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Stanislav LASEK¹, Jaromír DRÁPALA², Marie BLAHETOVÁ¹, Jiří VRBICKÝ³**ELECTROCHEMICAL CORROSION PROPERTIES OF LEAD-FREE SOLDERS****KOROZNĚ ELEKTROCHEMICKÉ VLASTNOSTI BEZOLOVŇATÝCH PÁJEK**¹ *Department of materials engineering, VŠB-Technical University Ostrava, 17. listopadu 15, Ostrava-Poruba, 735 64, Czech Republic – stanislav.lasek@vsb.cz*² *Department of non-ferrous metals, refining and recycling, VŠB-TU Ostrava, Czech Republic*³ *Department of mathematics and descriptive geometry, VŠB-TU Ostrava, Czech Republic***Abstract**

In the contribution the electrochemical corrosion properties of selected and/or new tin base lead-free solders with additions of Ag, Bi, Cu, In, Sb are compared and evaluated by means of potentiodynamic cyclic method using 0,1 mol/l NaCl water solution and by standard salt spray test. For testing were used these solders: Sn-0,5Ag-56Bi, Sn-2,5Ag-2Bi, Sn-3,1Ag-6,1Bi, Sn-3,4Ag-4,8Bi, Sn-3,5Ag-7Bi, Sn-3,5Ag-10Bi, Sn-3,3Ag-4,8Bi; Sn-5Ag-8,6In, Sn-3,3Ag-4,8In, Sn-0,5Ag-5In, Sn-1,5Ag-5In; Sn-5Bi-1In; Sn-1,5Ag-3Cu-5In, Sn-0,5Ag-3Cu-5In, Sn-0,5Ag-1Cu-5In, Sn-1,5Ag-1Cu-5In; Sn-3Ag-2Bi-2Sb, Sn-0,5Ag-1,5Bi-3Sb, Sn-2,5Ag-11,2Bi-5,5In, Sn-2Ag-7,5Bi-5,5In, Sn-2,9Ag-1,9Bi-2,9In, Sn-2Ag-7,5Bi-0,5Cu. The samples were made of casted rods Ø10-12 mm in the shape of discs. According to potentiodynamic test and pitting potentials (depassivation, repassivation) values, the solders with addition of Bi and/or Bi-Ag are more resistant in comparison with indium containing ones. The interpretation of individual alloying elements influence is difficult with respect to their low content and distribution among different phases and areas, as confirmed by metallography and microanalysis. Application of statistical methods made a possibility to compare the influence of individual elements on the corrosion parameters, e. g. the linear regression relation has been used for depassivation potential values: $E_d = -388 + 18,0 \cdot Ag + 0,35 \cdot Bi - 5,0 \cdot Cu - 11,1 \cdot In - 16,3 \cdot Sb$, where Ag and Bi have shown positive and In or Sb negative influence. The similar relation were obtained for corrosion mass loses after the salt spray test and gravimetric measurements. For a better interpretation of results, the pure metals for solders were also tested and ranking in pitting resistance based on potentiodynamic testing was confirmed in the order Ag, Bi, Cu, Sb, Sn and In. The dark spots, pits, matt surfaces and coloured areas on solders were observed by microscopy after corrosion tests.

Abstrakt

V práci jsou porovnány a zhodnoceny korozně elektrochemické vlastnosti vybraných anebo nových bezolovnatých pájek na bázi cínu s přísadami Ag, Bi, Cu, In, Sb na základě potenciodynamické cyklické metody s použitím vodného roztoku 0,1M NaCl (25°C) a expoziční zkoušky v komoře solné mlhy. Pro zkoušení byly použity tyto pájky: Sn-0,5Ag-56Bi, Sn-2,5Ag-2Bi, Sn-3,1Ag-6,1Bi, Sn-3,4Ag-4,8Bi, Sn-3,5Ag-7Bi, Sn-3,5Ag-10Bi, Sn-3,3Ag-4,8Bi; Sn-5Ag-8,6In, Sn-3,3Ag-4,8In, Sn-0,5Ag-5In, Sn-1,5Ag-5In; Sn-5Bi-1In; Sn-1,5Ag-3Cu-5In, Sn-0,5Ag-3Cu-5In, Sn-0,5Ag-1Cu-5In, Sn-1,5Ag-1Cu-5In; Sn-3Ag-2Bi-2Sb, Sn-0,5Ag-1,5Bi-3Sb, Sn-2,5Ag-11,2Bi-5,5In, Sn-2Ag-7,5Bi-5,5In, Sn-2,9Ag-1,9Bi-2,9In, Sn-2Ag-7,5Bi-0,5Cu; vzorky byly vyrobeny z odlévaných tyčí Ø10-12mm. Podle hodnot potenciálů bodové koroze (depasivace, repasivace) odolnější jsou pájky obsahující Bi, případně Bi-Ag, naopak méně odolné jsou pájky s indiem. Interpretace výsledků s ohledem na vliv jednotlivých přísad je poměrně obtížná z důvodu jejich nízkého obsahu a rozdělení do různých fází a oblastí, jak potvrzují výsledky metalografického rozboru a mikroanalýzy. Aplikace statistických metod umožnila porovnat vlivy jednotlivých prvků na parametry koroze, např. pro potenciál depasivace byl zjištěn regresní vztah: $E_d = -388 + 18,0 \cdot Ag$

+0,35.Bi -5,0.Cu -11,1.In -16,3.Sb, podle něhož pozitivní vliv vykazuje Ag a Bi, avšak negativně působí další prvky. Podobné vztahy byly získány pro korozní úbytky na základě gravimetrické metody po expozici v komoře se solnou mlhou. Pro porovnání a lepší interpretaci výsledků byly také zkoušeny potenciodynamickou metodou čisté kovy na výrobu pájek, přitom z měření plyne pořadí odolnosti proti pittingu: Ag, Bi, Cu, Sb, Sn, In. Pomocí mikroskopů byly pozorovány korozní body, tmavé skvrny, zmatnění povrchu i barevné oblasti na pájkách po korozních zkouškách.

Key words: Tin alloys, lead-free solders, pitting corrosion, potentiodynamic polarization method, salt spray test

1. Introduction

New types of lead-free tin base solders are studied from the ecological and health purposes, as well as for improving their mechanical and technological properties. The corrosion problems of lead-free solders can be divided into the areas:

- oxidation of solders at heating up and melting in air,
- corrosion of solders joints in atmosphere during equipment lifetime,
- negative influence of chlorides (halogenides) containing fluxes,
- possibility of galvanic corrosion between solder and base metal,
- influence of melted solders on the materials and devices at wave soldering,
- superposition of corrosion and mechanical factors on degradation of joints or contacts.

Corrosion resistance of tin is given by the oxide layers (SnO , SnO_2 films) that are stable in the pH 3,5-9 range. In diluted acids or alkali solution the tin corrosion is mainly influenced by oxide content or other oxidative component. The average general corrosion rate of tin is around $0,5 \mu\text{m/a}$ (annual) in clean atmosphere and $\approx 3 \mu\text{m/a}$ in polluted one. The corrosion of lead is 3-6 times lower at the same conditions, so that atmospheric corrosion lead-free solders can be probably higher than Sn-Pb alloys [1].

Assessment of alloying elements on the properties and corrosion resistance of solders is given in contribution [2]. Silver improves mechanical strength and corrosion resistance in solid solution, but silver containing intermetallics can cause microgalvanic and localized corrosion. Bismut lowers melting temperature and improves wetting ability, in some solders it can form phase $\text{BiPb}_{32}\text{Sn}_{16}$ (with melting temperature only 95°C), which can cause degradation similar to intergranular corrosion. Antimon is added for strengthening, without influence on corrosion at low concentration. The problem with indium is its higher price, lower corrosion resistance and oxide formation at melting. Copper improves wettability and thermal fatigue resistance. Some of these alloying elements can improve general corrosion resistance, but can facilitate localized (pitting) corrosion.

The electrochemical corrosion measurements were conducted on Sn-3,8Ag-0,8Cu solder strengthened by Cu or Ni particles [3]. The differences among solders, with and without these particles, were measured in values of corrosion potential and passive current, but not in pitting potential. Microelectrochemical measurements on the particles and pores free surface revealed its better corrosion resistance.

The aim of this contribution is comparison and evaluation of corrosion resistance of selected and new tin base lead-free solders with Ag, Bi, Cu, In and Sb addition on the basis of standard potentiodynamic polarization method and salt spray test.

2. Tested lead-free solders

The selected solders were made in department of non-ferrous metals, refining and recycling VŠB-TU by melting and casting into circular rods (diameters Ø10-12 mm) of which were cut out samples of 4-7 mm thickness. Chemical composition of tested Sn solders is given in Tab. 1.

The metallography and microanalysis of solder phases have been presented in the work [4]. Nearly eutectic structures and dendritic grains with some particles were predominantly observed. For better interpretation and comparison of individual element influence the potentiodynamic test were conducted with pure metals used for production (Sn, Bi, Ag, Cu, In, Sb) of solders. Flat surfaces of samples were ground by new metallographic SiC papers up to no. 1200 under water, cleaned by spirit and rinsed by demineralised water before testing.

Table 1 Nominal composition of selected lead-free solders

sample	solder	sample	solder
E3	Sn-3Ag-2Bi-2Sb	F34	Sn-3,33Ag-4,76In
E19	Sn-2,5Ag-11,2Bi-5,5In	F36	Sn-2,91Ag-1,94Bi-2,91In
F1	Sn-2Ag-7,5Bi-5,5In	F41	Sn-3,5Ag-7Bi
F23	Sn-0,5Ag-1,5Bi-3Sb	F42	Sn-3,5Ag-10Bi
F25	Sn-0,5Ag-56Bi	F44	Sn-1,5Ag-3Cu-5In
F47	Sn-5Bi-1In	F45	Sn-0,5Ag-3Cu-5In
E5	Sn-2,5Ag-2Bi	F51	Sn-0,5Ag-1Cu-5In
E11	Sn-5Ag-8,6In	F52	Sn-1,5Ag-1Cu-5In
E14	Sn-3,1Ag-6,1Bi	F55	Sn-0,5Ag-5In
F9	Sn-2Ag-7,5Bi-0,5Cu	F56	Sn-1,5Ag-5In
F17	Sn-3,4Ag-4,8Bi	Q1	Sn-3,33Ag-4,83Bi

3. Applied corrosion test method

3.1 Potentiodynamic cyclic polarization measurements

Electrochemical corrosion tests were conducted according the standard [5,6] and published works [2-6]. For electrochemical test were used 0,1 mol/l water solution NaCl at room temperature with free access of air. Exposed surfaces of samples in corrosion cell were in the range 0,5 cm². At the beginning of tests the corrosion potential values were measured. Polarization measurements were realised in wider potential range with respect to corrosion potential values at potential scanning rate 1,0 mV/s by means of the potentiostat-galvanostat PGP201 and software Voltmaster 1. For better reproducibility and precision (as well as evaluation and compare surface state) the measurements were repeated 2-4 x. On the basis of potentiodynamic polarization curves the values of pitting and/or passive state stability potentials were determined:

E_d – depassivation potential for conventional current density 0,10 mA/cm², which is connected with resistance to macro pitting initiation and growth,

E_r – repassivation potential at which current density drop down to conventional value 0,01 mA/cm², during return polarization - at transition to passive state.

Before pitting initiation the values of polarization resistance ($R_p = \Delta E / \Delta J$, $E \rightarrow E_{cor}$, $J \rightarrow 0$) that are indirectly proportional to general corrosion rates, were also calculated at corrosion potential (E_{cor}).

3.2 Salt spray test

Before this standard test [7] the samples were cleaned and weighed by digital scales Sartorius CP224S-OCE. All solders (Table 1) were exposed then under neutral salt, formed by spraying (atomizing) of 5% NaCl water solution in corrosion testing system Liebisch S400M-TR. After exposition time 100 and 240 hour at 35°C the samples were observed, photographed, rinse by water, dried and weighed again.

4. Description and discussion of results

4.1 Electrochemical method

At testing of passive state and pitting resistance of selected solders the polarization curves were measured and recorded, see example in Fig. 1. The depassivation (E_d) and repassivation (E_r) potential values were determined than and compared for tested lead-free solders, Fig. 2. According to values of pitting potentials, the Bi and/or Ag-Bi containing solders are more resistant, on the other hand indium (In) containing solders have shown a lower resistance.

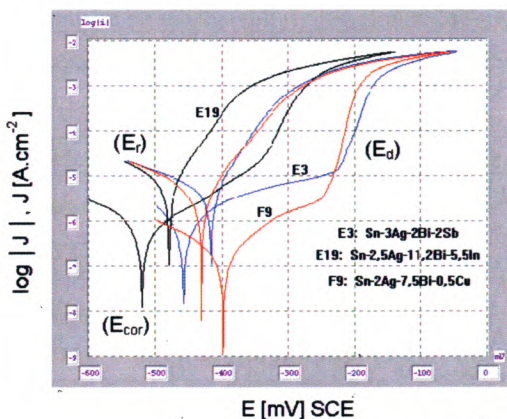


Fig. 1 Typical potentiodynamic cyclic curves of selected solders (0,1mol/l NaCl, 25°C)

Interpretation of measured values is difficult with respect of individual elements influence because of their low content and distribution in different phases. For comparison and evaluation of corrosion resistance, the results of metallographic observation and microanalysis have to be taken into mind, especially an occurrence of intermetallic phases with mikrogalvanic influence and real content and distribution of alloying elements in structure.

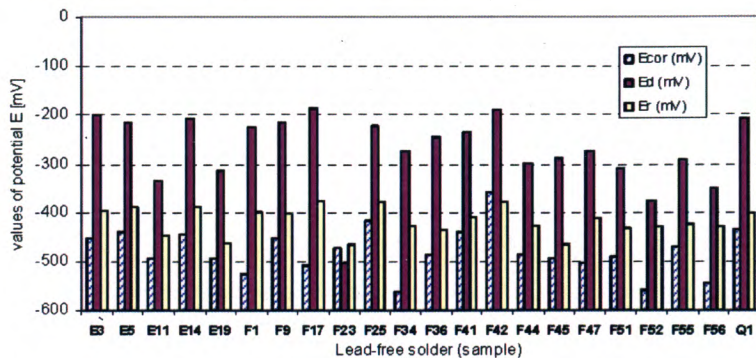


Fig. 2 The comparison of pitting potentials and passive state stability of tested solders

The application of statistical methods made possible the comparison of individual elements influence on the corrosion parameters. For example, by the means of linear regression model the relation for depassivation potential was calculated (with correlation index $I=0,91$):

$$E_d = -388 + 18,0.(Ag) + 0,35.(Bi) - 5,0.(Cu) - 11,1.(In) - 16,3.(Sb), \quad (1)$$

where positive influence have shown Ag and Bi, and negative other element (In, Sb). Tin as base elements was not incorporated into regression model and the content of alloying elements is given in % wt. The similar relation were found out for other potentials (E_r , E_{cor} , $E_d - E_{cor}$), e.g.

$$E_r = -4,1 + 3,9.(Ag) + 1,64.(Bi) - 3,9.(Cu) - 8,34.(In) - 16,3.(Sb), \quad (I=0,87) \quad (2)$$

The stated influence of elements is in good agreement with their resistance to pitting corrosion as pure metals by potentiodynamic method. The sequence of pitting resistance was determined: Ag, Bi, Cu, Sb, Sn and In. This order also corresponds to standard potential (E_o) values: Ag +0,80V; Bi +0,30V; Cu +0,34V; Sb +0,15V; Pb -0,13V; Sn -0,14V a In -0,34V (HSE). The galvanic corrosion between lead-free solders and base metals (Cu, brass) is also possible and could be tested. The intermetallic phases rich in Ag, Bi and Cu can initiate microgalvanic corrosion of tin base matrix.

The example of typical structure of solders (F1: Sn-2Ag-7,5Bi-5,5In) is documented in Fig. 3, where the dendritic grains with different orientations and heterogeneities are evident.

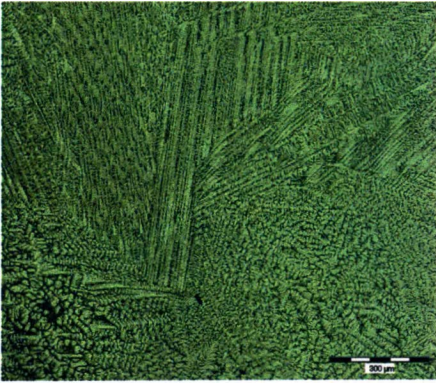


Fig. 3 Microstructure of solder (F1) after polishing and etching



Fig. 4 Surface of solder (E14, Ø12) after salt spray test, exposition 240 h

4.2 Salt spray test

After exposition test the spots, pits and mat surfaces were observed, and on same samples the coloured areas have occurred, Fig. 4. The results of gravimetric method are compared in Fig. 5, where the positive influence of Ag and /or Bi (solder E3, F25, F42, F47, Q) is indicated but negative effect of In (see solders: E11, F51, F52, F55).

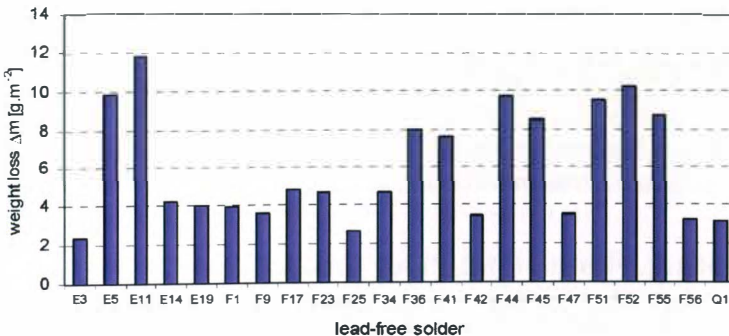


Fig. 5 Corrosion weight losses after salt spray test

Within of framework of linear regression model the positive influence of alloying elements on the general corrosion was shown, except for indium. Tin as base metal is not incorporated in the model. The positive influence of Sb must be carefully evaluated, because of its low content (2-3%) in solders, and behaviour of Cu is in relation with its electrochemical properties.

$$\Delta m/S = -9,10 + 0,432.(Ag) + 0,489.(Bi) + 0,615.(Cu) - 0,353.(In) + (1,49).(Sb) \quad (3)$$

The lower value of correlation index ($r = 0,64$) can be explained by smaller mass losses and relative higher dispersion on smaller samples or more complex non-linear regression models might be used, including products among elements (interactions).

The qualitative results of salt spray test are in agreement with potentiodynamic measurements. None of tested combinations of elements caused significant ($\geq 5x$) increasing or decreasing of corrosion resistance of selected lead-free solders.

5. Conclusion

In the contribution is compared and evaluated the corrosion resistance of selected and/or new tin base lead-free solders with additions of Ag, Bi, Cu, In and Sb. On the basis of potentiodynamic cyclic polarization measurements and statistical treatment of results (mainly values of depassivation and repassivation potentials) was shown the positive influence of Ag and Bi, and negative one of indium on pitting corrosion. Similar results were obtained by gravimetric method after salt spray test. On the exposed solder surfaces the pits, black spots and mat areas have been observed. The pitting corrosion resistance of pure metals was also confirmed by potentiodynamic test in ranking Ag, Bi, Cu, Sb, Sn, In.

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