https://doi.org/10.37434/tpwj2021.08.04

INFLUENCE OF ALLOYING ELEMENTS ON SOLIDUS AND LIQUIDUS TEMPERATURES OF ALLOYS OF Cu–Mn–Ni–Si SYSTEM

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Plasma brazing of steels is performed using brazing filler metals having liquidus temperature higher than 1000 °C. This work shows the possibility of lowering the brazing temperature by applying brazing filler metals having a lower melting temperature. The method of high-temperature differential thermal analysis was used to establish the influence of manganese, nickel and silicon on solidus and liquidus temperatures of experimental alloys of the Cu–Mn–Ni–Si system. Empirical data and mathematical processing methods were applied to determine the influence of chemical elements on calculated coefficients of the impact of alloying elements on solidus and liquidus temperatures of alloys of the Cu–Mn–Ni–Si system that promotes lowering of melting temperature. The influence of nickel and silicon content at a fixed quantity of manganese of 10 and 16 wt.% on the spreading area over 08kp (rimmed) steel and melting temperature range was studied. High-quality formation of brazed joints from 08kp alloy produced by plasma brazing with application of the studied alloys was proved experimentally. 16 Ref., 2 Tables, 5 Figures.

Keywords: plasma brazing, spreading area, solidus and liquidus temperature, high-temperature differential thermal analysis, melting temperature range

Currently, as an alternative to MIG brazing, the process of plasma brazing is developed, in which two independent arcs are used — pilot and primary one. Pilot arc is burning between the nozzle and tungsten electrode, and primary arc is burning between the tungsten electrode and a product. Brazing is performed using an direct constant and modulated current, the brazing filler metal is supplied automatically. Plasma brazing is quite successfully applied to join parts in the manufacture of car bodies, metal-plastic windows and ventilation boxes [1–6]. For plasma brazing, a wide range of standard copper based alloys is proposed, which are divided into three groups, depending on the nature of alloying (Table 1).

Most often bronzes alloyed with silicon (SG–$CuSi_3$) and aluminium (SG–$CuAl_8$) are used. All brazing filler metals have a liquidus temperature of about 1000 °C and higher. A decrease in the melting temperature of the brazing filler metal allows reducing the input energy required to produce high-quality brazed joints [6, 9, 10]. This leads to a decrease in residual stresses and an increase in the life of brazed joints.

Table 1. Chemical composition of brazing filler metals and melting temperature [7, 8]

Order number	Bronze grade	Melting temperature interval, °C
1	SG–CuSi3	910–1025
2	SG–CuSn6	910–1040
3	SG–CuAl8	1030–1040

The aim of the work is to establish the regularities of the influence of Mn, Ni and Si on the solidus and liquidus temperature of alloys of the Cu–Mn–Ni–Si system, which are used as brazing filler metals in plasma brazing.

Procedure of experiment. For investigations, cast brazing filler metals were produced in a laboratory electrode installation (Figure 1) on a copper water-cooled substrate in a purified argon.

As the source components, materials with cleanliness of not lower than 99.95 wt.% were used. The solidus and liquidus temperature of the produced alloys was determined by the method of high-temperature differential thermal analysis in the VDTA-8M installation in helium at heating and cooling rates of 40 °C/min. Based on the multifactorial planning method [11] and the analysis of binary diagrams of the state Cu–Mn, Cu–Ni and Cu–Si [12, 13], a matrix with a variable composition of alloying elements Mn, Ni and Si was plotted. Cu–13Mn–2Ni–2Si** alloy with a solidus temperature of 823 °C, and a liquidus one of 962 °C (interval of crystallization temperature is 139 °C) was selected as the base one. Concentration borders of manganese

**Here and further wt.%.

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Figure 1. Laboratory installation for melting brazing filler metals in argon

(10–16 wt.%) were selected based on the analysis of binary diagrams of the state copper-manganese [12] with the account of the melting temperature interval.

The wetting of the experimental brazing filler metals of steel 08kp was performed using arc (TIG) method that contributes to the uniform heating of the larger area of the base metal substrate as compared to plasma heating [14]. The heating temperature was monitored using the Cr/Al thermocouple and the TRM device.

The ends of the thermocouple were welded-on from the reverse side of the base metal (substrate) to produce a hot brazing filler metal. The calculation of the obtained experimental data from spreading (spreading area) was carried out using AutoCard software.

For plasma brazing of specimens from steel 08kp, the power source KEMPPI Master TIG 2300 with a plasma module was used.

According to the standard procedure, microsections were prepared that were investigated without chemical etching using the TescanMira 3 LMU electron scanning microscope.

Results of experiments and their analysis. The influence of alloying elements Mn, Ni and Si to the liquidus and solidus temperature of copper-based alloys was evaluated using formulas (1) and (2). In fact, this implies the decomposition of the function of influence in a series of Taylor [15, 16] in the area of melting pure copper.

$$T^{\mathrm{sol}}_{(\mathrm{Cu})} = T_{\mathrm{Cu}} + \left(\frac{\partial T_{\mathrm{Cu}}}{\partial C_{\mathrm{Mn}}}\right)^{\mathrm{sol}} C_{\mathrm{Mn}} + \left(\frac{\partial T_{\mathrm{Cu}}}{\partial C_{\mathrm{Ni}}}\right)^{\mathrm{sol}} \times \times C_{\mathrm{Ni}} + \left(\frac{\partial T_{\mathrm{Si}}}{\partial C_{\mathrm{Si}}}\right)^{\mathrm{sol}} \times C_{\mathrm{Si}}; \quad (1)$$

$$T^{\mathrm{lic}}_{(\mathrm{Cu})} = T_{\mathrm{Cu}} + \left(\frac{\partial T_{\mathrm{Cu}}}{\partial C_{\mathrm{Mn}}}\right)^{\mathrm{lic}} C_{\mathrm{Mn}} + \left(\frac{\partial T_{\mathrm{Cu}}}{\partial C_{\mathrm{Ni}}}\right)^{\mathrm{lic}} \times \times C_{\mathrm{Ni}} + \left(\frac{\partial T_{\mathrm{Si}}}{\partial C_{\mathrm{Si}}}\right)^{\mathrm{lic}} C_{\mathrm{Si}}, \quad (2)$$

where $\frac{\partial T_{\mathrm{Cu}}}{\partial C_i}$ is the tangent of the inclination angle of the solidus and liquidus lines near the melting point of pure copper on the diagrams of the state of the respective binary systems [13]. The area of the used alloying concentrations show that the dependence of solidus and liquidus temperature can be accepted as close to the linear and the ratio $\frac{\partial T_{\mathrm{Cu}}}{\partial C_i}$ can be changed for $\frac{\Delta T_{\mathrm{Cu}}}{\Delta C_i}$, which indicates the influence of Mn, Ni and Si on the solidus and liquidus temperature of copper-based alloys within the alloying complex, %: 1–3 of silicon; 1–3 of nickel and 10–16 of manganese. According to the results of calculations, it was determined that silicon greatly affects a decrease in the solidus and liquidus temperature (Table 2).

The calculated coefficients of the influence of alloying elements on the solidus and liquidus temperature in the alloys of the Cu–Mn–Ni–Si system show that at a set change in the concentration interval of the alloying elements, a decrease in the solidus and liquidus temperature is more strongly influenced by a silicon content with a coefficient of –40.5 for solidus temperature and –23.5 for liquidus one. The amount of manganese affects the decrease in the solidus and liquidus temperature to a lower extent, which is indicated by lower values of the coefficients: –8.3 and –0.33 (for solidus and liquidus temperature, respectively).

Based on the experimental data, which were obtained while spreading of the investigated alloys, it was found that the presence of nickel within 1–3 % in the brazing filler metal of the Cu–Mn–Ni–Si system at a fixed concentration of manganese of 10 and silicon of lower than 2 %, leads to a decrease in spreading area (as

Table 2. Coefficients of influence of alloying elements on solidus and liquidus temperature of copper-based alloys (calculated data)

Alloying element *i*	$\Delta T_i^{\mathrm{lic}}$, °C	$\Delta T_i^{\mathrm{sol}}$, °C	ΔC_i, wt.%	$(\Delta T/\Delta C)^{\mathrm{lic}}$	$(\Delta T/\Delta C)^{\mathrm{sol}}$
Mn	–62	–50	6	–10.33	–8.33
Ni	12	7	2	6	3.5
Si	–47	–81	2	–23.5	–40.5

Note. ΔC is the change of concentration interval, in which a decrease in melting temperature by the value of ΔT is observed. ΔT is a change in the temperature range, which depends on the concentration of the constituent elements.

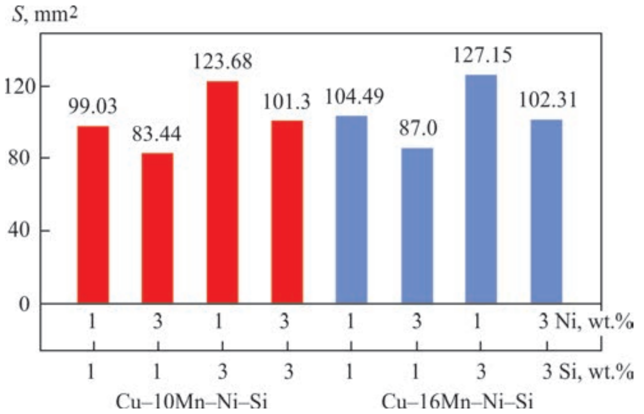

Figure 2. Dependence of spreading area of experimental alloys of the Cu–Mn–Ni–Si system at a fixed Mn content on the amount of Mn and Si

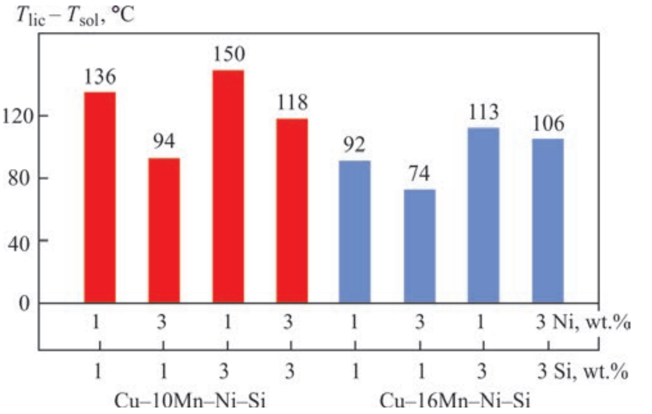

Figure 4. Dependence of temperature interval of melting experimental alloys of the Cu–Mn–Ni–Si system on content of manganese, nickel and silicon

compared to the base one). An increase in the concentration of silicon to more than 2 % and a decrease in the nickel content contribute to an increase in the spreading area as compared to the base alloy (Figure 2).

At a concentration of manganese of 16 % and silicon of lower than 2 %, a reduction in nickel content (up to 1 %) as compared to the base one increases the spreading area, and an increase in nickel to higher than 2 %, leads to a decrease in the spreading area. In the alloys with the content of manganese of 16 % and nickel of lower than 2 % and silicon within 1–3 %, a gradual increase in the spreading area to 104.49 and 127.15 mm^2, respectively, is observed. With an amount of nickel being higher than 2 %, a reduction in the silicon content as compared to base one reduces the spreading area.

The results of investigations of experimental brazing filler metals by high-temperature differential thermal analysis showed that with a manganese content of 10 % and of silicon being lower than 2 %, nickel alloying in the range of 1–3 % increases the solidus and liquidus temperature. While reducing the amount of nickel in the alloy containing 10 % of manganese and more than 2 % of silicon, a decrease in the solidus and liquidus temperature of the alloy is observed. An increase in the content of the nickel increases the solidus temperature (Figure 3, *a*).

In the alloy containing 16 % of manganese and lower than 2 % of silicon, alloying by nickel contributes to an increase in the solidus temperature. The liquidus temperature also grows, but slightly (Figure 3, *b*). Doping of the alloy by silicon (up to 3 %), containing an increased concentration of nickel (up to 3 %) contributes to reduction in the solidus and liquidus temperature (Figure 3, *a, b*).

It is known that the temperature interval of melting is the difference between the solidus and liquidus temperature of the alloy. From the obtained results of investigations, it follows that at the concentration of manganese of 10 % and silicon being lower than 2 %, alloying by nickel reduces the crystallization interval as compared to the base alloy.

The content of silicon being higher than 2 % and a decrease in the amount of nickel lead to an increase in the temperature interval of melting as compared to the base values, whereas an increase in the nickel content reduces it (Figure 4).

Nickel doping within 1–3 % of the alloy of the Cu–Mn–Ni–Si system containing 16 % of manganese and less than 2 % of silicon leads to a decrease in the temperature interval of melting, which is also observed in the alloys, containing more than 2 % of silicon.

Based on the obtained results of experimental investigations, the optimal components of brazing filler metals with an acceptable temperature interval were selected, which were used in plasma brazing. Structur-

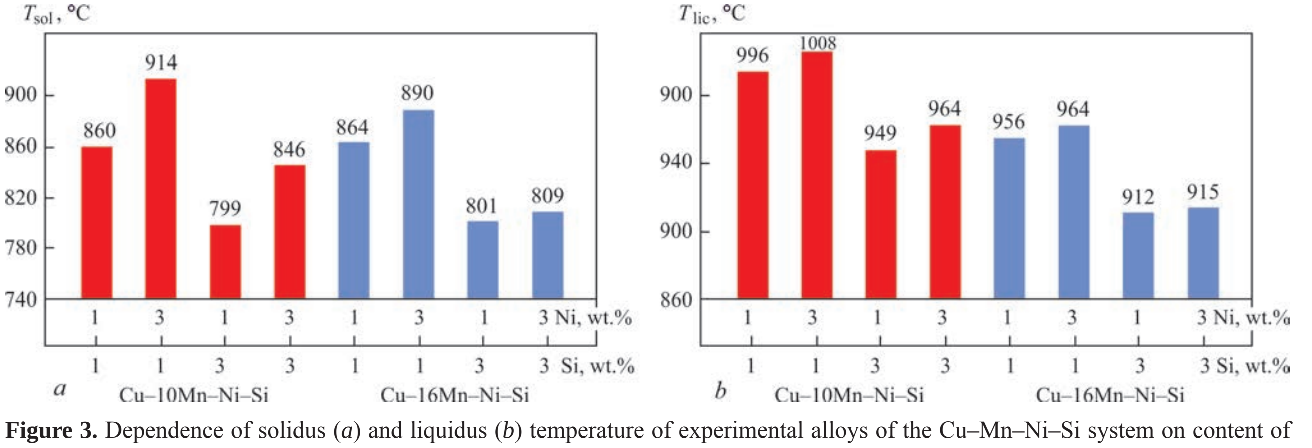

Figure 3. Dependence of solidus (*a*) and liquidus (*b*) temperature of experimental alloys of the Cu–Mn–Ni–Si system on content of manganese, nickel and silicon

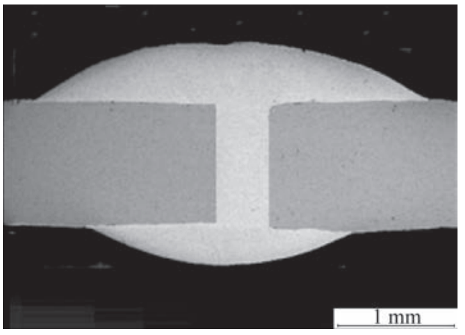

Figure 5. Brazed joint of steel 08kp, produced in plasma brazing

al investigations of brazed joints showed a high-quality formation of dense defect-free welds while using the brazing filler metal Cu–16Mn–1Ni–3Si (T_{lic} = = 912 °C) (Figure 5).

Conclusions

Applying the calculation method, the coefficients of influence of alloying elements on the solidus and liquidus temperature in the alloys of the Cu–Mn–Ni–Si system were determined, which show that at a set change in the concentration interval of alloying elements, a decrease in the solidus and liquidus temperature is more strongly influenced by a silicon content with a coefficient of –40.5 for solidus temperature and –23.5 for liquidus one. The amount of manganese affects a decrease in the solidus and liquidus temperature to a lower extent, which is indicated by lower values of the coefficients: –8.3 and –10.33 (for solidus and liquidus temperature, respectively).

It was experimentally proved that alloying with nickel within the range of 1–3 % of the alloy of the Cu–Mn–Si system, which contains a fixed amount of manganese of 10 %, silicon of lower than 2 %, leads to a decrease in the spreading area (to 99.03–83.44 mm^2) and an increase in the solidus temperature to 860–914 °C and the liquidus one to 996–1008 °C as compared to the base alloy. At an increase in the concentration of silicon to 3 %, a decrease in the content of nickel promotes an increase in the spreading area to 123.68 mm^2 as compared to the base alloy.

The results of experimental studies show that an increase in the nickel content at a manganese concentration of 10 % and that of silicon being lower than 2 % reduces the melting temperature interval from 136 to 94 °C as compared to the base one. Reducing the amount of nickel in the alloy with an increased concentration of silicon (more than 2 %) increases the of melting temperature interval to 150 °C as compared to the similar indices of the base alloy.

Nickel doping of the alloy containing 16 % of manganese and less than 2 % of silicon reduces the temperature interval of crystallization to 74–92 °C as compared to the base values. At an increased concentration of silicon, alloying with nickel leads to an increase in the melting interval to 106–113 °C.

On the basis of a comprehensive evaluation of empirical data, the concentration limits of alloying elements were selected, wt.%: 10–16 Mn, 1–3 Ni, 1–3 Si, which provide an acceptable solidus and liquidus temperature of the brazing filler metal on the base of copper and high-quality formation of brazed joints from steel 08kp.

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Received 28.04.2021