

<https://doi.org/10.37434/tpwj2022.05.05>

FEATURES OF THE STRUCTURE OF MOLYBDENUM–KOVAR BRAZED JOINTS

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ABSTRACT

The work presents the results of metallographic and X-ray microspectral studies of molybdenum–Kovar overlap joints, which were produced by vacuum brazing with application of brazing filler metal based on Cu–Mn–Co system. The influence of soaking at brazing temperature on brazed seam structure formation was studied. Local X-ray microspectral analysis was used to determine the number of structural components of the brazed seam: copper-based solid solution, individual single iron-based grains, reaction layer in the form of a continuous band on molybdenum–brazing filler metal interface. It was found that longer soaking at the brazing temperature promotes an increase of the reaction layer width from 1 to 3 μm and leads to formation of a faceted morphology from the brazed seam side and to microcracks initiation in it, but it does not affect molybdenum concentration, which at different soaking (1–15 min) is in the range of 55.81–59.05 wt.%. In the solid solution (matrix) manganese concentration decreases with longer soaking, copper concentration rises, but the quantity of iron practically does not change, and it is in the range of 4.52–4.95 wt.%. In single grains of the dark phase, observed near the interface with Kovar, longer soaking promotes an increase of iron and nickel concentration and lowering of manganese and copper content.

KEYWORDS: Kovar, molybdenum, vacuum brazing, brazing filler metal, structure, brazed seam, soaking, reaction layer, X-ray microspectral analysis

INTRODUCTION

Under the conditions of modern industry, alloys with specified physical characteristics have become widely applied as individual brazed assemblies, which are the components of different structures. Special attention is attracted by dissimilar brazed joints, for instance, molybdenum–Kovar pair. Molybdenum is an important structural material of electrovacuum, rocket, aviation, and nuclear power engineering. A successful combination of a complex of valuable physico-mechanical and corrosion properties makes this metal one of the main high-tech structural materials [1–3]. It is rather difficult to join molybdenum and Kovar, because of the difference in their chemical composition and physico-mechanical properties. As is known, there exist different methods of joining this pair of materials: diffusion, electron beam and laser welding [3–5], but the technology of joining these materials by vacuum brazing became the most widely applied.

Molybdenum brazing runs into problems, because of its high affinity to oxygen, as well as its proneness to grain growth at high temperature. Molybdenum recrystallization temperature (850–1220 °C) depends on many factors and, primarily, on the purity and degree of deformation. At transition through the recrystallization threshold, molybdenum becomes brittle, which should be taken into account at selection of the filler metal for its brazing. In addition, molybdenum has a small temperature coefficient of linear expansion ($\alpha = 5.6 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) which distinguishes it from

metals and alloys, with which it is usually joined at brazing (copper, nickel, iron, etc.) [6].

Considerable problems arise at brazing of dissimilar materials [7, 8]. At their brazing copper [2], copper–titanium [9] and ductile silver brazing filler metals [10] are used as brazing materials.

At brazing temperature the brazing filler metal should wet both the base materials equally well, otherwise it will spread over the surface of one of the materials, which is better wetted, instead of filling the brazing gaps. Molybdenum and iron (which is a Kovar component) have considerable areas of solubility at high temperature, but at temperature lowering these areas quickly become narrower and at room temperature the mutual solubility is practically absent [11]. Between the considered elements, there is a number of intermetallic phases, which have a negative role, leading to brittleness of both the welded and brazed joints [5, 8]. Therefore, studying structure formation on molybdenum–brazing filler metal–Kovar interface is highly important when producing molybdenum–Kovar dissimilar permanent joints.

The objective of this work is studying the influence of soaking time on brazed seam structure formation and reaction layer width at brazing of molybdenum–Kovar dissimilar joints (with application of a brazing filler metal of copper–manganese system) in vacuum.

EXPERIMENTAL PART

Used as base metal were plates of 12Kh18N10 stainless steel (Fe–(17–18)Cr–(8.0–10)Ni– \leq 2.0Mn– \leq

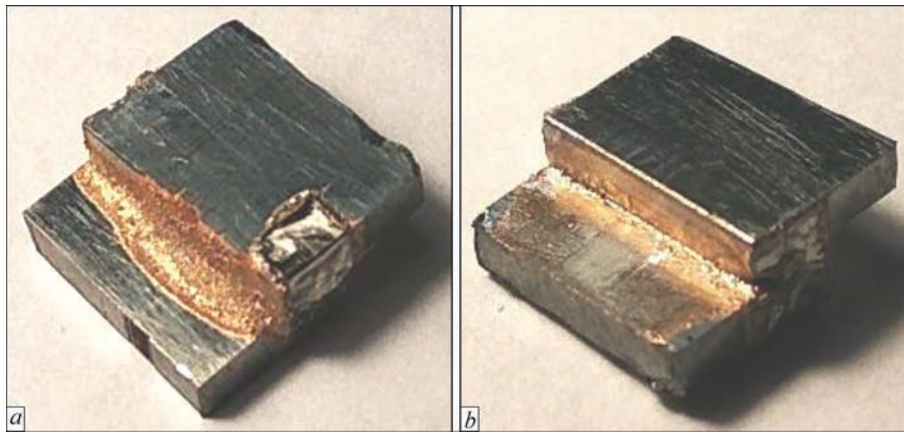


Figure 1. Appearance of dissimilar molybdenum–Kovar brazed joint at 15 min soaking: straight (*a*) and reverse fillets (*b*)

$\leq 0.8\text{Si}$ – $\leq 0.12\text{C}$), characterized by high anti-corrosion properties, precision Kovar alloy of 29NK grade (Fe–29Ni–17Co) and brazing filler metal of copper–manganese system (Cu–Mn–4.5Co) with the structure of solid solution. The latter was obtained by melting in a laboratory installation in a shielding atmosphere of argon, and it was used in the cast state in the form of pieces (of not more than 2 mm size). Before brazing the surfaces of materials to be joined were ground on a diamond disc with 125 μm granularity.

Brazing dissimilar overlap joints (with a capillary gap) was conducted in a vacuum furnace with radiation heating at a temperature exceeding the liquidus temperature ($T_1 = 966\text{ }^\circ\text{C}$) of the brazing filler metal by 30 $^\circ\text{C}$, soaking time was 1, 3 and 15 min. Obtained samples were cut normal to the plate surface, macro-sections were prepared by a standard procedure and chemical inhomogeneity was studied in a scanning electron microscope TescanMira 3 LMU. Micro-X-ray spectral studies and determination of local distribution of elements in the individual phases were conducted with application of energy-dispersive spectrometer “Oxford Instruments X-max 80 mm²”, fitted with INCA software. Microsections were examined without chemical etching [12]. Hardness was studied

using PMT-3 microhardness meter with loading $P = 50\text{ g}$ ($\tau = 0.15\text{ min}$).

EXPERIMENTAL RESULTS AND THEIR ANALYSIS

Dense brazed lines (Figure 1, *a*) and reverse fillet areas (Figure 1, *b*) form at brazing overlap dissimilar molybdenum–Kovar joints.

The brazing filler metal spreads readily over the base metal and flows into the capillary gap [13]. Results of metallographic studies and X-ray microspectral analysis of molybdenum–Kovar brazed joints ($\tau = 1\text{ min}$) showed that the welds are characterized by a homogeneous structure (Figure 2, *a, b*).

The brazed seam structure is represented by solid solution based on copper–manganese–nickel–cobalt system, containing a small quantity of iron (4.52 %), and it is the matrix. Moreover, individual iron-based dark grains are observed against the background of this matrix, which are weakly visualized (Table 1, spectrum 1, Figure 2, *c*).

It can be assumed that diffusion processes (or Kovar dispersion) run at brazing, and individual base metal grains (Table 1, spectrum 1, Figure 2, *c*) in the form of dark grains precipitate against the background of matrix–solid solution. With greater distance from

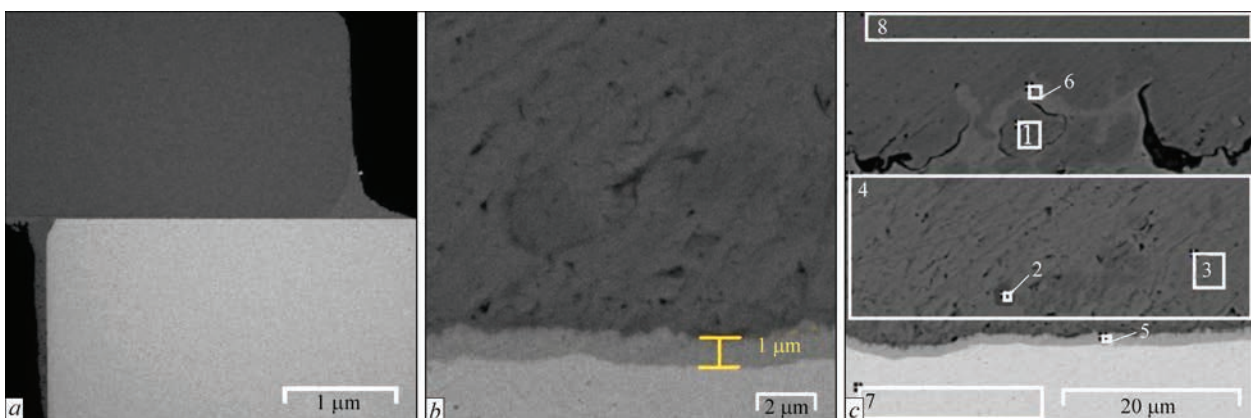


Figure 2. Appearance (*a*), reaction layer (*b*) and areas (*c*), where chemical heterogeneity of Mo–Kovar brazed joint ($\tau = 1\text{ min}$) was determined

Table 1. Chemical heterogeneity of Mo–Kovar brazed joint ($\tau = 1$ min)

Spectrum number	Chemical elements, wt.%					
	Mn	Fe	Co	Ni	Cu	Mo
1	22.12	39.49	17.62	13.50	6.42	0.85
2	29.99	28.25	21.43	5.06	10.07	5.21
3	26.53	4.52	4.41	5.37	59.17	–
4	26.33	5.71	5.02	5.15	57.79	–
5	10.25	18.26	11.80	0.69	2.57	56.42
6	24.06	8.87	5.62	9.15	52.30	–
7	–	–	–	–	0.48	99.52
8	0.69	52.79	17.75	28.77	–	–

Table 2. Chemical heterogeneity of Mo–Kovar brazed joint

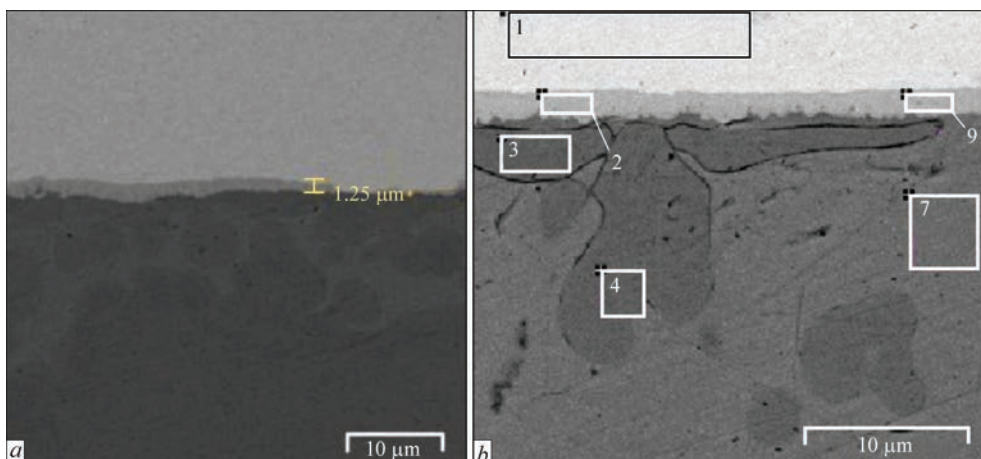
Spectrum number	Chemical elements, wt.%					
	Mn	Fe	Co	Ni	Cu	Mo
1	–	–	–	–	–	100.00
2	8.64	19.78	11.08	1.29	2.78	56.43
3	26.51	30.35	20.89	5.62	1.06	5.56
4	26.54	28.36	18.20	7.17	19.73	–
7	24.01	4.43	3.16	5.19	63.21	–
8	23.68	10.09	6.48	6.14	52.24	1.39
9	7.76	19.97	10.98	1.17	1.07	59.05

them to Kovar, the nickel and iron concentration in these grains is reduced, and that of manganese, cobalt and copper becomes higher (Table 1, spectrum 2, Figure 2, *c*) that is indicative of their saturation by the constituent chemical elements of the brazing filler metal (or partial dissolution in the liquid brazing filler metal at brazing). It should be noted that iron concentration in the solid solution of the brazed seam, adjacent to molybdenum, does not change, remaining on the level of 4.52 %. A higher concentration of iron of 5.71 % was found, when studying the chemical composition of the solid solution in the areas which are located closer to Kovar.

From the side of molybdenum, bordering on the weld metal, a molybdenum-based layer with 56.42Mo–18.26Fe–11.80Co–10.25Mn 1 μ m wide is formed, which contains a small amount of copper and

nickel (Figure 2, *a–c*, Table 1, spectrum 5). Increase of soaking time at vacuum brazing from one up to three minutes leads to a light increase of its width up to 1.25–2.0 μ m (Figure 3, Table 2, spectrum 2), but molybdenum concentration remains on the same level (Table 2, spectrum 2, Figure 3, *b*).

In keeping with binary constitutional diagram of Fe–Mo (Figure 4), iron and molybdenum have limited solubility and form several intermetallic phases: more stable FeMo (α -phase) and $\text{Mo}_{38}\text{Fe}_{62}$ intermetallic phases form at high temperature; two more intermetallic phases, namely Fe_2Mo and Fe_7Mo_6 , form in the solid state by the peritectic reactions. A feature of high-temperature phases FeMo (σ -phases) and $\text{Mo}_{38}\text{Fe}_{62}$ (R-phases) is the fact that as a result of temperature lowering they transform into μ -phase, whose


Figure 3. Microstructure (*a*) and electronic image (*b*) of Mo–Kovar brazed joint ($\tau = 3$ min)

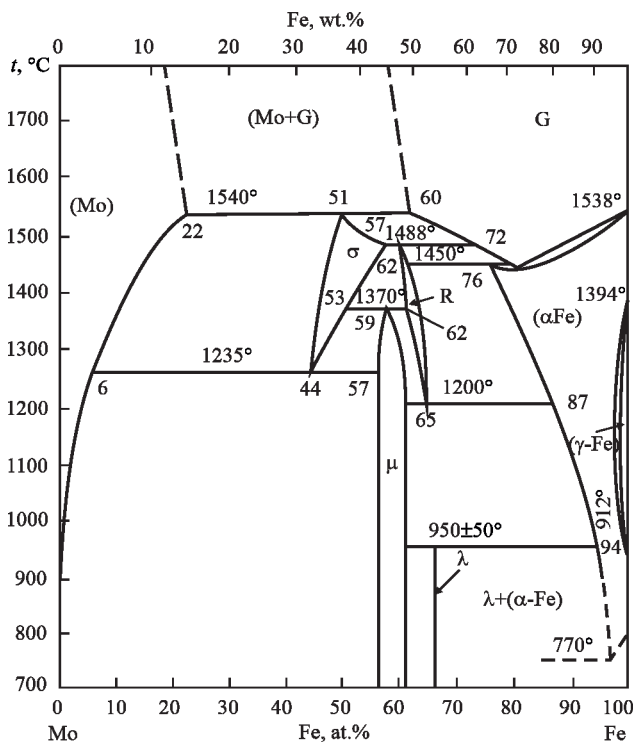


Figure 4. Binary constitutional diagram of Fe–Mo metallic system

homogeneity region is 44–58 at.% and into Mo- and α Fe-based solid solutions (respectively) [11].

MoFe₂ compound (Laves phase) with homogeneity region of 66.3 ± 0.2 at.% (at the temperature of 950 ± 50 °C) forms by the peritectic reaction. Such a phase composition is characteristic for binary alloys of this system that were brought into the equilibrium state by heat treatment [11].

It should be noted that solidification of brazed seam metal runs under nonequilibrium conditions in the presence of diffusion processes and concentration gradient on base metal–brazing filler metal interface that influences the chemical composition of the brazed seam and its morphology [14]. Proceeding from the obtained results of local X-ray microspectral analysis, it can be assumed that such conditions of solidification of brazed seam metal promote formation of a complex molybdenum-based intermetallic phase of Mo₅₆(Fe, Co, Mn, Cu, Ni)₄₄, which is observed in the form of a continuous band — reaction layer along the brazed seam, and contains other constituent elements of the brazing filler metal and base metal, in addition to iron and molybdenum. A continuous series of solid solutions are formed by γ -iron and α -cobalt

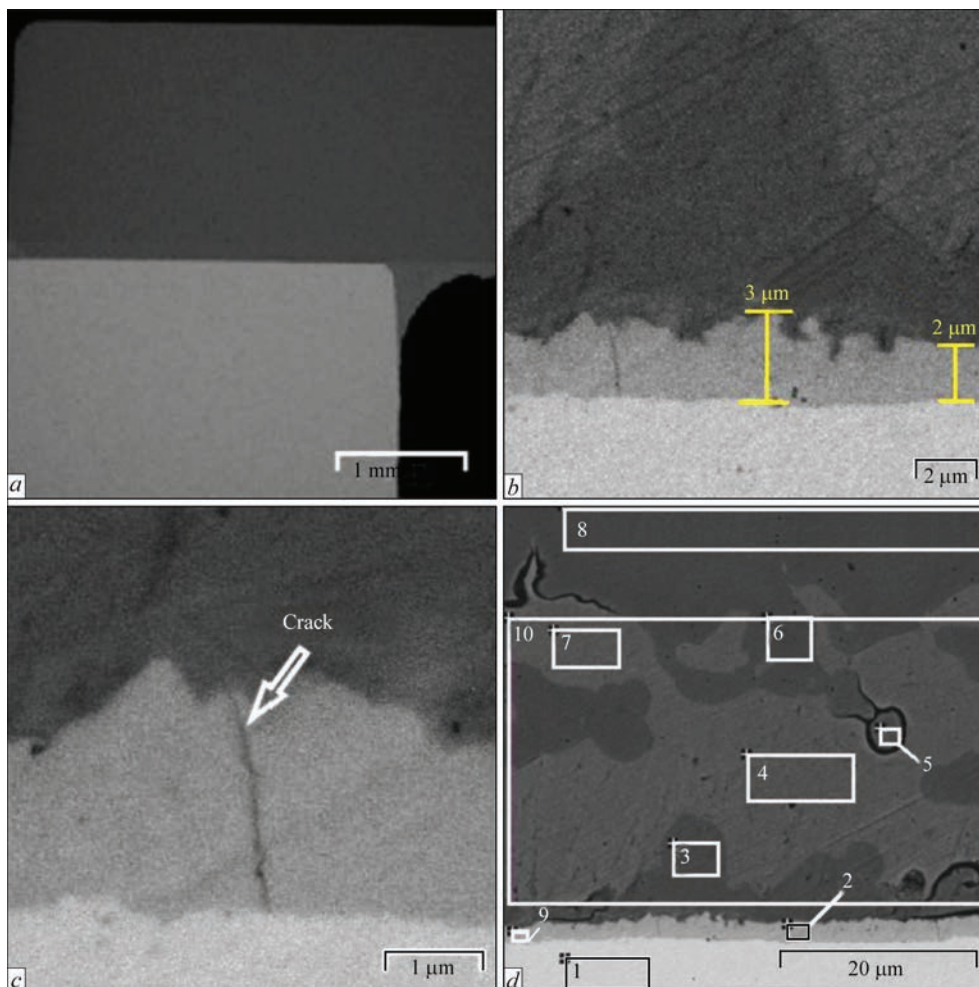


Figure 5. Appearance (a), reaction layer (b, c) and electronic image (d) of Mo–Kovar brazed joint microstructure ($\tau = 15$ min)

Table 3. Chemical heterogeneity of Mo–Kovar brazed joint ($\tau = 15$ min)

Spectrum number	Chemical elements, wt. %					
	Mn	Fe	Co	Ni	Cu	Mo
1	0.00	0.19	0.00	0.00	0.00	99.81
2	7.00	22.47	12.58	1.79	0.00	56.16
3	21.03	31.97	17.42	8.31	17.18	4.10
4	19.11	4.95	3.71	6.21	66.01	0.00
5	20.36	31.69	16.14	10.58	18.39	2.85
6	9.15	47.56	16.34	24.07	2.41	0.47
7	18.71	6.15	4.14	6.45	64.36	0.19
8	4.44	48.94	16.63	24.78	5.20	0.00
9	6.57	21.92	12.63	1.76	1.31	55.81
10	17.24	12.60	6.60	6.90	55.98	0.69

between high-temperature modifications, similar to the high-temperature region of iron-manganese binary system [11]. As to copper and nickel concentration, it is negligible in this phase and cannot have any significant influence on its properties.

Further increase of soaking time up to 15 min leads to increase of the reaction layer width within 2–3 μm (Figure 5).

Molybdenum concentration practically does not change and remains on the same level as in the previous samples (Table 3, spectra No. 2 and No. 9). In individual areas of the reaction layer (from the brazing filler metal side) its morphology undergoes changes and it is transformed into the faceted surface (Figure 5, *b, c*).

More over, increase of soaking time leads not only to increase of its width but also to initiation of micro-cracks which propagate only in some regions of this reaction layer in the direction normal to its surface (Figure 5, *b, c*) that is indicative of its brittleness.

Concentration of constituent elements of individual phases of the brazed seam also changes (Table 3). In the solid solution manganese concentration is equal to 18.71–19.11 wt.% that is much smaller, compared to previous samples. It is obvious that at increase of the temperature of soaking at brazing temperature the high manganese vapour pressure results in its partial evaporation that leads to lowering of its concentration in the brazed seam metal (brazing filler metal).

In the dark phase iron concentration increases slightly, and it is in the range of 31.69–47.56 %, while cobalt concentration is equal to 16.34–17.42 % (Table 3). X-ray microspectral analysis proved that increase of soaking from one up to 15 min at brazing temperature of Mo–Kovar samples promotes an increase of iron, and nickel concentration and lowering of manganese and copper content in the dark phase grains located near Kovar (Figure 6).

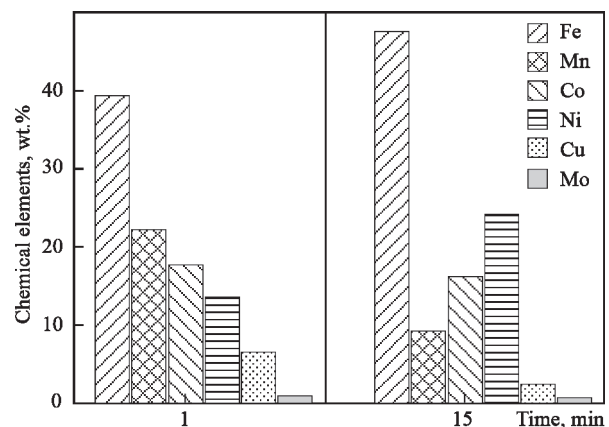
More over, it should be noted that increase of iron concentration is manifested to a greater extent in the grains of this phase, which are located closest to Ko-

var. In the grains located in the weld central zone an increase of iron concentration is also observed but it is less pronounced.

Analysis of the obtained results of X-ray microspectral analysis shows that increase of soaking time at brazing of dissimilar molybdenum–Kovar joints promotes increase of copper concentration in the solid solution–matrix of brazed seam metal, but the quantity of iron practically does not change and it is in the range of 4.52–4.95 % (Figure 7, *a*). Cobalt and nickel concentration practically does not change, and that of manganese is considerably reduced.

It follows from the conducted studies that with increase of soaking time from 1 up to 15 min the width of the reaction layer is increased (molybdenum-based phase), but molybdenum concentration remains on the same level, as at soaking for 1, 3 and 15 min (Figure 7, *b*). A slight reduction of manganese concentration with a simultaneous increase of iron concentration is observed. Such features of structure formation are due to the pattern of binary constitutional diagrams of metal systems [11] and high elasticity of manganese vapours.

Obtained data correlate well with the results of studying element distribution in the Mo–Kovar brazed joint ($\tau = 15$ min) that are determined by scan-


Figure 6. Dependence of chemical element content in iron-based phase on soaking time at brazing dissimilar Mo–Kovar joints

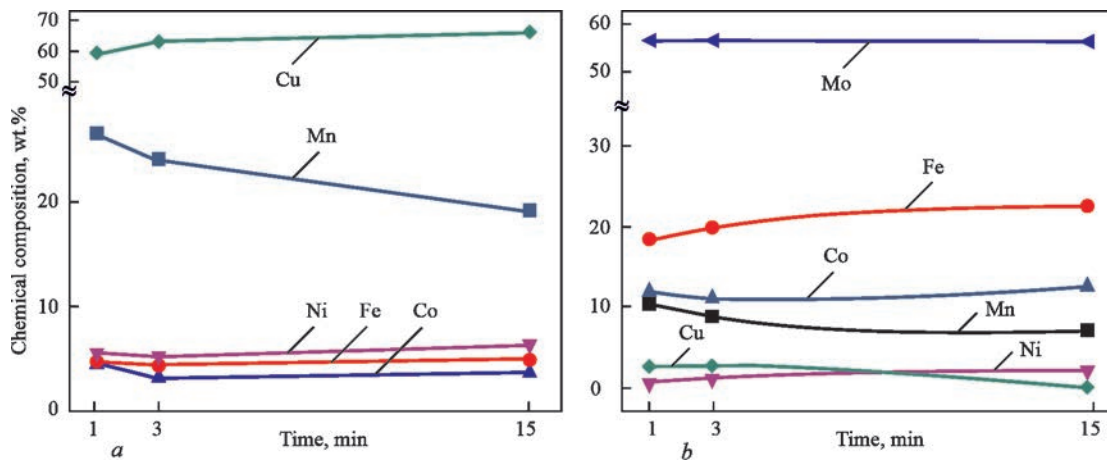


Figure 7. Influence of soaking time on chemical element concentration in the following phases: in the solid solution (*a*); in the reaction layer — molybdenum-based phase (*b*) at brazing dissimilar Mo–Kovar joints

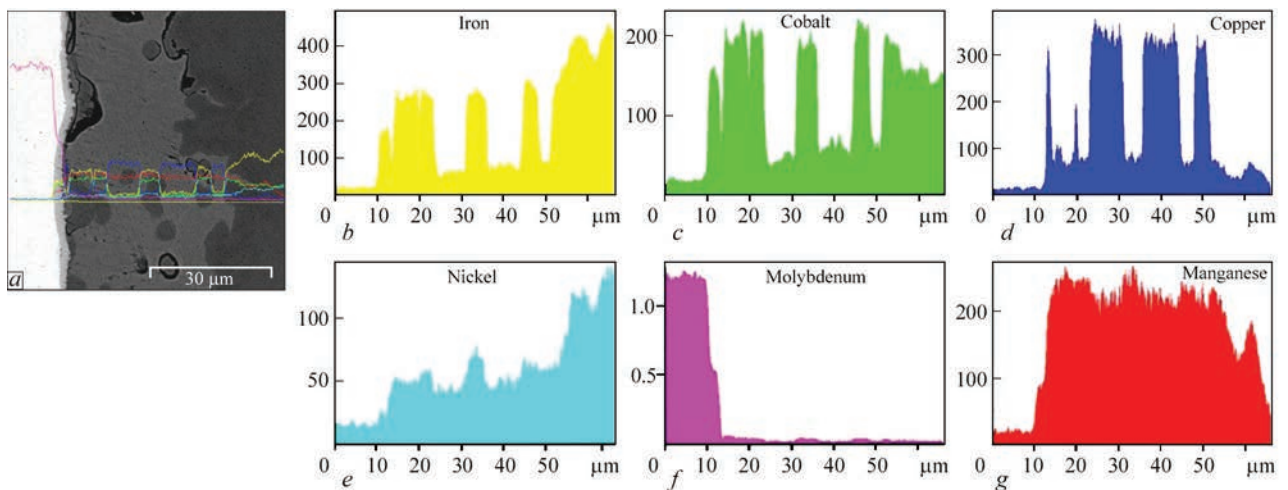


Figure 8. Electronic image (*a*) and qualitative distribution of elements: iron (*b*), cobalt (*c*), copper (*d*), nickel (*e*), molybdenum (*f*) and manganese (*g*) in a brazed seam of a dissimilar joint at application of brazing filler metal of Cu–Mn–4.5Co system

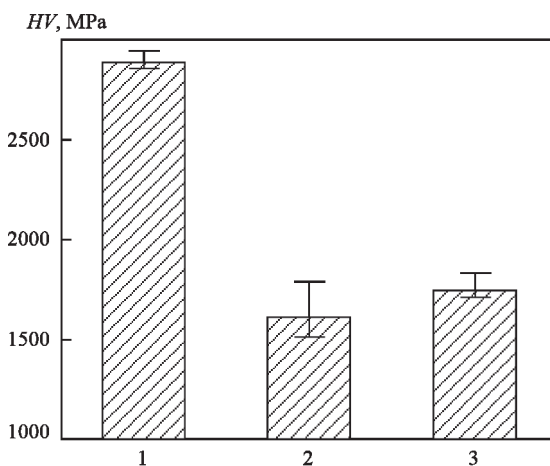


Figure 9. Microhardness of dissimilar molybdenum–Kovar joint: 1 — molybdenum; 2 — seam; 3 — Kovar

ning of the brazed seam cross-section by the electron beam. Presence in the weld central part of a phase based on Fe–Co–Mn system and molybdenum-based phase, which solidifies in the form of a continuous band along the brazing filler metal–molybdenum interphase, is confirmed (Figure 8).

Results of studying the brazed joints ($\tau = 3$ min) showed that the brazed seam microhardness is characterized by essentially lower values, compared to those for molybdenum, but differs only slightly from these values for Kovar (Figure 9).

The obtained data lead to the conclusion that microhardness (*HV*) of the brazed seam (1513–1791 MPa) and Kovar (1678–1831 MPa) is in close ranges, which it can have a positive influence on the mechanical properties and relaxation of stresses, arising at brazing the dissimilar joints.

CONCLUSIONS

X-ray microspectral studies showed that the main phase (matrix) of the brazed seam in molybdenum–Kovar joints is a copper-based solid solution, in which up to 4.95 % is dissolved. A molybdenum-based phase in the form of a continuous (reaction) layer forms along the brazing filler metal–molybdenum interphase. Moreover, individual single iron-based grains are observed, which solidify against the background of the matrix–solid solution. Increase of soaking from

1 up to 15 min promotes an increase of the concentration of iron and nickel (in the dark phase grains located near Kovar) and lowering of manganese and copper content.

In the solid solution (matrix) of brazed seam metal manganese concentration decreases with longer soaking, that of copper becomes higher, but the amount of iron practically does not change and is in the range of 4.52–4.95 %.

Local X-ray microspectral analysis proved that increase of soaking time from 1 up to 15 min at brazing molybdenum–Kovar joints promotes an increase of the width of the reaction layer, forming on molybdenum–seam metal interface, from 1 up to 3 μm , but it does not influence its chemical composition. Molybdenum concentration at different soaking (1, 3, 15 min) is within 55.81–59.05 %. Widening of the molybdenum-based reaction layer (up to 3 μm) leads to formation of a faceted morphology from the side of brazed seam metal and to appearance of microcracks in it.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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SUGGESTED CITATION

S.V. Maksymova, P.V. Kovalchuk, V.V. Voronov (2022) Features of the structure of molybdenum–kovar brazed joints. *The Paton Welding J.*, **5**, 33–39.

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<https://pwj.com.ua/en>

Received: 07.04.2022

Accepted: 08.08.2022