New types of lead-free solders on the base of tin and their properties

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Abstract

The aim of the work is an experimental study of binary, ternary and quaternary systems on the base of tin alloys. 22 alloys with different ratios of individual elements Ag, Cu, In, Sb, Bi, and Sn were prepared experimentally. In addition, 6 alloys of lead-free solders produced commercially (Kovohutě Příbram nástupnická, a.s.) were used and the Pb-Sn solder served as a comparative etalon. The following characteristics were studied: temperatures and enthalpies of phase transformations (DTA, TG, DSC) of individual solders at the rates of re-heating and cooling of specimens of about $4\,^{\circ}\mathrm{C\,min^{-1}}$, microstructural analysis (optical metallography) and microhardness of specimens, chemical analysis, microanalysis of individual phases in the structure of solders (WDX, EDX), measurement of surface tension and density of solders in dependence on the temperature, test of wettability with or without use of fluxes, measurement of corrosion properties, measurement of electrical resistivity.

Key words: lead-free solders, alloys, tin, properties, structure, wettability

1. Introduction

The international European project COST Action 531 Lead-free Solder Materials was in the period 2002–2007 focused on the basic scientific research of materials suitable for lead-free solders and on the problem of their practical application, reliability during long-term utilization in all types of equipment and their recycling. The main objective of the COST Action 531 was to increase the fundamental basic knowledge on possible alloy systems that can be used as lead-free solder materials and to provide a scientific basis for deciding which of these materials should be used for different soldering purposes in order to replace the currently used lead-containing solders in the future.

Lead-containing solders have two main fields of applications: electronic assemblies and heat exchangers. In both cases, replacement of lead causes problems, which are of entirely different kinds. The electronic industry sees a change in melting temperature and processing ability to be major problems, while manufacturers of heat exchangers are much more sensitive to cost and strength. There are a number of lead-free solders with varying properties available today. The problem is not only a question of developing solders with the right properties, but also a lack of knowledge about the existing alternatives and their properties. In this stage some of the most important properties, such as electrical and heat conductivity, wettability, mechanical properties and melting temperature should be studied for the basic alloys considered in the literature survey. These properties are examined and compared to tin-lead solder.

In this work we present an experimental study of selected physical, chemical, mechanical and utility properties of 28 alloys on the base of tin with different ratios of individual elements Ag, Cu, In, Sb, and Bi.

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T a b l e 1. DTA, DSC analysis (re-heating and cooling rate 4 °C min^{-1}) and microhardness HV_m of tin alloys

Specimen	Chemical composition (wt.%)	T_S (heating) (°C)	T_L (heating) (°C)	ΔH (heating) (J g^{-1})	ΔH (cooling) (J g^{-1})	HV_m
E3	Sn-3Ag-2Bi-2Sb	202	228	60.9	62.0	26
E5	Sn-2.5Ag-2Bi	204	226	54.8	55.7	22
E11	Sn-5Ag-8.6In	185	213	49.9	48.3	18
E14	Sn-3.1Ag-6.1Bi	183	220	53.4	54.2	30
E19	Sn-2.5Ag-11.2Bi-5.5In	132	199	51.8	53.1	44
F1	Sn-2Ag-7.5Bi-5.5In	132	205	59.6	51.3	34
F9	Sn-2Ag-7.5Bi-0.5Cu	171	215	52.0	51.8	31
F17	Sn-3.4Ag-4.8Bi	187	222	54.0	53.6	32
F23	Sn-0.5Ag-1.5Bi-3Sb	209	238	59.9	61.1	21
F25	Sn-0.5Ag-56Bi	137	144	47.6	47.6	18
F34	Sn-3.33Ag-4.76In	194	217	53.5	45.9	20
F36	Sn-2.91Ag-1.94Bi-2.91In	190	218	54.8	54.5	24
F41	Sn-3.5Ag-7Bi	180	218	51.6	49.7	31
F42	Sn-3.5Ag-10Bi	165	214	49.7	47.7	30
F44	Sn-1.5Ag-2Cu-5In	194	218	51.1	49.6	19
F45	Sn-0.5Ag-3Cu-5In	192	222	47.7	47.3	19
F47	Sn-5Bi-1In	194	225	55.6	55.9	25
F51	Sn-0.5Ag-1Cu-5In	195	222	51.5	50.6	18
F52	Sn-1.5Ag-1Cu-5In	190	218	54.2	52.3	17
F55	Sn-0.5Ag-5In	196	226	48.8	49.6	16
F56	Sn-1.5Ag-5In	187	222	51.6	51.2	18
Q1	Sn-3.33Ag-4.83Bi	186	222	54.1	53.7	30
P1	Sn-1Cu	225	235	56.2	57.9	11
P2	Sn-1.5Cu-3.5Sb	228	240	56.7	56.6	11
P3	Sn-4Ag	219	229	58.7	58.9	13
P4	Sn-5Sb	233	247	53.8	55.5	11
P5	Sn-3.8Ag-0.7Cu	211	226	59.2	59.8	16
P6	Sn-37Pb	182	189	39.5	38.2	8

2. Experimental samples

The aim of our work was an experimental study of binary, ternary and quaternary systems on the base of tin alloys. 22 alloys with different ratios of individual elements Ag, Cu, In, Sb, Bi, and Sn were prepared experimentally – see Table 1. The alloys were prepared by smelting of input metals in the graphite crucible followed by casting into graphite boats. In addition, 6 alloys (specimens P1–P5) of lead-free solders produced commercially (Kovohutě Příbram nástupnická, a.s.) were used and the Pb-Sn solder (specimen P6) served as a comparative alloy.

3. Experimental methods of the study

The following characteristics of prepared experimental solders were studied:

1. Temperatures and enthalpies of phase transformations (DTA, TG, DSC) of individual solders at the rates of re-heating and cooling of specimens of about 4 °C min^{-1} – Table 1;
2. Microstructural analysis (optical metallography) – Fig. 1, and microhardness of specimens – Table 1;
3. Chemical analysis (ICP-AES and Optical Emission Spectrometry OES), microstructural analysis (SEI, BEI), and chemical microanalysis of individual phases in the structure of solders (X-ray spectroscopy WDX, EDAX);
4. Measurements of density and surface tension of solders in dependence on the temperature;
5. Tests of wettability of solders with copper, brass and nickel using fluxes or without them – see Fig. 2;
6. Corrosion behaviour of individual alloys in various chemical-corroding mediums;
7. Measurements of electrical resistivity of solders.

The measurements of individual characteristics of solders were carried out at the Faculty of Metallurgy and Materials Engineering (VŠB – Technical University of Ostrava) – Department of Non-ferrous Metals, Refining and Recycling, Department of Physical Chemistry and the Theory of Technological Processes, Department of Material Engineering, Institute of Materials Chemistry, Masaryk University in Brno, Institute of Physics of Materials AS CR in Brno, Czech Technical University in Prague, Faculty of Electrical Engineering, Charles University in Prague, Department of Physics of Materials.

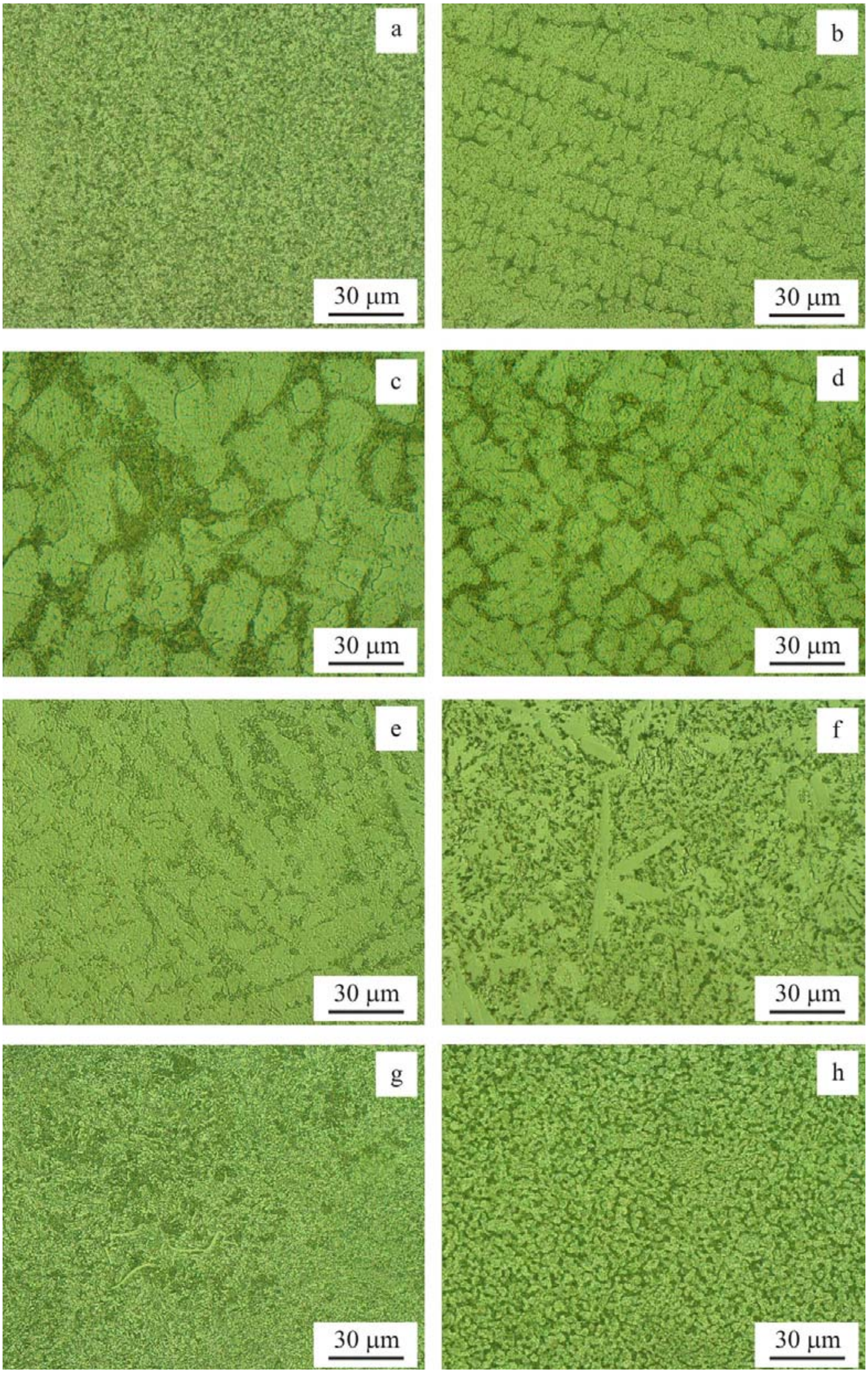

Fig. 1. Metallographic study of selected tin alloys: a) F56, b) F9, c) F34, d) F36, e) F41, f) F44, g) P5, h) P6.

4. Experimental results

The differential thermal analysis (DTA) and the thermo-gravimetry & differential scanning calorimetry (DG/DSC) were carried out in the device SETARAM SYSTEM 18_{TM}. The results of the measurements of

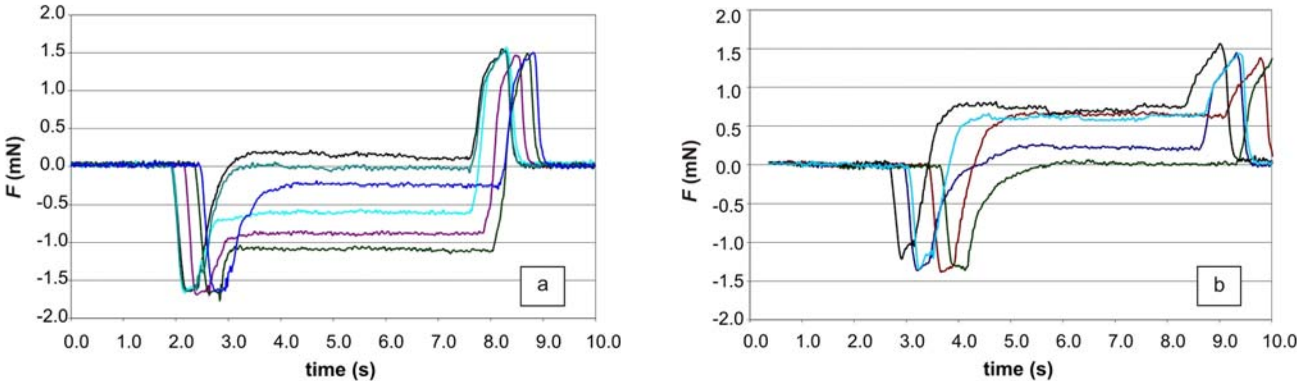

Fig. 2. Examples of the curves of wettability measurements (Cu wire diameter 1.0 mm, flux Epsilon 5), F is wetting power. a) copper/Sn95.5Ag3.8Cu0.7, b) copper/Sn63Pb37.

Table 2. Summary results of the course of wetting

Wire	Flux	Solder								
		P1	P2	P3	P4	P5	P6	P7	P8	P9
Copper	without flux	10	10	10	10	10	10	10	10	10
	Epsilon M5	8	10	9	10	8	5	9	9	9
	Epsilon 5	8	10	8	10	6	4	9	9	8
	Epsilon 2	8	10	4	10	4	1	9	9	7
Nickel	without flux	10	10	10	10	10	10	10	10	10
	Epsilon M5	7	6	2	9	2	2	8	7	5
	Epsilon 5	5	6	2	8	2	2	5	5	3
	Epsilon 2	3	6	2	8	2	1	3	4	3
Brass	without flux	10	10	10	10	10	10	10	10	10
	Epsilon M5	8	10	7	9	8	5	9	9	8
	Epsilon 5	6	8	6	8	5	5	6	7	6
	Epsilon 2	4	7	3	9	4	4	4	6	4

Other solders: P7 – Sn97Cu3, P8 – Sn99.75, P9 – Sn97Bi2Cu1

the temperatures T_S (solidus) and T_L (liquidus) were acquired at the heating rate 4 ℃ min^{-1} and enthalpies of phase transformations were acquired at the heating/cooling rate 4 ℃ min^{-1}, see Table 1.

4.1. Metallographic study

Microstructures of specimens acquired by the microscope Neophot 32 using the camera Olympus DP 11 differed very slightly with respect to the history of their preparation. Metallographic analyses discovered practically in all the cases fine-grained two-phase structures, mostly of a eutectic type, often with present dendritic formations. A primary precipitated phase, which was not identified more precisely, was sometimes found in specimens P1 to P6. Microstructures of selected specimens of solders are shown in Fig. 1. All the photos have a uniform magnification presented in the picture lower right corner (the line segment length corresponds to 30 μm). The microhardness tester LECO applying the load 0.05 N measured microhardness according to Vickers in all the specimens. The measurement results are presented in Table 1.

4.2. Measurement of wettability

Wettability is a property of metal surface that expresses the material diffluence. Formation of an intermetallic compound is a necessary condition of good wetting and linking of the solder and wetted metal. A tested component is suspended on the dynamometer above the vessel with the molten solder. The measurement itself was carried out on the meniscograph solderability tester GEC. The device consists of a measuring head with a spring microbalance, a holder for gripping the measured object, a soldering bath and electronic control unit. The tested specimens of copper, nickel and brass (Ms66) were in the form of wire, diameter 1 mm. Rinsing-

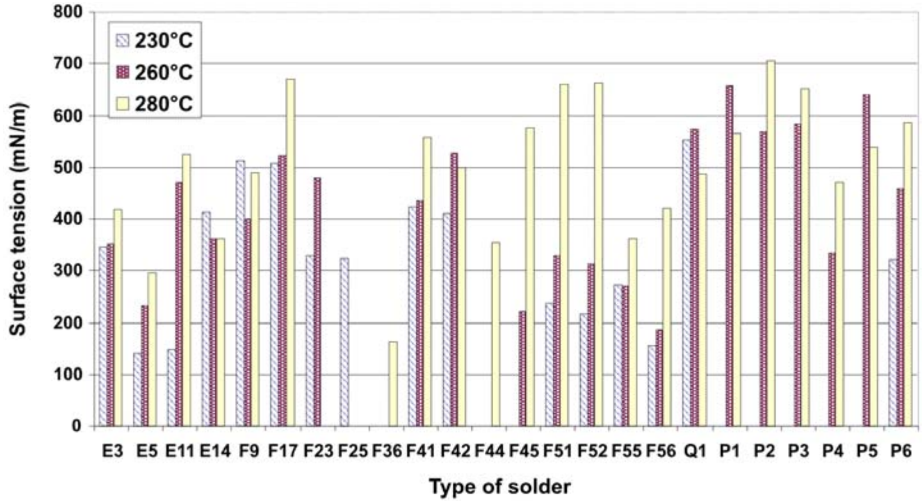

Fig. 3. Comparison of surface tensions of individual solders at the temperatures 230 ℃, 260 ℃ and 280 ℃.

-less fluxes were used for lead-free solders Epsilon 5 and Epsilon 5M and a universal flux for soldering in electronics Epsilon 2, producer SLUVIS Prague.

The wettability tests were carried out at ČVUT Prague. Copper, nickel and brass wires were tested at the soldering temperature 250 ℃ applying various fluxes. For the solder Sn63Pb37 the temperature was 235 ℃. All the combinations of the solders, fluxes and test specimens were measured. Several measurements were performed for each combination solder-flux-test specimen. All the measured combinations were rated by marks from 1 (best wettable combination) to 10 (worst wettable combination). The classification was carried out on the basis of the measured courses of the wetting force and on the basis of the visual control of the measured specimens under the microscope. The results are summarized in Table 2.

4.3. Measurement of surface tension of alloys (method of lying drop)

The study of surface tension contributes considerably to the explanation of processes determining the forming of structure and chemical composition of given systems in the molten state. The surface tension of molten solder is a key parameter related to both the wetting and solderability. The surface tension is defined as the force acting normally to the unit of length on the surface of liquid striving to minimize its surface. The surface tension is a consequence of non-compensated forces acting on atoms and molecules on the surfaces of all substances. Its intensity depends on the temperature and composition of neighbouring substances and on the surface of the substance in question. This phenomenon, when the liquid surface behaves as an elastic film, means thermodynamically that the liquid surface strives to reach the state with the least energy. The greater the surface tension is, the "rounder" this liquid drop is. If a drop of a liquid solder comes into contact with another metal surface, cohesion forces striving to keep it in the original state, i.e. with the least surface at a given volume, and adhesion forces tending to extend the contact of both the metals on the surface start to act on it. It generally holds for metals that the surface tension as well as the melt density decreases linearly with the growing temperature.

The principle of the lying drop method consists in evaluating the geometric parameters of a melt drop on a solid base. The base is not wetted, shape stable even at higher temperatures and does not react with the melt. A base made of Al_2O_3 is used for metal melts most frequently. The wetting angle is required to be greater than 90° and the drop created on the base should have a circular cross-section. The surface tension measurements were executed in a horizontal Tammann furnace. The specimens were tested in the temperature interval the lower limit of which was given by the material melting temperature. The CCD camera SONY DKC 5000 which enables to work with the maximum resolution 1520 × 1144 pixel acquired a photographical record. The camera is placed on a stand in front of the furnace.

The values of surface tension of individual specimens at the temperatures 230 ℃, 260 ℃ and 280 ℃ were selected as evaluating criteria and they were compared with the value of surface tension of the lead solder. The values measured at the selected temperatures are compared in Fig. 3.

The most convenient specimens include the solders E5, F55, F56, and P4 – they present the lowest values of surface tension in the given temperature range of measurement. On the contrary, the worst evaluated specimens were F17, P2 and P3. Significant changes

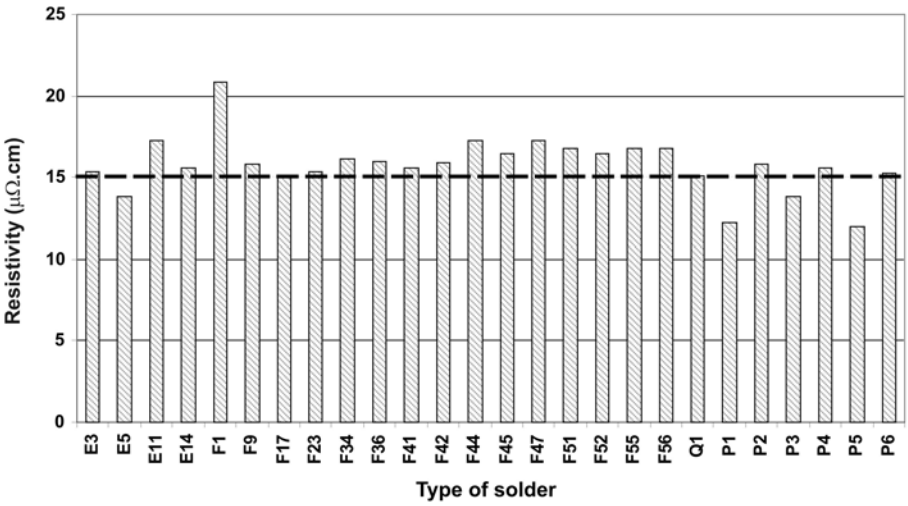

Fig. 4. Comparison of resistivity of the solders.

in behaviour of particular systems were proved from the surface properties view, which resulted from interchange of individual components and their per cent contents.

4.4. Measurement of resistivity

The resistivity is an important property when determining suitable types of lead-free solders. To be able to measure the resistivity of solders it was necessary to roll down the specimens into the form of film 0.2 mm thick. Stampings of a required shape, 50 mm long, 5 ± 0.1 mm wide, with notches 5 × 1 mm on both sides, were prepared by means of a special cut jig with a flat stamping die. The measurement itself was carried out at the Department of Physics of Materials UK in Prague. The classical four-point method at room temperature 23 ℃ was used for the resistivity measurement. The apparatus Keithley 221 was used as a power supply, a real current value was determined from the voltage measurement on the normal Tettex Zürich with the indicated nominal value 0.0099995 Ω. The voltage measurement was executed by the nanovoltmeter Keithley 2182. All the measurements were performed at the current value ~ 0.5 A. The electrical resistance measured in this way was converted to resistivity applying the finite elements method. This requires the knowledge of the specimen dimensions.

Resistivity of metals is dependent on the purity of individual elements and on the structural perfection of materials. Even a slight amount of impurities can change it considerably. It is obvious from the results of the resistivity measurements of lead-free solders, see Fig. 4, that the lowest resistivity is that of the solder P5 – SnAg3.8Cu0.7. On the contrary, the highest resistivity showed the solder F1 – SnAg2Bi7.5In5.5.

If we compare the results of our measurements with the published data [1–3], then e.g. the value for indium is $\rho = 8.34\ \mu\Omega$ cm [3] and our value is 9.8 μΩ cm. For the alloy Sn-Pb, [1] presents the value $\rho = 14.4\ \mu\Omega$ cm, [2] the value 15.0 μΩ cm compared to our value 15.3 μΩ cm. Similarly, the values presented for SnAg4 are 10.0 and 12.3 μΩ cm [1, 2], 11.8 μΩ cm [4], our value was 13.8 μΩ cm. We can conclude from the above mentioned than our measured values are in average by 12 % higher that the published data. It can be caused by the initial state of our specimens, which were deformed by cold rolling and the foils 0.2 mm thick were not annealed before the measurement. Nevertheless, the results can be regarded as objective and mutually comparable since all the results had the same geometrical form, dimensions and history. The column chart in Fig. 4 enables us a comparison between individual alloys of solders from the resistivity point of view.

4.5. Test of solderability

Good solderability of materials is an essential presumption for creating a quality joint. It influences significantly the reliability of the whole electronic system. The material solderability is a function of the solder material, flux, substrate, temperature, and time. Lead-free solders generally have higher surface tension than the solder Sn-Pb, which causes smaller diffluence and worse wettability and therefore the soldered surface has to be physically and chemically stable. Six industrial fluxes with the best adhesion were chosen for the test of solderability. The fluxes were in the liquid form (supplier firm Sluvis) and in the solid or gel form (from Germany). A suitable amount of flux was applied on a copper substrate by means of soldering iron and a solder, diameter 4 mm, thickness 0.2 mm, was placed on the warm flux. Pre-

Table 3. Comparison of solderability of individual solders with Sn-Pb alloy

Solder		FB 12-11	MT-SW 24/3	MT-SW 24/2	F1	Epsilon 5M	Epsilon 5
E3	SnAg3Bi2Sb2	0	+			0	–
E5	SnAg2.5Bi2	–	0	+	0	+	0
E11	SnAg5In8.6	–	0	0	+	+	–
E14	SnAg3.1Bi6.1	–	0	+	+	+	+
F1	SnAg2Bi7.5In5.5	–	0	0	+	–	+
F9	SnAg2Bi7.5Cu0.5	–	+	+	+	+	+
F17	SnAg3.4Bi4.8	–	+	+	+	0	+
F23	SnAg0.5Bi1.5Sb3	0	+	0	+	–	–
F25	SnAg0.5Bi56	–	–	–	0	–	–
F34	SnAg3.33In4.76	–	+	+	+	+	+
F36	SnAg2.9Bi1.94In2.91	–	0	+	+	–	+
F41	SnAg3.5Bi7	–	+	–	+	–	+
F42	SnAg3.5Bi10	–	+	–	+	+	+
F44	SnAg1.5Cu2In5	–	+		+	+	+
F45	SnAg0.5Cu3In5	–	+	+	+	–	+
F47	SnBi5In1	–	+	0	+	–	+
F51	SnAg0.5Cu1In5	–	+	+	+	+	–
F52	SnAg1.5Cu1In5	–	+	+	+	–	–
F55	SnAg0.5In5	–	+	+	+	0	+
F56	SnAg1.5In5	–	+	+	+	–	0
Q1	SnAg3.33Bi4.83	–	+	+	+		–
P1	SnCu1	–		+	+	–	–
P2	SnCu1.5Sb3.5	–	+	+	+	–	–
P3	SnAg4	–	+	+	+		0
P4	SnSb5			0	0	–	–
P5	SnAg3.8Cu0.7	–	+	+	+		
P6	SnPb37	0	0	0	0	0	0

Note: (+) better than Sn-Pb, (0) same as Sn-Pb, (–) worse than Sn-Pb

pared specimens were inserted into the furnace heated up to 210 ℃, 260 ℃ and 280 ℃ according to the solder melting temperature for the time of 4 minutes.

After a preliminary test of solderability of the two alloys P3 and P5, six fluxes with good effects were chosen from 20 fluxes. From these six fluxes the flux F1 appeared to be the best and FB 12-11 the worst ones. The test of solderability was carried out on a copper base with various fluxes, the results are presented in Table 3 in the form of items up, graded into three categories according to the joint quality. The alloy PbSn was taken as a reference sample with the mark "0". Solders with worse solderability have a mark with "–" sign, solders with better solderability have a mark with "+" sign. Blank places in the table mean that the solder did not join with the Cu base, these solders would need either a higher temperature in the furnace or longer time for soldering. Based on the visual observation, the solders F9 and F34 were chosen as the solders with the best solderability.

Lead-free solders generally show worse wetting properties than classical Sn-Pb solders due to a higher surface tension in the solder as well as due to a higher tendency to oxidation because of a higher soldering temperature.

4.6. Corrosion tests of lead-free solders

Electrochemical corrosion properties of selected lead-free solders (see Table 4) were studied on the base of potentiodynamic polarization method using three 0.1 mol l^{-1} aqueous solutions of NaCl, KOH and H_2SO_4 at 25 ℃ and the results were compared with the Sn-Pb solder (Sn67Pb37). In the basic KOH solution all the tested solders exhibited an active-passive transition. Relatively high differences were found out among the values of corrosion potentials, critical current densities (Table 4) and other measured parameters for lead-free solders. On Sn63Pb37 solder the manifold current densities were measured in the passive state in comparison with lead-free solders. Higher current densities and considerably wider active ranges were measured on lead-free solders in acid H_2SO_4 solution compared with Sn-Pb solders. Lead-free solders containing Ag showed to be more resistant to pitting corrosion in the neutral NaCl solution comparing to solders containing Cu or Sb – see Fig. 5. Dark spots and/or surface corrosion pits created on lead-free solders in salt spray unlike the Sn-Pb solder with light general corrosion products.

Table 4. The results of polarization measurements of lead-free solders using 0.1 mol l^{-1} KOH solution and salt spray test

Specimen No.	Solder	E_{cor} (mV)	J_p (mA cm^{-2})	Δm_c (g cm^{-2})
E3	Sn-3Ag-2Bi-2Sb	–1064	2.18	2.4
E19	Sn-2.5Ag-11.2Bi-5.5In	–497	0.011	4.03
F1	Sn-2Ag-7.5Bi-5.5In	–585	n	3.98
F23	Sn-0.5Ag-1.5Bi-3Sb	–1054	2.79	4.65
F25	Sn-0,5Ag-56Bi	–1043	2.21	2.67
F47	Sn-5Bi-1In	–1001	0.799	3.5
E5	Sn-2,5Ag-2Bi	–1059	2.86	9.86
E11	Sn-5Ag-8,6In	–502	n	11.8
E14	Sn-3,1Ag-6,1Bi	–1048	2.704	4.24
F9	Sn-2Ag-7,5Bi-0,5Cu	–1058	3.014	3.58
F17	Sn-3,4Ag-4,8Bi	–1078	2.67	4.8
F34	Sn-3.33Ag-4.76In	–570	0.135	4.65
F36	Sn-2.91Ag-1.94Bi-2.91In	–469	0.27	7.96
F41	Sn-3.5Ag-7Bi	–1060	3.49	7.61
F42	Sn-3.5Ag-10Bi	–1035	2.32	3.42
F44	Sn-1.5Ag-3Cu-5In	–533	0.061	9.67
F45	Sn-0.5Ag-3Cu-5In	–540	0.085	8.48
F51	Sn-0.5Ag-1Cu-5In	–495	0.099	9.5
F52	Sn-1.5Ag-1Cu-5In	–590	0.119	10.2
F55	Sn-0.5Ag-5In	–640	0.116	8.67
F56	Sn-1.5Ag-5In	–850	0.128	20.2
Q1	Sn-3.33Ag-4.83Bi	–1054	2.22	3.18
P1	Sn-1Cu	–1086	3.61	0.547
P2	Sn-1.5Cu-3.5Sb	–1071	3.84	0.795
P3	Sn-4Ag	–1085	3.75	0.503
P4	Sn-5Sb	–1079	2.78	1.71
P5	Sn-3.8Ag-0.7Cu	–1082	3.4	2.32

Note: E_{cor} is corrosion potential, J_p is critical passivation current density, n is polarization curves without peak, Δm_c is corrosion losses on samples after salt spray test exposition 240 h. Linear multiply regression model: $\Delta m_c = -9.1 + 0.432\text{Ag} + 0.49\text{Bi} + 0.62\text{Cu} + 0.353\text{In}$.

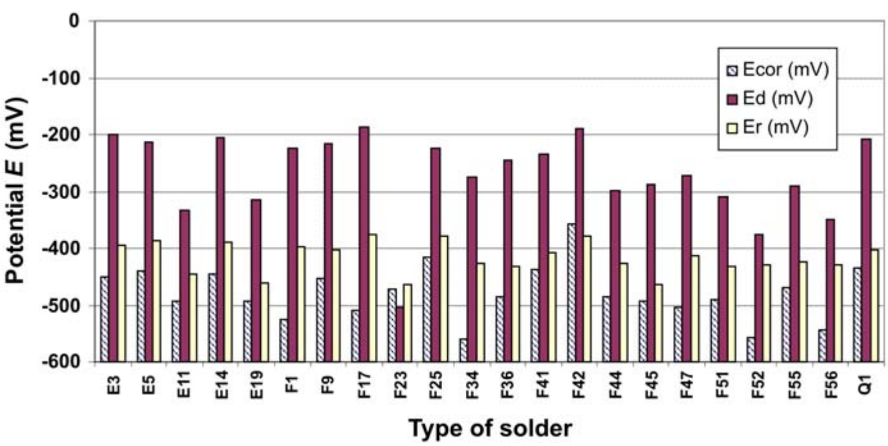

Fig. 5. Comparison of potentials of pitting corrosion for the studied solder types in 0.1 M NaCl solution. E_{cor} is corrosion (free) potential, E_d is potential of depassivation, E_r is potential of repassivation.

On the basis of accelerated corrosion test in salt spray, relatively small differences of corrosion losses were found for selected lead-free solders on the base of tin as well as for the Sn-Pb solders. Considerable differences were discovered in the corrosion products appearance. Corrosion in the form of dark points or spots in lead-free solders was determined by the occurrence of phases with higher Ag and Cu contents. An even corrosion without dark spots was observed on the Sn-Pb solders.

5. Discussion

Metallographic analyses discovered practically in all the cases fine-grained two-phase structures, mostly of a eutectic type, often with present dendritic formations. A primary precipitated phase was sometimes found in specimens P1 to P6. From the *micro-hardness* point of view, the softest solder was Pb/Sn (HV_m = 8), the hardest solders were E19, F1, containing Sn-Ag-In-Bi (HV_m > 40). The solders of eutectic type delivered from Kovohutě Příbram exhibited a relatively low microhardness (HV_m = 11 to 16), while our alloys had the values of microhardness HV_m = 16 to 34. This is connected with the manner of the preparation of alloys and their further mechanical-thermal treatment. The specimens prepared at VŠB – TU Ostrava in the form of button tests were, after smelting and the melt homogenization under a protective layer of a reduction agent, cast into graphite crucibles, thus the cooling rate was relatively high.

It follows from the *differential thermal analysis* that the solder F25 containing the greatest amount of Bi has the lowest temperature of melting since bismuth lowers the Sn temperature of melting considerably. Alloys Sn-Bi are suitable for applications with parts little sensible to heat while a high strength in the solid state is preserved. The solders E19 and F1 have the temperatures of melting close to lead containing solder. The solder P4 on the Sn-Sb base has the highest measured temperature of melting, which is more suitable for high-temperature applications. Ternary as well as quaternary systems on the Sn-Ag or Sn-Cu bases have considerably higher temperatures of melting than Sn-Pb, by 35 °C in average. Due to higher temperatures of melting of lead-free solders it will be necessary to solve the problem of optimum temperature regimes at the soldering procedure (e.g. a gradual wave) to prevent excessive overheating of parts and boards.

Table 1 presents also the values of enthalpy of phase transformations of alloys, mostly of eutectic composition. It is obvious that a classic Sn-Pb solder has the value ΔH_m around 39.5 J g^{-1}, while all lead-free solders on the base of tin exhibit the value ΔH_m, which is substantially higher, in the range of 48 to 60 J g^{-1}. It means that at the process of crystallization of lead-free solders a considerably higher amount of heat per mass unit will have to be conducted away from the crystallization front, which will again mean a higher load of electronic components. It is interesting that from the view of the phase transformation entropy, all solders behave practically in a similar way ($\Delta S_m = 14 \pm 1$ J K^{-1} mol^{-1}).

The surface tension of molten solders is a key parameter connected with both the wetting and solderability. The lying drop method was used for determination of *surface tension* of individual specimens of solders. The surface tension of melts, as well as their density, depends on the alloy temperature and chemical composition. These problems in the area of lead-free solders are treated by the group led by Moser from Krakow [4–9]. It can be concluded from their works that both the melt surface tension and density of the studied solders are linearly dependent on and decrease with the temperature. The dependence between the surface tension and composition of alloys in a binary or ternary system has a more complicated character and it mostly exhibits a negative deviation from the linear course. Disproportions were found when comparing our results measured by the lying drop method with the "maximum bubble pressure method" [6]. In most our measurements the melt surface tension exhibited a slight non-linear increase in a relatively narrow temperature interval. Forming an oxide layer on the specimen surface during its heating, even though high purity argon 4N was used as a protective atmosphere probably caused this anomalous behaviour. However, the furnace was not sufficiently close shut. The authors Moser et al. [6] used the mixture Ar + H_2 for their experiments. Despite of this circumstance, our results can be considered significant since they enable us to compare the values of surface tensions of individual types of solders in a relative way – see Fig. 3. For further experimental measurements, the temperature range will have to be extended up to 400 °C and an inert-reduction atmosphere on the furnace will have to be ensured so that the results can be comparable with the literature.

When comparing the values of surface tension of pure tin melt, the mean value determined by our measurements was 545 and 567 mN m^{-1} at the temperatures close above the tin melting point, authors [6] found the value 540 mN m^{-1} applying another method of measurement, other authors presented the values in the range 550 to 580 mN m^{-1}. An excellent conformity of our results can be concluded from the above mentioned.

The test of solderability was performed on the copper base with various fluxes. The results are summarized in Table 3 in the form of subjective evaluation according to the joint quality. The solders were divided into three groups pursuant to the temperature of melting. After a preliminary test of solderability of the two alloys P3 and P5, six fluxes with good effects were chosen from 20 fluxes. The fluxes F9 and F34 appeared to have the best solderability.

The wettability was determined for the specimens P1 to P6 and several other solders produced commercially. The wires of Cu, Ni and brass Ms66 were used for the wettability and commercial rinsingless fluxes Epsilon 2, Epsilon 5 and Epsilon M5 were applied on their surface, in some cases no flux was used. All combinations of the solders, fluxes and test specimens were used, and several measurements were carried out for

Table 5. A summary of properties of the best selected solders

Solder		Sn-Ag2.5-Bi2	Sn-Ag3.1-Bi6.1	Sn-Ag2-Bi7.5-Cu0.5	Sn-Ag3.8-Cu0.7	Sn-Pb37
Solidus temperature (℃)		204	183	171	211	182
Liquidus temperature (℃)		226 (–)	220 (–)	215 (–)	226 (–)	189
Surface tension	230 ℃	140 (+)	413.8 (–)	511 (–)	–	511 (–)
($mN\ m^{-1}$)	260 ℃	232.3 (+)	363 (+)	400.9 (+)	638.5 (–)	400.9 (+)
	280 ℃	295.5 (+)	361 (+)	489 (+)	538.5 (0)	489 (+)
Solderability	F1	(0)	(+)	(+)	(+)	(+)
with flux	MT-SW 24/3	(0)	(0)	(+)	(+)	(+)
of type	Epsilon 5	(0)	(+)	(+)	(+)	(+)
Resistivity (μΩ cm)		13.83 (+)	15.55 (0)	15.79 (0)	11.98 (+)	15.26 (0)

Note: (+) better than Sn-Pb, (0) as good as Sn-Pb, (–) bad, worse than Sn-Pb

each combination. All the materials of test specimens (Cu, Ni, Ms66) are not wetted for all types of the solders if fluxes are not used. The best results were reached for nickel. The lead containing solder and from the lead-free solders, the P5 solder had the best wetting properties. The solder P4 is not wetted with all the fluxes mentioned above. The Epsilon 2 flux appears to be the most universal flux. The fluxes Epsilon 5 and in particular Epsilon M5 have a considerably greater dispersion variance among the measured courses of wetting forces compared to the flux Epsilon 2. These fluxes are obviously much more volatile and can be recommended especially for manual soldering.

Interaction of the solders with metals during the wettability tests. The specimens obtained from the wettability tests were submitted to metallographic analysis and chemical point microanalysis EDAX. Very good compatibility of both the solder and base was found from the metallographic analysis of all the tested solders with use of the flux Epsilon 2 even with real time of wettability test 10 s. It means that a transitional interlayer of an intermetallic compound (Cu_6Sn_5 or Ni_3Sn_4) had been created. The point microanalysis was performed in three typical areas, namely in the central area where the wire was used, in the area of the solder layer and in the transitional layer.

At the EDAX chemical analysis in the area of solder existence the presence of metals (Cu, Ni, brass) was discovered in the distance of 5 μm from the solder/metal interface. It means that under the given experimental conditions, a considerable dissolving of the core by the solder happens at the given temperature and time regimes. At the same time the interdiffusion of atoms takes place and a corresponding intermetallic phase ensuring the solder and base compatibility creates. An important role is also played by a used flux, whose principal function is to dissolve surface films, especially oxides of metals, and to ensure the solder good wettability. In addition, the point analysis showed that the created intermetallic compound corresponds approximately to the stoichiometric formula, but it also contains other elements of the solder. The thickness of the formed intermetallic compound was less than 1 μm and therefore it was impossible to determine precisely its stoichiometry.

5.1. Overall evaluation of alternative solders

As a substitution of lead solders we recommend the alloys E5 – SnAg2.5Bi2, F9 – SnAg2Bi7.5Cu0.5, E14 – SnAg3.1Bi6.1 and P5 – SnAg3.8Cu0.7.

All the selected substitutions of lead solders have higher temperatures of melting; their range of melting is 215 to 226 ℃. They have very good solderability and wettability because they exhibit lower surface tension. The best candidate is the solder E5 – SnAg2.5Bi2. It has lower surface tension and resistivity than lead solder. The solder SnAg3.8Cu0.7 appears to be the most balanced if its properties are compared with the alloys SnPb37.

The worst alloy of all was found to be the solder F25 – SnAg0.5Bi56. Although it has the lowest temperature of melting due to bismuth, its mechanical properties are unsatisfactory, especially from the view of brittleness. It is badly solderable and wettable. The solder P4 – SnSb5 can also be regarded as unsuitable, its wetting properties are very bad and Sb has toxic effects on human organism.

The detailed evaluation of selected types of solders is summarized in Table 5.

6. Conclusion

The study of 28 low-fusing alloys on the base of tin was performed with the aspect of observing their selected physical, chemical, structural, and technological properties. The experimental specimens of lead-free solders were submitted to the following examinations: metallography, chemical and structural microanalysis, microhardness, differential thermal analysis, surface tension, solderability, wettability, corrosion tests, and resistometry. In the further stage, the chosen types of alternative solders will be tested in working conditions.

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