EFFECT OF TIN ADDITIONS ON STRUCTURE AND TECHNOLOGICAL PROPERTIES OF BRAZING FILLER METALS OF THE Ag–Cu–Zn SYSTEM

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The effect of tin and silicocalcium additions on structure, melting temperature ranges and spreading of alloy of the Ag–Cu–Zn system was investigated. It was found that cadmium-free brazing filler metals are characterised by good performance and provide strength properties of the joints close to those provided by brazing filler metal PSr-40.

Keywords: *brazing, brazing filler metals, cadmium-free brazing filler metal, eutectic, thermal analysis, structure, technological properties*

Silver-base brazing filler metals found practical application several thousands years ago. They have become strongly established in modern market of brazing consumables. Silver in its pure form can be applied as a brazing filler metal. However, most of the filler metals are based on eutectic of the Ag–Cu system [1], having a melting point of 779 °C and containing approximately 28 wt.% Cu. Adding zinc to the Ag–Cu system alloys leads to formation of ternary eutectic 56Ag–24Zn–20Cu (point *E* in Figure 1) with a melting point of 665 °C [2].

To decrease their melting point, alloys of this system are doped with the fourth (fifth, sixth) element. Wide acceptance has been received by the Ag–Zn–Cu–Cd system filler metals, which are plentiful in the market. Their different modifications are included both in catalogues of all companies manufacturing brazing filler metals and in standards of industrialised countries [3]. The main advantage of this system of the filler metals is that they have the lowest brazing temperature among a wide range of silver-base brazing filler metals. For example, temperature of eutectic of this quaternary system (45Ag–15Cu–16Zn–24Cd) is approximately 615 °C [4], whereas the most widely applied brazing filler metal PSr-40 has a solidus temperature of 590 °C and liquidus temperature of 610 °C. These filler metals are used to advantage for brazing different materials, and for the extensively applied iron- and copper-base alloys they provide joints with good mechanical properties.

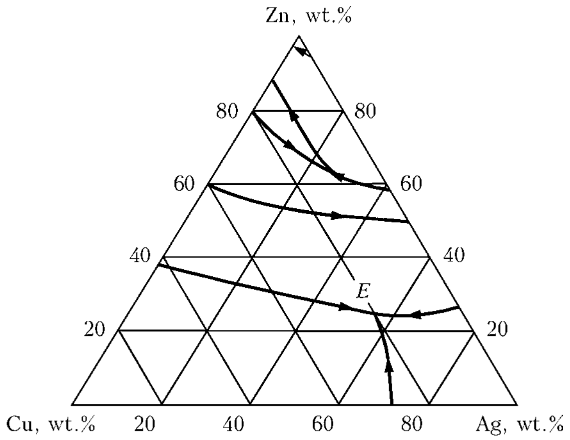
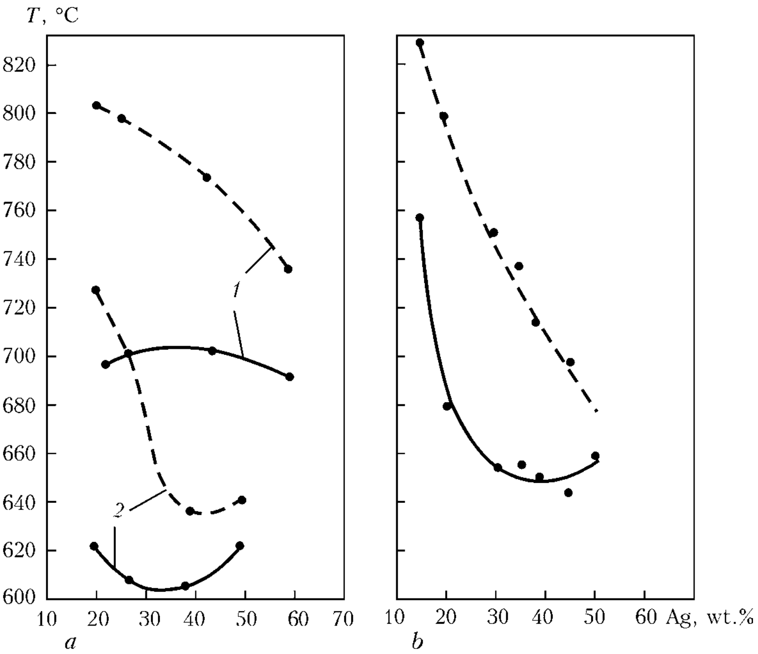


Figure 1. Projection of solidification surface of constitutional diagram for Cu–Ag–Zn system [2]

Meanwhile, the problem of replacing cadmium in brazing filler metals has arisen long ago. The European Parliament and United Europe Consulate Council adopted a directive that prohibits application of hazardous materials, including cadmium, in particular. Tin was chosen as an alternative to it [5, 6].

Study [5] gives data that in alloys of the Ag–Cu–Zn, Ag–Cu–Cd and Ag–Cu–Zn–Sn systems (Figure 2) the solidus and liquid temperatures can be considerably decreased due to a tin addition, compared with the ternary system. However, in this case the melting temperature range is higher. To reach a solidus temperature of the alloys equal to about 630 °C, it is necessary that the silver content of alloy Ag–Cu–Zn–Sn be about 55 wt.%, i.e. a bit higher than in the widely applied filler metals. In opinion of the author of study [5], this may lead to a 15–20 % increase in the cost of work. Later, the similar task was posed in study [6], which, by the way, made a wide use of the data of study [5], in particular data on alloys 1 and 4 (Table 1). It should be noted that the range of brazing filler metals considered in study [7] has been much widened. That study contained the data on strength properties of brazing filler metal in the as-cast state, and compared alloys of the Ag–Cu–Zn, Ag–Cu–Zn–Sn and Ag–Cu–Zn–Cd systems.

It follows from the data given in Table 1 that brazing filler metals of the Ag–Cu–Zn–Sn system are not inferior to the ternary system filler metals and to those containing cadmium, which is very important for their practical application. At this point, one should note the following interesting fact. Filler metals 3–5 (Table 1) have close chemical composition, which corresponds to standard American filler metal BAg-28. At the same time, they are markedly differing



a *b*

Figure 2. Variations in solidus (solid curve) and liquidus (dashed curve) temperatures in alloys of the Ag–Cu–Zn (*1*), Ag–Cu–Zn–Cd (*2*) (*a*) and Ag–Cu–Zn–Sn (*b*) systems depending on their silver content

in their mechanical properties, filler metal 5 having the lowest strength, and filler metal 4 having the highest strength among all the alloys investigated. Study [6] gives no explanation to this fact. It gives no strength characteristics of the brazed joints either.

Judging from the ranges of products present in the market, the filler metals under consideration have not yet ousted the cadmium-containing ones. More information on alloys of the Ag–Cu–Zn–Sn system is required to reveal the cause of low popularity of these filler metal in the world market.

The purpose of the present study was to investigate the effect of tin additions (3–10 wt.%) in alloys of the Ag–Cu–Zn system on structure of the latter, spreading area and strength of the resulting brazed joints in steel 12Kh18N10T, as well as on the same parameters with the silicocalcium addition.

The E.O. Paton Electric Welding Institute carried out investigations of the effect of tin on the melting range, structure and strength of the joints. The charge was made from pure materials (silver of the SrA-1 grade, cathode copper M0k, and zinc of the TsV grade). Allowing for a high pressure of the saturated zinc vapour, the zinc content in the charge was 2 % higher than in the filler metal. Filler metals were melted by high-frequency heating in the graphite crucible, and flux PV200 was used for shielding. First copper and silver were melted, then heating was stopped, and zinc and cadmium were added after the metal temperature decreased to 400–500 °C. To provide a homogeneous melt by induction and mechanical stirring, a filler metal was subjected to repeated short-time heating until it melted down.

Steel 12Kh18N10T 2 mm thick was chosen as a base metal. Billets measuring 100 × 20 × 2 mm were brazed by using gas-flame heating and flux PV209. Overlap was 2 mm. The flux was preliminarily applied to the brazing zone in the form of paste mixed with

Table 1. Chemical composition, melting ranges and strength of brazing filler metals [6]

Number of filler metal	Chemical composition of elements, wt.%					Melting temperature range, °C	Tensile strength in cast state, MPa
	Ag	Cu	Zn	Sn	Cd		
1	30	36	32	2	–	665–755	448
2	35	34	30	1	–	660–740	476
3 (BAg-28)	39	31	28	2	–	645–725	473
4 (BAg-28)	39	31	27	3	–	635–710	497
5 (BAg-28)	40	30	28	2	–	649–710*	406
6 (BAg-1a)	50	15	16	–	19	627–635*	457
7	40	30	28	–	–	–	441
8	45	25	30	–	–	–	425

*The data are taken from study [3].

Table 2. Results of tests of brazing filler metals of the Ag–Cu–Zn–Sn system to spreading and shear strength of the brazed joints in steel 12Kh18N10T

Number of filler metal batch	Filler metal system	Spreading area, mm^2	Shear strength, MPa
1	56Ag–22Cu–17Zn–5Sn	130.3	$\frac{242.7–297.9}{267.4}$
2	57.5Ag–22.5Cu–17Zn–3Sn	125.9	$\frac{267.3–288.5}{275.4}$
3	55Ag–21.5Cu–16.5Zn–7Sn	140.9	$\frac{251.4–263.9}{259.5}$
4	55Ag–20Cu–15Zn–10Sn	127.9	$\frac{158.1–214.1}{187.8}$
5	56Ag–22Cu–17Zn–5Sn–0.25SiCa	117.5	$\frac{250.3–277.2}{263.1}$
6	57.5Ag–22.5Cu–17Zn–3Sn–0.25SiCa	119.2	$\frac{284.9–298.8}{290.5}$
7	55Ag–21.5Cu–16.5Zn–7Sn–0.25SiCa	139.2	$\frac{234.5–261.2}{251.1}$
8	55Ag–21.5Cu–15Zn–10Sn–0.25SiCa	152.1	$\frac{168.4–203.0}{183.1}$

water, which was dried before heating. After heating to a melting temperature of the flux, a filler metal preform was placed on the joining zone, and heating was continued till melting of the preform and formation of the joint. The samples after brazing were machined to remove reinforcement, and then tensile tested using the MTS-20 testing machine.

The experiments on spreading of brazing filler metals were carried out according to GOST 23904–79. Filler metal preforms (0.50 + 0.01) g in weight were placed on a plate measuring 40 × 40 mm. The flux was poured from above on the filler metal placed on the substrate. The samples were heated for 3 min in the furnace preliminarily heated to 700 °C. The area of spreading of each filler metal was calculated using the AutoCard 2002 software. Compositions of the investigated filler metals and results of the experiments on spreading and strength of the brazed joints are given in Table 2.

Analysis of the obtained data showed that the area of spreading of filler metals with a different tin content is approximately within the same ranges, i.e. the tin content has an insignificant effect on this characteristic, including in the silicocalcium-containing alloys. Some increase in the spreading area can be noted only at a tin content of 7 wt.%. It follows from Table 2 that strength of the joints decreases with increase in the tin content of a filler metal. While strength of the joints brazed with the filler metal containing 3 wt.% Sn is 275 MPa, that with the filler metal containing 10 wt.% Sn is 187 MPa. Moreover, consistency of the results decreases with increase in the tin content.

The brazing filler metals containing silicocalcium exhibit the same trend: strength of the joints brazed with the filler metal containing 3 wt.% Sn is 290 MPa, and that with the filler metal containing 10 wt.% Sn is 183 MPa. Consistency of the test results decreases accordingly. At the same time, the data presented show some increase in strength of the joints with a silicocalcium addition to the alloy containing 3 wt.% Sn. In this case, doping with silicocalcium should be considered useful. At a considerable tin content the effect of silicocalcium is levelled. It means that adding it is inexpedient.

New data were obtained from investigation of melting ranges and structures of the considered alloys with a different tin content. Melting ranges of the alloys were determined by using the VDTA-8 unit in the helium atmosphere. Weight of the investigated sample was 1.03 g, and rate of its heating and cooling was 80 °C/min. The samples were heated two times to achieve a good fit of the preform to the crucible bottom and provided reliable data on thermal effects. The thermal effects were fixed on the second heating curve, the solidus and liquidus temperatures of the alloy were also determined from this curve (overcooling prior to solidification has a substantial effect in cooling of the alloy). At the same time, the level of the thermal effects is better reflected on the alloy cooling curves.

Analysis of the obtained data showed that doping with tin has a substantial effect on the phase transformation temperature and melting range. For instance, the composition of alloys with 3 wt.% Sn is practically single-phase (Figure 3, *b*). The solidus temperature is 640 °C, and the liquidus temperature is 690 °C. A hardly perceptible thermal effect takes place at a temperature of 680 °C. It does not show up appreciably even in cooling, i.e. the second phase content is insignificant. Emergence of the thermal effect

Table 3. Chemical composition (wt.%) of alloys determined by thermal analysis

Investigated region	Ag	Cu	Zn	Sn	Si
57.5Ag–22.5Cu–17Zn–3Sn (eutectic)					
Dark phase	32.072	47.222	19.359	1.344	0
Light phase	75.732	6.880	13.305	3.833	0.252
Eutectic	74.127	12.133	12.948	0.711	0.085
57.5Ag–22.5Cu–17Zn–3Sn–0.25SiCa (eutectic)					
Dark phase	18.212	58.161	21.811	1.285	0.528
Light phase	75.835	7.609	13.046	3.333	0.189
Eutectic	73.486	7.144	13.534	5.716	0.120
56Ag–22Cu–17Zn–5Sn					
Dark phase	15.638	59.222	22.458	2.517	0.160
Light phase	74.588	9.837	11.880	3.696	0
Eutectic	69.885/68.269	6.400/6.867	9.698/10.379	13.917/14.257	0.091/0.219
56Ag–22Cu–17Zn–5Sn–0.25SiCa					
Dark phase	17.153	55.552	24.570	2.486	0.236
Light phase	72.037	8.520	12.320	6.838	0.285
Eutectic	58.129	18.081	14.749	7.846	0.393
55Ag–21.5Cu–16.5Zn–7Sn–0.25SiCa					
Dark phase	17.706	60.295	20.517	1.182	0.298
Light phase	77.668	3.793	10.968	7.274	0.305
Eutectic	74.851	4.467	11.466	8.798	0.423
55Ag–21.5Cu–16.5Zn–10Sn–0.25SiCa					
Dark phase	9.551	64.382	22.305	3.357	0.402
Light phase	76.841	5.075	7.932	10.027	0.963
Eutectic	72.816	6.234	8.343	12.312	0.290

becomes noticeable at a temperature of 480–490 °C, which can hardly be associated with melting of a low-melting point component. Most likely, this is a result of phase transformation in the solid phase, which is indirectly confirmed by the presence of a number of transformations occurring in the solid phase of the Sn–Cu system [7].

The results obtained for the alloy with 5 wt.% Sn are approximately identical to those obtained for the alloy with 3 wt.% Sn (Figure 3, *a*), i.e. it is almost single-phase in melting and solidification, the thermal effect taking place at a temperature of 490 °C. The insignificant increase of the liquidus temperature is hard to explain. Moreover, the thermal effect in this case is located lower on the cooling curve than for the alloy with 3 wt.% Sn. Strength of the joints decreases to some extent.

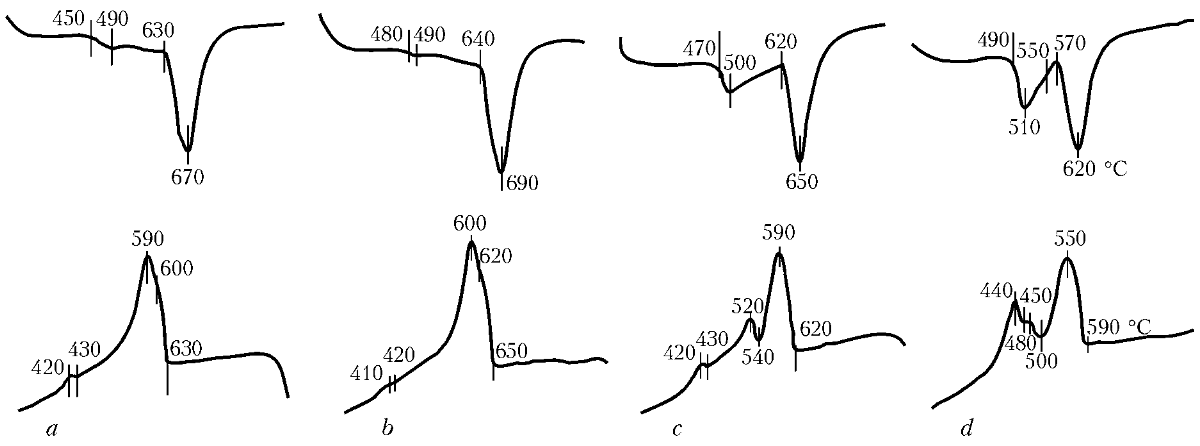


Figure 3. Data of differential thermal analysis of alloys of the 56Ag–22Cu–17Zn–5Sn (*a*), 57.5Ag–22.5Cu–17Zn–3Sn (*b*), 55Ag–21.5Cu–16.5Zn–7Sn (*c*) and 55Ag–20Cu–17Zn–10Sn (*d*) systems

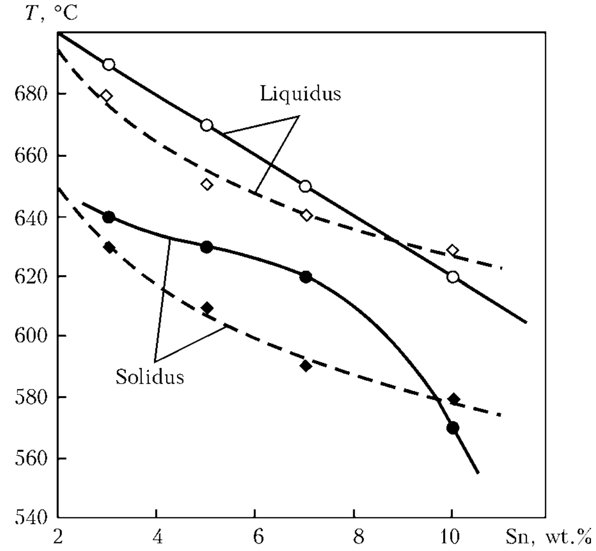


Figure 4. Variations in liquidus and solidus temperatures in alloys of the Ag–Cu–Zn–Sn (solid curve) and Ag–Cu–Zn–Sn (SiCa) (with the silicocalcium addition) (dashed curve) systems

The presence of the two thermal effects emerging at temperatures of 620–650 and 470–500 °C is clearly fixed in the alloy with 7 wt.% Sn. The presence of the third effect can be seen in the cooling curve at a temperature of 420–430 °C (Figure 3, *c*). Strength of the joints brazed with this filler metal is markedly lower.

The presence of the thermal effect, but in a more explicit form, was fixed in the alloy with 10 wt.% Sn (Figure 3, *d*). Strength of the joints is much lower (approximately by 90 MPa, compared to the joints brazed with the alloy with 3 wt.% Sn). Approximately the same phenomena are fixed in the alloys containing a silicocalcium addition with increase in the tin content as in the alloys without the silicocalcium addition (Figure 4).

Examination of structure and chemical heterogeneity of alloys with 3 wt.% Sn showed that they can be classed with the eutectic structures with a higher or lower content of the primary phase. The silicocalcium addition does not change the general character of structure (Figure 5, *a, b*). The eutectic composition is difficult to identify in a complex structure. However, it is possible to judge on the composition of individual phases. The dark phase (based on copper) contains approximately 32 wt.% Ag, 19 wt.% Zn and 1.3 wt.% Sn (Table 3), and the light phase (based on silver) contains about 6.8 wt.% Cu, 13.3 wt.% Zn and

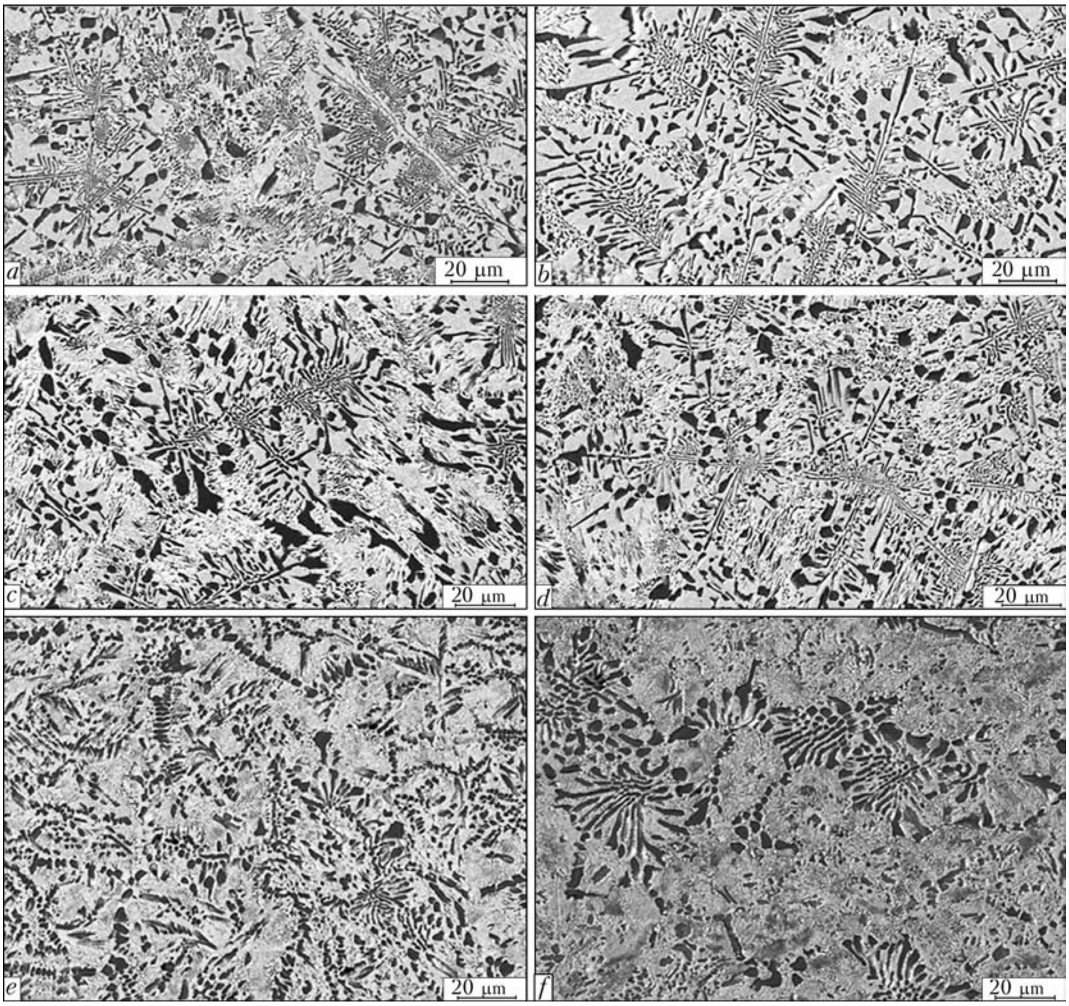


Figure 5. Microstructure of alloys of the 57.5Ag–22.5Cu–17Zn–3Sn (*a*), 57.5Ag–22.5Cu–17Zn–3Sn–0.25SiCa (*b*), 56Ag–22Cu–17Zn–5Sn (*c*), 56Ag–22Cu–17Zn–5Sn–0.25SiCa (*d*), 55Ag–21.5Cu–16.5Zn–7Sn–0.25SiCa (*e*) and 55Ag–20Cu–15Zn–10Sn–0.25SiCa (*f*) systems

3.8 wt.% Sn. The first composition is in a higher temperature range than the second one. Therefore, the first alloy should be a bit more high-temperature one, and should be the first to solidify, which can be seen in Figure 5, *a, b*. The alloys containing tin solidify in almost indiscernible temperature ranges (see Figure 3, *c*). Supposedly, solidification of the alloys occurs as follows. Primary dendrite of the copper-base phase precipitate from the liquid, and then the second phase starts solidifying around the first one in a close temperature range, i.e. solidification of the conglomerate eutectic takes place, and solidification of the normal (lamellar) eutectic begins in the intervals. As the primary crystals are few, the normal eutectic takes a larger part of a section. It should be noted that in some cases the eutectic has a sort of the dendrite stem, and the eutectic colony looks like the «eutectic dendrite». Similar eutectic solidification was noted in filler metal of the Ni–Mn–Cu–Si system [8].

Adding silicocalcium does not have a marked effect on structure of a brazing filler metal, as well as on distribution of elements into structural components.

As noted above, the curves plotted with the help of high-temperature differential analysis for alloys with 3 and 5 wt.% Sn are very similar to each other. The same can be said about structure of these alloys (see Figure 5, *a*–*d*). It should be noted that the tin content of structural components of alloys with 5 wt.% Sn increases, especially with the silicocalcium addition.

With increase in the tin content to 7 wt.%, the content of the dark high-temperature phase based on copper also grows, and structure as a whole (especially the eutectic component) becomes greatly refined, like in the case with 10 wt.% Sn (Figure 5, *e*). At the same time, the alloys with 10 wt.% Sn and siliconcalcium addition comprise the eutectic regions with coarser grains (Figure 5, *f*). Probably, this depends upon the ingot cooling conditions.

It can be concluded on the basis of the results obtained that the additions of tin to the alloys of the Ag–Cu–Zn system have a less efficient influence than the additions of cadmium. For example, the minimal achieved liquidus temperature is about 650 °C even in the alloys with 7 wt.% Sn, i.e. it is much higher than in the alloys with a high cadmium content. However, at a tin content of 7 and more than 10 wt.%, the melting range is two-phase and very wide, this deteriorating the technological properties of the filler metal. In addition, strength characteristics of the joints become much worse (see Table 3). It can be stated on the basis of the results obtained that alloys with 3 or maximum 5 wt.% Sn are most suitable for the application. Moreover, the silicocalcium addition should be considered useful.

CONCLUSIONS

1. The investigated compositions of environmentally clean brazing filler metals of the Ag–Cu–Zn–Sn system have structure close to the eutectic one, suitable melting range, and provide good technological properties of the joints.

2. Utilisation of these filler metals instead of those of the Ag–Cu–Zn–Cd system for brazing stainless steels provides the comparable strength values at a tin content of the filler metals equal to no more than 5 wt.%.

3. Filler metals of the system under consideration do not require any changes in heating methods and compositions. They require no special approaches, and can be easily applied under industrial conditions.

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