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# VACUUM BRAZING OF KOVAR–MOLYBDENUM DISSIMILAR JOINTS

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The features of spreading of brazing filler metals of Cu–Mn–Co system over molybdenum and Kovar were established based on the performed studies. Micro X-ray spectral analysis determined that zonal crystallization of a brazing filler metal drop on the base metal substrate occurs during spreading: pronounced areas of copper-based solid solution (Cu–12.92Mn–4.69Co) form along the outer perimeter of the drop, and dendrites of manganese-based solid solution, characterized by a higher melting point, are crystallized in the drop central part. It has been experimentally proven that an increase in the heating temperature contributes to an increase in the spreading area of the brazing filler metal by improving the spreading of copper-based solid solution. It was found that a copper-based solid solution forms in the brazed seam of dissimilar Kovar–molybdenum joints, and a molybdenum-based reaction layer (about 1 μm wide), crystallizes at the molybdenum-brazing filler metal interface. This layer is enriched in cobalt (15.80 %) and manganese (14.12 %) and contains a small amount of copper (1.63 %). As a result of mechanical tests of Kovar–molybdenum overlap joints under static loads at room temperature, destruction occurs partly along the brazed seam and partly along the base metal–molybdenum. 14 Ref., 2 Tables, 6 Figures.

*Keywords: Kovar, molybdenum, vacuum brazing, dissimilar joints, copper-manganese-cobalt alloys, microstructure, strength, spreading*

Individual components from dissimilar materials are often used to obtain certain properties of structures. Producing them by brazing involves a number of problems that is due to chemical composition of the materials being joined, and different physicomechanical properties.

At brazing dissimilar joints of molybdenum-stainless steel (Kovar), it is necessary to take into account the features of each material. Molybdenum belongs to refractory high-temperature materials due to a high melting temperature (2600 °C), and considerable specific strength under the conditions of high temperature. Its brazing is conducted under vacuum or in shielding gases, as it actively reacts with oxygen at heating in air that promotes its oxidation and lowers its mechanical properties [1]. Brazing temperature should not exceed its recrystallization temperature. At transition through recrystallization threshold, molybdenum becomes brittle [2] that is important to take into account at selection of the brazing filler metal and its melting ranges. Moreover, the difference in the coefficients of thermal expansion of both the metals leads to appearance of residual stresses, product deformations and crack initiation [3–5]. Therefore, at their combination copper and its alloys are usually used as brazing filler metal, which act as a damper between the parts being joined and promote relaxation of the arising stresses. Special ductile interlayers can be used, which are effective at joining dissimilar metals, with considerably different physicomechanical properties [4].

Much fewer works are devoted to joining molybdenum to Kovar (Fe–29Ni–17Co), compared to brazing molybdenum to stainless steel. Still, such work has been performed for many years, and it became particularly urgent in connection with development of new units and structural elements in instrument-making. At present, joining dissimilar Kovar–molybdenum materials, designed for high-temperature application, is urgent [5, 6]. Kovar belongs to precision alloys with specified temperature coefficient of linear expansion (TCLA), which is close to that of borosilicate glass [7] that promotes its application in optical instruments operated in a broad temperature range. Brazing of these metals involves problems of a different nature. On the one hand, their TCLA are close: for Kovar it is equal to ~ $4.6–5.29 \cdot 10^{-6}$ $°C^{-1}$ (in the temperature range of 20–400 °C and it grows rapidly with increasing temperature) [8], and for molybdenum it is equal to $5 \cdot 10^{-6}$ $°C^{-1}$ (in the temperature range of 0–100 °C) that is a positive moment when making Kovar–molybdenum brazed joints. On the other hand, however, based on melting diagram of Mo–Fe system one can see that molybdenum and iron have considerable areas of solubility at high temperature. With its

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**Table 1.** Chemical composition of experimental materials, wt.%

| Composition | Fe | C | Si | Ni | Co | Mo |
|---|---|---|---|---|---|---|
| Mo | Up to 0.01 | Up to 0.005 | Up to 0.01 | Up to 0.005 | – | min 99.96 |
| 29NK | 51.14–54.5 | – | – | 28.5–29.5 | 17.0–18.0 | – |

lowering, however, these areas rapidly become narrower and at room temperature the mutual solubility is practically absent. A series of intermetallic phases forms between the considered elements, which can have a negative role, leading to brittleness of the brazed joint [9]. Formation of intermetallic phases has a negative influence on the mechanical properties of dissimilar joints, which were produced by different methods, also by welding [6, 10]. Detailed studies of microstructure of the joints produced at electron beam braze-welding of Kovar with molybdenum showed that three zones form on the joint interphase, where an iron-based and molybdenum-based solid solutions were found, as well as brittle intermetallic phases: $Fe_5Mo_3$, FeMo, which are the cause of brittle fracture and low strength [10].

At vacuum brazing of Kovar to molybdenum (at the temperature of 1115 °C), using pure copper 100 μm thick as brazing filler metal, the joint strength is equal to 72–75 MPa [5].

This work presents the results of investigations on spreading of experimental brazing filler metals of Cu–Mn–Co system on Kovar and molybdenum and features of formation of the structure of dissimilar Kovar–molybdenum brazed joints that were produced by vacuum high-temperature brazing.

**Experimental part**. Molybdenum sheets of MCh grade (3 mm thick) and Kovar precision alloy (2 mm thick, Table 1) were used as base metal to conduct the experiments.

Experimental brazing filler metals were produced on a copper backing in an argon atmosphere with application of arc heating. In order to study the influence of cobalt on solidus and liquidus temperature, a number of experimental alloys of Cu–Mn–(0.5–4.5)Co system were produced and their melting ranges were determined by high-temperature differential thermal analysis (HTDTA) (Table 2), using VDTA-8M3 unit in high-purity helium at the heating rate of 40 °C/min (±5 °C).

In order to conduct the experiments, Cu–Mn–(0.5–4.5)Co polycrystalline alloys in the cast and rolled state were used in the form of a strip of ~ 100 μm thickness.

Experiments on spreading of the studied alloys were conducted on molybdenum substrates of 15×15 mm size. Brazing filler metals in the quantity of 300 mg were placed in the central zone of base metal substrate, heating was conducted in a vacuum furnace with radiation heating at the temperature that exceeds the liquidus temperature by 30 °C at rarefaction of the working space of $1.33 \cdot 10^{-4}$ Pa for 180 s. The spreading areas of experimental brazing filler metals were measured using scanning and KOMPAS-3Dv17.1 program.

Brazing dissimilar overlap joints (with a capillary gap) was also performed at the temperature which exceeds $T_L$ by 30 °C, soaking time was 180 s. Obtained samples were cut normal to the sheet surface and microsections were prepared by a standard procedure and their chemical heterogeneity was studied, using a scanning electron microscope TescanMira with LMU. Micro X-ray spectral studies and determination of local distribution of elements in individual phases were conducted using energy-dispersive spectrometer Oxford Instruments X-max 80 $mm^2$, which is fitted with INCA program package. Microsections were studied without chemical etching.

**Experimental results and their analysis**. Obtained investigation results showed that experimental alloys have a quite narrow melting range, not exceeding 22–35 °C, but increasing cobalt concentration leads to its widening due to increase of liquidus temperature. With increase of cobalt concentration from 0.5 to 4.5 wt.%, the alloy solidus temperature rises by 14 °C.

When conducting the experiments, the maximum overheating above the alloy solidus temperature was equal to 65 °C (Figure 1).

Ternary alloys of Cu–Mn–(0.5–4.5)Co system are characterized by a cast structure that is formed by two solid solutions based on copper and on manganese. The latter is observed in the form of dark dendrites of the solid solution with pronounced liquation by the

**Table 2.** Experimental alloys and temperature of spreading (brazing)

| Alloy number | Composition, wt.% | Spreading temperature, °C | Melting temperature range, °C | Heating above solidus temperature, °C |
|---|---|---|---|---|
| 1 | Cu–Mn–0.5Co | 939 | 22 | 52 |
| 2 | Cu–Mn–1Co | 946 | 21 | 51 |
| 3 | Cu–Mn–2Co | 955 | 26 | 56 |
| 4 | Cu–Mn–4.5Co | 966 | 35 | 65 |

component elements that is inherent in alloys of this system [11]. Cobalt is a component element of both the solid solutions. Kovar structure is single-phase and is formed by γ-solid solution, which is resistant at the temperature higher than –70 °C. At an unfavourable ratio of nickel and cobalt and present impurities, partial γ→α transformation (of martensite nature) is possible at $T$ = –70 °C, which may lead to TCLA increase that should be taken into account at creation of structures and components from such dissimilar materials as Kovar and molybdenum.

It is known that one of the important physicochemical characteristics of producing a sound joint is the ability of brazing filler metal to wet the base metal and spread over it [12]. The quality of brazed products depends on the completeness of running of this complex metallurgical process. Proceeding from the conducted investigations, it was found that at spreading of cast brazing filler metal (Figure 2, *a*) of Cu–Mn–CO system on molybdenum, a drop of inhomogeneous structure forms, which can be conditionally divided into zones (Figure 2, *b*, *c*).

In the central zone (No.1), a manganese-based solid solution crystallizes as dispersed dendrites, which form the tip of brazing filler metal drop. They are located against the background of the copper matrix, but their liquidus temperature is higher than that of copper-based solid solution [13]. The results of micro X-ray spectral analysis revealed considerable chemical inhomogeneity of the intermediate zone (No.2) which is a copper-based solid solution of varying concentration. The morphology of this zone differs considerably from the previous one, and consists of rather coarse dendrites of the solid solution with a pronounced liquation by component elements (Figure 2, *d*) that is determined by the cooling rate and crystallization temperature range [11]. Manganese concentration is in the range of 16.2–32.15 %.

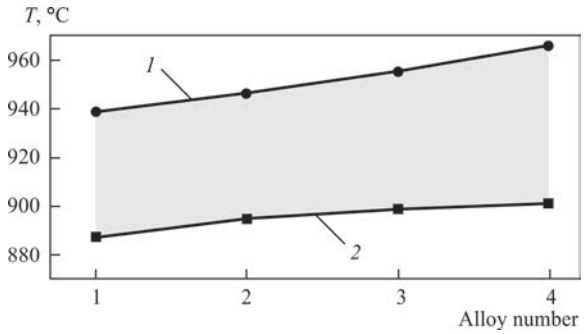


**Figure 1.** Brazing temperature (*1*) and solidus temperature (*2*) of experimental alloys

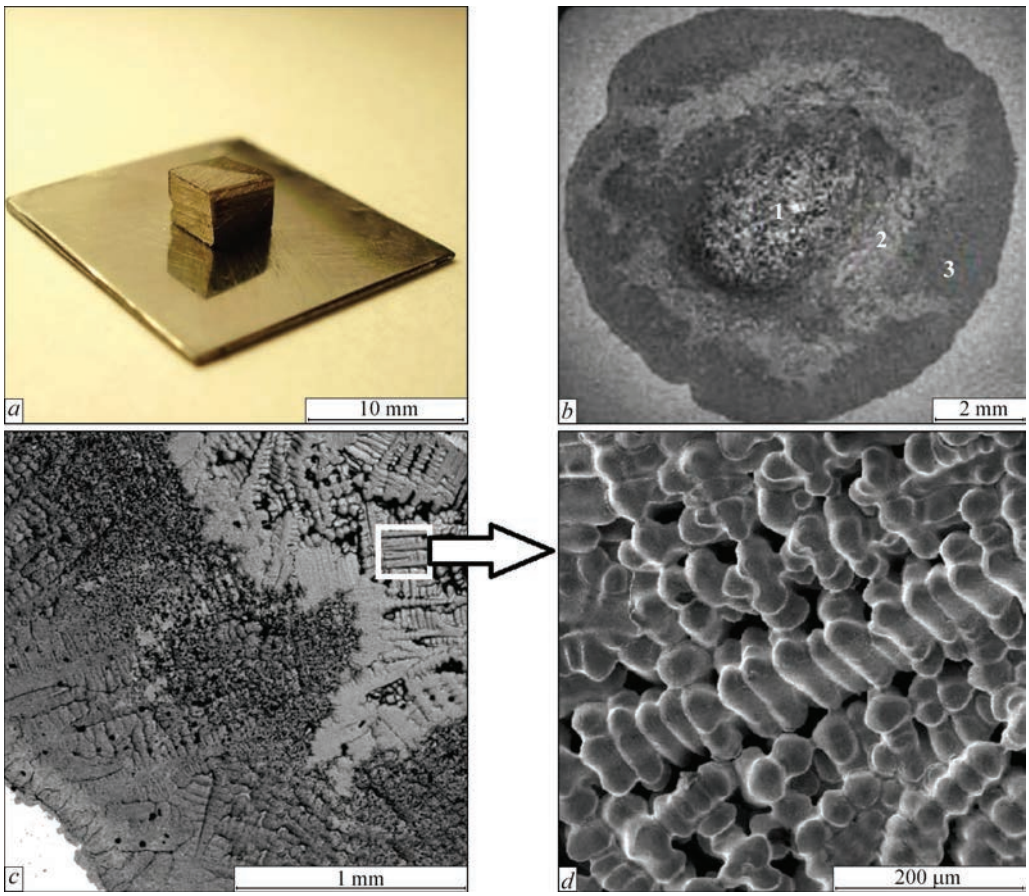


**Figure 2.** Cu–Mn–4.5Co brazing filler metal on a molybdenum substrate (*a*), after spreading (*b*, *c*) and structure of the intermediate zone – dendrites of copper-based solid solution (*d*)

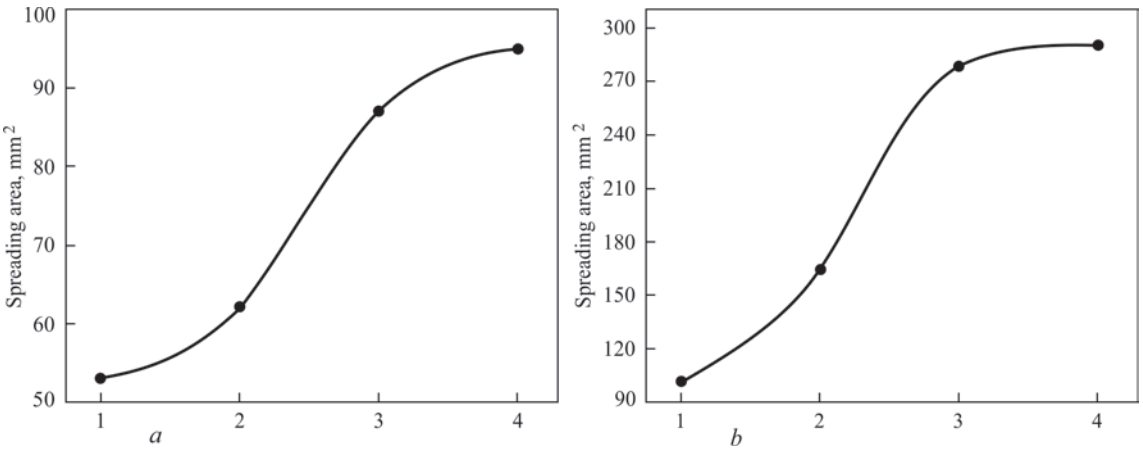


**Figure 3.** Spreading area of brazing filler metals Nos 1–4 of Cu–Mn–Co system, on molybdenum (*a*) and on Kovar (*b*)

A halo in the form of a plane crystallization front is observed around the drop perimeter (zone No.3), which is formed by a copper-based solid solution with minimum manganese concentration (12.92Mn), which is characterized by the lowest melting temperature and is the last to crystallize. The low concentration of manganese in this zone is due to high vapour pressure and time of brazing filler metal staying in the liquid state under vacuum. Note that zonal formation of the structure at molybdenum spreading is characteristic for all the studied brazing filler metals (see Table 1).

It was proved experimentally that at increase of heating temperature the area of brazing filler metal spreading increases (Figure 3, *a*) due to improvement of spreading of copper-based solid solution, which crystallizes around the perimeter of brazing filler metal drop in the form of a halo. The tendency to increase of the area is observed at spreading of experimental brazing filler metals both on molybdenum (Figure 3, *a*), and over Kovar (Figure 3, *b*). Obtained data show the good capillary properties of brazing filler metals of Cu–Mn–Co system.

Dissimilar reference-samples were brazed simultaneously with samples for mechanical testing, in order to study the brazed seam properties and conduct metallographic examination. External examination of the samples showed that at brazing of dissimilar molybdenum-Kovar joints (by Cu–Mn–4.5Co brazing filler metal) formation of a full direct and reverse fillet section is observed (Figure 4, *a*, *b*).

Micro X-ray spectral analysis showed that the brazed seam metal consists of a matrix — copper-based solid solution of Cu–Mn–Ni, which contains 2.87 % cobalt and 3.73 % iron. A molybdenum-based reaction layer (about 1 μm wide), enriched in cobalt (15.80 %), and manganese (14.12 %) and having a small amount of copper (1.63%), forms on molybdenum–brazing filler metal interphase.

Moreover, a small amount of discrete grains based on iron (27.05–28.29 %) and enriched in manganese (27.94–26.93 %) is observed against the background of the solid solution that is confirmed by investigations at electron beam scanning of the brazed sample (Figure 5).

Note that such features of structure formation are due to nonequilibrium conditions of crystallization of brazed seam metal, presence of concentration gradient on base metal – brazing filler metal interphase and diffusion processes running during brazing. Owing to

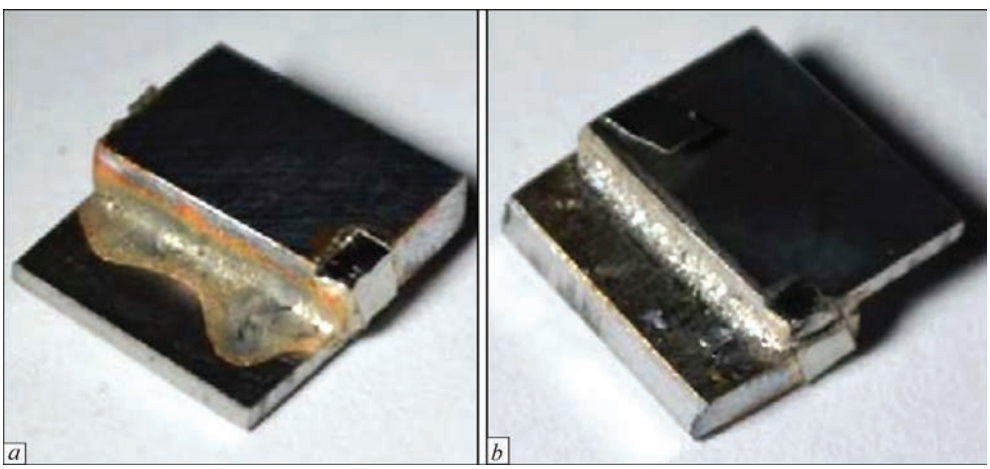


**Figure 4.** Appearance of a brazed dissimilar Kovar–Mo joint: direct (*a*) and reverse fillets (*b*)

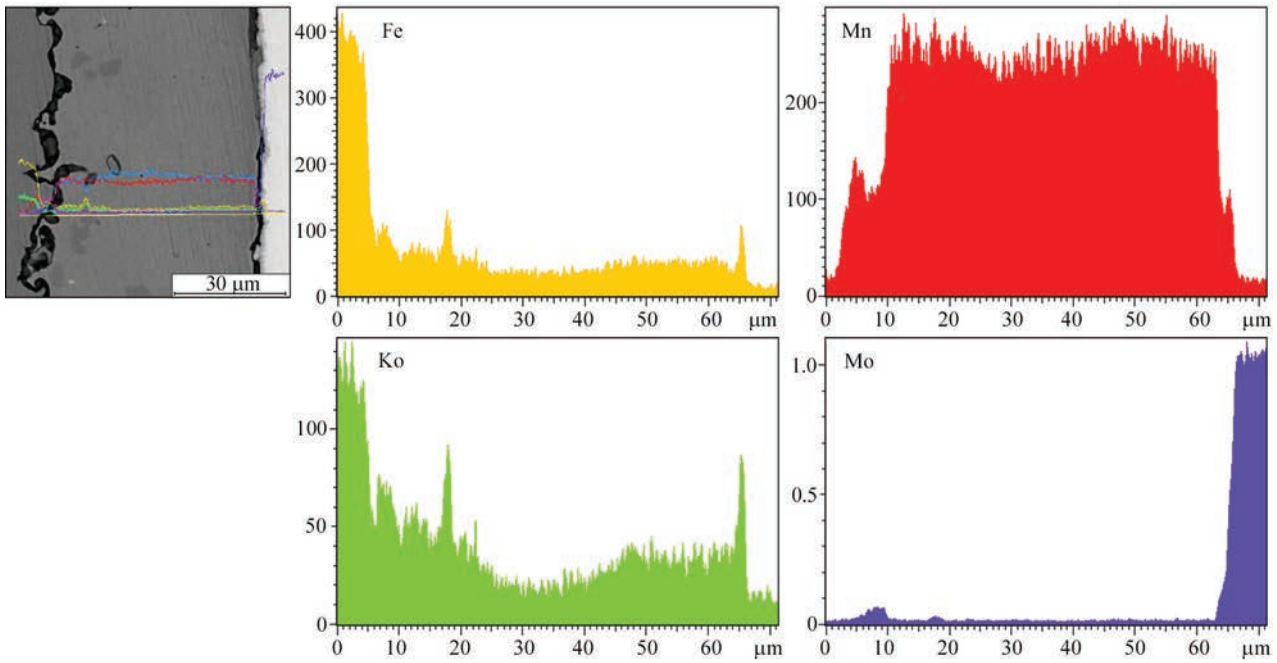


**Figure 5.** Electron image and distribution of iron, manganese, cobalt, and molybdenum in the weld of brazed dissimilar Kovar–Mo joint

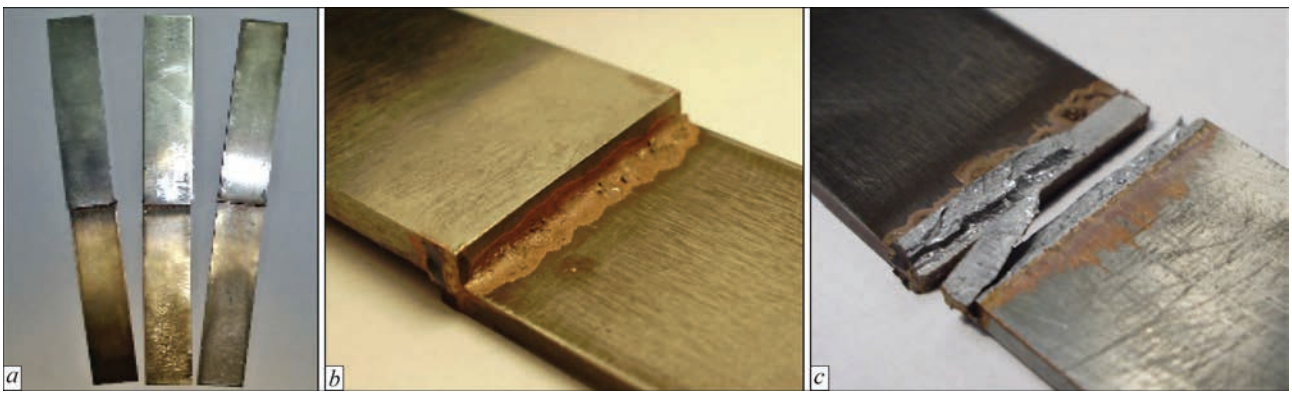


**Figure 6.** Appearance of brazed Kovar–molybdenum samples before (*a*, *b*) and after testing (*c*)

diffusion processes, the brazed seam meal is saturated by base metal elements, and, as a result, it differs from the initial brazing filler metal by chemical composition, that affects the mechanical properties of the brazed joints.

Overlap sheet brazed Kovar–molybdenum samples were used to study the mechanical properties under static loading conditions at room temperature [14] which were produced with application of brazing filler metal (No.4) Cu–Mn–4.5Co. Their appearance in the initial condition (as-brazed) is indicative of sound formation of the fillet sections and absence of pores in the welds (Figure 6, *a*, *b*).

During testing destruction of the samples occurs partially in the brazed seam and partially in the base metal–molybdenum (Figure 6, *c*). Proceeding from mechanical testing results, it was determined that the shear strength of brazed Kovar–molybdenum samples is in the range of 168.18– 278.87 MPa.

## Conclusions

Obtained investigation results showed that at spreading of brazing filler metals of Cu–Mn–4.5Co system on molybdenum, zonal crystallization of brazing filler metal drop takes place. Pronounced regions with plane fronts of crystallization of copper-based solid solution (Cu12.92Mn–4.69Co) form around the drop perimeter. In the intermediate zone, dendrites of copper-based solid solution, containing a varying concentration of manganese (16.2–32.15 %) are observed that is due to dendritic segregation at crystallization.

Dendrites of manganese-based solid solution form in the drop central (upper) zone against the background of copper-based solid solution. Their melting temperature is higher than that of copper-based solid solution.

It is found that increase of the heating temperature leads to increase of brazing filler metal spreading area

that is due to melting temperature of copper-based solid solution which practically does not change.

Shear strength at room temperature of brazed overlap dissimilar Kovar–molybdenum samples is in the range of 168.18–178.87 MPa. Destruction of the samples runs partially through the brazed seam and partially–through base metal–molybdenum.


1. Tits, T., Wilson, J. (1969) *Refractory metals and alloys.* Ed. by P.K. Novikova, I.I. Novikov. Moscow, Metallurgiya [in Russian].
2. Gurevich, S.M., Nerodenko, M.M., Kharchenko, G.K. et al. (1982) *Metallurgy and technology of welding of refractory metals and alloys on their base.* Kiev, Naukova Dumka [in Russian].
3. Yermolayev, H.V., Kvasnytskyi, V.V., Kvasnytskyi, V.F. et al. (2015) *Brazing of materials:* Manual. Ed. by V.F. Khorunov, V.F.,Kvasnytskyi. Mykolaiv, NUK [in Ukrainian].
4. Liu, G.W., Valenza, F., Muolo, M.L. et al. (2010) SiC/SiC and SiC/Kovar joining by Ni–Si and Mo interlayers. *J. Mater. Sci.*, 45, 4299–4307. DOI: https://doi.org/10.1007/s10853-010-4337-3
5. Kumar, S., Upadhyay, A., Dinesh Kumar, P., Agarwal, A. (2015) *Vacuum brazing of molybdenum–Kovar and evaluation of its joint strength*. MSF 830–831, 282–285. DOI: https://doi.org/10.4028/www.scientific.net/msf.830-831.282
6. Chen, G., Yin, Q., Guo, C. et al. (2019) Beam deflection effects on the microstructure and defect creation on electron beam welding of molybdenum to Kovar. *J. Materials Proc. Technology*, 267, 280–288. DOI: https://doi.org/10.1016/j.jmatprotec.2018.12.017
7. (1983) *Precision alloys:* Refer. Book. Ed. by B.V. Molotilov. 2nd Ed. Moscow, Metallurgiya [in Russian].
8. Buturlya, E.A., Bugaenko, B.V., Petrenko, L.M., Golub, D.M. (2019) Features of active brazing of ceramics with metals. *Visnyk DDMA*, 45(**1**), 38–42 [in Ukrainian].
9. (1997) *State diagrams of binary metal systems:* Refer. Book. Ed. by N.P. Lyakishev. In: 3 Vol., Vol. 2. Moscow, Mashinostroenie [in Russian].
10. Chen, G., Yin, Q., Dong, Z. et al. (2020) Microstructure evolution analysis for the reaction interface between molybdenum and Kovar acquired by electron beam welding-brazing. *Materials Characterization*, 171. DOI: https://doi.org/10.1016/j.matchar.2020.110781
11. Favstov, Yu.K., Shulga, Yu.N., Rakhshtadt, A.G. (1980) *Metals science of high-damping alloys*. Moscow, Metallurgiya [in Russian].
12. Krasovskyi, V.P., Gab, I.I., Stetsyuk, T.V., Krasovska, N.O. (2017) Wetting of quartz glass by low-melting brazing melts. *Adgeziya Rasplavov i Pajka Materialov*, **50**, 18–27 [in Russian].
13. Drits, M.E. (1979) *Binary and multicomponent copper-based systems:* Refer. book. Moscow, Nauka [in Russian].
14. Maksymova, S.V., Kovalchuk, P.V., Voronov, V.V. (2019) Influence of cobalt on structure and technological properties of Cu-Mn system alloys. *Metalofiz. Novitni Tekhnologii*, 41(**10**), 1365–135. DOI: https://doi.org/10.15407/mfint.41.10.1365


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