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Investigations of corrosion behaviour of SnSb12Cu6Pb alloy in 0.1M H_2SO_4 and 0.5M NaCl solution

J. Hrabia-Wiśnios [a],*, B. Leszczyńska-Madej [a], R. Kowalik [b]

[a] Department of Materials Science and Non-Ferrous Metals Engineering, Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Mickiewicza 30 Av., Cracow 30059, Poland

[b] Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals, Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Mickiewicza 30 Av., Cracow 30059, Poland

* Corresponding e-mail address: hrabia@agh.edu.pl

ORCID identifier: https://orcid.org/0000-0002-7554-8893 (J.H.-W.); https://orcid.org/0000-0003-0232-9080 (B.L.-M.); https://orcid.org/0000-0002-3942-2521 (R.K.)

ABSTRACT

Purpose: The results presented the microstructure and corrosive behavior of SnSb12Cu6Pb alloy (B82) in H_2SO_4 aqueous solution and NaCl aqueous solution.

Design/methodology/approach: The electrochemical corrosion has been investigated in two different aqueous solutions: 0.1M sulfuric acid (H_2SO_4) and 0.5M sodium chloride (NaCl) solution measuring of potential changes relative to immersion time and conducting mass loss test. Microscopic investigations before and after corrosion tests were made using scanning electron microscopy.

Findings: The obtained results indicate very good corrosion resistance of the alloy tested in NaCl solution. Corrosion progresses faster in a sulfuric acid aqueous solution compared to sodium chloride aqueous solution. Also, it was found that the dominant mechanism of corrosion degradation in both solutions is selective corrosion which is a particularly undesirable type of corrosion because it involves the loss of one alloying component and the formation of porous structure on the alloy surface.

Research limitations/implications: The aqueous solutions used in this study are not a natural working environment of the bearing. However, a comparison of acidic and neutral solutions allows explaining the corrosion behavior of tin babbitts due to contaminants of oil lubricants. Further research should be conducted in more aggressive environments characteristic of industrial conditions.

Practical implications: One of the important properties of bearing alloys are corrosion resistance. Corrosion properties are extremely important for the transport and storage of metallic components before they are used. Also, the working environment can have a destructive effect on the properties of the materials used. Industry environment, aging stagnant oil, and some acids may lead to selective corrosion of the tin, copper, lead, or antimony components and leaving a rough and weakened the babbitt surface. Electrochemical corrosion can contribute to the acceleration of bearing wear and consequent to bearing damage.

Originality/value: Studies of the corrosion of tin-babbitt bearings are not extensive in the literature due to rare tin corrosion. This study could be an important complement to knowledge about the corrosion behavior of tin-based bearing alloys.

PROPERTIES

1. Introduction

Tin based bearing alloys otherwise known as tin babbitts are used as a surface layer in slide bearings mainly cast on bronze or steel [1,2]. Tin-based Babbit is a material that contains more than 80% of tin. The alloy may also contain smaller parts of antimony, copper, and lead. These alloys are characterized by a multi-phase microstructure, predominantly three-phase: α, β, η, where α – solution of antimony and copper in the tin, constitutes a soft and ductile matrix β – irregular crystals of compound SnSb, η – acicular precipitates of compound Cu_6Sn_5 [3-5].

The corrosion behavior of tin-based bearing alloys is more complicated than other tin alloys and pure tin. Previous studies have shown that the attack of metal surfaces by electrolytes results either in the pitting of the surface or in the oxidation of the alloy [3,6,7]. According to the literature, tin can passivate in aqueous environments over a wide pH range (from about pH 1 to pH 12). The corrosion resistance of tin babbitt alloys is good except under conditions of water contamination of the oil [3,6] and sulfur compounds, originating from inadvertent contamination or some oil additives [7]. The tin matrix can converse to tin oxide in the electrochemical process and form a layer on the bearing surface. This formation generates hard regions on the surface which may build in thickness up to 100 μm, to cause abrasive damage. Consequently, it can lead to bearing failure. Aging stagnant oil and some acids may lead to selective corrosion of the tin, copper, lead, or antimony components and leaving a rough and weakened the babbitt surface. Selective removal of the micro constituents of a bearing will generally embrittle the structure so that it finally fails by cracking. In a less common type of corrosion, the copper phase of the tin-rich alloy is attacked. The result is the formation of copper sulfates, from the copper in the Babbitt and sulfur present in the oil or atmosphere. The damage results in the etching away of the tin matrix leaving tin-antimony cuboids on the surface [3,6,7].

Local corrosion of tin by dilute chloride solutions depends on time. Oxide film growth occurs and the potential of the metal rises. Local dissolution may begin after many days and manifested at first by small black spots and later by small pits. Furthermore contact with a more noble metal such as copper increases the number and intensity of pits [8]. In turn, in sulfuric acid solution confirmed that the electrochemical behavior of alloys containing Sn, Pb, Sb, Cu is related to the electrochemical property of the individual phase involved in the internal galvanic couples formed [9,10].

The results presented herein show the microstructure and corrosive behavior of SnSb12Cu6Pb alloy (B82) in H_2SO_4 aqueous solution and NaCl aqueous solution. The aqueous solutions used in this study are not a natural working environment of the bearing. However, a comparison of acidic and neutral solutions allows explaining the corrosion behavior of tin babbitts due to contaminants of oil lubricants.

2. Material and methodology

2.1. Chemical composition

The tests concerned tin-based casting alloy SnSb12Cu6Pb (B82). The alloy was cast into cast iron chills, then cooled in ambient air. Table 1 presents the chemical composition of the tested alloy.

Table 1.
Chemical composition of investigated alloys, wt.% (PN-ISO 4381: 1997)

Alloy name		Chemical composition, wt.%				
Grade mark	Designation	Sn	Pb	Sb	Cu	As
SnSb12Cu6Pb	B82	balance	1-3	11-13	5-7	0.1

2.2. Material characterisation

The microstructure of the samples, before and after the corrosion test was investigated using scanning electron microscopy, along with an analysis of the chemical composition in the micro-areas by energy dispersive spectroscopy (microscope Hitachi SU 70).

2.3. Electrochemical measurement

The corrosion resistance of the tin babbitt samples was evaluated in 0.1M H_2SO_4 and 0.5M NaCl solutions by measuring of Open Circuit Potential (OCP) changes relative to immersion time. Alloy samples were mounted in epoxy raisin. Samples with 4 cm^2 of surface area were exposed to the solution. All samples were polished with SiC paper to have a smooth surface and then were washed with demineralized water. The OCP measurement system is shown schematically in Figure 1. B82 samples were used as working electrodes. The reference electrode was a saturated calomel electrode and the auxiliary electrode was a platinum sheet. The OCP vs. time was measured for 24 hours.

2.4. Weight loss measurements

Corrosion resistance was determined by measuring weight change after immersing cubic samples in 0.1M H_2SO_4 and 0.5M NaCl solutions at room temperature for 5 days. The samples were placed in polypropylene screw cap bottles with 200 ml of solution. During the corrosion test,

the bottles were placed in laboratory shaker type 357 (Elpin+). Every 24 hours, samples were extracted, cleaned in distilled water, dried with cold air, and weighed.

3. Results and discussion

3.1. Electrochemical results (OCP)

The corrosion resistance of the samples was evaluated in 0.1M H_2SO_4 and also in 0.5M NaCl solutions testing of potential changes relative to immersion time. The OCP indicates the thermodynamical tendency of a material to electrochemical oxidation in a corrosive medium. Results from the electrochemical tests are presented in Figure 2. The OCP curves showed differences in the corrosion resistance of the investigated alloy in both solutions.

The shape of the OCP curves in 0.1M H_2SO_4 solution indicates high electrochemical activity. After a period of immersion the E_{OCP} stabilized around a stationary value and, on average, come to about -0.51 V which would indicate that corrosion occurs uniformly however the results of the SEM study indicate that only the tin matrix corrodes (Fig. 3). It can be noticed that tin matrix contacts with a more noble phase such as SnSb or Cu_6Sn_5 and galvanic couples are formed. According to the literature tin spontaneously corrode in acidic solutions and the presence of more noble phases only accelerates this process (Fig. 3b) [8,16]. The OCP value is dominated by selective tin dissolution, though additionally lead sulphate formation on the surface is observed (Fig. 4).
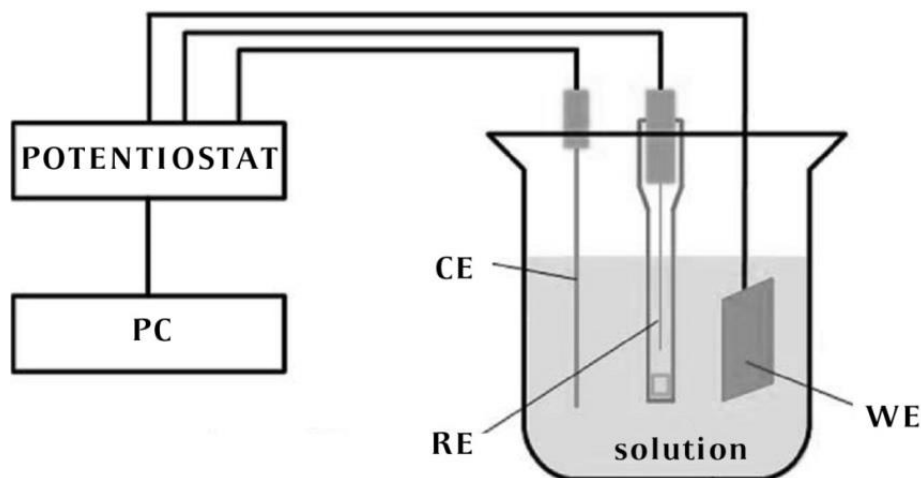

Fig. 1. Schematic view of the basic design OCP measurement system; WE – working electrode; RE – reference electrode; CE – the counter electrode
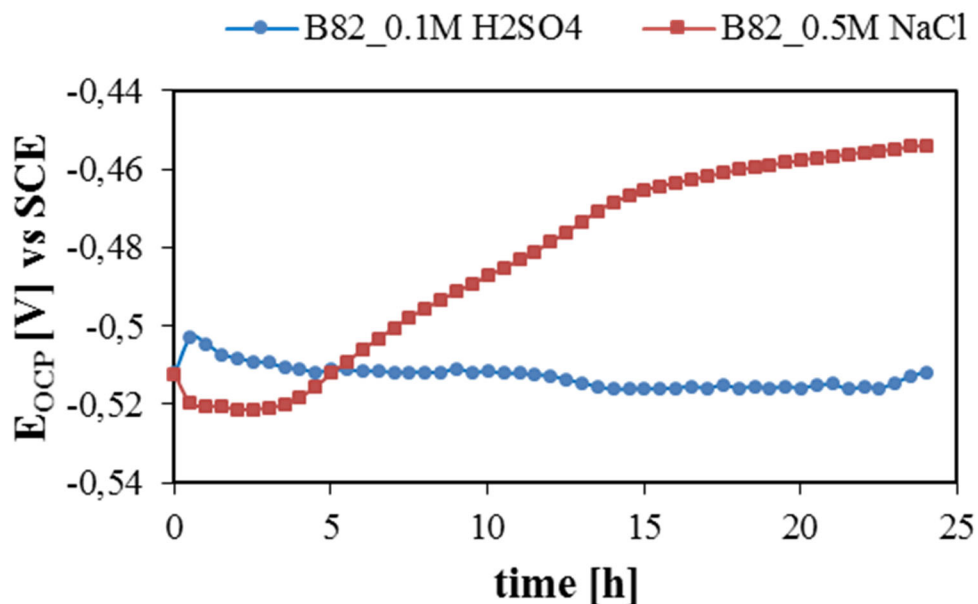
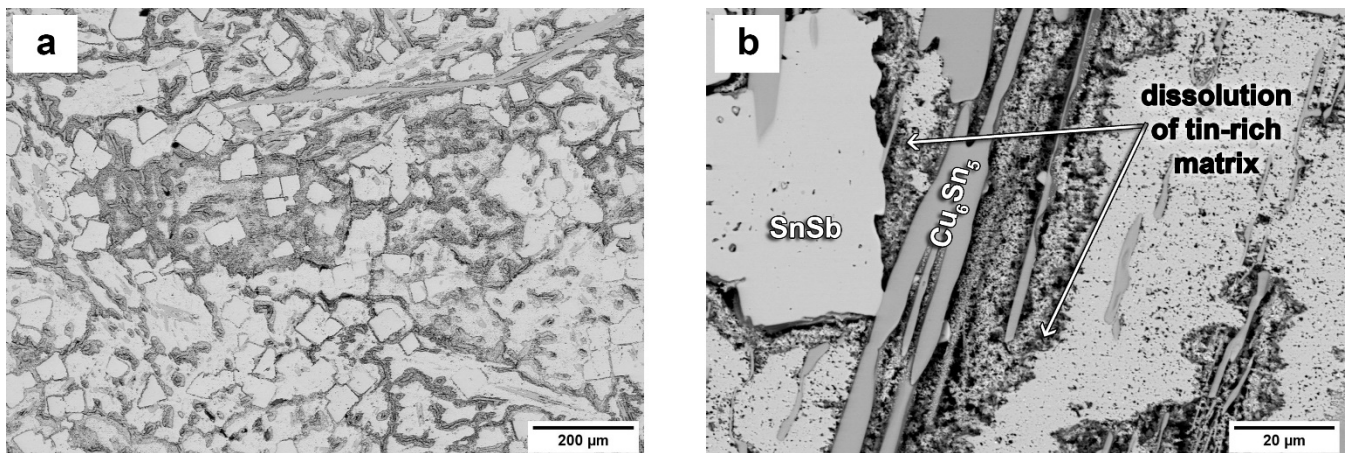Fig. 2. Potential OCP (E_{OCP}) with immersion time for B82 in 0.1M H_2SO_4 and 0.5M NaCl solutions

Fig. 3. Microstructure of B82 after 24h corrosion in 0.1M H_2SO_4; magnification a) 100x, b) 1000; SEM/BSE

The value of E_{OCP} determined in 0.5M NaCl solution at the beginning is at the same level as registered in 0.1M H_2SO_4 solution. However it should be noted it is very unstable and it is changing systematically over the initial 15 hours, ranging from -0.52 V to -0.46 V. It begins to stabilize only after 15 hours of immersion. Increases in the curve of OCP potential for 15 hours may suggest the growth of the passive film onto the sample surface. According to literature, the oxide film consists mainly of $Sn(OH)_4$ or more stable SnO_2, which is one of the reasons for the excellent corrosion resistance of a tin-based alloy [8]. On the other hand, this passive layer is not desirable in bearings because is very hard and can damage the cooperating steel surface of the shaft spigot [11]. Oxide particles probably may break off the compact layers and act as an abradant during friction.
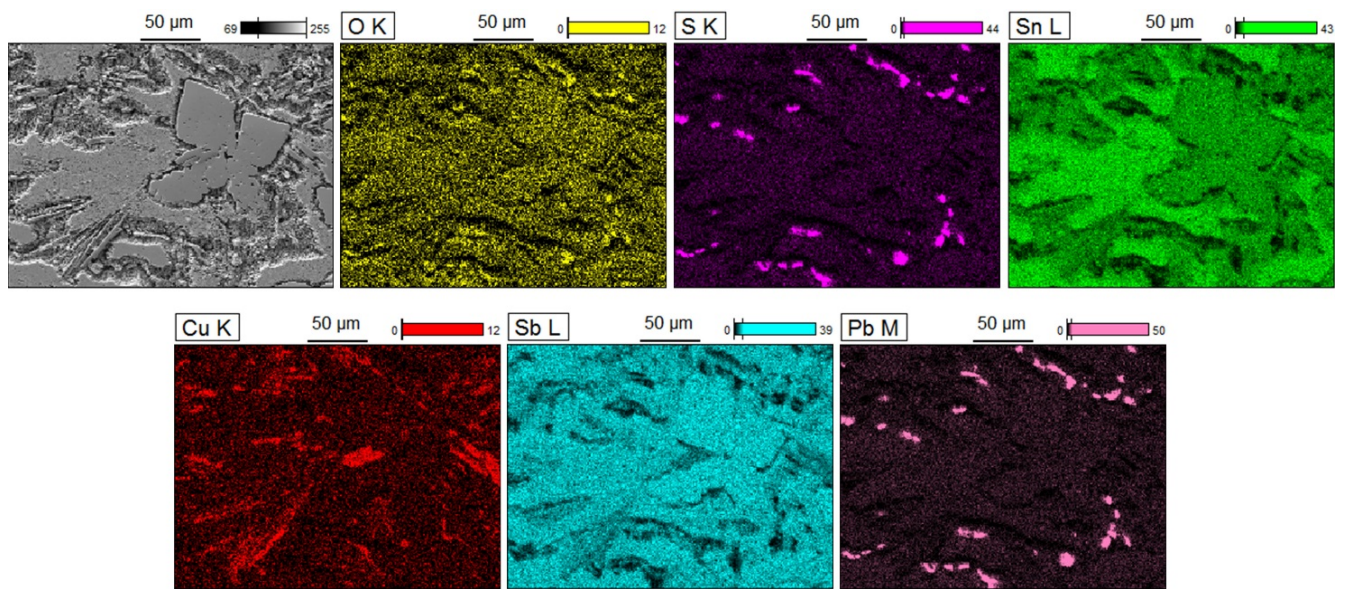
Fig. 4. Microstructure and distribution maps of O, S, Sn, Cu, Sb and Pb in the B82 alloy after 24 h immersion in 0.1M H_2SO_4 solution; SEM/EDS

3.2. Corrosion rate (weight loss)

One of the measures of material corrosion resistance is weight loss measurement. Figure 5 showed a variation of the corrosion rate (weight loss) with immersion time for SnSb12Cu6Pb in two different solutions for comparison: 0.1M H_2SO_4 and 0.5M NaCl solutions. As might be expected determined corrosion rates show a higher value of weight loss rate in a sulfuric acid environment compared to corrosion in NaCl aqueous solution. The above predictions result from the weaker tin corrosion resistance in an acidic environment.

The curve of the corrosive rate determined for 0.1M H_2SO_4 solution showed an upward trend from 70 g/(m²·day) after 1 day to 90 g/(m²·day) after 5 days. The occurrence of a slight increase in corrosion rate (weight loss) could be caused by selective corrosion of the tin matrix (Fig. 3). The etching away of the tin matrix leaving tin-antimony cuboids and copper-tin phases on the surface. These phases may fall out of a porous, rough, and weakened surface leaving holes and resulting in faster weight loss (Fig. 5).

In 0.5M NaCl solution the value of the corrosion rate of the investigated alloy was below 10 g/(m²·day). The decrease in the corrosion rate noted on the second day (Fig. 5) may indicate the formation of a passive layer on the sample surface of B82.

3.3. Microstructure results

Selected photographs of the microstructure of SnSb12Cu6Pb alloy made by using a scanning electron microscope are shown in Figures 3,4, 6-9. The microstructure of investigated alloy before corrosion tests (Fig. 6 and Fig. 8) consists of large hard cubic crystals of the SnSb phase and precipitates of the Cu_6Sn_5 phase, both needle-shaped and nearly globular-shaped dispersed in a softer tin-reach matrix [3-5]. Lead in the alloys is arranged uniformly inside the tin-rich matrix grains as dispersion precipitates. But also may locate as larger clusters on the grain boundaries (Figs. 6, 8).

Characteristic surfaces of the investigated alloy after 24 hours corrosion test in 0.1M H_2SO_4 solution are shown in Fig. 3 and 4. Selective corrosion of the tin-matrix and leaving SnSb cuboids and CuSn both needle-shaped and nearly globular-shaped on the surface are observed (Fig. 3). This type of galvanic corrosion can occur when two electrochemically different metallic phases are in contact with the electrolyte and form a galvanic cell. The cell is corrosive to one metal at the expanse of the other. According the galvanic series (Tab. 2) tin (Sn/Sn^{2+} E_0=-0.14 V) and lead (Pb/Pb^{2+} E_0=-0.13 V) are less noble, than copper (Cu/Cu^{2+} E_0=+0.34 V) and antimony (Sb/Sb^{3+} E_0=+0.20 V) [15].
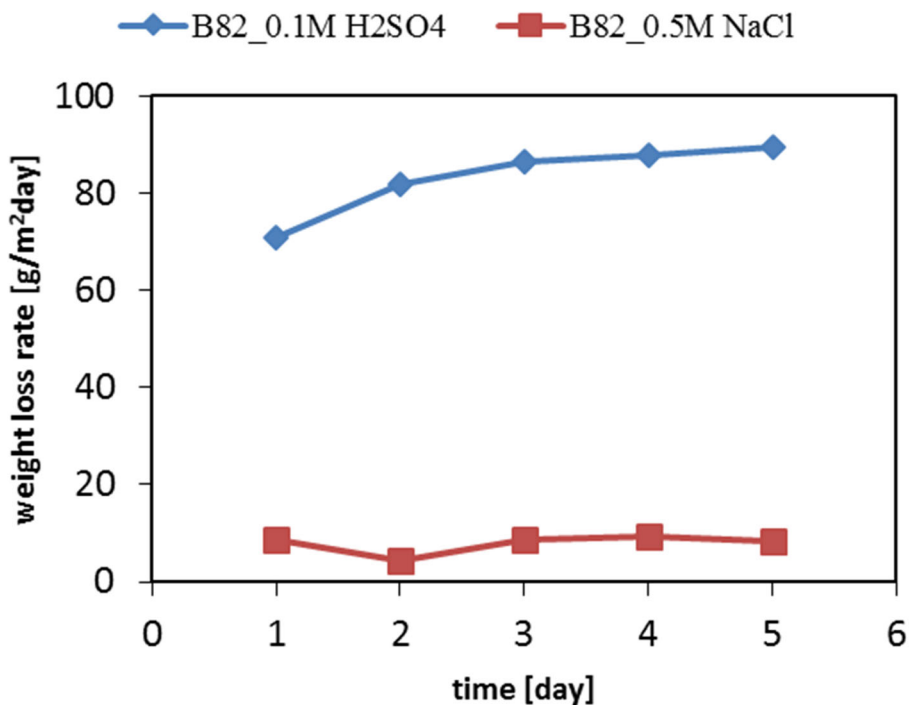
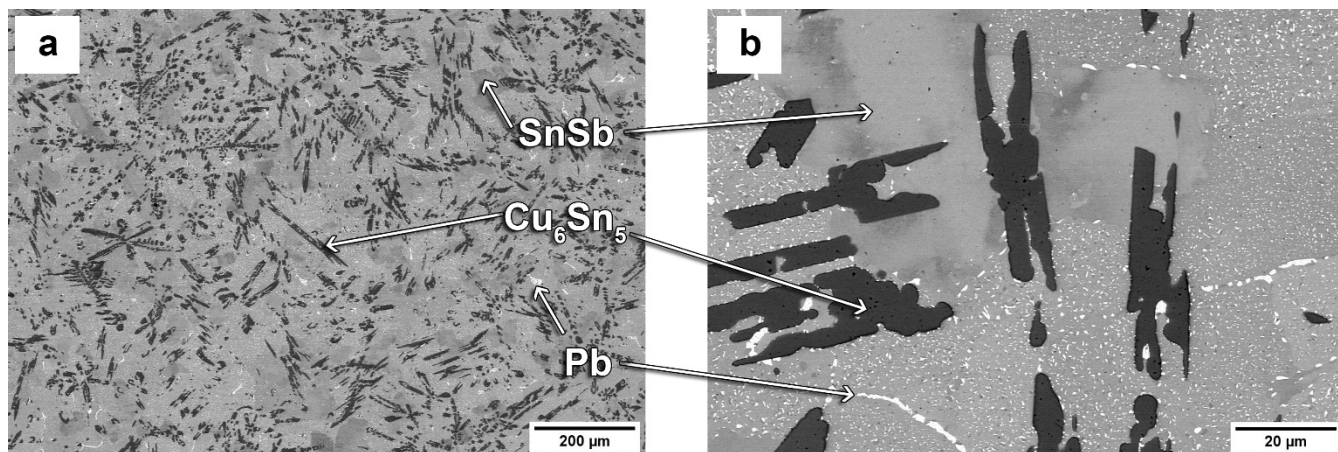Fig. 5. Corrosion rate (weight loss) with immersion time for B82 in 0.1M H_2SO_4 and 0.5M NaCl solutions

Fig. 6. Microstructure of B82 before corrosion; magnification a-100x, b-1000; SEM/BSE

Table 2.
Standard reduction potentials E°values for selected metals (25°C, 1 atm) [15]

Electrode	Sn/Sn^{2+}	Pb/Pb^{2+}	Sb/Sb^{3+}	Cu/Cu^{2+}
E^0, V	-0.14	-0.13	0.15	0.34

Therefore Cu_6Sn_5 phase and SnSb phase have a higher reduction potential than tin-rich matrix or clusters of lead and create a corrosive microcell in an electrolyte solution.

Analyzing the change in OCP over time, it could be assumed that the corrosion process of the examined alloy is uniform. Nevertheless, the SEM images clearly show

that only the tin matrix corrodes. However, it is worth noting another important fact related to the mechanism of tin dissolution. Namely, the tin matrix is intensively dissolved primarily in the very close vicinity of the more noble phases (SnSb, Cu_6Sn_5) (Fig. 3). The above mechanism may be responsible for the falling out of SnSb and Cu_6Sn_5 grains from the porous, rough, and weakened surface leaving holes. Thus there is no enrichment in the more noble phases on the alloy surface and the corrosion process is not slowed down. Hence, the weight loss of the samples immersed in the sulfuric acid solution was systematic for 5 days and showed no slowdown, and was also much faster compared to the same samples immersed in the NaCl neutral solution (Fig. 5). The above mechanism clearly explains the stable value of OCP during the 24 hours' immersion test.
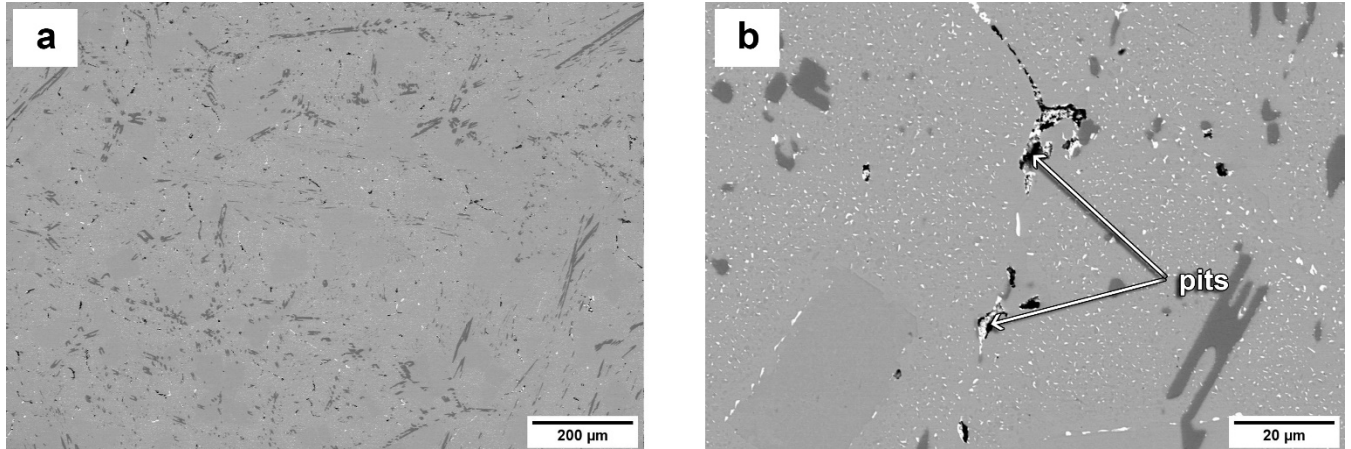

Fig. 7. Microstructure of B82 after 24h corrosion in 0.5M NaCl solution ; magnification a-100x, b-1000; SEM/BSE
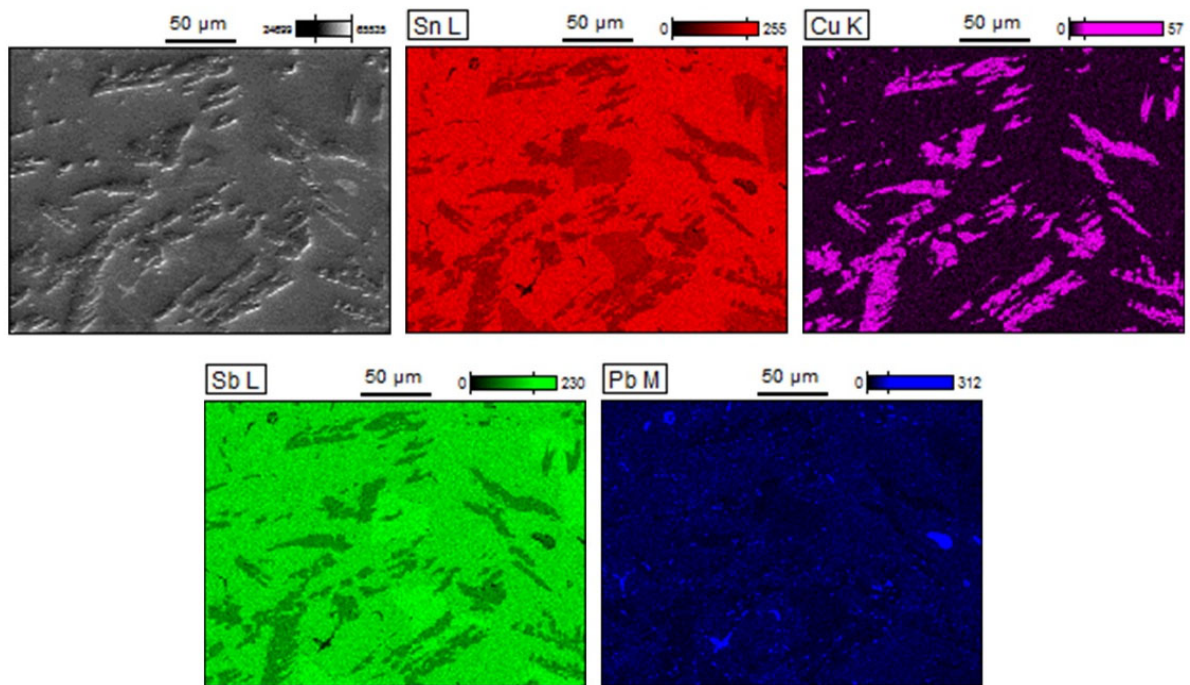

Fig. 8. Microstructure and distribution maps of Sn, Cu, Sb and Pb in the B82 alloy; SEM/EDS
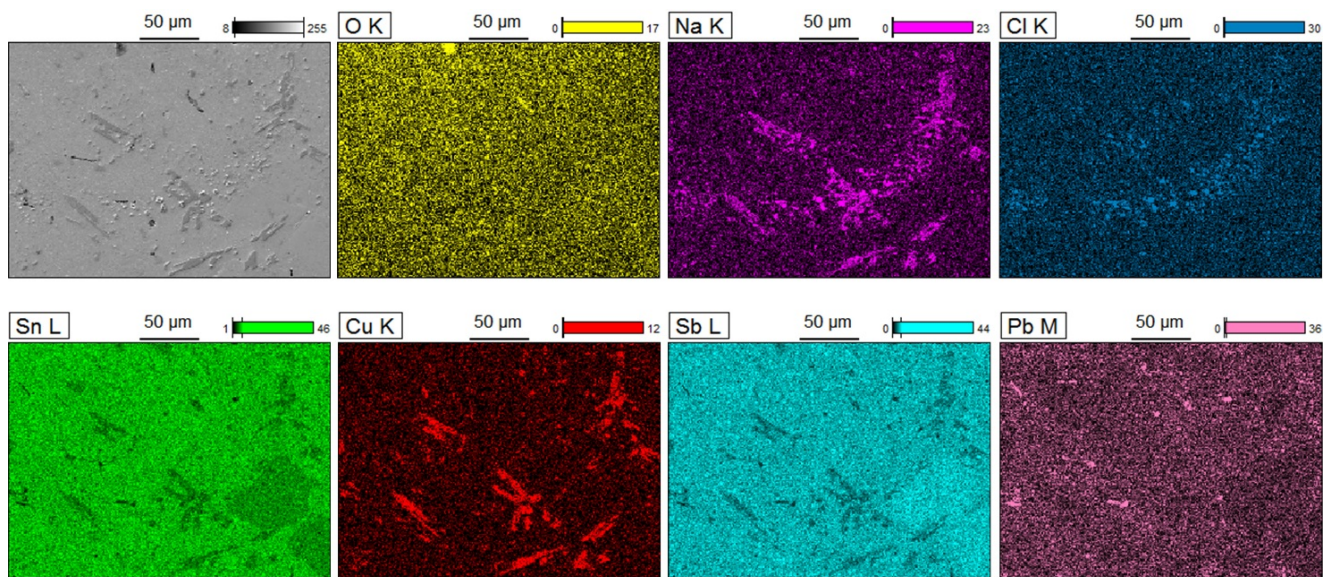
Fig. 9. Microstructure and distribution maps of O, Na, Cl, Sn, Cu, Sb and Pb in the B82 alloy after 24 h immersion in 0.5M NaCl solution; SEM/EDS

Based on the other experimental corrosion tests carried out with an Sn-Cu alloy [17,18], such resulting electrochemical behaviour is intimately associated with both metallurgical and electrochemical aspects. According to literature the boundaries between tin-rich matrix and intermetallic Cu_6Sn_5 is not be perfectly conformed which is related to the solidification process and more specifically the different growth natures of the Sn-rich (non-faceted) and the intermetallic (faceted) phases. It seems that these regions could be more susceptible to the corrosion action because of certain strain in the atomic level along the boundaries between these phases [17,18].

Based on the distribution maps of selected chemical elements, surface oxidation, and chemical interaction of lead with sulfate ions from the solution was found (Fig. 4). According to literature in terms of corrosion behavior, Pb-Sb, and Pb-Sn alloys in sulfuric acid solutions, the corrosion layers of these alloys can include $PbSO_4$ and lead oxides: PbO, PbO_n, PbO_2 [9,10].

Characteristic surfaces of the investigated alloy after 24 hours corrosion test in 0.5M NaCl solution are shown in Figures 7, 9. Distribution maps of particular alloying elements (Fig. 9) indicated oxidation of tin and lead which also was confirmed by the increases of the value of OCP potential (Fig. 2) and the decreases in the corrosion rate (Fig. 5). As well, pits located mainly at the grain boundaries were observed (Fig. 7b). This may indicate the type of intergranular corrosion. This situation can happen when the

grain boundaries are depleted with tin in favor of lead which is located at the grain boundaries. As mentioned above, tin is the least noble metal among alloy components (Tab. 2), and therefore the selective dissolution of tin is most likely which was confirmed distribution map of Sn in the investigated alloy after 24 h immersion in 0.5M NaCl solution (Fig. 9). According to previous corrosion studies performed in NaCl solution [12,13] and concerning Sn-based solders, a corrosion product on the surface of tin-based alloys can be tin oxide chloride hydroxide ($Sn_3O(OH)_2Cl_2$) with a platelet-like shape and loosely distributed on the surface with different orientations. The corrosion product of Pb in NaCl solution can be $PbCl_2$, PbO, and Pb_2O_3 [14].

4. Conclusions

The microstructure and corrosion resistance of SnSb12Cu6Pb (B82) in 0.1M sulfuric acid (H_2SO_4) and 0.5M sodium chloride (NaCl) solution were studied. The tests allowed the formulation of the following conclusions:

1. The investigated alloy B82 is characterized by a multi-phase microstructure consisting of precipitates of Cu_6Sn_5 and SnSb phases, as well as a tin-rich matrix. Lead is evenly distributed in the matrix and located as larger clusters on the grain boundaries.

2. The electrochemical and microstructure results determined in 0.1M H_2SO_4 solution indicate selective corrosion of tin-matrix in the vicinity of the more noble phases (SnSb, Cu_6Sn_5) and formation on the surface the corrosion layers include $PbSO_4$ and also lead and tin oxides.

3. In turn, the growth of the passive film and selective dissolution of tin mainly at the grain boundaries dominates in the case of sample immersion in 0.5M NaCl solution.

4. Determining corrosion rates show a higher value of corrosion velocity in sulfuric acid aqueous solution, while in NaCl aqueous solution corrosion is occurred very slowly. The weaker tin corrosion resistance in an acidic environment can contribute to the acceleration of bearing wear and consequent to bearing damage. The dominant selective corrosion of tin may be responsible for the falling out of SnSb and Cu_6Sn_5 grains from the porous, rough and weakened surface leaving holes.

5. Corrosion behavior of B82 alloy is related to the electrochemical property of the individual phase involved in the internal galvanic couples formed.

Acknowledgements

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