Electrochemical and wetting behavior of as-cast Sn–Zn–Sb lead free solder alloys

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Abstract
Ternary alloys SnZn12Sb8, SnZn10Sb10, SnZn8Sb12, SnZn6Sb14 and SnZn2Sb18 were prepared by induction melting. The electrochemical and wetting (contact angle) behavior of prepared as-cast samples were investigated using open circuit potential measurements and the sessile drop technique. The results of the electrochemical investigation show that the open-circuit potential, a few seconds after the immersion of electrodes, shifts toward more negative values, indicating a relatively smaller rate of dissolution during the spontaneous dissolution process under curentless conditions. After that period, the values of the potential tend to remain constant with time. It was found that all investigated alloys have poor wettability on copper substrates and that the contact angle values decrease with increasing superheat temperature.

Keywords: open-circuit potential, contact angle, step soldering alloys, sessile drop technique.

Available online at the Journal website: http://www.ache.org.rs/HI/

SCIENTIFIC PAPER

UDC 544.6:544.632.4:669.4

Hem. Ind. **67** (3) 477–484 (2013)

doi: 10.2298/HEMIND120608084M

Lead is a heavy poisonous metal harmful to human health, but, in spite of that, lead–tin alloys have been widely used as soldering materials. Multicomponent alloys based on the Sn–Zn eutectic belong to a group of materials with perspectives to apply in the industry of electronic systems apart from near-eutectic Ag–Sn–Cu alloys. Bismuth, indium and antimony are the most popular metals among the modifiers of soldering properties of the Sn–Zn eutectic [1].

Sn–Sb alloys are important high-temperature solders. The melting points of Sn–Sb alloys are higher than that of conventional eutectic Sn–Pb solder and they have been used as high-temperature solders in step soldering processes. Step soldering refers to the circumstance in which soldering processes occur at various steps because more than one soldering process is needed for some electronic products. To avoid remelting of the earlier solder joints in the later soldering processes, solders with different melting points are used [2].

Various Sn–Sb based alloys have been developed as high-temperature solders in compliance with recent Pb-free requirements for electronic products. Among various lead-free solders, Sn–Sb based alloy is one of the promising candidates for the replacement of the high-melting-point Sn–95wt%Pb alloy. Hence, ternary Sn–Zn–Sb alloys may also be considered as promising lead-free solders. Investigations of Sn–Zn–Sb alloys with constant atomic percent of tin and high, variable contents of Zn and Sb (calculated phase diagram presented in Figure 1 [3,4]) are conducted in very small scale.

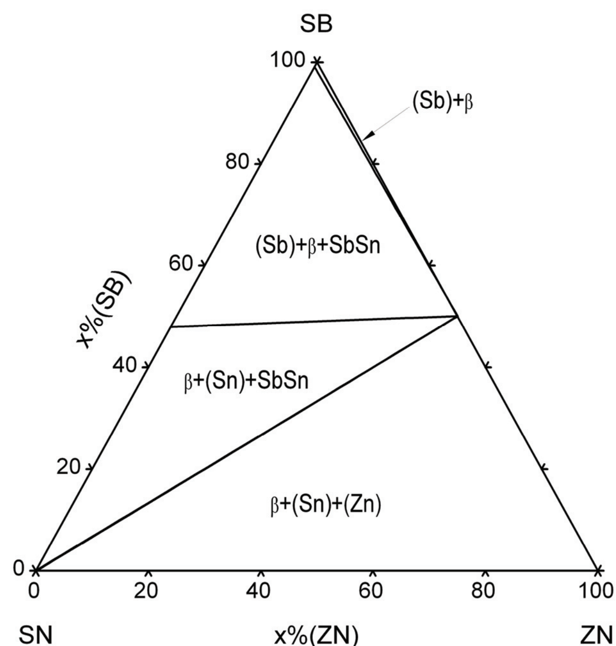

Figure 1. The calculated isothermal section of the Sn–Zn–Sb system at room temperature.

The electrochemical behavior of pure tin in different media has been studied previously [5,6] but the electrochemical behavior studies of complex Sn–Zn–Sb alloys have not yet been done.

Solder spreading on a substrate is fundamental for the development of new solders. It is a complex pheno-

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Paper received: 8 June, 2012
Paper accepted: 11 July, 2012

menon involving joint configuration, flux selection, substrate finishing and many other factors [7]. When the solder melts, the increase in contact area indicates the wetting behavior of solder [8]. The extent of wetting is measured by the contact angle that is formed at the juncture of solid and liquid (molten solder), as shown in Figure 2.

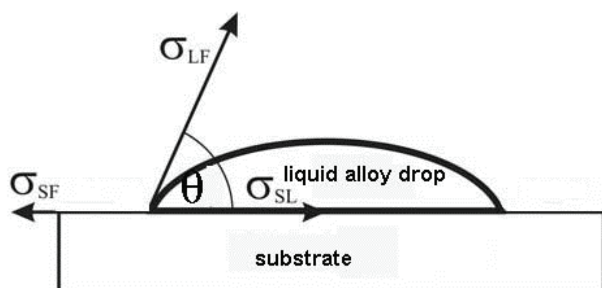

Figure 2. Schematic presentation of the contact angle, θ, between an alloy drop and a substrate, where σ_{SL}, σ_{SF}, and σ_{LF} refer to the surface tension of liquid/substrate, substrate/environment, and liquid/environment, respectively.

In this work, electrochemical and wetting (contact angle) behavior of Sn–Zn–Sb alloys with high amount of antimony were studied, and several results were obtained.

EXPERIMENTAL

Electrochemical investigations

The investigations were performed in 0.1 mol/dm^3 H_2SO_4 (pH 1) and 0.01 mol/dm^3 NaOH (pH 11) by open circuit potential measurements at 25 °C, using a saturated calomel electrode as a reference. For the open-circuit measurements, a counter electrode was not used. The body of the electrochemical cell was a double-wall vessel made of Pyrex glass. The body was covered with a lid with five holes, where electrodes, thermometer, and gas inlet (if used) are put through. The solution was prepared from p.a. NaOH and H_2SO_4 (Zorka, Serbia) and distilled water. The system for electrochemical measurements consisted of hardware (PC, AD-DA converter NI–6251 produced by National Instruments (Austin, TX) and analog interface) and software for excitation and measurement (Lab-View 8.2 platform and application software; National Instruments) both fully developed by the Technical Faculty in Bor [9]. Good reproducibility was proven by repeating the experiments under the same conditions.

All investigated samples were prepared in the form of electrodes (Figure 3). Electrical contact between the copper wire and the electrode material was achieved by using conducting silver glue IM-P3014 (Iritel, Belgrade, Serbia) and then mounted in cold polymerized SIMGAL mass (Galenika, Belgrade, Serbia). For each set of experiments, the working electrodes were ground, polished, washed out, dried, and finally, immersed into lectrolyte. Grinding was performed by the finest grinding paper, polishing by alumina (0.05 µm), and washing by distilled water and alcohol.

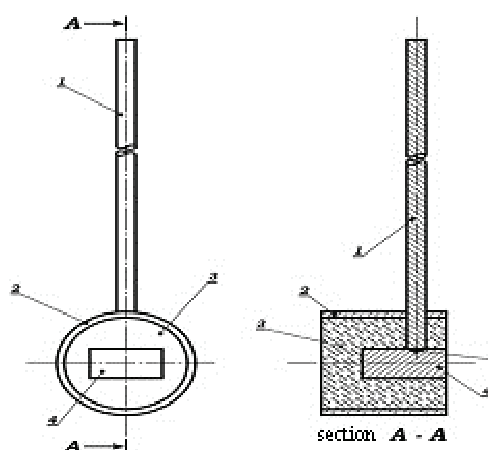

Figure 3. Working electrode construction: 1 – copper wire, 2 – mold, 3 – SIMGAL mass, 4 – alloys samples, 5 – conducting silver glue.

The electrochemical investigations were conducted using the setup shown in Figure 4.

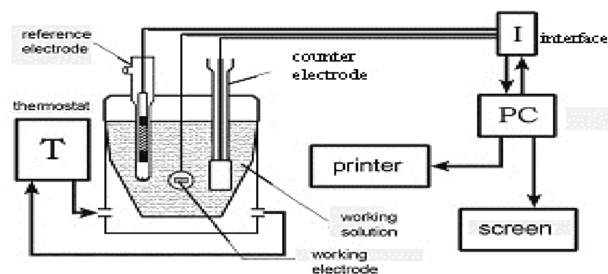

Figure 4. Experimental set-up for electrochemical investigations.

Wetting investigation

The five investigated alloys from Sn–Zn–Sb system were prepared from high purity (99.9 wt.%) tin, zinc and antimony. They were melted in a graphite crucible at 450 °C in an electrical furnace under an inert argon atmosphere. The chemical compositions of the investigated alloys are presented in Table 1.

Table 1. Composition (wt.%) of investigated alloys

Alloy	Sn	Zn	Sb
A1/ (Sn-12Zn-8Sb)	80.31	11.72	7.97
A2/ (Sn-10Zn-10Sb)	80.39	9.57	10.04
A3/ (Sn-8Zn-12Sb)	80.37	7.93	11.70
A4/ (Sn-6Zn-14Sb)	80.38	5.49	14.13
A5/ (Sn-2Zn-18Sb)	80.52	1.91	17.57

The investigated alloys were remelted at 400 °C and poured into a mold to make a disc of 20 mm in diameter and 5 mm in thickness. Then, the disc was cut into cylinders 10 mm in diameter, with mass around 4 g.

The aforementioned samples of alloys were remelted and sessile drops of about 4 g for each studied alloy were deposited on copper substrate (with thickness of about 0.8 mm for substrate) under two different melt superheats (50 and 100 °C above liquidus temperature of the alloy). Both superheat and substrate materials were chosen in order to simulate various industrial applications. The substrates were sequentially degreased in a 5% NaOH solution at room temperature for 15 s, and finally washed in ethanol for quick drying. Each solidified alloy drop was examined using an image processing system (stereomicroscope and Adobe Photoshop 7.0). Contact angles were measured using Image J®. The images of the melted alloy drop and the analytical analyzing process are presented in Figures 5 and 6.

Figure 5. Formed alloy Sn–12Zn–8Sb drop on Cu substrate inside electrical resistance furnace (temperature superheat 100 °C above liquidus temperature).

Figure 6. Analytical determination of contact angle for alloy Sn–12Zn–8Sb and Cu substrate (superheat temperature, 100 °C above liquidus temperature).

RESULTS AND DISCUSSION

Electrochemical investigation

The microstructural investigations of the alloys showed that in system Sn–Zn–Sb, at room temperature, the following phases were present: β-phase, which is actually the ZnSb-phase and represents an intermetallic compound of antimony and zinc, the Zn-phase, representing primary crystals of Zn, Sn-matrix, and intermetallic SbSn-phase, occuring at higher antimony contents. The primary Sb crystals are also present at higher antimony contents [10]. The characteristic microstructure for A2 alloy is presented in Figure 7.

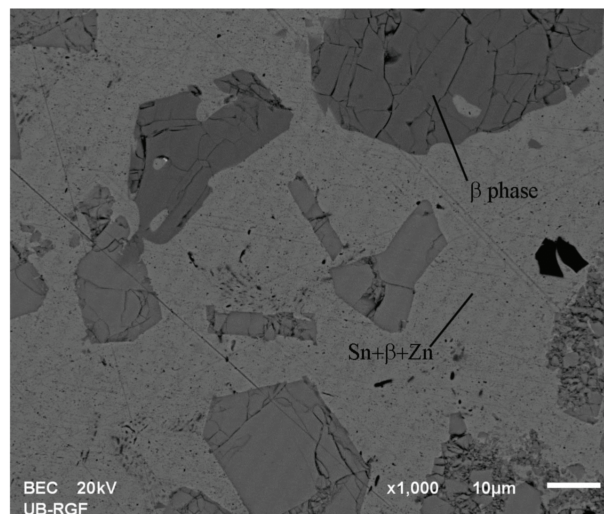

Figure 7. SEM micrograph of A2 alloy.

These results are in good agreement with the results obtained from analytically determined Sn–Zn–Sb system for the investigated concentration area presented in Figure 1. Considering the chemical composition of investigated alloys presented in Table 1, for electrochemical investigations, the Pourbaix diagrams for Sn, Zn and Sb were calculated using the CALPHAD method and shown in Figure 8.

The Pourbaix diagrams give insight into the thermodynamic possibilities of some reactions taking place at certain pH and potential values [11].

The examination of the potential *vs*. pH equilibrium diagrams indicated that a tin electrode could be active or passive, depending on the applied potential. In most neutral solutions, the resistance of tin to corrosive attack is good because of the presence of oxide films.

The Pourbaix diagrams for zinc show that under acidic conditions no surface oxides of zinc are stable, whereas under neutral or slightly alkaline conditions zinc corrosion products are formed, which are more stable [12].

The Pourbaix diagrams for antimony show that under acidic and alkaline conditions and positive values of applied potential, antimony oxide films are formed, whereas under negative values of applied potential the antimony is stable and doesn't dissolute. Considering all E *vs*. pH diagrams, it can be observed that zinc, as the active element, has a central role in the electrochemical behavior of the investigated alloys.

Open-circuit potential measurements (OCP) for five investigated alloys in acidic and alkaline solutions are

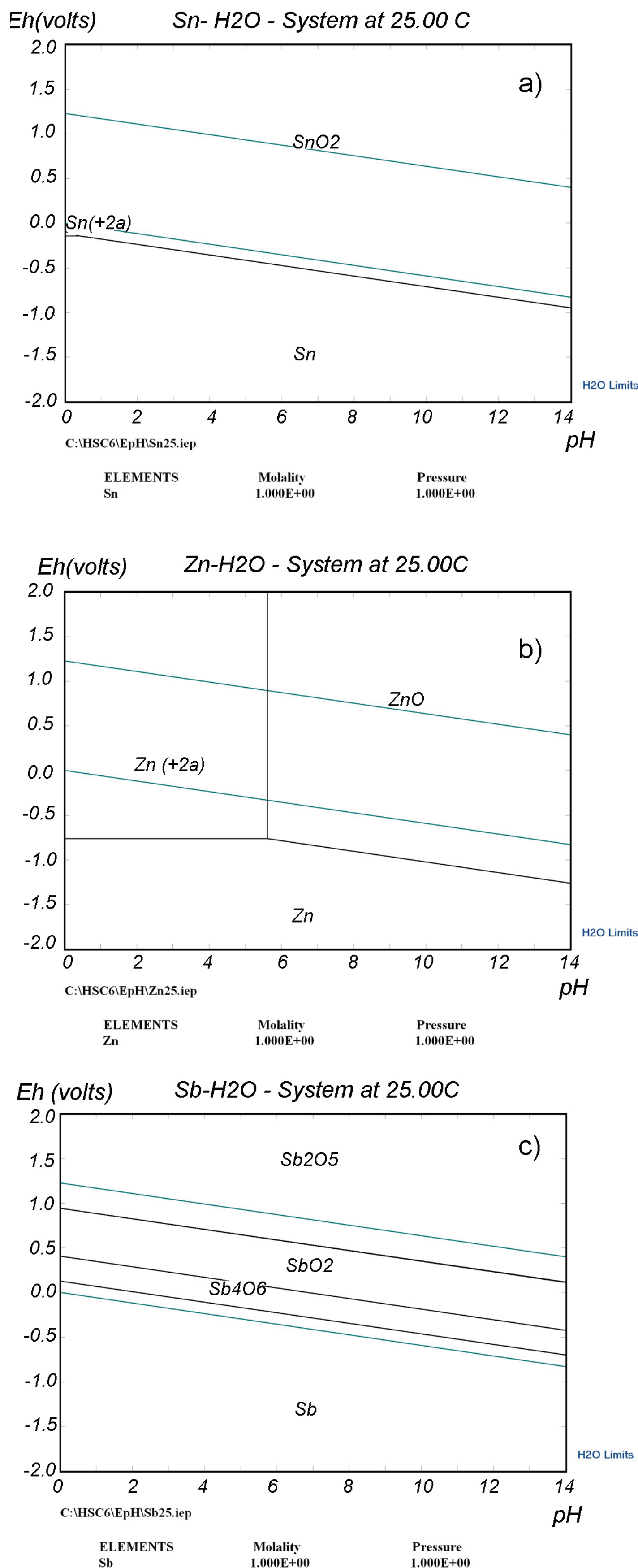

Figure 8. Calculated E–pH diagrams for the systems: a) Sn–H_2O, b) Zn–H_2O and c) Sb–H_2O at 25 °C.

presented in Figures 9 and 10, respectively. These measurements were conducted as a function of exposure time over a period of 20 s in naturally aerated, unstirred solutions. All electrodes had negative potentials and immediatly after imersing the electrodes in 0.1 M H_2SO_4 or 0.01 M NaOH, the potential values shifted to more negative values. This phenomenon is a result of dissolution of zinc in acidic and alkaline solutions. After that period, the potential values tend to remain constant with time, which is a result of the formation of stable oxides layers. Alloys with high Zn contents have more negative potential values and alloys in acidic solution have nobler potential than in alkaline solution.

Wetting investigation

The liquidus temperatures for the investigated alloys were determined by the CALPHAD method and calculated with Pandat Software, version 8.0. An example of the calculated solidification path for alloy A5 is showed in Figure 11.

These calculations were used for the determination of superheat temperature for the investigations of contact angle between the alloys and copper substrates. The superheat temperatures are given in Table 2.

Experimental results of contact angles on the copper substrate as a function of melt superheat (50 and 100 °C above the liquidus temperatures) for the five

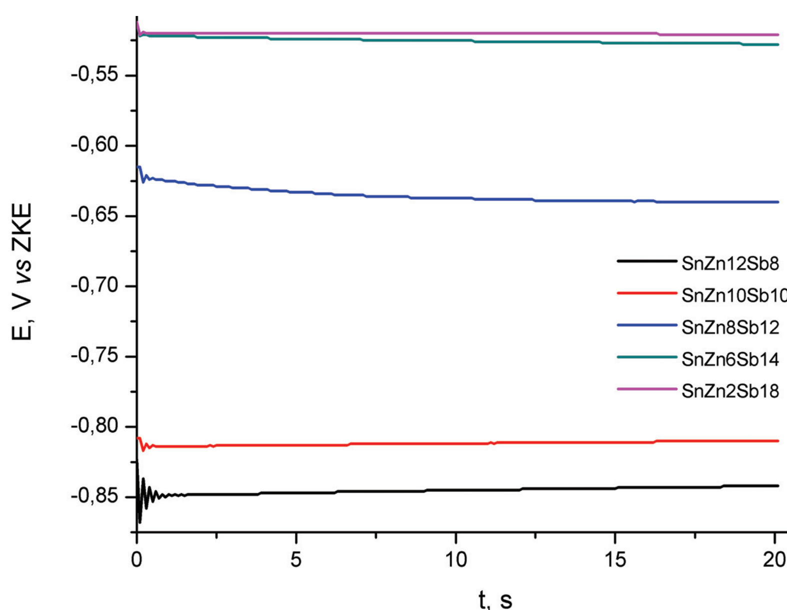

Figure 9. Open circuit potential of the Sn–Zn–Sb alloys in 0.1 M H_2SO_4 solution at 298 K.

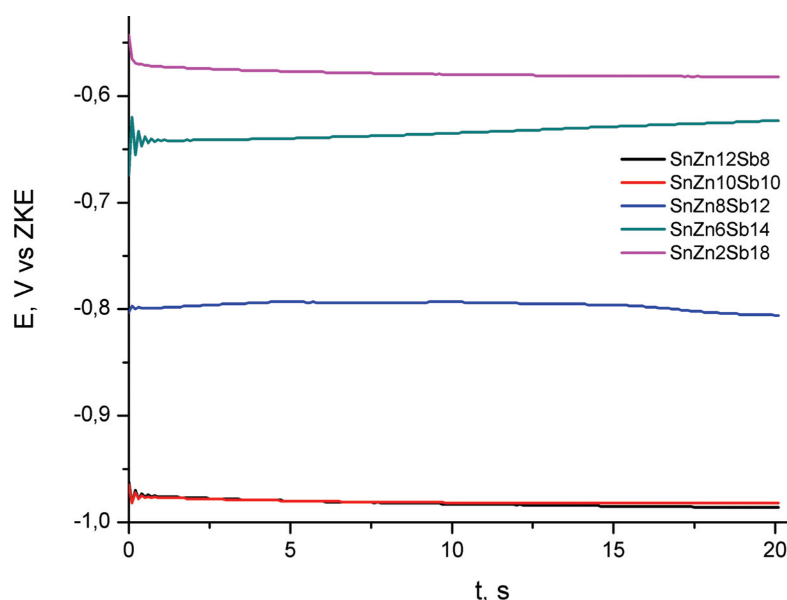

Figure 10. Open circuit potential of the Sn–Zn–Sb alloys in 0.01 M NaOH solution at 298 K.

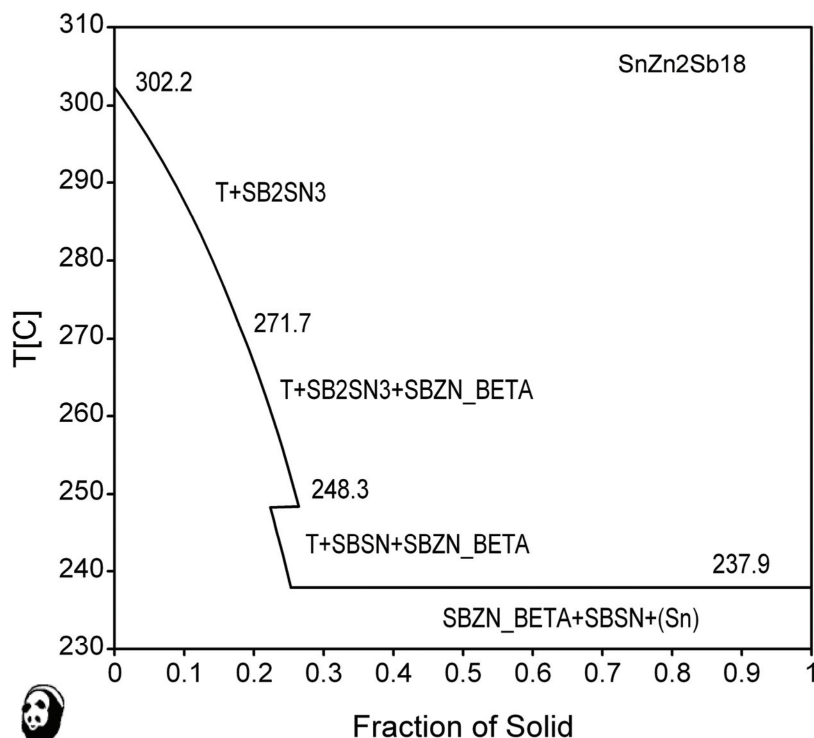

Figure 11. Calculated solidification path for alloy A5.

Table 2. Calculated superheat temperatures (°C) of investigated alloys

Alloy	50 °C above liquidus temperature	100 °C above liquidus temperature
A1	362	412
A2	367	417
A3	368	418
A4	364	414
A5	352	402

ternary alloys are shown in Figure 12. It is important to remark that the shape of the sessile drops of the investigated alloys was not perfectly ellipsoidal but irregular in about 5% of the experimental drops. These irregular drops were not considered for determination of average values of wetting angles. Leonardo *et al*. also reported this phenomenon and explained these irregular shapes as they were associated with oxidation [13]. The presence of surface-active elements such as oxygen will have a significant influence on measurements of contact angle. The formation of a zinc oxide film can provoke drop surface distortions. Atmospheric oxygen molecules pass through this oxide and promote a diffusion reaction within the solder to form a thick oxide layer. Suganuma *et al*. [14] have also reported that sessile drops can be distorted due to oxidation preventing the solders from uniform wetting and spreading.

The contact angles on the Cu substrate for all alloys examined generally tended to attain their lowest values for a melt superheat of 100 °C, as can be seen in Figure 12. However, based on the range of values of contact angles given by the error bars (maximum and minimum values), average values of about 138 and 130 °C can be considered for all investigated alloys. Many researchers have reported that the contact angle decreases with increasing melting temperature, which is associated with lower viscosity and consequent better metal/substrate wetting. Lower contact angles are associated with higher fluidity. It has been demonstrated that the best fluidity is generally attained for pure components, eutectics or phases that solidifies congruently, whereas fluidity decreases with increasing solidification range [15,16]. Comparing the experimental results of contact angle for all the studied alloys, it can be observed that alloy A1 had minimum values of contact angle 50 and 100° above the liquidus temperature. Alloy A2 had the highest values of contact angle with an average contact angle of about 140° for the first superheat temperature and 135° for the second.

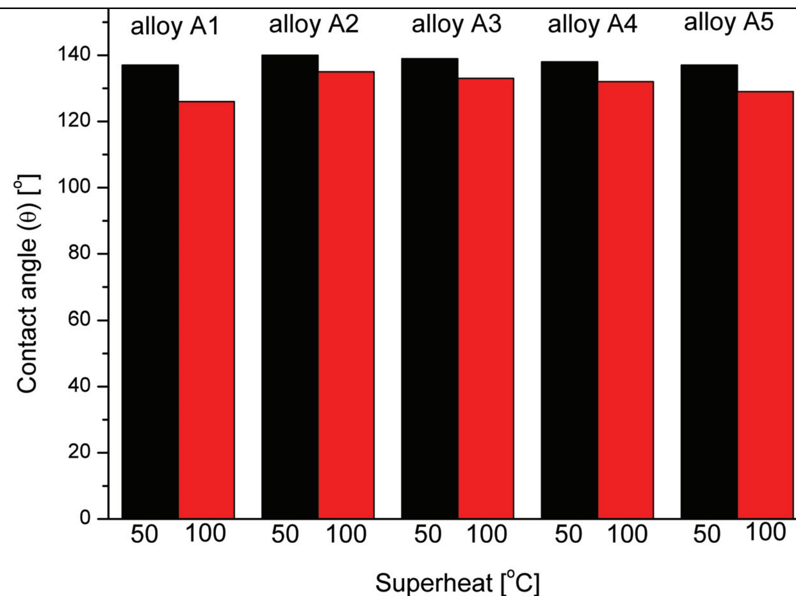

Figure 12. Contact angle values as a function of melt superheat for the investigated alloys.

CONCLUSION

These experimental investigations confirmed poor corrosion and wetting properties of the investigated alloys, which is in good agreement with some earlier investigations of alloys with similar chemical composition. Additional alloying of investigated Sn–Zn–Sb alloys can probably contribute to better electrochemical and wetting behavior, and further investigations are needed.

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IZVOD

ELEKTROHEMIJSKO PONAŠANJE I KVAŠLJIVOST LIVENIH BEZOLOVNIH LEMNIH LEGURA U SISTEMU Sn-Zn-Sb

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(Naučni rad)

Sprovedena istraživanja imala su za cilj pronalaženje adekvatnih zamena olovnim legurama u različitim aspektima njihove primene. Jedan od segmenata primene olovnih lemnih legura je kod tehnike stepenastog lemljenja, koja pretpostavlja spajanje elektronskih komponenti i substrata u nekoliko faza. Kako se ne bi prethodno zalemljene komponente odlemile koriste se lemni materijali sa različitim temperaturama topljenja. U ranijoj praksi jedna od korišćenih legura bila je SnPb95. Moguća zamena za ovu leguru pretpostavlja se da može biti i neka legura iz trojnog sistema Sn–Zn–Sb. U ovom radu ispitivano je elektrohemijsko ponašanje i kvašljivost legura sa konstantnim procentom kalaja (80 at.%) i promenljivim odnosom Zn i Sb. Elektrohemijska ispitivanja sprovedena su merenjem potencijala otvorenog kola legura iz ispitivanog sistema, dok je kvašljivost odnosno vrednost kontaktnog ugla između pomenutih legura i bakarnog substrata ispitivana pomoću metode ležeće kapi. Elektrohemijska ispitivanja su pokazala da se vrednosti potencijala otvorenog kola nekoliko sekundi nakon uranjanja elektroda kreću ka negativnim vrednostima ukazujući na relativno malo rastvaranje cinka prisutnog u leguri u kiselim i baznim reagensima. Nakon toga, vrednosti su skoro konstantne sa vremenom. Ispitivanjima sprovedenim u ovome radu ustanovljeno je da legure iz ispitivanog koncentracionog područja sistema Sn–Zn–Sb imaju veoma slabu kvašljivost bakarnog substrata i da se vrednosti kontaktnog ugla smanjuju sa povećanjem temperature pregrevanja rastopa legure. Potvrđeno je i zapažanje mnogih istraživača da najniže vrednosti kontaktnog ugla imaju legure koje se tope na konstantnoj temperaturi i da se sa povećanjem opsega između temperature solidusa i temperature likvidusa kvašljivost legura pogoršava.

Ključne reči: Potencijal otvorenog kola • Kontaktni ugao • Legure za stepenasto lemljenje • Metod ležeće kapi