EFFECT OF NICKEL AND MANGANESE ON STRUCTURE OF Ag–Cu–Zn–Sn SYSTEM ALLOYS AND STRENGTH OF BRAZED JOINTS

V.F. KHORUNOV, B.V. STEFANIV and **S.V. MAKSYMOVA**
E.O. Paton Electric Welding Institute, NASU
11 Bozhenko Str., 03680, Kiev, Ukraine. E-mail: office@paton.kiev.ua

It is a well-known fact that alloys of Ag–Cu–Zn–Sn system are a good basis for development of cadmium-free brazing filler metals (BFM) for brazing of different materials. However, as it follows from works of different authors, the BFM of this system are insufficiently active in brazing of hard-alloy materials. This work tries to eliminate these disadvantages. Effect of nickel and manganese alloying in 1–4 wt.% Ni and 2–6 wt.% Mn interval is investigated using method of experiment planning. Investigated are the intervals of alloy melting, areas of spreading and wetting angles on different substrates, strength characteristics of the joints in brazing of stainless steels and hard alloys. Structure of pilot alloys is investigated using the methods of optical and electron microscopy and microX-ray spectrum analysis. It is shown that manganese and nickel alloying of Ag–Cu–Zn–Sn system alloys allowed developing BFM, which provide good wetting of hard-alloy materials at the level of BFM of Ag–Cu–Zn–Cd system at filler relationship, approximately, 1.5–2.0 Mn:1.0 Ni. Technological properties of BFM deteriorate at 1.0 Mn:1.5–2.0 Ni relationship. Development of environmentally friendly BFM of Ag–Cu–Zn–Sn–Ni–Mn system for brazing of rock destruction and metal-cutting tool allows refusing from application of harmful BFM of Ag–Cu–Zn–Cd system and significantly (per 20–50 %) increasing strength of brazed joints. 5 Ref., 4 Tables, 7 Figures.

Keywords: *brazing, cadmium-free brazing filler metals, structure, melting interval, contact wetting angle, induction heating, temperature of phase transformations, nickel, manganese, silver brazing filler metal, joint strength*

Experimental investigations were carried out in works [1, 2] for the purpose of development of non-toxic brazing filler metals (BFM) containing no cadmium and having the same melting temperatures and mechanical properties as Ag–Cu–Sn–Cd system BFM. The investigations included analysis of phase composition, thermal analysis, extrusion, mechanical tests of Ag–Cu–Zn–Sn system alloys. The works of authors [3, 4] show that BFM of this system provide for strength of the brazed joints close to that in using of Cd-containing BFM. However, study of wetting of hard-alloy plates by these BFM determined that these characteristics are not sufficient for obtaining of quality joints. In [1, 2] it was noted the necessity of additional manganese and nickel alloying of the BFM of Ag–Cu–Zn–Sn system for their successful application in brazing of hard-alloy tool.

Aim of the present study lies in the investigation of effect of nickel and manganese alloying of Ag–Cu–Zn–Sn system alloys on structure, melting intervals, wetting of hard alloys and strength of the brazed joints. Alloy VK8 and stainless steel 12Kh18N10T were used as materials to be brazed.

Melting of pilot alloys of Ag–Cu–Zn–Sn–Ni–Mn system under laboratory conditions was carried out by induction heating using high-frequency generator of VChI4-10U4 type (frequency 440 kHz, power 10 kW) with double-coil inductor. Five alloys were melted in accordance with the selected matrix of experiment planning on specified procedure [3, 4]. General losses made 0.01–0.50 %.

Temperature interval of alloy melting was determined with the help of differential thermal analysis on VDTA-8M unit in crucibles, manufactured from zirconium oxide. Heating and cooling was carried out in helium atmosphere at 80 °C/min speed. Mass of investigated specimen made (1.25 ± 0.05) g. The specimens were heated twice in order to receive good fitting of sample to crucible bottom and provide accurate data on thermal effects. Therefore, thermal effects were registered according to second heating curve.

Analysis of the received data shows that nickel and manganese fillers significantly affect temperature of phase transformations and value of melting interval. Thus, only two phases are registered in Ag–Cu–Zn–Sn–2Mn–1Ni alloy (Figure 1). Solidus temperature makes 630 °C, and liquidus is 694 °C. Two thermal effects are clearly registered in Ag–Cu–Zn–Sn–6Mn–1Ni alloy, namely in 671–693 and 640–671 °C intervals. T_S makes 640 °C, and T_L = 693 °C. Ag–Cu–Zn–Sn–2Mn–4Ni alloy is also double phase, T_S = 618 °C, and T_L = 702 °C. The second phase in Ag–Cu–

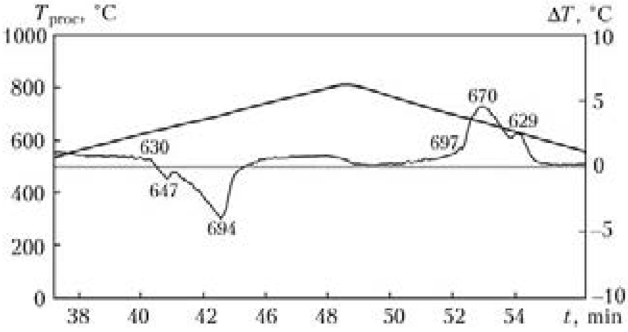

Figure 1. Results of differential thermal analysis of Ag–Cu–Zn–Sn–2Mn–1Ni system alloy

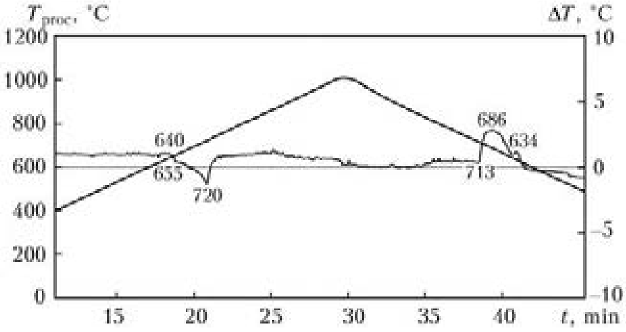

Figure 2. Results of differential thermal analysis of Ag–Cu–Zn–Sn–6Mn–4Ni system alloy

Zn–Sn–6Mn–4Ni alloy has weak thermal effect in heating, but it is clearly apparent in cooling (Figure 2). T_S = 640 °C, and T_L = 720 °C. Ag–Cu–Zn–Sn–4Mn–2.5Ni alloy is also double phase, T_S = 640 °C and T_L = 702 °C. Plates from hard-alloy material VK8 of 13.5 mm diameter and 4.5 mm thickness and BFM in form of blocks (4 × 4 × 4 mm) were used as a substrate for performance of experiments on spreading.

The specimens were degreased before brazing by acetone (alcohol), the investigated BFM was placed in the middle of the specimen, and PV209 flux, reactive temperature interval of which equals 600–850 °C [5], was applied on along the whole perimeter on the specimen. Heating of the specimens was carried out using mentioned above high-frequency generator. Single-coil inductor was used for the investigations. The specimens were positioned on ceramic support having internal channel for feeding of thermocouple, measuring the temperature of specimen heating. 3-second soaking was applied after melting of the BFM and then heating was switched on. A level of solid substrate wetting by BFM was determined through evaluation of area of spreading of melted BFM (three specimens for each BFM) and contact angle, formed between the substrate and spread drop of the BFM.

The contact angle was determined on microsections cut out from the specimens normal to wetting plane (Figure 3). Area of spreading of each BFM and contact wetting angle (Table 1) were calculated using AutoCard 2002 program.

Experiments on determination of strength of specimens of the brazed joint, manufactured from 12Kh18N10T grade stainless steel, were carried out using investigated BFM. The specimens were brazed with the help of gas heating and flux PV209. The flux was preliminary applied to the place of brazing in form of water-kneaded paste, and dried before heating. After heating to the flux melting temperature, the sample was put in the place of joining, and heating was performed up to melting of the latter and formation of the brazed joint. The brazed specimens were treated in order to remove reinforcement and break tests were carried out on MTS-20 machine.

The experiments on stainless steel were carried out according to GOST 23047–75. As can be seen from given data (Table 2), alloys of Ag–Cu–Zn–Sn system, alloyed by nickel and manganese, significantly increase shear strength of the brazed joints (from 300 to 400 MPa). In particular, rise of shear strength is observed in the joint, made using BFM No.5 (more than 450 MPa).

BFM of Ag–Cu–Zn–Sn–6Mn–4Ni, having the best indicies on wetting as well as strength char-

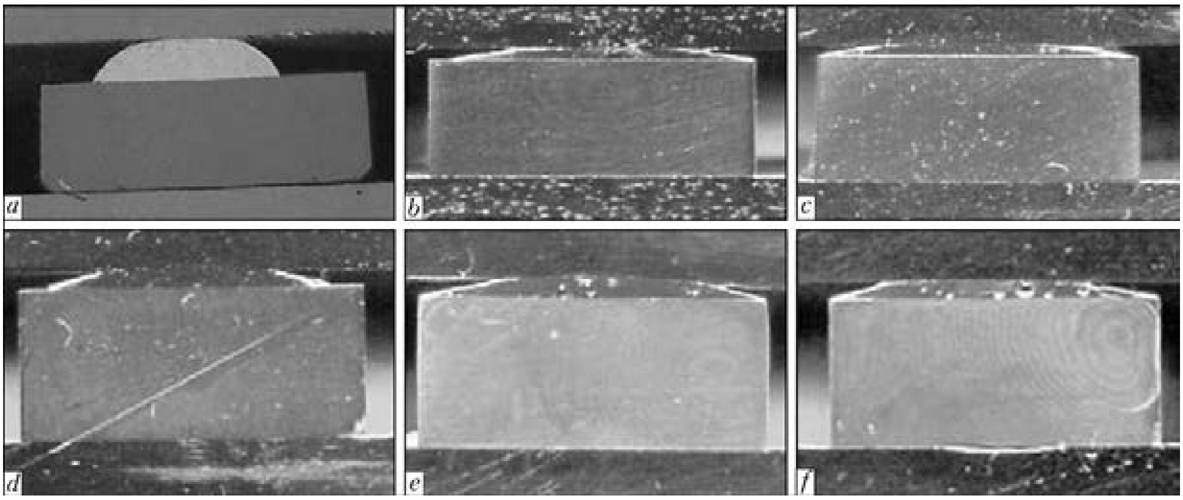

Figure 3. Cross section of specimens 1–6 (*a*–*f*) (see Table 1) after spreading test

Table 1. Melting temperature, contact wetting angle and area of spreading over hard-alloy plates of experimental alloys

BFM number	BFM system	Contact wetting angle θ, deg	Temperature of melting, °C		Temperature of BFM heating, °C	Average area of spreading BFM* S, mm^2
			T_S	T_L		
1	Ag–Cu–Zn–Sn (BAg-7)**	50	618	651	750	51
2	Ag–Cu–Zn–Sn–2Mn–1Ni	20	630	694	750	123
3	Ag–Cu–Zn–Sn–6Mn–1Ni	17	640	693	750	136
4	Ag–Cu–Zn–Sn–2Mn–4Ni	35	618	702	750	87
5	Ag–Cu–Zn–Sn–6Mn–4Ni	10	640	720	760	144
6	Ag–Cu–Zn–Sn–4Mn–2.5Ni	12	640	702	750	143

*Determination of area of spreading was carried out using high-frequency heating by nonstandard procedure.
**Interval of BFM meting is taken from USA standard.

Table 2. Average strength characteristics of brazed lap joints on 12Kh18N10T steel

BFM number	BFM system	b, mm	B, mm	S, mm^2	P, kg	τ, MPa
1	Ag–Cu–Zn–Sn (BAg-7)	2.35	20.10	47.23	1300	275.2
2	Ag–Cu–Zn–Sn–2Mn–1Ni	2	20.06	40.12	1640	408.7
3	Ag–Cu–Zn–Sn–6Mn–1Ni	2	20.06	40.12	1400	348.9
4	Ag–Cu–Zn–Sn–2Mn–4Ni	3	20.06	60.18	1860	309.3
5	Ag–Cu–Zn–Sn–6Mn–4Ni	2	20.03	40.06	1820	454.3
6	Ag–Cu–Zn–Sn–4Mn–2.5Ni	2	20.06	40.12	1658	413.2

acteristics for stainless steel joints, was selected determination of shear strength of hard-alloy plates. 13.5 mm diameter, 6 and 3.5 mm height hard-alloy plates of VK8 type were used in determination of the brazed joint shear strength. The values of shear strength, received using special device of tensile-testing machine R-05 (V.N. Bacul Institute for Superhard Materials of the NASU), lie in 489–524 MPa range.

As mentioned above, the investigations were carried out using the method of experiment planning. Two-factor experiment was performed and data of two recalls were received. The results of processing of experimental data were obtained from «Statistica 6.0» program. Regression equations of dependence of area of spreading and joint strength on manganese and nickel content are the following:

$$S_{\mathrm{spr}} = 54.1014 + 24.5059\mathrm{Mn} + 25.061\mathrm{Ni} - 2.7492(\mathrm{Mn} \times \mathrm{Mn}) + 2.8052(\mathrm{Mn} \times \mathrm{Ni}) - 8.0526(\mathrm{Ni} \times \mathrm{Ni});$$

$$\tau_{\mathrm{av}} = 432.7222 - 12.3333\mathrm{Mn} - 15.3333\mathrm{Ni} - 2.4375(\mathrm{Mn} \times \mathrm{Mn}) + 17.0833(\mathrm{Mn} \times \mathrm{Ni}) - 10.2222(\mathrm{Ni} \times \mathrm{Ni}).$$

In graphic form these dependencies are shown in Figures 4 and 5. The analysis of received results allows stating that the best values of strength and area of spreading are achieved at manganese

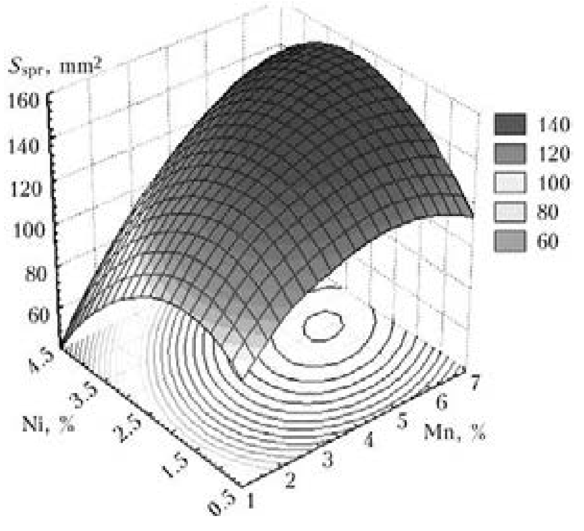

Figure 4. Dependence of BFM spreading area on manganese and nickel content

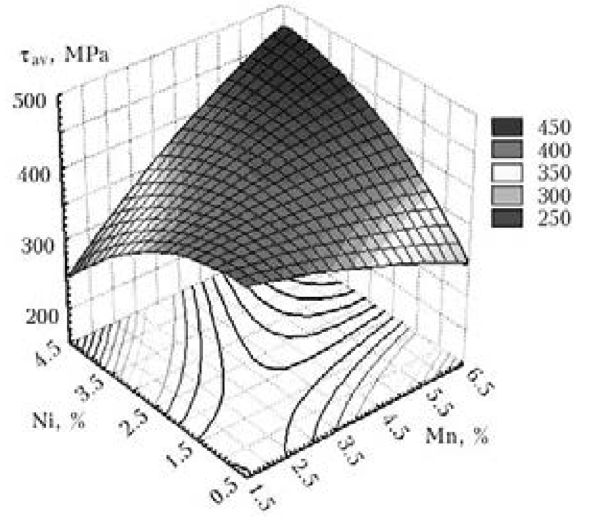

Figure 5. Dependence of BFM strength on manganese and nickel content

Table 3. Element composition of structural constituents of Ag–Cu–Zn–Sn–2Mn–1Ni alloy, wt.%

Spectrum number	Mn	Co	Ni	Cu	Zn	Ag	Sn
1	0.35	0.42	5.76	61.35	23.66	8.09	0.37
2	0.19	–	3.16	44.52	19.64	32.18	0.31
3	0.16	–	–	9.41	12.88	76.69	0.87
4	0.28	–	–	14.44	17.16	61.42	6.70

Table 4. Element composition of structural constituents of Ag–Cu–Zn–Sn–6Mn–4Ni alloy, wt.%

Spectrum number	Mn	Co	Ni	Cu	Zn	Ag	Sn
1	8.70	2.25	26.08	37.32	21.42	2.74	1.48
2	1.48	–	–	8.64	11.67	78.22	–
3	1.76	–	0.36	15.97	13.52	65.50	2.89

to nickel relation, approximately, 1.5:1.0 (see Tables 1 and 2).

Metallographic investigations were carried out on specimens after determination of temperature interval of melting, i.e. all alloys were cooled to room temperature at similar rate.

Structure and chemical inhomogeneity of Ag–Cu–Zn–Sn–Ni–Mn system alloys with different level of manganese and nickel alloying were investigated with the help of optic microscope MIM-8M and scanning electron microscope TescanMira3LMU. The results of investigations of alloys containing 1.5 Mn:1.0 Ni showed that in general they can be related to the eutectic structures with larger or smaller amount of primary phase (Figures 6 and 7).

Thus, Ag–Cu–Zn–Sn–2Mn–1Ni system alloy refers to the eutectic structure with small content of Cu-based primary dendrites. This alloy has two well-defined phases with different melting temperatures, that is verified by VDTA unit results. Probably, Cu-based solid solution, containing small amount of silver and tin (see Figure 6), appears as a primary phase. Light Ag-based phase with smaller content of copper, zinc and tin from 0.87 to 6.70 % (Table 3), is solidified around the primary dark dendrites. The Ag–Cu–Zn–Sn–6Mn–4Ni system alloy has the same structural constituents (see Figure 7; Table 4).

Comparison of data of the microX-ray spectrum analysis of both alloys shows significant increase of nickel, copper and tin in Cu-based solid solution (see Tables 3 and 4) in the second alloy and significant reduction of content of tin in the eutectic. The latter can explain the rise of brazed joint strength.

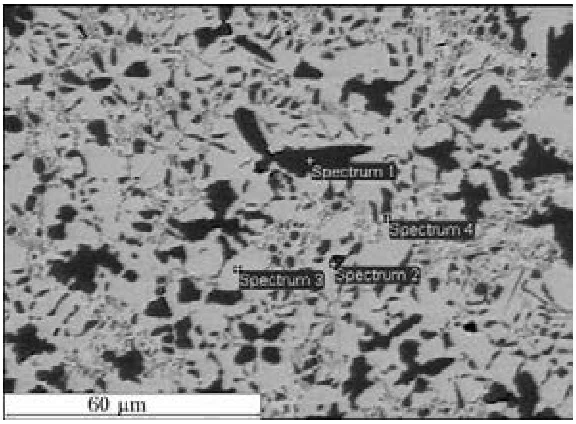

Figure 6. Microstructure (×400) of Ag–Cu–Zn–Sn–2Mn–1Ni system alloy

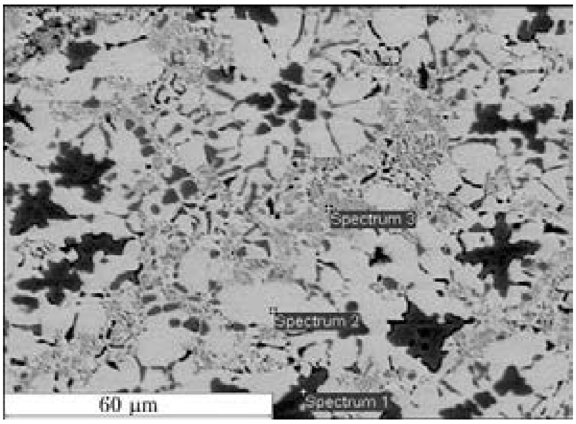

Figure 7. Microstructure (×400) of Ag–Cu–Zn–Sn–6Mn–4Ni system alloy

Conclusions

1. Nickel and manganese alloying of Ag–Cu–Zn–Sn system alloys allowed receiving the brazing filler metals, which provide good wetting of hard-alloy materials and stainless steel, and higher strength properties of brazed joints from stainless steel (up to 450 MPa) and hard alloys (up to 500 MPa).

2. Application of the brazing filler metals of investigated system requires no change of heating methods, flux composition, use of any special techniques and can be easily mastered in industrial conditions.

1. Roberts, P.M. (1978) Recent developments in cadmium-free silver brazing alloys. *Welding J.*, **10**, 23–30.
2. Timmins, P.F. (1994) The development of Ag-based brazing alloys. *Ibid.*, **10**, 31–33.
3. Khorunov, V.F., Maksymova, S.V., Stefaniv, B.V. (2010) Effect of tin additions on structure and technological properties of BFM of the Ag–Cu–Zn system. *The Paton Welding J.*, **7**, 16–21.
4. Khorunov, V.F., Maksymova, S.V., Stefaniv, B.V. (2012) Effect of palladium on structure and technological properties of Ag–Cu–Zn–Ni–Mn system brazing filler alloys. *Ibid.*, **9**, 20–25.
5. Klochko, N.A. (1981) *Principles of technology of brazing and heat treatment of hard-alloy tool.* Moscow: Metallurgiya.

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