemical composition. Therefore, development of new methods of joining Ti6-4 alloy that will ensure a lowering of the level of thermal impact on the alloy is urgent. It is known that application of intermediate multilayers, in which at heating the diffusion processes of the component mixing proceed at an anomalously high rate, allows lowering the temperature of the joint formation process [11]. From this viewpoint, it is rational to perform joining of Ti6-4 alloy with application of multilayers based on systems with an eutectic with melting temperature < 980 °C, which will prevent degradation of the alloy structural characteristics. The advantage of such an approach is fast formation of a thin interlayer of the liquid phase in the butt, due to intensive diffusion mixing of the components of the multilayer that will ensure wetting of the joint surfaces and their physical contact at a low compressive force. The work is a study of the regularities of formation of the structure and mechanical properties of Ti6-4 alloy joints, produced by diffusion bonding through intermediate multilayers based on systems with Ti–Cu and Ti–Cu–Ni eutectic in the temperature range of 920–950 °C.

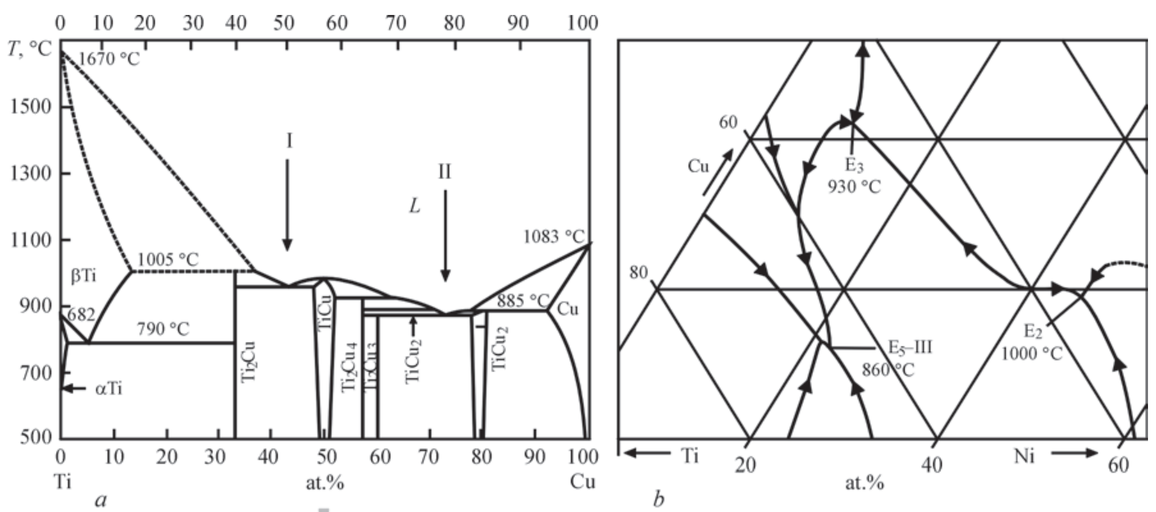
MATERIALS AND METHODS

Interlayers in the form of multilayer foil (MF) of a chemical composition close to that of binary eutectics I and II of Ti–Cu system (Figure 1, *a*) and ternary eutectic III of Ti–Cu–Ni system (Figure 1, *b*) were produced by the method of layer-by-layer electron beam deposition of components into a rotating substrate, described in detail in [14]. Scheme of producing the MF is shown in Figure 1, *c*.

The thickness ratio of binary MF component layers is determined by the ratio of their vapour flow intensities. The layer alternation period (sum of the two component layer thicknesses) at a certain evaporation intensity is determined by the substrate evaporation rate. Pressure in the chamber during deposition is maintained at the level of 10^{-3} Pa. Substrate temperature was kept below 300 °C that prevented diffusion mixing of the component layers. At substrate rotation speed of 2 min^{-1} an MF with layer alternation period of 500 nm and 35 μm thickness was produced. The required chemical composition of ternary Ti–Cu–Ni MF was ensured by cladding the Ti–Cu interlayer with layers of nickel of a certain thickness by evaporation of an additional nickel ingot. Figure 2, *a* shows the microstructure of a binary Ti–Cu MF, and Figure 2, *b* is the general view of a ternary Ti–Cu–Ni foil. Table 1 gives the chemical composition of binary and ternary MF. Foil melting temperature was determined by the method of differential thermal analysis (DTA) in VDTA-2000 unit. Figure 2, *c* shows fragments of DTA curves in the melting range of foils of different composition, and Table 1 gives their melting ranges.

Bonding of Ti6-4 alloy was conducted by heating an assembly, which consisted of samples of the alloy and MF placed between them, in a vacuum chamber in a fixture which allowed fixing the position of the samples and the foil (Figure 3, *a*). Sample dimensions are shown in Figure 3, *b*.

Grinding of the sample surfaces on R1200 abrasive paper and ultrasonic cleaning of the samples and



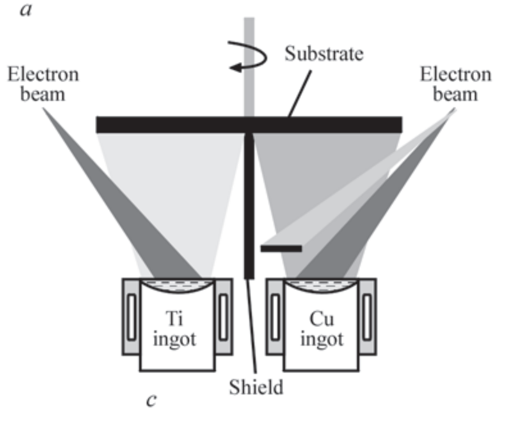


Figure 1. Constitutional diagram of Ti–Cu [12] (*a*), Ti–Cu–Ni [13] (*b*) and scheme of producing MF (*c*)

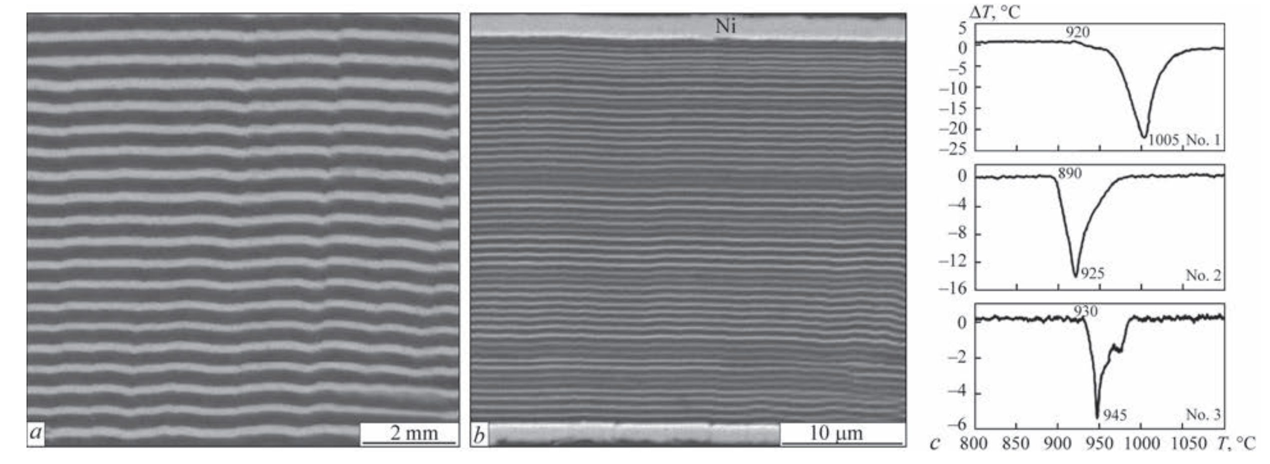


Figure 2. SEM image of the cross-section of Ti–Cu MF No. 1 with 500 nm layer period (*a*), Ti–Cu–Ni MF No. 3 (*b*), fragments of MF DTA curves (*c*)

Table 1. MF characteristics

MF number	MF structure	MF overall chemical composition, at.%			Melting range, °C
		Ti	Cu	Ni	
1	Ti/Cu	55.7	44.3	–	920–1005
2	Ti/Cu	22.6	77.4	–	890–925
3	Ni+Ti/Cu+Ni	67.1	18.1	14.8	930–945

the foil in acetone were performed before the bonding process. The bonding process was conducted at temperatures of 920 and 950 °C for 60 min, and 980 °C for 30 min at the compressive force of 70 kPa. The process temperature was selected according to MF melting temperature. The vacuum in the chamber was maintained at the level of 10^{-3} Pa.

The microstructure and chemical composition of different regions of the joint were studied with application of scanning electron microscope CamScan-4, fitted with energy-dispersive analysis system EDX INCA 200. Samples for metallographic investigations were prepared by a standard procedure in grinding-polishing equipment of Struers Company. Shear testing of the samples using special fixtures was conducted to assess the quality of the joints (Figure 3, *c*). Tensile strength of samples of a standard shape to GOST was determined in ZDM 4 tensile testing machine. Average strength value was found by the results of testing not less than three samples.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Table 2 gives the characteristics of the joints produced with MF application in different modes.

Figures 4–6 show the joint microstructure. Chemical and phase composition of the respective regions of the diffusion zone are given in Tables 3–5. At bonding through MF No. 1 and No. 2 regions of different chemical and phase composition form in the diffusion zone (Figures 4, 5) that is the consequence of diffusion mixing of the components of MF and titanium alloy due to the alloy surface wetting by the liquid phase which forms at MF melting.

In the diffusion zone central part a layer based on Ti_2Cu and TiCu intermetallics forms as a result of re-

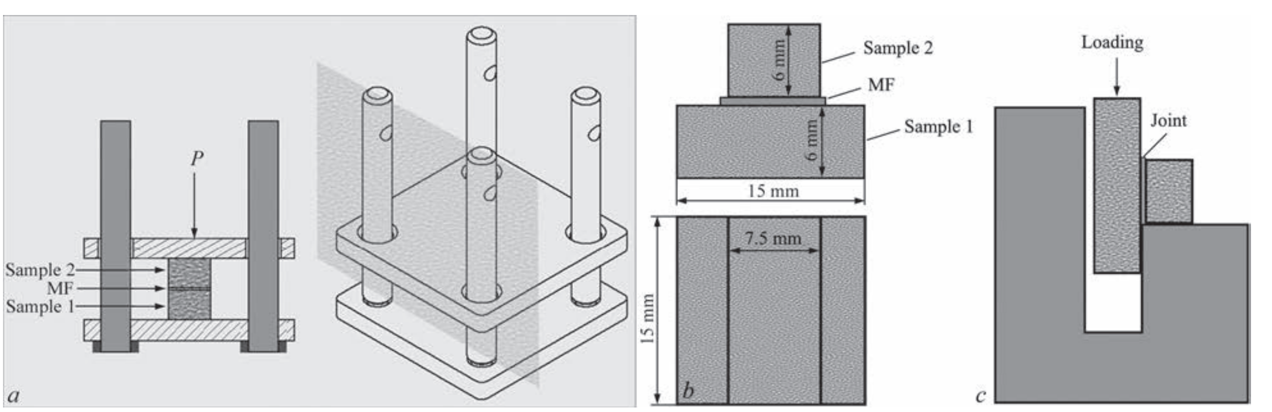


Figure 3. Schematic image of the fixture for conducting the bonding process (*a*), samples (*b*) and fixture for shear testing (*c*)

Table 2. Properties of joints produced in different modes

MF number	Temperature, °C	Duration, min	Diffusion zone width, μm	Shear strength τ, MPa
1	920	60	120	180
	950	60	150	190
2	920	60	123	160
	950	60	190	409
3	920	60	190	453
	950	60	250	532

action interaction of MF components at heating and counter diffusion of copper and titanium on MF/alloy interface. The thickness and phase composition of the intermetallic layer were determined by MF chemical composition and heating temperature. At temperature rise the intermetallic layer thickness decreases and its fragmentation takes place. Its simultaneous enrichment in titanium leads to formation of Ti_2Cu intermetallic. Note that the intensity of diffusion mixing of titanium and copper at application of MF No. 2 is two times higher. This is attributable to increase of the

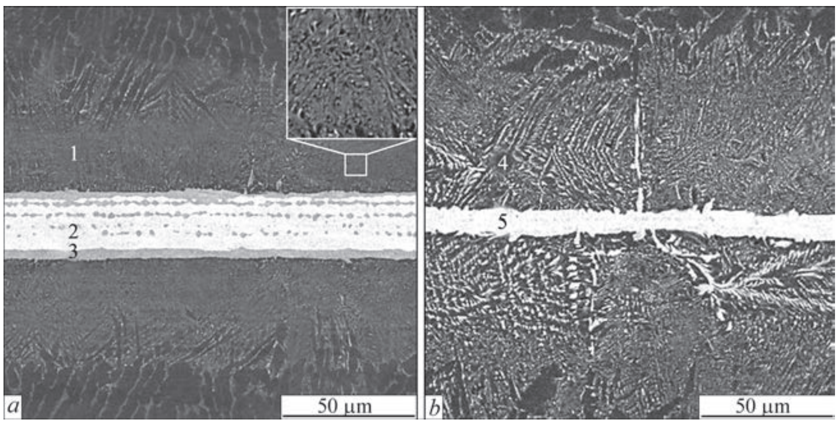


Figure 4. Microstructure of the joints produced using intermediate MF No. 1 in the following modes: 920 °C, 60 min (*a*) and 950 °C, 60 min (*b*)

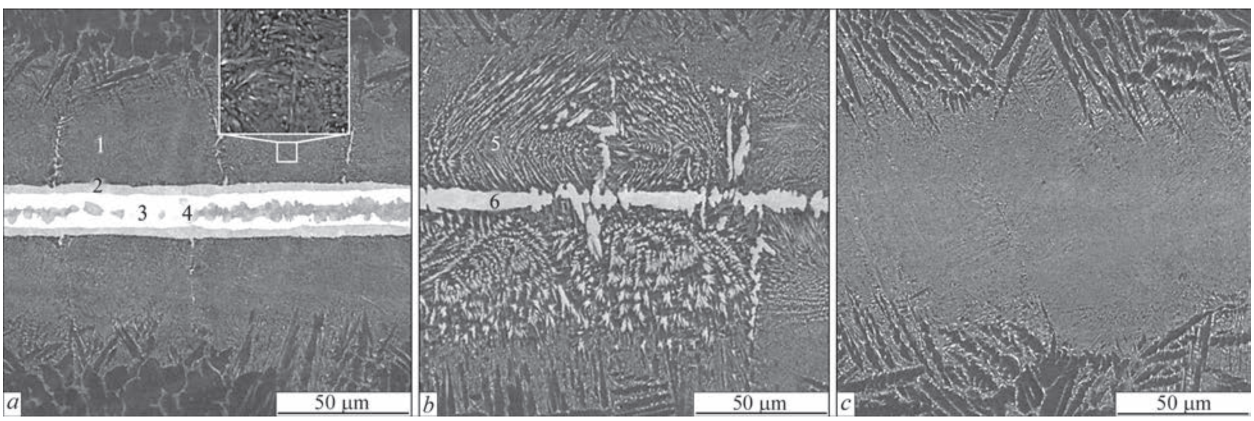


Figure 5. Microstructure of joints produced with application of intermediate MF No. 2 in the following modes: 920 °C, 60 min (*a*), 950 °C, 60 min (*b*), 980 °C, 30 min (***c***)

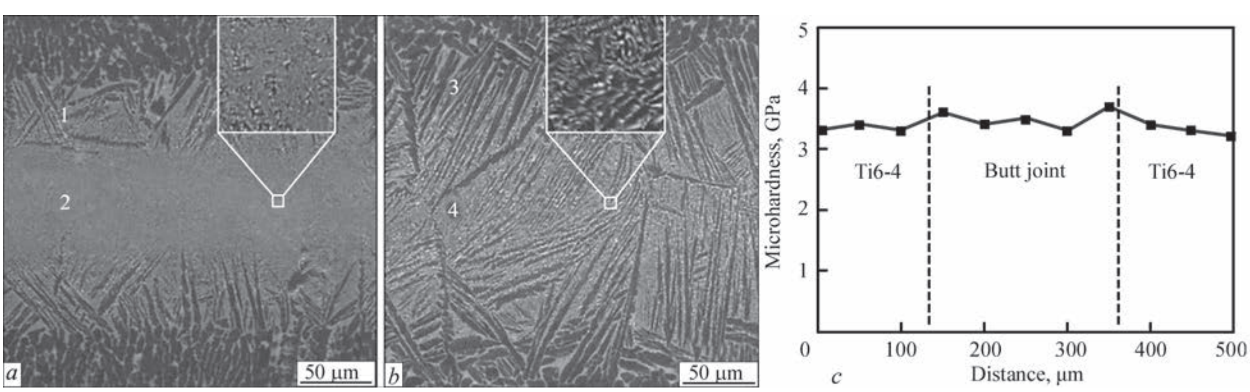


Figure 6. Microstructure of joints produced with application of intermediate MF No. 3 in the following modes: 920 °C, 60 min (*a*) and 950 °C, 60 min (*b*) and microhardness distribution in the butt joint (*c*)

Table 3. Chemical and phase composition of regions of the joints in Figure 4

Region	Chemical composition, at.%				Phase composition	*HV*20, GPa
	Al	Ti	V	Cu		
1	7.81	80.6	3.1	8.49	α-Ti+Ti_2Cu	3.7
2	–	53.96	–	46.04	TiCu+Ti_2Cu	3.4
3	1.95	66.4	–	31.65	Ti_2Cu	–
4	7.31	80.11	2.54	10.04	α-Ti+Ti_2Cu	3.8
5	2.37	67.69	–	29.94	Ti_2Cu	3.0

Table 4. Chemical and phase composition of joint regions in Figure 5

Region	Chemical composition, at.%				Phase composition	*HV*20, GPa
	Al	Ti	V	Cu		
1	8.95	77.29	4.21	9.55	α-Ti+Ti_2Cu	3.7
2	2.43	65.66	–	31.91	Ti_2Cu	–
3	–	50.43	–	49.57	TiCu	3.2
4	7.6	59.09	–	33.31	Ti_2Cu	3.0
5	8.64	77.53	3.57	10.27	α-Ti+Ti_2Cu	3.9
6	2.7	66.81	–	30.49	Ti_2Cu	3.2

Table 5. Chemical and phase composition of regions of the joints in Figure 6

Region	Chemical composition, at.%					Phase composition
	Al	Ti	V	Ni	Cu	
1	7.86	82.03	3.51	3.35	3.25	α-Ti+Ti_2Cu+Ti_2Ni
2	5.99	81.52	2.52	4.03	5.94	
3	9.44	83.87	3.64	1.47	1.59	
4	8.07	82.46	2.5	2.61	4.35	

volume fraction of the liquid phase in the butt joint at heating temperature of 920–950 °C that is ensured by smaller melting range of MF No. 2 (Table 1).

Intermetallic layer formation in the butt joint can be explained as follows. At Ti–Cu MF heating up to the melting temperature appearance of the liquid phase in the butt joint promotes titanium diffusion from the alloy into the interlayer, leading to formation of excess TiCu and Ti_2Cu intermetallics with melting temperature higher than that of the bonding process. We can assume that this leads to reduction of the liquid phase volume fraction in the butt and limits diffusion mixing of the components. This assumption is supported by absence of an intermetallic layer in the joint produced at the temperature of 980 °C (Figure 5, *c*) that is higher than the melting temperature of TiCu and Ti_2Cu intermetallics. Copper diffusion into the titanium alloy leads to lowering of α↔β transformation temperature. It results in βTi decomposition in the diffusion zone during cooling by an eutectoid reaction of βTi→αTi+Ti_2Cu with formation of an eutectoid of hyper eutectoid composition with a dispersed structure (region 1 and its enlarged view in Figures 4, *a* and 5, *a*), the phase components of which become larger at temperature rise (regions 4 in Figures 4, *b* and 5, *b*). A region with Widmanstatten structure forms between the region of eutectic structure and Ti6-4, as a result of βTi transformation into acicular αTi.

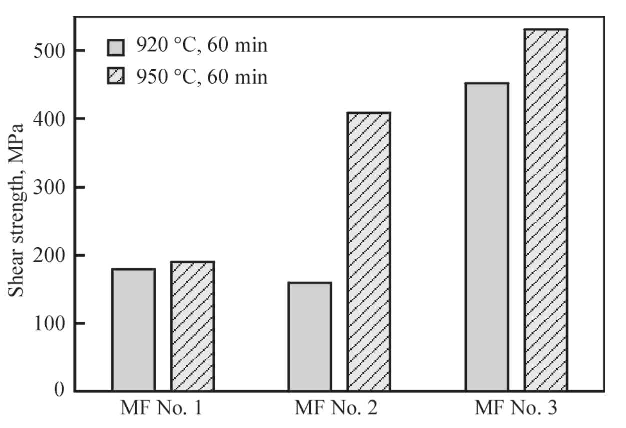


Figure 7. Shear strength of the joints

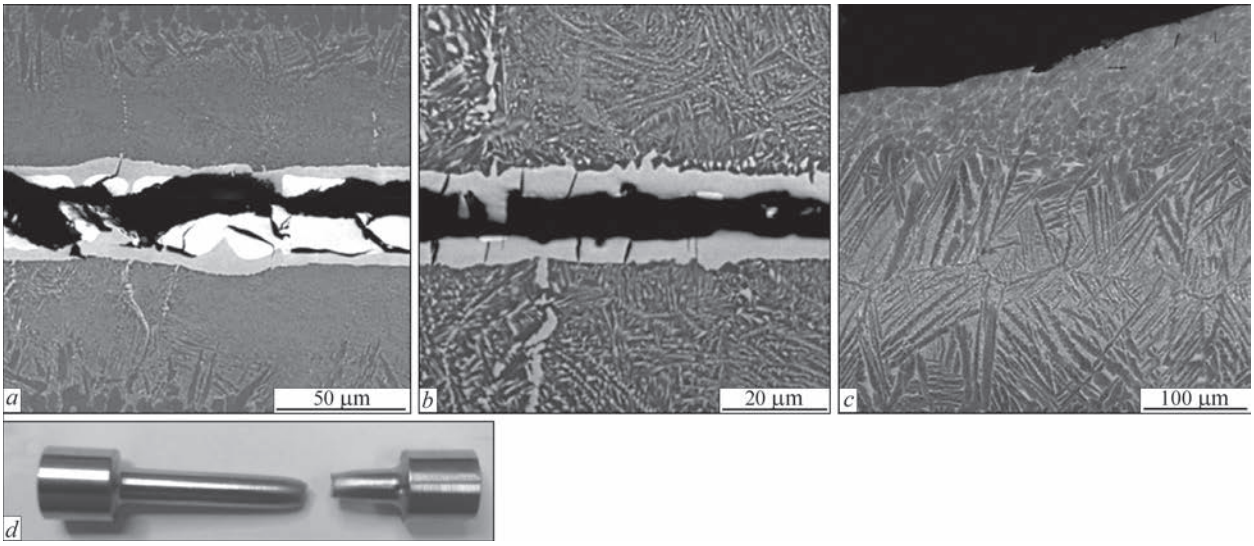


Figure 8. Joint microstructure after shear testing: MF No. 1, T = 920 °C (*a*), MF No. 1, T = 950 °C (*b*), MF No. 3, T = 950 °C (*c*) and sample image (MF, No. 3, T = 950 °C) after tensile testing (*d*)

No formation of an intermetallic layer in the butt joint is observed at Ti6-4 alloy bonding through MF No. 3 at the temperature of 920 and 950 °C (Figure 6).

It can be assumed that a significant volume of the liquid phase of a homogeneous composition forms at foil melting that is indicative of a narrow melting range of the foil (Table 1). This ensures intensive diffusion mixing between the foil and alloy components and formation of a continuous βTi interlayer in the butt joint as a result of a lowering of α→β transformation temperature. Two structural regions form in the joint at cooling. In the joint central part (regions 2, 4 in Figure 6, *a*, *b*) an eutectoid with a dispersed structure forms by eutectoid reaction of $\beta Ti \rightarrow \alpha Ti + Ti_2(Cu) + Ti_2(Ni)$. A region with Widmanstatten structure is present between the eutectoid region and the alloy metal. At increase of process temperature, a coarsening of structural components of the regions takes place (Figure 6, *b*). On the other hand, temperature rise ensures an increase of the intensity of diffusion mixing of MF and alloy components and of the diffusion zone width and formation of the Widmanstatten structure over its entire width that promotes the homogeneity of the chemical composition and microhardness of the butt joint (Figure 6, *b*, *c*).

Shear testing of the joints was conducted to assess their mechanical properties. Figure 7 shows a comparative diagram of shear strength of the joints produced at application of different MF.

One can see that formation of a continuous intermetallic layer in the butt joint results in the low strength of the joint. The latter fails in the area of the intermetallic layer (Figure 8, *a*, *b*), which has the microhardness lower than that of the adjacent regions (Tables 3, 4). One can assume that formation of Ti_2Cu and TiCu intermetallics as a result of reaction diffusion of titanium and copper at heating is accompanied by formation of vacancy type defects and pores, owing to volume effect at phase transformations. Note that formation of a fragmented intermetallic interlayer in the butt joint (Figure 5, *b*) promotes an increase of the joint shear strength. Absence of an intermetallic interlayer in the butt joint and formation of a homogeneous structure of the diffusion zone ensures an increase of the joint mechanical properties. So, the highest shear strength (532 MPa) and tensile strength (930 MPa) is demonstrated by the joint produced using MF No. 3 at the temperature of 950 °C, in which the content of intermetallic-forming components (Ni+Cu) in the butt joint is < 7 at.%. The joint strength corresponds to the strength level of Ti6-4 alloy (σ = 935 MPa in tensile testing) that is ensured by homogeneity of mechanical properties of the joint regions (Figure 6, *c*).

At shear and tensile testing the joint fails in the region of Ti6-4 alloy (Figure 8, *c*, *d*). Our result is in agreement with experimental data of the authors of [15] obtained at brazing Ti6-4 alloy using traditional Ti–Zr–Ni–Cu braze alloys at the temperature of 950–990 °C. The advantage of the diffusion bonding method with application of an intermediate MF layer of eutectic composition is the possibility of lowering the temperature required to produce an equal-strength and defect-free joint of the titanium alloy.

CONCLUSIONS

1. Application of intermediate multilayers of eutectic composition based on Ti–Cu and Ti–Cu–Ni systems ensures production of a permanent and defect-free joint of Ti6-4 alloy by the method of diffusion bonding at the temperature of 920–950 °C.

2. Joint microstructure depends on MF temperature and melting range, and it is determined by reac-

tion interaction of the foil and titanium alloy components at heating. Formation of a layer of Ti_2Cu and TiCu intermetallics in the butt joint leads to lowering of the joint mechanical properties.

3. Producing a joint with shear and tensile strength matching that of Ti6-4 alloy, is ensured by formation in the butt of a dispersed Widmanstatten structure with copper and nickel content < 7 at.% and homogeneous microhardness distribution.

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ORCID

T.V. Melnychenko: 0000-0002-1460-5532,
A.I. Ustinov: 0000-0002-8855-3499,
O.Yu. Klepko: 0000-0003-2014-1938

CONFLICT OF INTEREST

The Authors declare no conflict of interest

CORRESPONDING AUTHOR

T.V. Melnychenko
E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine.
E-mail: melnychenko21@ukr.net

SUGGESTED CITATION

T.V. Melnychenko, A.I. Ustinov, O.Yu. Klepko, O.V. Samofalov (2025) Diffusion bonding of Ti6-4 alloy through multilayer interlayers of an eutectic composition based on Ti–Cu system. *The Paton Welding J.*, **1**, 3–9.
DOI: https://doi.org/10.37434/tpwj2025.01.01

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Received: 31.07.2024
Received in revised form: 23.10.2024
Accepted: 23.01.2025