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PRODUCING DISSIMILAR JOINTS OF MOLYBDENUM–STAINLESS STEEL USING VACUUM BRAZING

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In this work the possibility of using brazing alloys with the structure of a solid solution based on Cu–Mn–Ni system for brazing dissimilar joints of molybdenum-stainless steel was shown, the results of micro X-ray spectrum examinations and strength characteristics of brazed joints were presented. The micro X-ray spectrum examinations revealed that in producing dissimilar joints of molybdenum-stainless steel using brazing alloys based on Cu–Mn–Ni system the central zone of a brazed weld is composed of a solid solution on copper base. The diffusion zone of weld (on the side of molybdenum) is formed by the phase based on molybdenum, which is precipitated in the form of a continuous band along the brazed weld. The application of brazing alloy based on Cu–Mn–Ni system with the structure of a solid solution provides formation of dense brazed welds without cracks. The shear strength is at the level of 200–210 MPa during fracture in the brazed weld and at 300 MPa during fracture in the base metal (molybdenum). 9 Ref., 3 Tables, 10 Figures.

Keywords: *dissimilar joints, vacuum brazing, brazing alloy, structure, solid solution, weld, mechanical properties*

The optimum service properties of a number of structures can be provided by applying the composite combined units of dissimilar metals. In this case, the advantages of each of them are most completely realized and the expensive metals are saved [1]. The joints of dissimilar materials produced using brazing, are in demand in different branches of industry [2, 3].

In particular, the joints of molybdenum-stainless steel are used in manufacturing parts operating for a long time at a high temperature in the nozzles of rockets and electric vacuum devices, in nuclear power industry in manufacture of nuclear reactors, in production of round anodes of X-ray tubes, heat exchangers, for manufacture of equipment operating in aggressive environments and a number of other products [4, 5]. It was managed to reach the higher manufacturability of many modern structures mainly due to the use of the latest achievements in the field of brazing. The selection and use of dissimilar metals as structural materials are determined by the service requirements specified for the structure and by economic indicators.

It is naturally, that the joining of dissimilar metals represents a more complicated problem than joining of similar joints. This is due to the difference in chemical composition and physical and mechanical properties of materials being joined. Thus in brazing dissimilar metals a big problem is to provide wetting of both materials and overcoming the difference in the coefficients of thermal expansion, which may lead to formation of brittle intermetallic interlayers at the interface, occurrence of inner stresses, appearance of cracks.

Each pair of the dissimilar materials being joined requires an individual approach in choosing brazing alloys and parameters of technological brazing process [6]. The applied brazing alloys should provide good wetting of both metals, the melting temperature of brazing alloy should not exceed the solidus temperature of a more low-melting base metal. The final aim of the technological process of brazing is the formation of serviceable joints with the specified service characteristics.

In brazing of refractory, chemically active metals (molybdenum, etc.) with corrosion-resistant steels it is necessary to apply brazing alloys with the structure of a solid solution or plastic brazing alloys based on the copper-silver system, which will contribute to relaxation of stresses in the brazed joint and serve as a damper between two metals being joined. However, brazing alloys based on silver are characterized by a low melting temperature and a low resistance under the conditions of neutron radiation.

In this work the features of formation of brazed joints of molybdenum-stainless steel using brazing alloys with the structure of a solid solution based on the copper-manganese system, and the results of micro X-ray spectrum examinations of brazed joints and their strength characteristics are presented.

As the base metal, molybdenum, stainless steel 09Kh18N10T and brazing alloys based on cop-

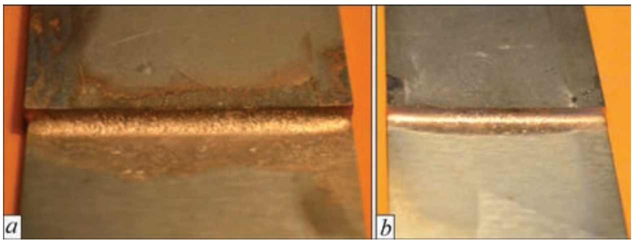

Figure 1. Appearance of brazed specimens of molybdenum-steel 09Kh18N10T: *a* — straight; *b* — reverse fillet

per-manganese system were applied. The brazing alloys were applied in the cast form and were produced by melting in the laboratory installation in the shielding atmosphere of argon. The produced ingots were overturned and remelted (up to 5 times) in order to average the chemical composition and provide a uniform distribution of elements. The solidus and liquidus temperatures of cast brazing alloys were determined using the installation of high-temperature differential analysis in the shielding atmosphere of helium at constant heating and cooling rate (40 °C/min).

For metallographic examinations the overlapped joints were brazed, the specimens were cut out perpendicular to the weld, the microsections were manufactured according to the standard procedure and examined using the scanning electron microscope TescanMira 3 LMU. The distribution of chemical elements was examined using the method of a local micro X-ray spectrum analysis applying the energy dispersion spectrometer Oxford Instruments X-max (80 mm^2) under the control of the software package INCA. The locality of micro X–ray spectrum measurements did not exceed 1μm, the filming of microstructures was carried out in back-scattered electrons

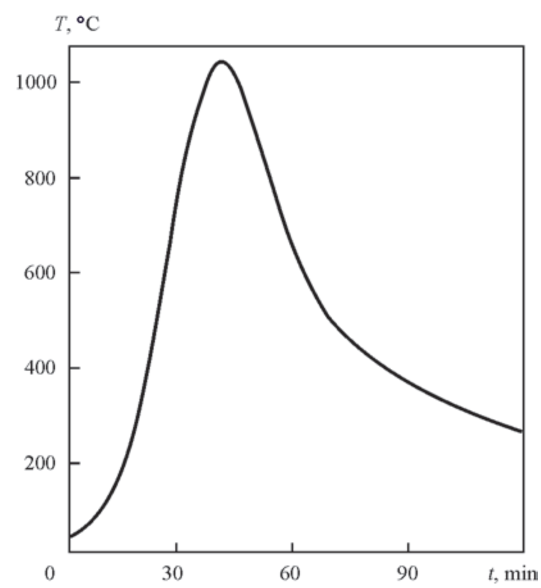

Figure 2. Thermogram of heating during brazing of molybdenum with stainless steel applying brazing alloy No.1

Table 1. Applied brazing alloys and brazing modes

Number of brazing alloy	Basic alloying system of brazing alloy	Brazing temperature, °C/time, min
1	Cu–Mn–Ni–Fe–Si	1050/3
2	Cu–Mn–Ni–Si	1100/5
3	Cu–Mn–Ni	1084/3

(BSE), which allowed examining the microsections without chemical etching.

For mechanical tests the plane overlapped joints of the 100×30×3 mm size were brazed and tested using the installation MTS-810.

Among the peculiarities of molybdenum there is a low resistance to oxidation at high temperatures. Above 500 °C the sublimation of MoO_3 begins and at 600 °C it becomes more significant and at higher than 800 °C the MoO_3 is melting which leads to hyperactive oxidation in the air atmosphere [7]. Therefore, brazing of molybdenum was carried out in vacuum. During assembly of specimens for brazing the brazing alloy was placed near the brazing gap. During heating the brazing alloy was melted and due to capillary forces it flowed into the gap.

The visual inspection of appearance of brazed specimens showed that while using brazing alloys (Table 1) a smooth straight complete fillet (Figure 1, *a*) is formed. The inverse fillet differs from a straight one by a smaller size (Figure 1, *b*).

In brazing of dissimilar joints of stainless steel-molybdenum applying brazing alloy No.1 at the mode, shown in Figure 2, *a* wide brazed weld based on copper is formed (Figure 3, *a*).

In the central area of the brazed weld the solid solution based on copper (92.58 %) is crystallized which except of the constituent elements of brazing alloy contains also a small amount of iron, which is 2.87 %.

In some areas the brazing alloy penetrates into stainless steel to the maximum depth of 20 μm (Figure 3, *a*).

In the peripheral zone of brazed weld, which borders with molybdenum, two diffusion layers are observed, which are distinguished in the form of narrow solid bands along the brazed weld. One of them, based on molybdenum, (51.21 %) is enriched with iron (31.71 %), silicon (up to 5.88 %) and located closer to molybdenum (Figure 3, *b*). The second one is based on iron (68.02 %) and does not contain molybdenum but also enriched with silicon and borders with a solid solution based on copper. Their width is variable, but it does not exceed 5 μm for each one. The common feature for these layers is the presence of increased concentration of silicon from 4.83 to 5.88 % (Table 2).

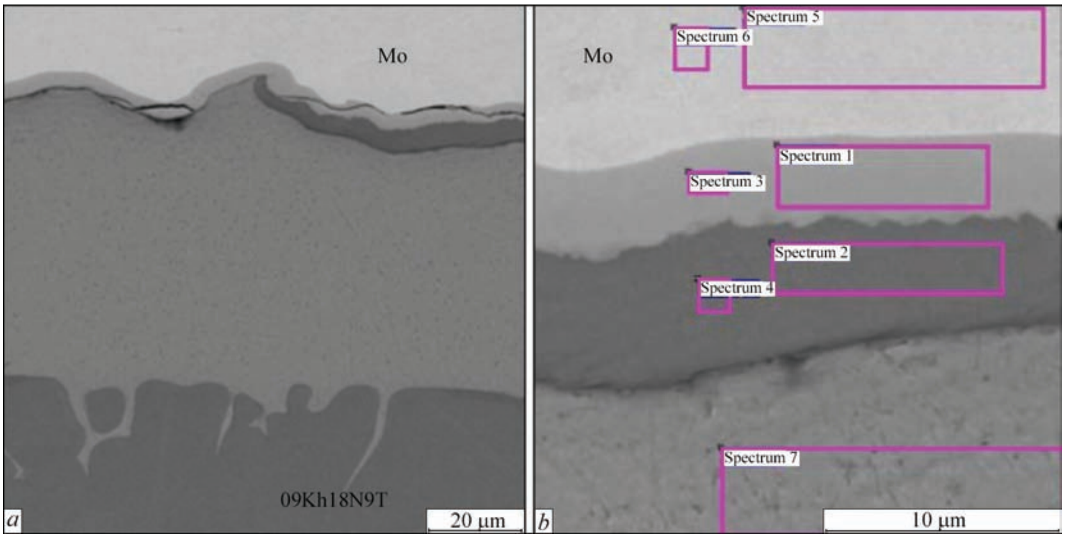

Figure 3. Microstructure (*a*) and examined regions of brazed joints (*b*), produced applying brazing alloy No.1

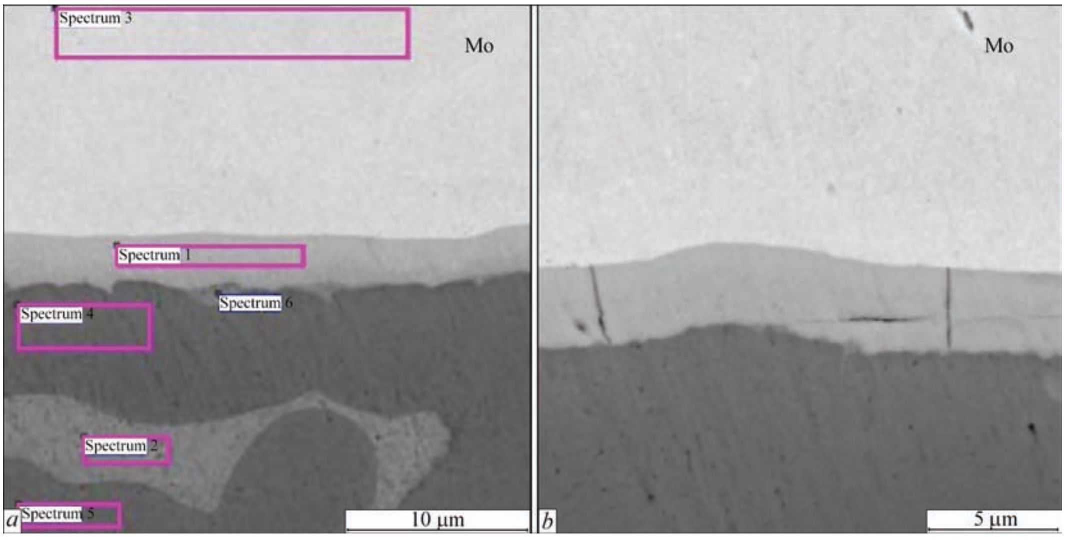

Figure 4. Examined regions of weld of brazed joint, produced applying brazing alloy No.2

It is obvious that during brazing the silicon interacts with iron and molybdenum, but during cooling of brazed joints under non-equilibrium conditions (at the drop of temperature and limited solubility of silicon) the phases are formed enriched with the latter.

The presence of gradient of concentration of chemical elements in these areas promotes the formation of longitudinal cracks (Figure 3, *a*) along the weld on the side of molybdenum over the diffusion layer based on molybdenum (51.21–52.59 %), enriched with iron (31.71–32.07 %) (Table 2, spectrum 1, 3). Such a formation of brazed joints is caused by mutual diffusion processes, occurring at the brazing alloy-stainless steel interface.

In brazing applying the brazing alloy with a reduced (0.2 %) concentration of silicon (No.2) the formation of fillet areas does not differ externally from the previous specimen. The brazing alloy provides a good wetting of base metals, it also penetrates into the base metal (stainless steel) along the grain bound-

Table 2. Results of micro X-ray spectrum analysis of individual phases of brazed joint applying brazing alloy No.1

Number of spectrum	Chemical elements, wt.%							
	O	Si	Cr	Mn	Fe	Ni	Cu	Mo
1	–	5.88	7.08	0.77	31.71	2.54	0.81	51.21
2	–	4.83	16.79	2.23	68.02	4.46	3.67	–
3	–	5.65	6.56	0.86	32.07	2.27	0.00	52.59
4	–	4.92	16.50	2.48	66.79	4.63	4.68	–
5	1.74	–	–	–	–	–	–	98.26
6	1.85	–	–	–	–	–	–	98.15
7	–	–	0.30	3.04	2.87	1.21	92.58	–

Table 3. Chemical composition of investigated areas applying brazing alloy No.2

Number of spectrum	Chemical elements, wt.%							
	Si	Ti	Cr	Mn	Fe	Ni	Cu	Mo
1	0.92	0.00	8.41	0.69	23.55	2.52	0.49	63.41
2	0.09	0.00	0.98	4.93	4.65	2.22	87.13	0.00
3	0.08	0.11	0.00	0.00	0.17	0.00	0.00	99.65
4	0.69	0.qq	13.66	2.92	61.36	9.84	5.66	5.87
5	0.61	0.00	15.52	2.55	64.90	8.75	6.12	1.55
6	1.11	0.00	11.55	1.97	36.83	3.43	4.27	40.84

aries. The examination of structure of brazed welds at high magnifications showed that between stainless steel and molybdenum a diffusion layer is observed in the form of a continuous band of 2.5 μm width based on molybdenum, which contains up to 23.55 % of iron but the concentration of silicon in it is lower and does not exceed 0.92 % (Figure 4, Table 3).

In accordance with the binary diagrams of metal systems there are significant regions of solubility in the molybdenum-iron system at high temperatures, but these regions are reduced rapidly at lower temperatures and at room temperature the mutual solubility is practically absent. Between the elements being considered there is a number of intermetallic phases, which can play a negative role, leading to the brittleness of a brazed joint [8].

The obtained results of investigations show that in some regions over the diffusion layer the microcracks are observed (Figure 4, *b*), they are located perpendicular to the plates being brazed, but they are absent in the brazed weld.

In order to eliminate the formation of cracks the brazing alloy No.3 was used in the brazed joints for brazing, which contains no silicon. The ternary alloys of Cu–Mn–Ni system are characterized by unlimited solubility in the liquid and solid state (Figure 5).

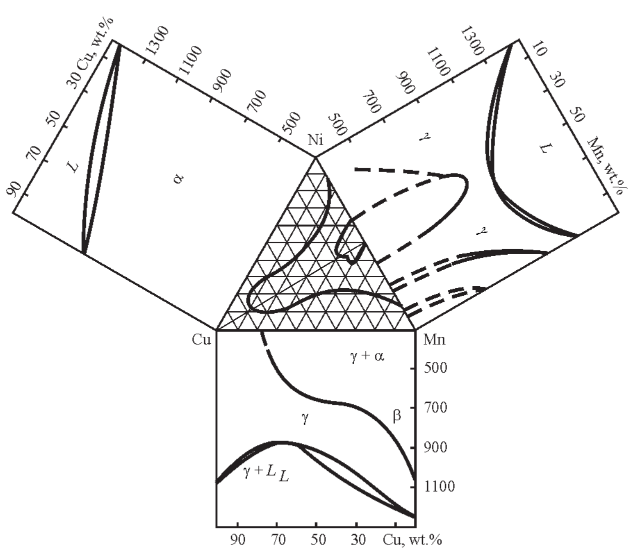

Figure 5. Ternary diagram of state Cu–Mn–Ni with adjacent binary systems [9]

In the system Mn–Ni the ordering of solid solution with the formation of phase Mn–Ni occurs at decrease in temperature [8].

The application of brazing alloys with the structure of solid solution during brazing of dissimilar joints with extended brazed welds allows reducing the influence of difference in thermal expansion coefficients. The brazing alloy acts as a soft interlayer, which provides relaxation of inner stresses occurring during heating and cooling.

The results of high-temperature differential thermal analysis are in good correlation with the diagrams of state of metal systems. At the thermal curve of heating a thermal effect was registered, which shows the melting range and corresponds to the solidus and liquidus temperature of the alloy (Figure 6).

The brazing mode applying the mentioned brazing alloy corresponded to the temperature of 1084 °C, however during investigation of brazed welds the cracks were not detected but the dense brazed joints are observed (Figure 7, *a*).

The use of a slight pressure during brazing has no effect on formation and chemical composition of diffusion layers, at the same time providing formation of dense brazed welds without cracks (Figure 7, *b*).

After metallographic and micro X-ray spectrum examinations the parameters of technological process of brazing were optimized and plane specimens of overlapped joints (three specimens for each brazing alloy) were manufactured for mechanical tensile tests at room temperature (Figure 8, *a*, *b*).

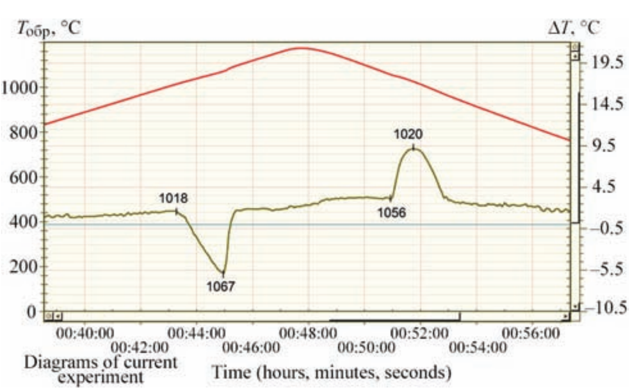

Figure 6. Temperature intervals of melting alloy of Cu–Mn–Ni system

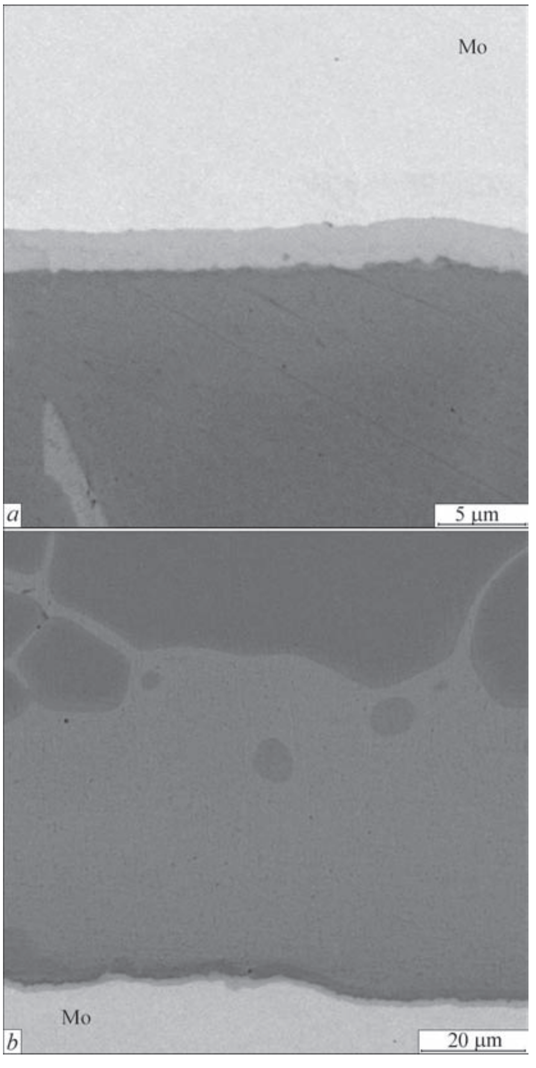

Figure 7. Microstructure of brazed joint, produced in brazing without (*a*) and with pressure (*b*) applying brazing alloy No.3

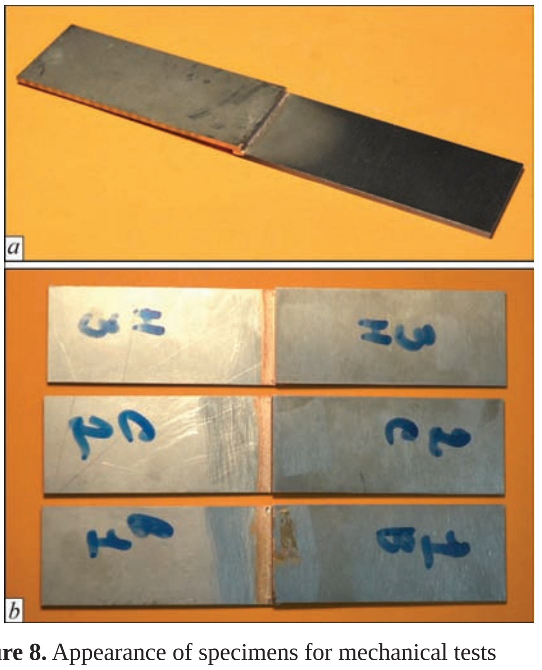

Figure 8. Appearance of specimens for mechanical tests

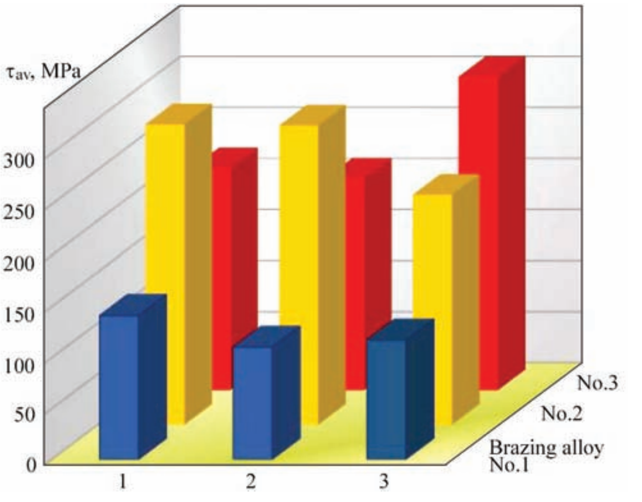

Figure 9. Shear strength of brazed joints of molybdenum-stainless steel

The carried out tests showed that the application of brazing alloy based on the system Cu–Mn–Ni, containing silicon (1 %), can not provide the shear strength higher than 110 MPa (Figure 9).

The reduction in concentration of silicon in the brazing alloy No.2 provided increase in shear strength. The application of brazing alloy based on the system Cu–Mn–Ni (No.3) with the structure of solid solution,

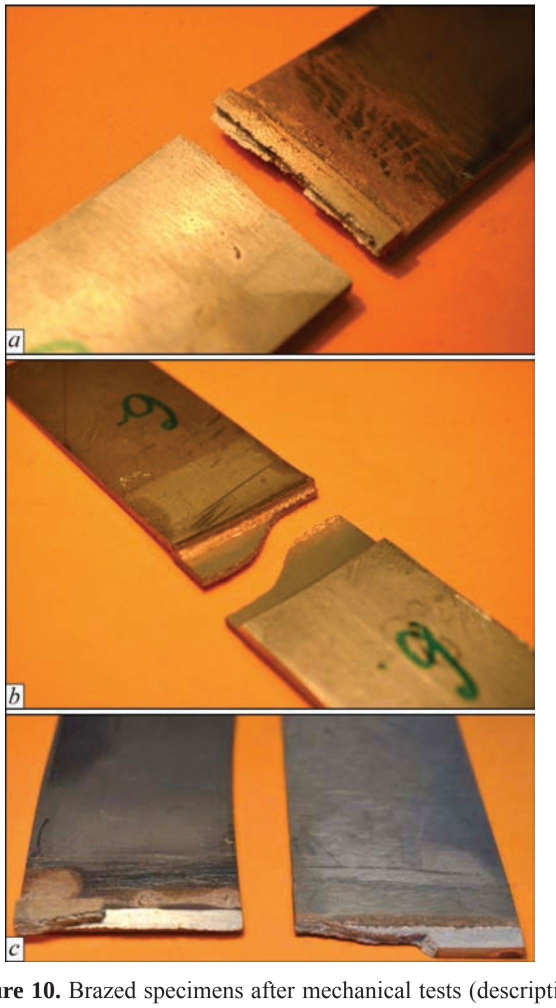

Figure 10. Brazed specimens after mechanical tests (description *a*–*c* see in the text)

containing no silicon, allowed increasing strength of the brazed joints up to 300 MPa (Figure 9).

It should be noted that during tests of brazed specimens produced applying the brazing alloy No.3 the fracture of specimens occurred along the brazed weld (Figure 10, *a*) and also along the base metal, i.e. molybdenum (Figure 10, *b*).

During fracture in weld the shear strength was at the level of 200–210 MPa (average value was 205). During fracture along molybdenum the maximum shear strength was 300 MPa. In some cases, a mixed character of fracture was observed: partially in weld and partially in base metal (see Figure 10, *c*).

Conclusions

Micro X-ray spectrum examinations revealed that in producing dissimilar joints of molybdenum-stainless steel using brazing alloys based on Cu–Mn–Ni–(Fe–Si) system, the central zone of a brazed weld is composed of a solid solution based on copper. The peripheral weld zone (on the side of molybdenum) is formed by diffusion phases based on iron and molybdenum, which are precipitated in the form of continuous bands along the brazed weld. At the 1 % concentration of silicon in the brazing alloy these areas are enriched by the latter, their composition and properties greatly differ from the chemical composition and properties of the brazed weld. Thus, the presence of a concentration gradient at the interface results in formation of longitudinal cracks and low mechanical properties of brazed joints.

The carried out mechanical tests of brazed joints showed, that the application of brazing alloy based on Cu–Mn–Ni system with the structure of solid solution provides formation of dense brazed welds without cracks. The shear strength is at the level of 200–210 MPa during fracture along the brazed weld and 300 MPa during fracture along the base metal (molybdenum).

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