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PROPERTIES OF LEAD-FREE TIN SOLDERS FOR METAL AND MECHANIC SECTOR

WŁAŚCIWOŚCI BEZOŁOWIOWYCH LUTÓW CYNOWYCH DLA ZASTOSOWAŃ W BRANŻY METALOWEJ

Beside electronic industry, soft soldering is quite widely used in the machine sector as well as for assembly, installation and tinsmith work. Technological processes of these industries usually involve copper, various grades of brass and unalloyed steel as parent metals, whilst tin-lead filler metals with Sn content of 40-60% usually serve as soft solders. In addition, active soldering fluxes based on chlorides and mineral acid are also applied.

The presented work investigated the possibility to substitute the aforementioned tin-lead solders with lead-free solder alloys as Sn-Ag, Sn-Ag-Cu, Sn-Ag-Bi, Sn-Ag-Zn, Sn-Zn and Sn-Zn-Ag with the lowest possible melting point and a narrow range of crystallization temperatures (nearly-eutectic alloys). The obtained results have revealed the most favourable properties of such solders as SnAg3.6Cu0.8 for unalloyed steel, brass and copper. Although the above solder alloy offered slightly poorer spreading properties, the wetting rate was sufficiently high and penetration into capillary gaps of soldered joints was comparable with conventional tin-lead solders. In return, its mechanical properties were much better than those of Sn-Pb solders as it provided higher strength parameters, in particular – the shear strength. The top value of shear strength was ascertained for the solders SnZn10Ag0.4 and SnAg3.03Zn0.95 but their applicability is limited due to relatively poor soldering properties, i.e. low wettability, poor capillary action and porosity of joints.

Keywords: Soldering, soft solder alloys, lead-free solder alloys, metal – mechanic sector, properties of solder alloys, properties of soldered joints

Lutowanie miękkie poza elektroniką jest także stosowane dość szeroko w przemyśle maszynowym a także w pracach instalatorskich i blacharskich. Jako materiały lutowane w tych procesach stosuje się przeważnie miedź, mosiądze i stale niestopowe, a spośród lutów miękkich spoiwa cynowo-ołowiowe o zawartości 40-60% Sn. W procesach tych stosuje się także aktywne topniki lutownicze na osnowie chlorków i kwasów nieorganicznych.

Przeprowadzone badania nad możliwością zastąpienia powyższych lutów cynowo-ołowiowych spoiwami bezołowiowymi typu Sn-Ag, Sn-Ag-Cu, Sn-Ag-Bi, Sn-Ag-Zn, Sn-Zn, Sn-Zn-Ag o najniższej temperaturze topnienia i możliwie wąskim zakresie krystalizacji (stopy zbliżone do eutektycznych) wykazały najkorzystniejsze wyniki w przypadku lutu SnAg3,6Cu0,8 dla stali niestopowych i mosiądzów oraz dla miedzi. Spoiwo to charakteryzowało się nieco niższą niż spoiwa typu Sn-Pb rozpływnością lecz wykazywało dużą szybkość zwilżenia i porównywalne wnikanie w szczeliny kapilarne połączeń. Wykazywało ono ponadto wyższe od spoiw typu Sn-Pb własności wytrzymałościowe i zapewniało znacznie wyższą wytrzymałość połączeń na ścinanie. Najwyższą wytrzymałość połączeń na ścinanie zapewniały luty SnZn10Ag0,4 i SnAg3,03Zn0,95 lecz ich przydatność praktyczną ograniczają stosunkowo słabe własności lutownicze tj. słaba zwilżalność niskie własności kapilarne i porowatość połączeń.

1. Introduction

The so-far investigations on properties of lead-free solders have been focused on assessment of their suitability for electronic applications [6–14]. Therefore the research used a limited scope of assessment criteria, specific for the relevant applications [1–4].

This paper aims to present results of research work that has been carried out at Instytut Spawalnictwa and was dedicated to properties of those lead-free tin solders with silver and zinc with a little admixture of copper and bismuth that are most frequently addressed in topic-related literature reference. The investigations examined suitability of such solders for general technical application in metallurgical industries, including workshop and industrial soldering of machine and equipment parts as well as other tin-smith and lock-smith work. The discussed technological processes mostly involve unalloyed and low-alloy steel, copper and brass as structural

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material whereas active mixtures of chlorides and acids perform as solder fluxes.

Investigation results outlined below cover soldering-related and mechanical properties of solder alloys along with strength parameters of soldered joints made by means of them, thus they constitute a valuable contribution to the knowledge on lead-free tin solders and the basis of tin-silver and tin-zinc alloys [14]. For comparison purposes the research have also taken into account tin-lead solders with content of 40% and 60% of Sn (respective grades S-Pb60Sn40 and S-Sn60Pb40 by PN – EN 29453:2000).

2. Investigated materials

2.1. Soldering filler metals and fluxes

To select the materials for the investigations, a series of existing tin solders was analyzed with regard to their anticipated suitability as substitutes for commonly used tin-lead solder alloys with Sn content of 40–63% and melting point between 183°C and 238°C. Eventually, the solders with chemical contents as listed in Table 1 were opted for further examination due to their application performance described in literature references [1–4, 6–11].

The selected solders on the basis of tin and silver as well as tin and zinc present the alloys with eutectic and nearly eutectic composition and melting point within the range between 198-221°C. Therefore they correspond to temperature performance of tin and lead alloys with Sn content of 40-60%. Moreover, the selected solders characterize relatively high strength parameters, as compared with other solder alloys and contain wetting components capable of adhering to the basic structural material (steel, copper and copper alloys). Thus, the selected solders can be considered as the most comprehensive for application, out of among all the tin-based solders.

The samples of solder alloys selected for investigations were melted in Instytut Spawalnictwa. Their chemical composition was analytically verified whereas the melting points were established on the basis of solidification curves.

As it was mentioned above, for comparison purposes the investigation included also tin- lead solders with Sn content of 40% and 60% (respectively, grades S-Pb60Sn40 and S-Sn60Pb40 by PN ? EN 29453:2000).

Technological tests and soldering of trial joints were carried out with use of highly active soldering flux composed on the basis of zinc and ammonia chlorides. The flux, with its commercial name Cynotop-S, developed and manufactured in Instytut Spawalnictwa in Gliwice. The flux is designed for soldering of copper and its alloys, unalloyed and low-alloy steels, zinc-plated steel as well as zinc and its alloys. Flux remnants, left on joints after soldering is completed, must be thoroughly removed as they are characterised by strong corrosive properties.

TABLE 1

Chemical composition of investigated solders and their melting points1)

No	Marking of heat or denomination of solder	Required chemical composition (remaining part up to 100% – Sn), %, m/m			Chemical composition "as is" (remaining part up to 100% – Sn), after analysis, %, m/m			Melting point, °C
		Ag	Zn	others	Ag	Zn	others	
1	1	3–4	–	–	3.35	–	–	221–223
2	2A	3–4	–	4.08–5.2 Bi	3.35	–	5.06 Bi	206–214
3	3	3–4	0.9–1.1	–	3.03	0.95	–	217–220
4	5	3–4	–	0.5–1 Cu	3.6	–	0.80 Cu	215–217
5	4A	0.3–0.5	8–10	–	0.40	10.0	–	199–206
6	Pb60Sb40			60 Pb			(39.20 Sn) remaining part – Pb	183–238
7	Sn60Pb40			40 Pb			(59.72 Sn) remaining part – Pb	183–190

1) The lead-free solders were melted in Instytut Spawalnictwa. Melting points were established on the basis of solidification curves.

2.2. Parent metals

The following parent metals were used to investigate soldering properties of filler metals as well as strength parameters of soldered joints:

- steel sheets of S235 J2G3 grade by PN-EN 10025;
- copper sheets of M1 grade by PN-77/H-82120;
- brass sheets of M63 grade by PN-92/H-87025.

3. Investigations on soldering properties of filler metals

Soldering properties of used solder alloys are strictly related to their capability of wetting of the materials that are to be joined. In order to determine soldering properties of the solder alloy samples under test, the following examinations were carried out:

- examination of wetting properties by means of the spreading method;
- examination of soldering material capability to penetrate capillary gaps.

3.1. Examination of spreading properties

Spreading properties of tin based and tin-lead solders were examined for samples of parent metals with dimensions of 30×30×0.1 mm and made of unalloyed steel (S235), copper (M1) and brass (M63). Prior to testing the samples were mechanically cleaned up to pure metal surfaces and then thoroughly degreased with acetone. Next, a spot of the 0.3 ml Cynotop-S flux was placed on the sample surface by means of measuring pipette and covered with a pill of soldering material with dimensions ⌀6×1.5 (ca. 0.5g) positioned on the spot centre. Finally, the entire arrangement was put on the top of heated table B 400R from Planer, Great Britain.

Respective temperatures of experiments were set to 250°C, 280°C and 310°C with thermostatic adjustment ±5°C. The hold time for the above samples at the specified temperatures was 60s as measured from the moment when the soldering material started to melt.

The spreading factor, as recommended by the topic-related literature references [2, 3] as well as the standard PN-EN ISO 9455-10:2004 was adopted as the major measuring parameter for spreading of solder alloys. The factor is defined in the following way:

$$K_H = \frac{D - H_{SR}}{D} \cdot 100\%, \tag{1}$$

where: $D = 1.24\ V^{\frac{1}{3}}$ (V – volume of the soldering alloy pill 42.39 mm^3); it is diameter of the soldering alloy drop if no wetting occurs, H_{SR} – arithmetical mean of the soldering material thickness after spreading (averaging over five samples).

Experimental results are shown on Fig. 1.

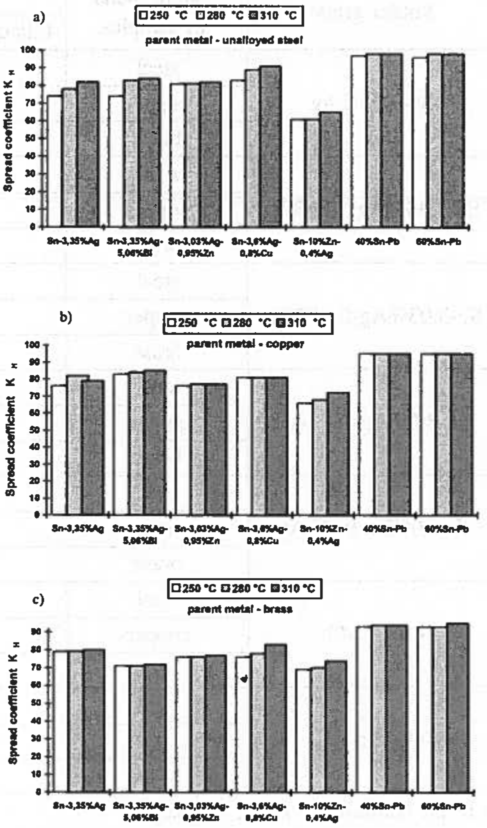

Fig. 1. Values of spread coefficient K_H for tin-lead solders at temperatures of 250°C, 280°C and 310°C on various parent metals: a) unalloyed steel, b) copper, c) brass

3.2. Examination of soldering material capability to penetrate capillary gaps

Examination of penetration capability and capillary action for tin based and tin-lead solders was carried out with T-shaped samples with the horizontal gap of the length of 60 mm and adjustable width from 0 to 1 mm, running in parallel to the axis of the T-bar web. Pills of the examined solder material with the dimension of ⌀6.5×1.5mm were placed on the samples on both sides of the web with the gap adjusted to the minimum width. The Cynotop-S flux was spread along the sample gap, on both sides of the sample web alike.

The experiments proceeded in an electric chamber furnace with heated walls of the chamber. Following that the samples were heated up to the temperature of 400±10°C and withheld at that temperature for 10 minutes. All the samples were heated in the same furnace; two samples for every combination of solder types and parent metals were inserted into the chamber for a single trial.

TABLE 2

Assessment of tin-based and tin-lead solders capability to penetrate capillary gaps with adjustable width of T-shaped samples

No	Solder grade	Parent metal of samples	Assessment of solders penetration into capillary gaps	
			Filled length of the gap[1], m	Remarks
1	Sn-3.35%Ag	steel	41	Uneven face of joint
2		copper	60	Smooth face of joint
3		brass	60	Smooth face of joint
4	Sn-3.35%Ag-5.06%Bi	steel	47	Uneven face of joint
5		copper	60	Smooth face of joint
6		brass	60	Smooth face of joint
7	Sn-3.03%Ag-0.95%Zn	steel	34	Porous face of joint
8		copper	60	Slightly porous joint surface
9		brass	60	Slightly porous joint surface
10	Sn-3.6%Ag-0.8%Cu	steel	46	Uneven face of joint
11		copper	60	Smooth face of joint
12		brass	60	Smooth face of joint
13	Sn-10%Zn-0.4%Ag	steel	37	Porous and uneven face of joint
14		copper	37	Poor spreading properties of solder
15		brass	44	Poor spreading properties of solder
16	40%Sn-Pb	steel	48	Uneven face of joint
17		copper	60	Smooth face of joint
18		brass	60	Smooth face of joint
19	60%Sn-Pb	steel	60	Uneven face of joint
20		copper	60	Smooth face of joint
21		brass	60	Smooth face of joint

[1] the result is averaged over 2 samples

Note – filling of the soldering gap along the distance of 60 mm with a specific solder is equivalent to filling the entire gap length

When the soldering process was completed the samples were subject to visual inspection and measurements. Examination results are summarized in Table 2.

4. Investigations on mechanical properties of solders and strength of joints

Investigation on essential mechanical parameters of filler metals, i.e. proof stress ($R_{0,2}$), tensile strength (R_m), elongation (A_5), transverse reduction of area (Z) was carried out by the procedure as specified in PN-EN 10002 for five round samples per each trial with a minimum primary cross-section diameter (d_o) of 5 mm.

The aforesaid samples (5 pieces for each solder type) were cast into split steel moulds and cooled in the open air at normal ambient temperature (20°C) with further machining. Tension and rupture tests were carried out one month after casting of samples; the tests were performed by means of a device for strength tests manufactured by Instron, model 115.

Results of the examinations for all the solder alloys under test are summarized in Table 3.

Soldered joints used in metal and mechanic sector are usually designed as lap type ones. That is why extensive knowledge of shear strength of such joints is of crucial importance. Therefore, tests for shear strength of the joints soldered with tin based and tin-lead solders were carried out for flat lap joints with the width of 10 mm, whereas the samples were made of copper sheets (M1 grade), brass sheets (M63 grade) and steel sheets (S235 grade); all the sheets being 1.5 mm thick.

A flat model of lap test samples, where a soldered joint during shearing is simultaneously subject to additional load from bending forces, was chosen by virtue of the desire to make the model as close as possible to the real structural shape of joints that are most frequently used in practice.

For the purpose of soldering the prepared samples were positioned horizontally by means of a special holder that assured nominal width of the joint gap amounting to 0.15 mm. The length of the overlap of joints, which is essential for rupture strength of joints and makes it possible to avoid deformations caused by squeezing (bend) stresses, was equal to 3+0.5 mm. An acetylene/air torch was used as a source of heat for the soldering of samples. The entire soldering process was carried out with the Cynotop-S flux.

TABLE 3

Basic mechanical properties of tin-based and tin-lead solder

No	Solder grade	Mechanical properties [1]							
		$Re_{0.2}$, MPa		R_m, MPa		A_5, %		Z, %	
		$\bar{X}$	S_X	$\bar{X}$	S_X	$\bar{X}$	S_X	$\bar{X}$	S_X
1	Sn-3.5Ag	22.81	2.02	50.9	2.12	20.78	1.41	66.90	4.94
2	Sn-3.35%Ag-5.06Bi	41.45	2.52	75.88	6.57	8.52	1.42	27.94	2.06
3	Sn-3.03%Ag-0.95%Zn	29.49	2.56	55.58	2.88	19.06	1.76	52.38	3.27
4	Sn-3.6%Ag-0.8%Cu	29.88	1.96	61.15	3.38	21.70	1.34	65.44	4.43
5	Sn-10%Zn-0.4%Ag	33.98	1.64	88.94	4.16	32.44	2.46	63.44	4.25
6	40%Sn-Pb	25.99	1.66	32.69	2.56	32.24	3.18	68.68	6.20
7	60%Sn-Pb	39.66	2.66	50.48	2.64	34.48	1.67	52.22	3.38

[1] $Re_{0.2}$ – proof stress, R_m – tensile strength, A_5 – relative elongation, Z – percentage reduction of area, $\bar{X}$ – averaged result for 5 measurements, S_X – standard deviation

Rupture tests of the soldered samples were performed in a manner similar to the tests of solder alloys at normal ambient temperature of 20°C, by means of the same machine from Instron (Great Britain), model 115 and with use of standard equipment.

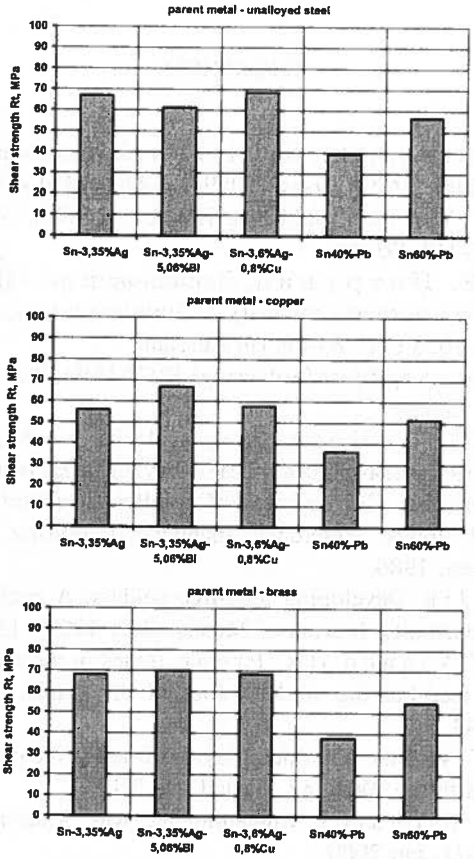

Fig. 2. Shear strength (Rt) for fillet-type joints of unalloyed steel, copper and brass after soldering with tin-based and tin-lead solders

Experimental results of strength tests of joints soldered with tin and tin-lead filler metals are shown in Fig. 2.

5. Analysis and recapitulation of test results

Assessment of soldering properties for various solder alloys by means of the spreading method has revealed that tin based solders are characterised by slightly poorer spreading on steel, copper and brass than tin-lead solders. The spreading factor calculated for solder alloys based on Sn-Ag alloys and taking into account thickness of the solder film after spreading fell into the range 70÷90%, which is classified as "good" and "very good" spreading. Visual observation of the spreading process proved that the phenomenon runs uninterruptedly during a single phase and full spreading is achieved as soon as after a dozen of seconds. In case of tin-lead solders the spreading process in subdivided into two phases and lasts not less than several dozens of seconds. The comparative results obtained for tin-lead solders within the range above 90% make it possible to classify the spreading capacity as "perfect". The best spreading factor for a variety of tin-based solders was revealed for steel base – the solder Sn-3.6%Ag-0.8%Cu whereas for copper base the best solders were Sn-3.35%Ag-5.06%Bi and Sn-3.6%Ag-0.8%Cu and for brass base – two solders, namely Sn-3.35%Ag and Sn-3.6%Ag-0.8%Cu. The worst spreading properties were observed for the solder Sn-10%Zn-0.4%Ag (spreading factor 61÷72% – "satisfactory" spreading).

No significant variations of spreading properties were observed for the examined solders with temperature increase over the entire range of investigation, from 250°C to 310°C.

Tests of capillary penetration into a horizontal gap of variable width in case of T shaped joints have revealed that for tin-based solders, namely for the solder alloys Sn-3.35%Ag, Sn 3.35%Ag-5.06%Bi and Sn-3.6%Ag-0.8%Cu, the results are comparable with tin-lead solders for copper and brass samples and just insignificantly poorer for steel samples. Much worse results were obtained for the filler metal Sn-3.03%Ag-0.95%Zn and definitely the worst for the solder Sn-10%Zn-0.4%Ag.

In addition, tin-based solders presented better strength parameters as compared with tin-lead solders. The highest tensile strength (75÷88 MPa), nearly twofold better than for Sn Pb solders, was found for the solder alloys Sn-10%Zn-0.%Ag and Sn-3.35Ag-5.06%Bi.

Tests of shear strength for fillet-type steel (unalloyed steel), copper and brass joints have provided excellent results, much better than in case of joints made with tin-lead solders (nearly twice higher that for the Sn40%-Pb solder).

The top strength for all the investigated structural materials, up to 70÷95 MPa, was reached for the solder Sn-10%Zn-0.4%Ag. In case of the tin-silver joints it was 67÷87 MPa for the solder Sn-3.03%Ag-0.95%Zn. Other joints, made with the remaining types of tin silver solders, presented comparable shear strength (55÷75 MPa), however it was higher than for joints that were soldered with tin-lead solders (35÷55 MPa).

All the foregoing experimental results make it possible to conclude that in presence of chemically active fluxes, Sn-Ag alloys-based solders are capable of rapid wetting of parent structural metals and convenient penetration into capillary fissures, however the spreading properties are slightly poorer than those of tin-lead alloys. The examined solders present relatively high strength properties and provide excellent shear strength of soldered steel, copper and brass joints, much higher than in case of tin-lead solder alloys. This quality is also specific for the solder on the base of Sn-Zn alloys with nearly-eutectic composition. However, its technical applicability is hindered by poor soldering properties for steel, copper and brass (poor wetting properties, low capillary action, porosity of joints) as well as by the threat to reduce the corrosion strength of joints. Even so, it should be emphasized that such types of solders are primarily recommendable in case of joining aluminium and its alloys [1–4].

6. Conclusions

1. From among solders developed to substitute tin-lead solders with a content of Sn within the range 40÷60%, tin- silver solder alloys, in particular with composition Sn-3.6%Ag-0.8%Cu presents the most advantageous properties.
2. Tin-based solders with admixture of silver-based alloys offer slightly poorer soldering properties, in particular spreading capacity, when used to join unalloyed steel, copper and brass parts than tin-lead solders with Sn content of 40÷60%. However, strength parameters of joints are much higher for all the foregoing materials.
3. Admixture of about 5% bismuth (Bi) to any tin-silver solder with eutectic composition advantageously reduces the temperature of the melting point, improves soldering properties for copper and brass as parent metals, increases strength of joints but lowers plasticity characteristics.
4. Admixture of about 0.8% of copper (Cu) to any tin-silver solder with eutectic composition slightly decreases melting temperature of such solders and improves soldering properties for unalloyed steel, copper and brass with a simultaneous increase in strength and plasticity of the solder.
5. The presented results of investigations prove that no essential technical hindrances should be expected in the programme of comprehensive implementation of tin-based lead-free solders in metal processing industries if the aforesaid solder alloys are applied instead of currently used tin-lead solders.

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