DOI: https://doi.org/10.37434/tpwj2024.09.02

PHASE AND STRUCTURAL TRANSFORMATIONS DURING HEATING OF MULTILAYER Ti/Cu FOILS OF EUTECTIC COMPOSITION OBTAINED BY THE EBPVD METHOD

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ABSTRACT

Phase and structural transformations in multilayer Ti/Cu foils of eutectic Composition I (Ti50–Cu50 wt.%) and Composition II (Ti22–Cu78 wt.%), obtained by layer-by-layer electron beam physical vapor deposition of components in vacuum, were investigated using differential thermal analysis (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) methods. It was found that during heating of the multilayer foils in the temperature range of 400–600 °C, due to the diffusion interaction between Ti and Cu layers, the following intermetallic compounds are formed: Cu_4Ti, Cu_4Ti_3, CuTi, and $CuTi_2$ in Composition I foils, and Cu_4Ti and Cu_4Ti_3 in Composition II foils. Upon further heating, melting of the multilayer foils of both eutectic compositions occurs. The Composition II foils begin to melt at a temperature of 879 °C, close to the equilibrium melting temperature of the eutectic alloy of the same composition (875 °C), while in the case of Composition I foils, the onset of melting occurs at a temperature of 915 °C, which is lower compared to the melting temperature of the eutectic alloy of Composition I (960 °C). Considering that Cu_4Ti and Cu_4Ti_3 metastable phases are formed in multilayer Composition I foils, which are components of the more fusible eutectic of Composition II, the reduction in the melting temperature of the foil may be due to its metastable structure. Such behavior of multilayer Ti/Cu foil of eutectic Composition I may facilitate softening of the temperature conditions required to establish physical contact in the material bonding zone during their reactive brazing.

KEYWORDS: Ti–Cu alloys, eutectic, electron beam physical vapor deposition, vacuum condensates, multilayer structures, phase transformations, melting

INTRODUCTION

It is known that multilayer foils (MF), consisting of interlayers of reactive components, are characterized by a pronounced heterogeneous structure and a considerable margin of internal energy: excess chemical energy, energy of elastic stresses in the layers, free energy of interphase boundaries [1, 2]. MF heating promotes solid phase reactions in it, running at a high rate. Nature of phase transformations in MF is determined by reaction interaction of the layer components, layer thickness, method of producing the foil, and it differs from the equilibrium one due to a considerable area of the contact zone between the components and a large number of grain boundaries in the layers [3]. The features of phase transformations and formation of the specific structural-phase state (presence of metastable phases, multiphase composition, structural elements of the nanoscale size, defects of vacancy type and pores) determine the physical properties of the foil and direction of its practical application. So, considerable heat evolution at running of SHS reaction, initiated by foil heating, which consists of layers of intermetallic forming components, allows using such MF as a local heat source at high-speed brazing [4, 5]. Formation of the nanostructured components and pores at MF heating ensures low-temperature plastic deformation of the foil under the conditions of thermomechanical loading, which determines the possibility of its application as an interlayer at diffusion welding of materials that are difficult to deform [6, 7]. On the other hand, formation of nanostructured and metastable components can lead to lowering of the temperature of phase and structural transformations at MF heating [8]. It may be useful at application of MF, which consists of layers of components of eutectic systems, as braze alloy at brazing of materials sensitive to thermal impact. From this viewpoint, MF of Ti–Cu system should be noted, the components of which are the base of the known braze alloys (for instance, Ticuni 70, BTi-1, MBF 5012, etc.) for brazing various materials.

The authors of [9] showed that in Ti/Cu contact reaction pair at its heating an interlayer of liquid based on a copper-enriched eutectic forms first, in keeping with the constitutional diagram. In view of that it can be assumed that the beginning of Ti/Cu MF melting will occur at the temperature of low-temperature eutectic transformation (875 °C in keeping with the constitutional diagram). Thus, it is possible to optimize the brazing process: lower the brazing temperature, reduce the braze alloy thickness through application of thin foil, and reduce the concentrational inhomo-

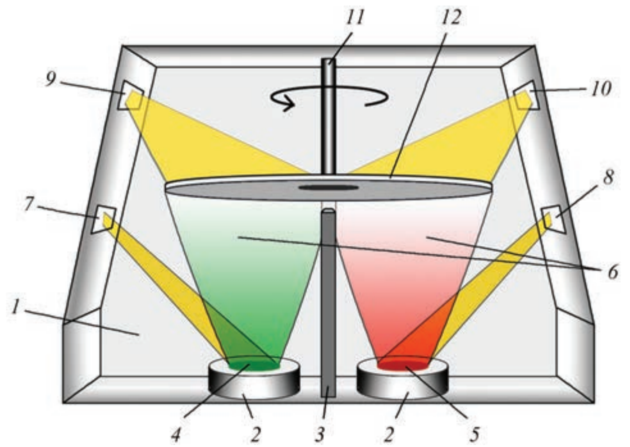

Figure 1. Scheme of electron beam deposition of condensates with a multilayer structure: *1* — work chamber; *2* — water-cooled crucibles; *3* — screen non-transparent for the vapour phase; *4*, *5* — titanium and copper ingots, respectively; *6* — vapour flows; *7*, *8* — electron beam guns for evaporation; *9*, *10* — electron beam guns for substrate heating; *11* — substrate holders; *12* — rotating substrate

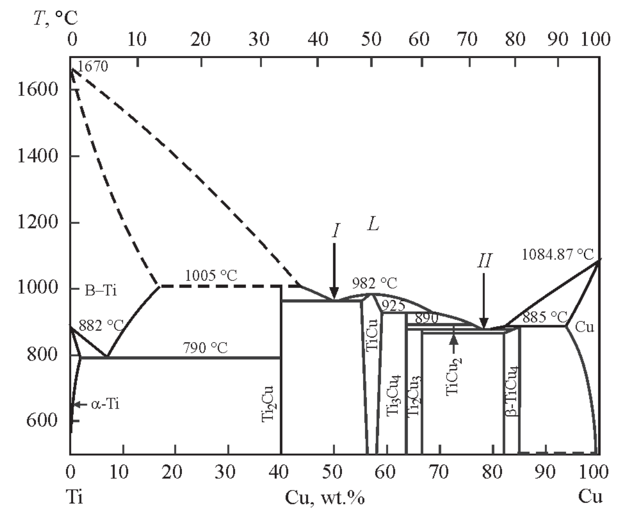

Figure 2. Ti–Cu binary alloy phase diagram [11]

geneity of the joint. In order to determine the nature of phase transformations in Ti/Cu MF, a study of the influence of layer thickness (layer period) and chemical composition of the foil produced by electron beam deposition of the component vapour phases, on the regularities of formation of its structure and phase composition at heating.

EXPERIMENTAL STUDIES

Ti/Cu MF were produced by the method of electron beam deposition of the components, in keeping with the scheme given in Figure 1.

Vapour flows, forming at evaporation of Ti and Cu ingots, are simultaneously deposited on a substrate rotating around the vertical axis in a vacuum chamber. An impermeable screen is mounted between the crucibles to prevent mixing of their vapour flows. As the substrate rotates, each section of it sequentially passes over the crucibles, which is accompanied by the deposition of the corresponding metal layer onto the substrate surface. The ratio of thicknesses of the layer components with such a deposition scheme is determined by the ratio of their evaporation velocities, and the period of modulation of the multilayer structure (sum of thicknesses for the two adjacent component layers) is determined by the speed of substrate rotation. Multilayer foils with the required component ratio were produced by changing the ratio of evaporation rates of each of the ingots, and the structure modulation period was varied at the change of the speed of rotation. To prevent diffusion interaction of the components during the deposition of vapor flows, the substrate temperature was stabilized at 200 °C.

Microstructural characteristics of the materials were studied by SEM method, using CamScan 4 electron microscope, fitted with energy-dispersive spectrometer EDS-200, on transverse sections prepared by the standard procedure of machining the surfaces in Struers Company equipment. Phase composition was studied by the method of XRD analysis in DRON-4M diffractometer in K_α radiation of the copper anode.

Temperature ranges of the phase and structural transformations in the investigated materials were studied by the method of differential thermal analysis in VDTA-2000 unit [10]. Specimens heating was conducted in the helium atmosphere at the rate of 20 °C/min.

In keeping with the phase diagram (Figure 2) [11], Ti–Cu system is characterized by existence of two alloys of an eutectic composition: eutectic I — at Ti50–Cu50 (wt.%) ratio with melting temperature of 960 °C and eutectic II with Ti22–Cu78 (wt.%) and melting temperature of 875 °C. In view of that, MF with component ratio corresponding to eutectic I and eutectic II were prepared for investigations (Table 1).

Table 1. Characteristics of manufactured MF and ingots

Eutectic alloy type	Foil/ingot number	Layer alternation period (Ti + Cu), nm	Ti		Cu	
			wt.%	at.%	wt.%	at.%
Eutectic I	Ingot I	–	49.9	56.9	50.1	43.1
	No. 1	500	48.7	55.8	51.3	44.2
	No. 2	150	47.5	54.6	52.5	45.4
Eutectic II	Ingot II	–	21.8	27.0	78.2	73.0
	No. 3	700	20.4	25.4	79.6	74.6

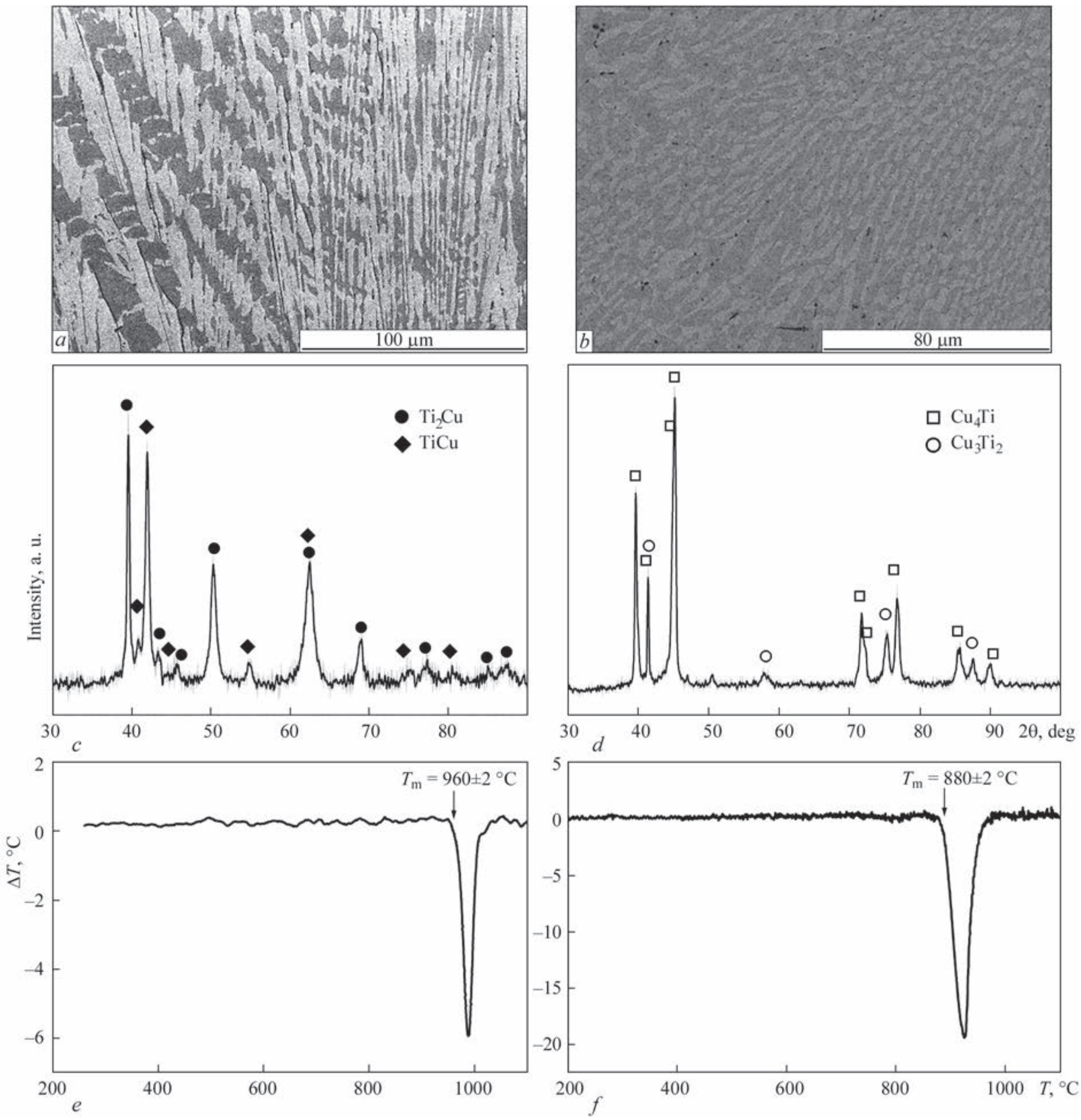

Figure 3. SEM image (*a*, *b*), diffraction patterns (*c*, *d*) and DTA thermograms of the produced Ti–Cu ingots of eutectic composition I and eutectic composition II, respectively

Investigations of the features of running of phase and structural transformations were conducted in comparison with cast ingots of Ti–Cu alloys of eutectic composition I and II (Figure 2, Table 1). Ingots were produced by the method of double electron beam remelting. Copper of M0k grade and VT1-0 titanium were used as the charge.

Cross-sectional microstructure of the prepared ingots is given in Figure 3, *a*, *b*. One can see that both the ingots have a microstructure characteristic for eutectic alloys and have two components, differing by their contrast. Chemical analysis of the sections showed that in the case of ingot 1 (Figure 3, *a*) the light-coloured regions have $Ti_{43.4}Cu_{56.6}$, composition, dark-coloured regions are $Ti_{60.2}Cu_{39.8}$, and in the case of ingot 2 (Figure 3*, b*) $Ti_{17.5}Cu_{82.5}$ composition corresponds to light regions, and $Ti_{25.7}Cu_{74.3}$ — to dark regions. X-ray diffraction analysis showed that ingot 1 consists of two phases: Ti_2Cu and TiCu (Figure 3, *c*) and ingot 2 consists of Cu_4Ti and Cu_3Ti_2 phases (Figure 3, *d*). DTA showed that the melting temperature of ingot 1 is equal to 959±2 °C (Figure 3, *e*), and that of ingot 2 is 880±2 °C (Figure 3, *f*). Maximal melting rate is observed at the temperature close to 900 °C. Complete melting of the ingot occurs at heating up to 920 °C temperature.

Thus, in keeping with the equilibrium phase diagram of Ti–Cu system, the chemical phase compositions of the produced ingots 1 and 2 correspond to eutectic alloys I and II, respectively (Figure 2).

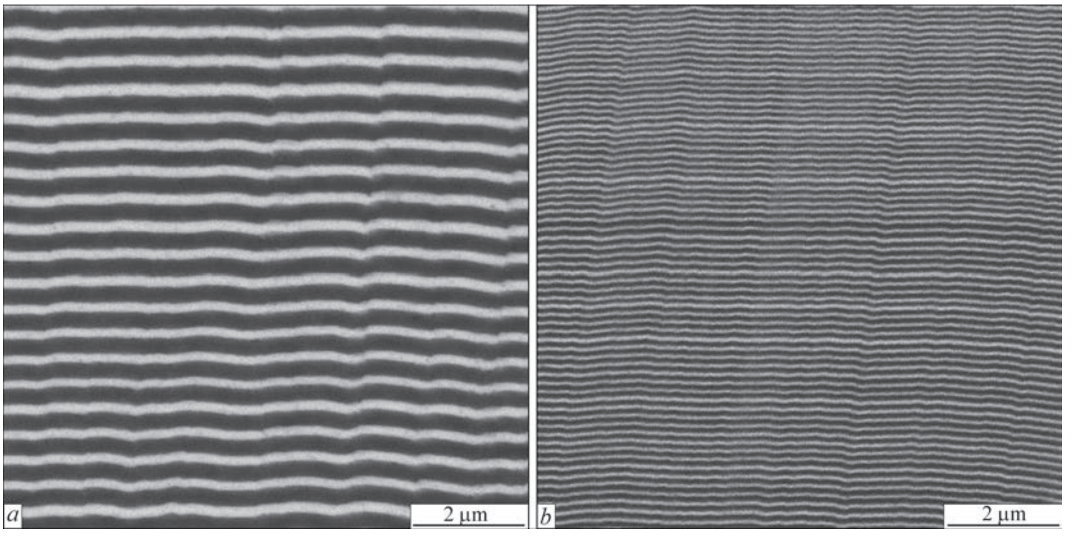

Figure 4. SEM images of the cross-section of Ti/Cu MF No. 1 (*a*) and No. 2 (*b*): dark layers — Ti; light layers — Cu

RESULTS AND THEIR DISCUSSION

Electron microscopic image of the characteristic microstructure of the produced Ti/Cu MF with different period of component layer alternation is given in Figure 4. One can see that the foil structure consists of layers with clearcut boundaries. There are no precipitates of other phases or structural defects such as pores or cracks on the layer interfaces.

X-ray diffraction analysis of as-deposited MF revealed the presence of diffraction peaks from just copper and titanium (Figure 5). This is indicative of a perfect physical contact between the layers of titanium and copper. The discrepancy between the experimentally revealed and theoretical intensity of the diffraction peaks is the consequence of formation of the crystallographic texture in the layers during deposition.

Figure 6, *a* gives a thermogram of Ti/Cu MF No. 3, in which the ratio of the components corresponds to eutectic composition II. One can see that unlike the ingot thermogram of the same chemical composition (Figure 3, *f*), a heat evolution peak is observed in the temperature range of 450–520 °C. In keeping with the diffraction studies after foil heating up to the temperature of 700 °C (higher than the heat evolution maximum), a change in its phase composition takes place compared with the initial condition. Diffraction peaks from titanium disappear, and peaks correspond-

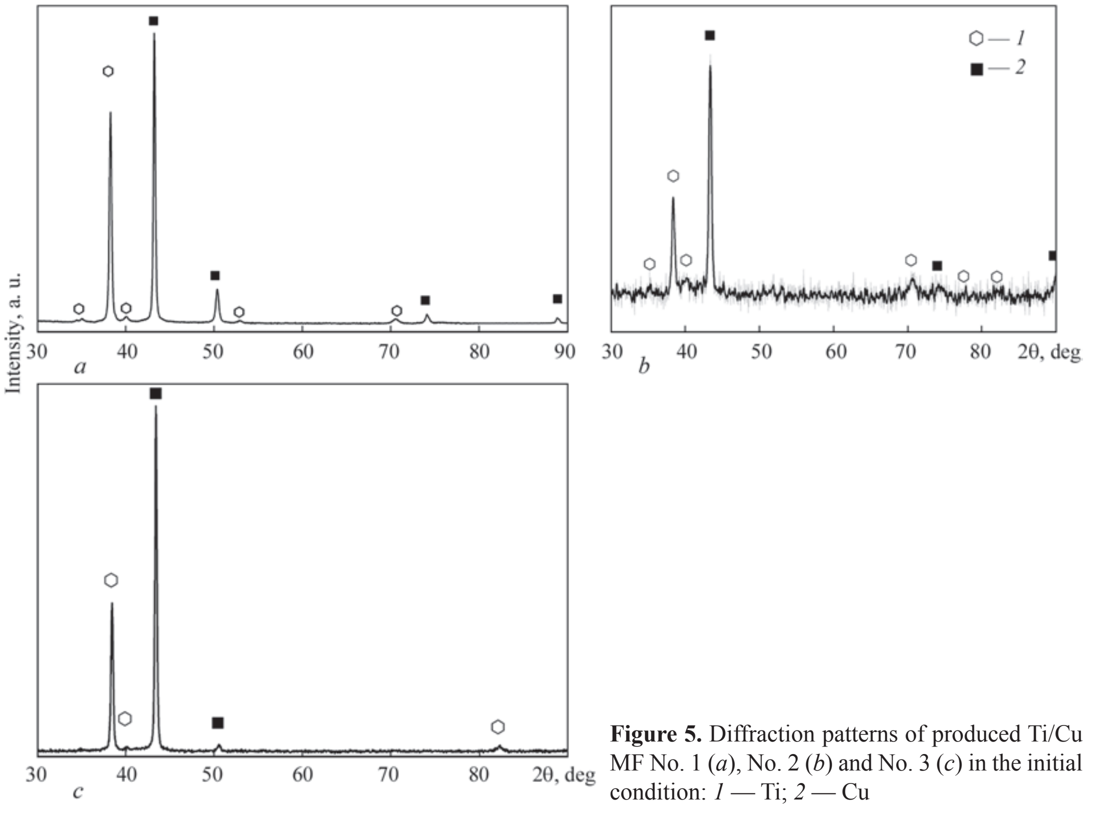

Figure 5. Diffraction patterns of produced Ti/Cu MF No. 1 (*a*), No. 2 (*b*) and No. 3 (*c*) in the initial condition: *1* — Ti; *2* — Cu

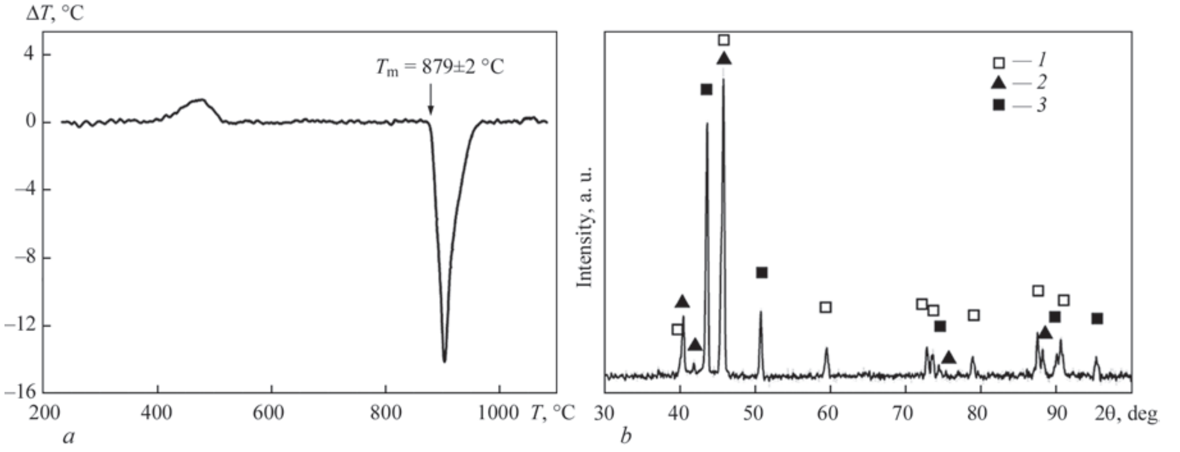

Figure 6. DTA thermogram of MF No. 3 (*a*) and its diffraction pattern after heating to the temperature of 700 °C (*b*): *1* — Cu_4Ti; *2* — Cu_4Ti_3; *3* — Cu

ing to Cu_4Ti and Cu_4Ti_3 intermetallic compounds are formed. Peaks from copper are also present in the diffraction pattern, which may be indicative of incomplete running of phase transformations, because of short duration of annealing or the need for heating to a higher temperature. At the same time in keeping with the phase diagram, Cu_4Ti_3 and Cu_3Ti_2 intermetallics have close chemical composition and crystalline structure, so that it can be assumed that longer annealing or heating to higher temperatures ensures an interaction of residual copper with Cu_4Ti_3 phase. As a result of such an interaction, a phase composition of Cu_4Ti and Cu_3Ti_2 forms, which corresponds to components of eutectic of composition II. This is confirmed by DTA data, according to which melting of MF No. 3 occurs at the temperature of 879±2 °C, which practically coincides with melting temperature of ingot No. 2 of the same chemical composition.

At heating of MF No. 1, where the ratio of the components corresponds to eutectic composition I a heat evolution maximum is also observed in the temperature range of 450–600 °C on DTA thermogram (Figure 7). At further heating, unlike an ingot of the same chemical composition (Figure 3, *e*), MF melting begins at the temperature of 915±2 °C, and at the temperature of 959±2 °C the melting process becomes much more intensive. The melting process is over at the temperature close to 1060±2 °C.

In keeping with the data of X-ray diffraction analysis at heating of MF No.1 to the temperature of 700 °C synthesis of a number of intermetallic compounds occurs through solid-phase reactions: $TiCu_4$, Ti_2Cu_3, Ti_2Cu and TiCu. Thus, the start of melting of MF No.1 with an averaged chemical composition, corresponding to eutectic I, at a lower temperature (compared to the ingot) can be the result of interaction between regions in MF, where $TiCu_4$ and Ti_2Cu_3 intermetallic compounds formed, which are the components of eutectic II. As the volume fraction of these phases is much smaller than that of Ti_2Cu and TiCu, the volume of molten metal and the respective thermal effect in the thermogram will be small.

In keeping with the theoretical models of melting of eutectic alloys, formation of the liquid phase occurs in regions of physical contact of the eutectic components at temperature lower than the melting temperature of each of the components [12, 13]. Formation of regions of physical contact creates the nec-

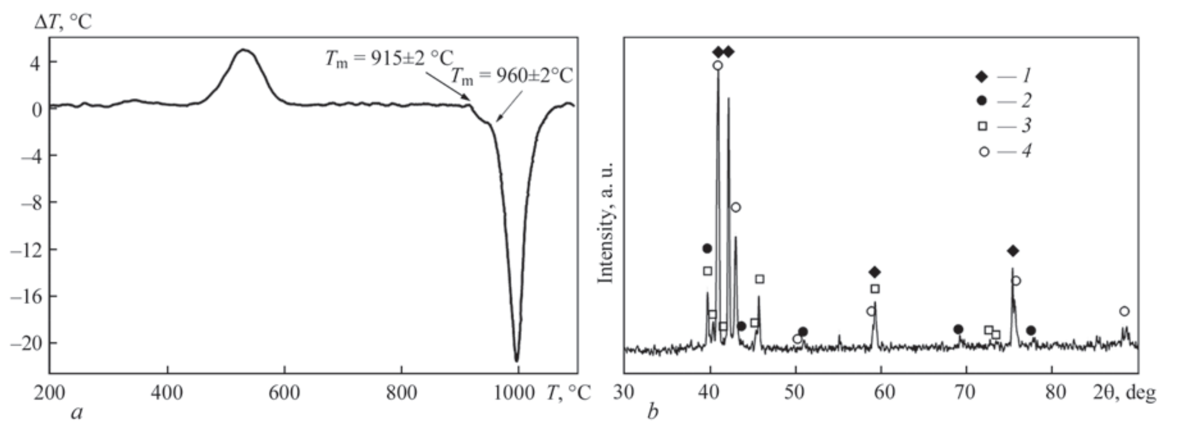

Figure 7. DTA thermogram of MF No. 1 (*a*) and its diffraction pattern after heating to the temperature of 700 °C (*b*): *1* — TiCu; *2* — Ti_2Cu; *3* — Cu_4Ti; *4* — Cu_3Ti_2

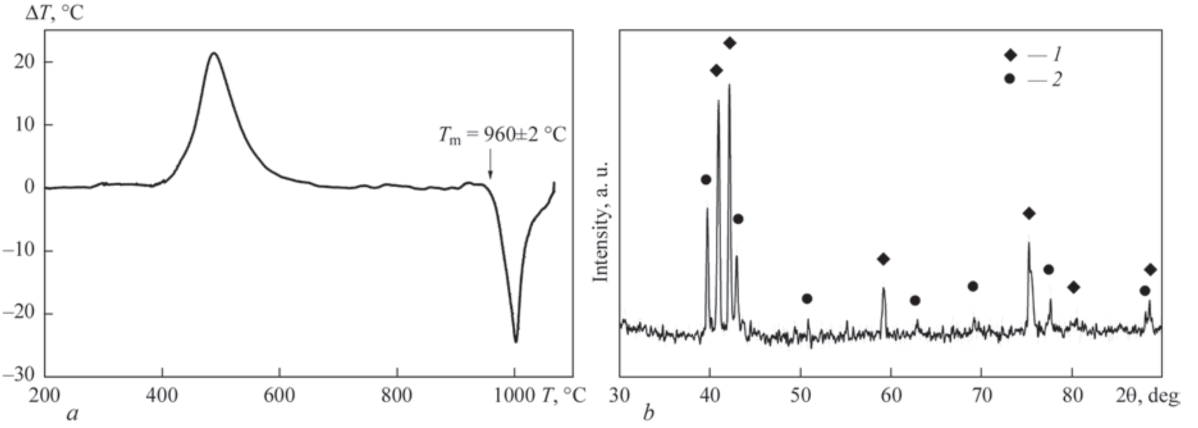

Figure 8. DTA thermogram of MF No. 2 (*a*) and its diffraction pattern after heating to the temperature of 700 °C (*b*): *1* — TiCu; *2* — Ti_2Cu

essary conditions for diffusion interaction between the components, resulting in appearance on the physical contact boundary of diffusion-related volumes of these components, where the chemical composition is close to that of the eutectic [14]. At eutectic temperature such dipoles provide the conditions necessary for appearance of liquid phase nucleus of a critical size on their base. Here, the proportion of the components contacting in the macrovolume is not important. It is clear that the volume fraction of the melt forming in the contact depends on how effectively the established contact will promote diffusion interaction between the components, as well as on the contact area.

Considering that Ti/Cu MF form under vacuum, there are no barriers for their diffusion interaction in the contacts between Ti and Cu layers over the entire area, and the density of contact surfaces per a unit of volume is inversely proportional to layer modulation period, it was anticipated that the volume fraction of the liquid phase can be increased by an order through increase of the number of boundaries between MF component layers due to reduction of the layered structure modulation period, i.e. presence of multiple contacts between MF components with an averaged component ratio, which corresponds to eutectic I, will promote its melting beginning at a temperature close to that of melting of the lower melting eutectic II.

To check this assumption, MF No. 2 with layer modulation period of 150 nm and component ratio close to the composition of eutectic I was studied.

One can see from DTA thermogram from MF No. 2 (Figure 8, *a*) that a heat evolution peak is present in the temperature range from 440 to 600 °C, similar to MF No. 1. At further heating of MF No. 2, however, its melting occurs at the temperature of 960 °C that corresponds to equilibrium melting temperature of the alloy of eutectic composition I. In this case, no low-temperature melting is observed. Results of X-ray diffraction studies of MF No. 2 showed that at heating up to the temperature of 700 °C (Figure 8, *b*) just two intermetallic compounds Ti_2Cu and TiCu form as a result of diffusion interaction. No diffraction indications of formation of additional $TiCu_4$ and Ti_2Cu_3

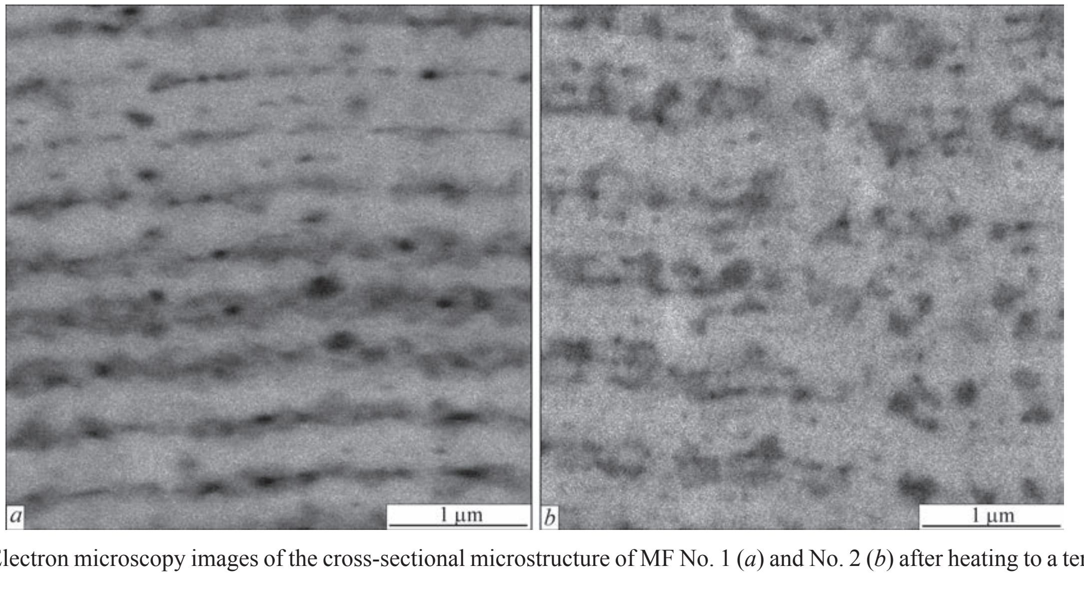

Figure 9. Electron microscopy images of the cross-sectional microstructure of MF No. 1 (*a*) and No. 2 (*b*) after heating to a temperature of 700 °C

intermetallics which are components of low-temperature eutectic II were revealed.

Electron microscopy images of cross-sectional microstructure of MF Nos 1 and 2 after heating up to the temperature of 700 °C are given in Figure 9. In the case of MF No. 1 (Figure 9, *a*) the layered structure is readily visible after heating, but precipitates in the form of individual particles and interlayers, differing by their contrast, appeared in place of titanium layers. On the whole, as one can see from images of MF microstructure, after formation of intermetallic compounds in it component distribution over the foil thickness is rather non-uniform. Analysis of the image of MF No. 2 microstructure (Figure 9, *b*) shows that reduction of the period of layer alternation leads to a more intensive diffusion mixing of the components during heating, which results in the layered structure becoming similar to the composite one (light-coloured regions as matrix, incorporating the dark-coloured inclusions).

Thus, attempts to increase the volume fraction of liquid phase formation in MF through reduction of the layer alternation period will promote more active running of the diffusion interaction between the layer components. It may lead to complete mixing of the component layers in the solid phase and to formation of quasi-equilibrium structure with phase composition of eutectic I already at the stage of heating at temperatures below the melting temperature of eutectic II. As a result, the MF melting temperature will correspond to its chemical composition, i.e. melting will start at the temperature of 960 °C.

In view of that it can be assumed that the layer modulation period should be greater than a certain value that will allow ensuring the conditions for preservation of a metastable structure, forming in the contact zone at the initial stages of diffusion interaction of the components, up to higher temperatures.

Thus, to ensure the conditions necessary for lowering the melting onset temperature of multilayer Ti/Cu foils with eutectic composition I, the modulation period of the layered structure must be greater than a certain critical value, at which the heterogeneous distribution of components across the thickness of the foil will be maintained up to the melting temperature of the more easily fusible eutectic II. It can be assumed that the critical value of the modulation period of the layered structure will depend on the foil heating rate. At lowering of the heating rate, the critical value of the modulation period should become greater.

Lowering of the temperature of the start of melting of MF of eutectic composition I can provide a softening of the conditions of producing permanent joints, both due to lowering of the bonding process temperature, and of the time of soaking at bonding temperature. The latter will be promoted by diffusion mobility of MF components due to heterogeneity and intensive process of intermetallic synthesis. Such a softening of the conditions of producing the joints will prevent lowering of the strength of materials being joined, for instance for titanium alloys after thermomechanical treatment, and reduction of the soaking time at a high temperature will promote preservation of their initial structural state.

CONCLUSIONS

1. It is shown for the first time that the start of melting of Ti/Cu MF with component ratio corresponding to high-temperature eutectic of Ti50–Cu50 (wt.%) composition can take place at a lower temperature, close to melting temperature of low-temperature eutectic of Ti28–Cu78 (wt.%) composition.

2. Lowering of melting temperature of MF of eutectic composition I can be related to formation of a heterogeneous structural state during heating, the composition of which includes metastable $TiCu_4$ and Ti_2Cu_3 intermetallics, which are components of low-temperature eutectic II.

3. To ensure a lowering of melting temperature of MF of eutectic composition I (Ti50–Cu50) the layered structure modulation period should be greater than a certain critical value, which will promote complete mixing of the component layers during heating and formation of the foil homogeneous structure up to the melting temperature of the low-melting eutectic.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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SUGGESTED CITATION

S.O. Demchenkov, T.V. Melnychenko, A.I. Ustinov, O.E. Rudenko, O.V. Samofalov (2024) Phase and structural transformations during heating of multilayer Ti/Cu foils of eutectic composition obtained by the EBPVD method.
The Paton Welding J., **9**, 12–19.
DOI: https://doi.org/10.37434/tpwj2024.09.02

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Received: 05.03.2024
Received in revised form: 06.06.2024
Accepted: 25.09.2024