

COMPARISON OF ELECTROCHEMICAL CORROSION PROPERTIES OF SELECTED LEAD-FREE SOLDERS

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POROVNÁNÍ KOROZNĚ ELEKTROCHEMICKÝCH VLASTNOSTÍ VYBRANÝCH BEZOLOV NATÝCH PÁJEK

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Abstrakt

Korozně elektrochemické vlastnosti vybraných bezolovnatých pájek (Sn99Cu1; Sn95Sb3,5Cu1,5; Sn95Sb5; Sn95,5Ag3,8Cu0,7; Sn96Ag4) a téměř eutektické Sn67Pb37 slitiny jsou porovnány na základě potenciodynamické polarizační metody (voltametrie) s použitím vodného roztoku 0,1 mol/l KOH za normální teploty. Uvedené slitiny byly zkoušeny ve tvaru dodaných drátů anebo tyčí. Poměrně malé rozdíly byly zjištěny mezi bezolovnatými pájkami v hodnotách korozních potenciálů, pasivačních proudových hustot a v šířce aktivní oblasti. Všechny tyto pájky vykazovaly aktivně-pasivní přechod. Značné rozdíly byly zjištěny mezi anodickými polarizačními křivkami bezolovnatých pájek a pájkou Sn63Pb37. Více anodických píků bylo zaznamenáno na polarizačních křivkách Sn-Pb pájky, kde přechod do transpasivní oblasti probíhal při nižších hodnotách potenciálu, než u bezolovnatých pájek. Rychlost koroze (podle proudové hustoty) v aktivním stavu byla vyšší na pájkách s obsahem antimonu, zatímco v pasivní oblasti tato rychlost byla významně vyšší pro pájku Sn-Pb. Měď a stříbro v malém množství se prakticky neprojeví na korozních vlastnostech v aktivní oblasti, avšak v transpasivní oblasti způsobily zvýšení proudové hustoty a vznik menších píků. Po provedených elektrochemických zkouškách byla pozorována na povrchu pájek rovnoměrná koroze. V příspěvku jsou také uvedeny výsledky chemické mikroanalýzy zkoušených pájek, včetně jejich minoritních fází a oblasti hranic zrn. Rovněž jsou porovnány základní vlastnosti zkoušených pájek (rozmezí teplot tavení, povrchové napětí, tvrdost, hustota).

Abstract

Electrochemical corrosion properties of lead-free solder alloys (Sn99Cu1; Sn95Sb3,5Cu1,5; Sn95Sb5; Sn95,5Ag3,8Cu0,7 and Sn96Ag4) and near eutectic Sn67Pb37 one are compared in the 0,1 mol/l KOH water solution at room temperature on the base of potentiodynamic polarization method (voltammetry). These tin alloys were tested in the form of as-received wires and rods. Relative small differences were found out in corrosion potential values, passivation current densities and active peak width among these lead-free alloys. All these solders exhibit active-passive transition. There were registered significant differences between anodic polarization curves of lead-free and Sn-Pb solders. More anodic peaks were

measured on the Sn63Pb37 solder, where transition to the transpassive region started at lower potential values in comparison with lead-free solders. Corrosion rate (according to current density and peak) was higher on Sb containing solders in the active state, on the other hand in the passive range the corrosion was higher for Sn-Pb one. The corrosion properties were not influenced by copper and silver in small quantity in the activity area, but in the transpassivity area they caused small peaks and current density increasing. The uniform corrosion was observed after potentiodynamic polarization tests. The results of chemical microanalysis of solders, including secondary phases and grain boundary areas are also given in the contribution. The main properties of tested tin solders (melting temperature range, surface stress, hardness, density) are compared too.

Key words: Tin alloys, lead-free solders, electrochemical corrosion, potentiodynamic polarization method.

1. Introduction

Tin is widely used as a protective coating for steel plates and for mild solders. The new types of lead-free solders have been developed and recommended for replacing Sn-Pb solders mainly for health and ecological requirements. Anodic behaviour and corrosion of tin base alloys under different conditions has been studied by electrochemical methods.

The formation and chemical composition of passivation layers on Sn and Sn-Cu alloys have been systematically studied in 0,1M KOH with potentiodynamic method and X-ray photoelectron spectroscopy (XPS) [1]. The potentiodynamic polarization curve of pure tin has two anodic peaks at potential $E = -1,05\text{V}$ and $E = -0,75\text{V}$ (SCE), which agree reasonably well with the formation of soluble HSnO_2^- and SnO_3^{2-} . A large passive range (with film or layer thickness ≤ 5 nm) follows between $-0,5$ and $1,2\text{V}$ with lower current density $J = 0,02\text{mA}\cdot\text{cm}^{-2}$ and a secondary passive range up to $1,9$ V with an increased current density $0,2\text{mA}\cdot\text{cm}^{-2}$. At $E > 1,9$ V follows a steep current increase attributed to oxygen evolution. The cathodic peak at $E = -1,25$ V is comparatively small which allows two explanations: only a very small amount oxide has been formed on the electrode or the reduction of the passive layer at this peak is not complete. The passive layer on tin consists of SnO/Sn(OH)₂ film in contact with the electrolyte followed by inner part of SnO₂/Sn(OH)₄ and Sn(II) fraction at the oxide/metal interface.

The electrochemical behaviour, microstructure and corrosive products of Sn-Zn9-Agx lead-free solders were investigated in study [2]. The Sn63-Pb37 and Sn-Ag3,5 solder alloys were also tested for comparison. The Sn-Ag3,5 solder alloy had higher equilibrium potential ($-0,44$ V SCE) than the ones Sn63-Pb37 ($-1,10$ V) and Sn-Zn9 ($-1,43$ V). The Ag addition enhanced the corrosion resistance of the Sn-Zn9 solder alloy. Passivation behaviour occurred in the solder alloys used [2], except the Sn63-Pb37 one. X-ray diffraction patterns showed that the Zn segregated in the Sn-Zn9 solder alloy as solidified, but it dissolved when 0,5% wt Ag was added to the solder alloy. The Ag₃Zn₃ and Ag₅Zn₈ were found in the Sn-Zn9-Ag1,5 solder alloy but they were substituted by Ag₃Sn when the Ag content in the solder was above 2,5 % wt. However, they are the initial sites for pitting. The corroded product of SnCl₂ was observed in all solder alloys tested. The potentiodynamic polarization method is applied for the corrosion study of lead-free solders in further studies [3,4]. The Sn-Pb base solders are used for the comparison purposes.

The aim of this contribution is the comparison of corrosion electrochemical properties of selected lead-free solders on the base potentiodynamic polarization method.

2. Experimental

The chemical composition of tested solders is given in Tab.1. The microanalysis results of their selected phases and grain boundary segregations are documented in the work [5] as well as structures. The solders were made in KOVO Příbram and in Department of Non-ferrous Materials, Refining and Recycling, VSB-TUO by technology of casting and forming into rods and wires.

Table 1 Chemical composition of tested soft solder alloys [weight %]

	solder / element	Ag	As	Bi	Cu	Fe	Pb	Sb	Sn
1	Sn99Cu1	0,0004	0,015	0,004	0,75	0,006	0,04	0,02	rest
2	Sn95Sb3,5Cu1,5	0,0025	0,005	0,007	1,40	0,022	0,060	3,3	rest
3	Sn95Sb5	0,0002	0,001	0,012	0,017	0,014	0,029	4,9	rest
4	Sn95Ag3,8Cu0,7	3,75	0,001	0,007	0,74	0,010	0,03	0,02	rest
5	Sn96Ag4	3,73	0,007	0,007	0,005	0,009	0,028	0,01	rest
6	Sn63Pb37	0,0003	0,001	0,009	0,001	0,003	rest	0,008	62,9

The content of other elements: Al <0,001, Cd < 0,001, In <0,01, Ni ≤ 0,001, Zn < 0,001 %.

The properties of tested solders are compared in Tab. 2, where T_h is high melting temperature at heating, T_c – low temperature of solidification at cooling, HV – Vickers hardness, ρ – density, σ – surface energy. The melting temperature interval is given by the temperature T_c and T_h . Some results of phase and grain boundary area microanalysis are also given in Tab. 2. The phases rich in Au and/or Cu can form micro-galvanic cells (cathodes) in the Sn base matrix (anode) and can cause pitting corrosion. The standard potential (E_o) of the main elements has values: Sn -0,14V, Pb -0,13V, Sb +0,15V, Cu +0,34, Au + 0,80 V. The Sn and Pb have near the same value of standard potential.

Table 2 Propertiešs of selected solders [5]

No.	property solder	T_h °C	T_c °C	HB	ρ Mg/m ³	σ mN/m	phases or areas
1	Sn99Cu1	231	210	10	9,51	509	Sn90Cu10
2	Sn95Sb3,5Cu1,5	237	222	16	9,06	507	Cu50Sb35
3	Sn95Sb5	245	225	12	8,84	494	Sn90Sb9
4	Sn95,5Ag3,8Cu0,7	222	206	17	7,54	428	Ag ₂ Sn ₂
5	Sn96Ag4	222	208	15	8,93	564	Ag ₃ Sn ₂
6	Sn63Pb37	188	169	8,5	10,68	425	Pb91Sn9

The working electrode were wires (Ø3mm, solder no. 1-3) with exposed area about 1,5 cm² and rods (Ø15mm, no. 4, cross section 24x13 mm, no. 5 and 6) with the one of 0,4 cm². The surface pre-treatment of the working electrodes from the rods was performed by mechanical polishing with SiC emery papers up to 1200 grit. These electrodes were then degreased with cleaning alcohol and washed by demineralised water. The solder wires were tested with the as received surface in vertical position by immersion into solution. The counter electrode was a platinum wire (5 cm²). The potential values were measured relative to a saturated calomel electrode (SCE).

The potentiodynamic polarization curves ($J=f(E)$) were recorded by sweeping the electrode potential (E) automatically from -1,5 to +1,5 V at the constant scan rate 5mV/s [6]. A potentiostat/galvanostat PGP201 and personal computer was used, Voltmaster 1 electrochemical

corrosion software was used for the technique mentioned above. All measurements were performed at constant temperature $25 \pm 1^\circ\text{C}$.

3. Results and discussion

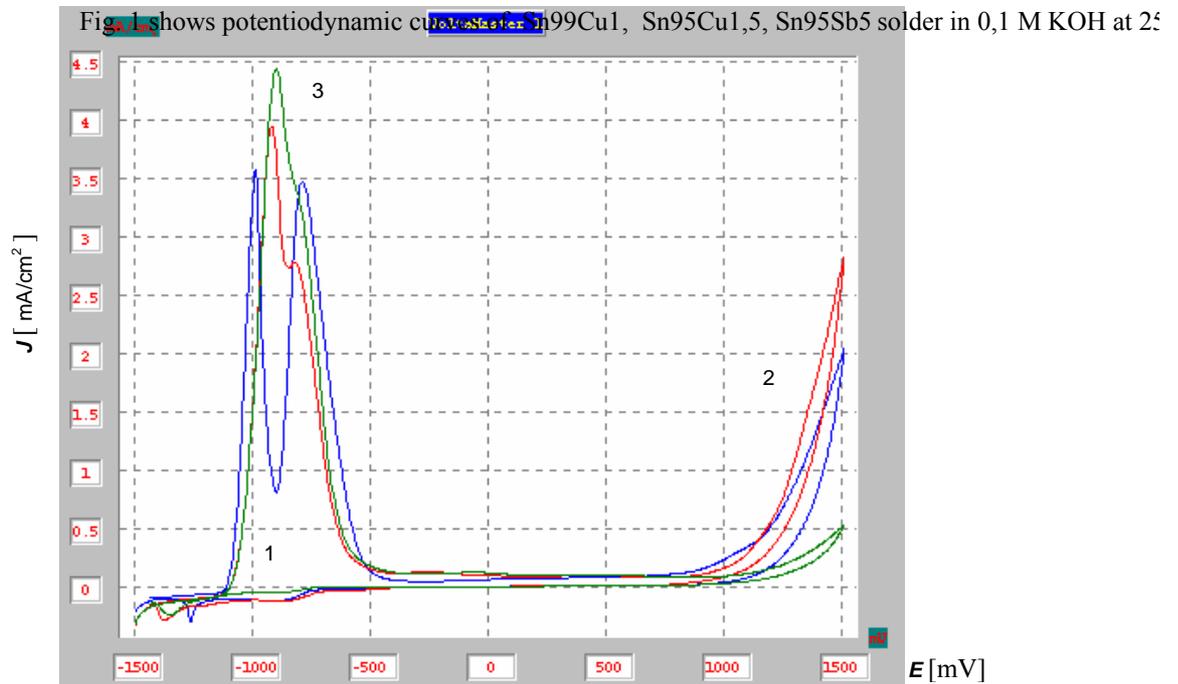


Fig.1 Polarization curves of lead-free solders: 1- Sn99Cu1, 2 - Sn95Sb3,5Cu1,5, 3 - Sn95Sb5

The anodic polarization curve exhibits active/passive transition, similar as in the case of clean tin [1] with characteristic peaks. The active dissolution region involves a well-defined two anodic peak for alloy Sn99Cu1, followed by a passive region, which extends up to 1,0 V with almost constant current density, which is further rising by one order up to 1,5 V. When scanning is back in the cathodic direction, one small cathodic peak appeared before the potential, where hydrogen evolution commences. Addition of Sb contributes to one higher peak, which is probably formed by connection of two peaks and it increases a little the current density in the passive area and decreases one in transpassive region. For interpretation of results is significant that according to the Faraday law the current density is proportional to the corrosion rate. The potential value corresponds to an oxidation capability of solution and/or environment. The potentiodynamic polarization curves of solders Sn95Ag3,8Cu0,7; Sn96Ag4; Sn63Pb37 are documented on Fig. 2. There are compared the measured values of electrochemical corrosion properties of selected solders in Tab. 3: E_{cor} – corrosion (free) potential measured before potentiodynamic test, J_p – passivation current density (maximum current density in active area, peak current density), ΔE_a – width of active area at current density $1,0\text{mA}/\text{cm}^2$, ΔE_p – passive range with current density below $0,1\text{mA}/\text{cm}^2$ (measured in a scale $\log J\text{-}E$).

The differences in values of measured parameters (Tab. 3) are rather small, except passive (pseudopassive) range. Passive surface state for the lead-free solders, characterized by current density below $0,10 \text{ mA/cm}^2$ is not perfect, but on the Sn63Pb37 alloy this value is few times higher ($0,5\text{-}0,8 \text{ mA/cm}^2$). This is in relation with salt spray test and gravimetric method results [7,8]. The higher mass loss and uniform corrosion was observed on Pb-Sn solders, on the lead-free ones the surface pitting and spot corrosion was characteristic.

In transpassive area appears smaller peaks (for alloy no. 4 and 5 at 1,0 V) and narrow secondary passivity with a local minimum of current density (at 1,1-1,2V).

Table 2 Electrochemical corrosion properties of solder alloys (solution 0,1M KOH).

parameter	E_{cor} mV	J_p mA/cm^2	ΔE_a mV	ΔE_p mV
solder				
Sn99Cu1	-1090	3,35	430	1220
Sn95 Sb3,5Cu1,5	-1075	3,70	325	980
Sn95Sb5	-1078	3,95	335	930
Sn95,5Ag3,8Cu0,7	-1090	3,69	380	1095
Sn96Ag4	-1090	3,73	450	870
Sn63Pb37	-1060	2,90	450	0

The Sn-Pb solder exhibits 3 peaks in anodic area and larger one in the passive range (see Fig. 2). Similar peaks and trends on polarization curves were registered on alloy Sn60Pb40, Pb51Sn47Sb, Pb72Sn27.

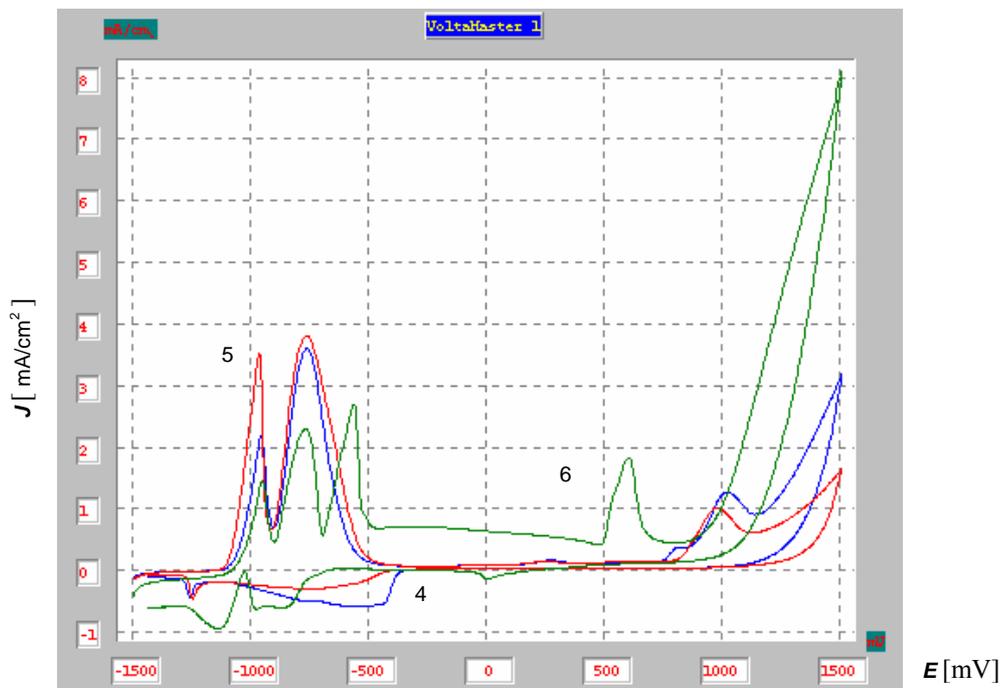


Fig.2 Polarization curves of solders: 4 – Sn95Ag3,8Cu0,7; 5 – Sn96Ag4; 6 – Sn63Pb37.

For alloy Sn63Pb37 these areas are shifted to the lower potential values (e.g. peak at 0,6 V, change of oxidation state). Above potential 1,0 V the steep current is caused by oxygen

evaluation. The surfaces after corrosion test exposition were cleaned and observed by stereomicroscope. Uniform corrosion was formed under testing conditions.

The selected solders have been also tested in neutral water solution (0,1M NaCl) and in acid solution (0,1 M H₂SO₄) and results will be published.

Conclusion

The electrochemical corrosion behaviour of tin base lead-free solders (Sn99Cu1, Sn95Sb3,5Cu1,5, Sn95Sb5, Sn95,5Ag3,8Cu0,7, Sn96Ag4) in water solution 0,1 mol/l KOH have been studied. For comparison the Sn63Pb37 solder was also tested. The results of potentiodynamic (voltametric) test have shown small differences among tested solders in the active area. The higher current density was measured in the passive area of Sn63Pb37 alloy in comparison with lead-free solders. Characteristic anodic peaks were registered for tested solders. The general corrosion of Sn lead-free solders is not worse than Sn-Pb one.

Acknowledgements

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