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Electrochemical migration of Sn-Pb and lead free solder alloys under distilled water

D. Q. Yu[a] · W. Jillek · E. Schmitt

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Abstract Electrochemical migration (ECM) is a potential reliability problem in electronic soldering which might become more dangerous in lead free electronic devices. In this paper, electrochemical migration tests on Sn-Pb and lead free solder alloys were conducted under distilled water by applying constant voltages with a power supply. The susceptibility of the solder alloys to ECM and the effect of the composition on ECM behavior were studied. It is found that both Sn-Pb and lead free solders investigated in present research have susceptibility on ECM. Dendrites grow from cathode to anode and show different morphologies with the different migration elements involved. In Sn-37Pb and Sn-36Pb-2Ag solders, the main migration element is Pb. While for Sn-Ag and Sn-Ag-Cu solder alloys, Sn leads the migration. For Sn-8Zn-3Bi, both Sn and Zn can migrate. Furthermore, the effect of applied voltage on the time to short and short resistance was also investigated. As could be expected, the higher the voltage is, the shorter the failure time is. The electrochemical migration mechanism of the solder alloys was also discussed.

Introduction

The trend towards compact and lightweight electronic devices asks for steadily decreasing clearances between adjacent tracks and pads. Surface mount technology is the primary process to produce such high functional electronic products. It is pointed out that the possibilities of integration are determined not only by the technological bases but also by the physical and chemical processes that can cause resistive shorts between adjacent metallization strips during the operation. One of the phenomena is the electrochemical migration [1].

Electrochemical migration is an electrochemical process where metal on an insulating material, in a humid environment and under an applied electric field, leaves its initial location in ionic form and redeposits somewhere else. The rate of electrochemical migration has four prerequisites: a mobile metal; a voltage gradient; a continuous film and soluble ions. Such migration may reduce isolation gaps and ultimately lead to an electrical short and cause catastrophic failure [2].

Nowadays, electrochemical migration has become one severe potential problem in electronic soldering for the following facts. The first arises from the narrow conductor spacing. At constant voltage, the electric field between the conductors rises inversely with the conductor spacing and the electrochemical migration would be enhanced under high electric field [3–4]. The second reason is that the solder alloys are composed of mobile metal elements. The most widely used solder systems are Sn-Pb nowadays and Sn-Ag-Cu in the lead free future [5–6]. It is known that silver is the metal most susceptible to migration, since it is a high anodic soluble metal and requires lower activation energy to initiate the migration process [7]. Copper, zinc and lead can also migrate, although under more severe conditions [1]. Thirdly, the cleaning process of the board after soldering has been changed due to regulation of chlorofluorocarbons such as Freon and other organic cleaning solvents which damage the ozone layer [3]. Recently, no-clean fluxes are in use to avoid the cleaning step after soldering. Many investigations on lead free solders indicate that their wetting behavior is poor compared to

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D. Q. Yu (✉) · W. Jillek · E. Schmitt
Georg-Simon-Ohm University of Applied Sciences,
D 90489 Nuernberg, Germany
Tel.: +49 (0) 30/37002434
e-mail: hansonydq@yahoo.com

[a] The author is now at Fraunhofer IZM, Berlin, Germany

the SnPb solder used so far [5–6]. This might encourage the manufacturers of lead free solder pastes to use more aggressive fluxes for achieving a satisfying wettability comparable with that of eutectic SnPb. In combination with decreasing clearances, this might enhance the undesired effect of electrochemical migration. This change in the cleaning and soldering processes provides a higher likelihood of corrosion and electrochemical migration [8–9].

Although a lot of research has been carried on ECM, most of them focus on the pure metal and the ECM of solder alloys has not been investigated in detail [1–4, 7–10]. Especially with the trend to lead free solders, many new elements such as Ag, Bi, Cu and Zn are selected as alloying elements [5–6]. The ECM of these new solders should be studied. This paper selected seven solder alloys containing five lead free solders to study the susceptibility of solder alloys to ECM and to clarify the effect of the composition on ECM behavior.

Experimental method and procedure

The solder alloys involved in this research are Sn-37Pb, Sn-36Pb-2Ag, Sn-3.5Ag, Sn-3Ag-0.5Cu, Sn-3.5Ag-0.75Cu, Sn-4Ag-0.5Cu and Sn-8Zn-3Bi. Solder alloys were cold rolled to 0.5 mm thickness and cut into rectangle shape with 6 mm width and 15 mm length. Specimens were mechanical grinded with waterproof silicon carbide paper # 2400 and then cleaned in ethanol and dried in air. Two solder specimens of the same composition were placed opposed to each other and attached with glue on the brominated epoxy-glass composite (FR4) board. The spacing between the two specimens was adjusted under a microscope using a micro-scale.

There are three main methods to get information or comparison the migration behavior: the water drop test, the accelerated climatic tests and cyclic voltammetry (CV) [11]. In this study, pure distilled water was used as the test environment which resistivity is about 0.18 MΩm. It is pointed out that to water drop test, the surface tension at the droplet edges would influence the process: dendrite shorts sometimes formed at these sites [11]. However, because it is not the determining factor for the dendrite formation, the effect of surface tension can be negated in present test. The distilled water was added using a thin capillary with a volume of 2 ml. The schematic of the test specimen for ECM is shown in Fig. 1.

A high performance picoammeter (model KEITHLEY 6487) can measure resistance under setting voltage on the device under tested. Varying voltage of 3V, 5V and 10V was applied and the change of the resistance as a function of time was recorded. For each voltage, at least 3 samples were tested for each solder alloy.

The test was carried out under stereomicroscope and we can observe the growth of the dendrites and take photos with setting time interval. We determined the occurrence of the time to short by two criterions: (1) the dendrites connecting the two electrodes exactly, (2) the sudden drop of the resistance.

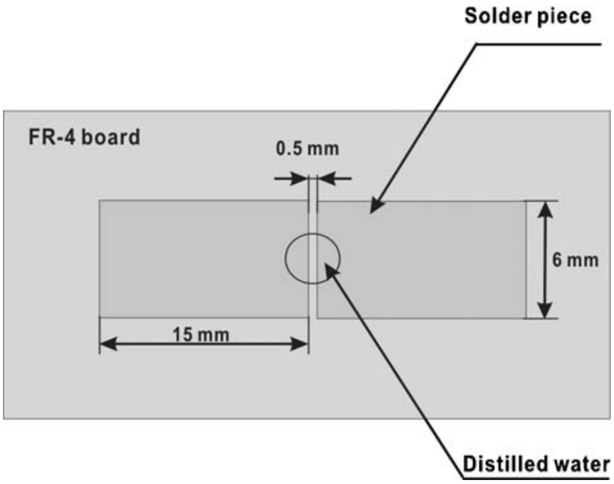

Fig. 1 Schematic of specimen for ECM test

The microstructure of the residual dendrites was examined by a scanning electron microscopy (SEM) (LEJTZ-AMR 1200) with a voltage of 20 KeV. Energy dispersive x-ray spectroscopy (EDS) (Oxford INCA 200) was also used to determine the elemental composition at selected areas. In order to facilitate the observation, the surface of the samples was sputtered with gold.

Results and discussion

A. In-situ observation of dendrites growth

Under a stereomicroscope, the whole growth process of the dendrites in the water can be observed. Figure 3 and 4 show the in-situ optical microscopy photos of the migration process of Sn-3.5Ag-0.75Cu and Sn-8Zn-3Bi solder alloys. From these photos, we can find some characters of the ECM. Through the whole process, we can find air bubbles are generated continuously at the cathode as shown in Fig. 3(b)–(d) and Fig. 4(b)–(d). To the Sn-Ag and Sn-Ag-Cu solders, milkiness precipitates can be detected in the water. The formation of the precipitates will be discussed later. The incubation period of the dendrites is longer comparing with its growth rate. It maybe takes tens of seconds for a dendrite nucleation and as soon as it grows up, it can reach the anode within several seconds as shown in Fig. 3 (c), 3(d) and Fig. 4 (c), 4(d).

The corresponsive curves for the change of the resistance with the test time of Sn-3.5Ag-0.75Cu and Sn-8Zn-3Bi which photos shown in Fig. 3 and Fig. 4 are shown in Fig. 5(a), (b) respectively. It can be seen that with the growth of the

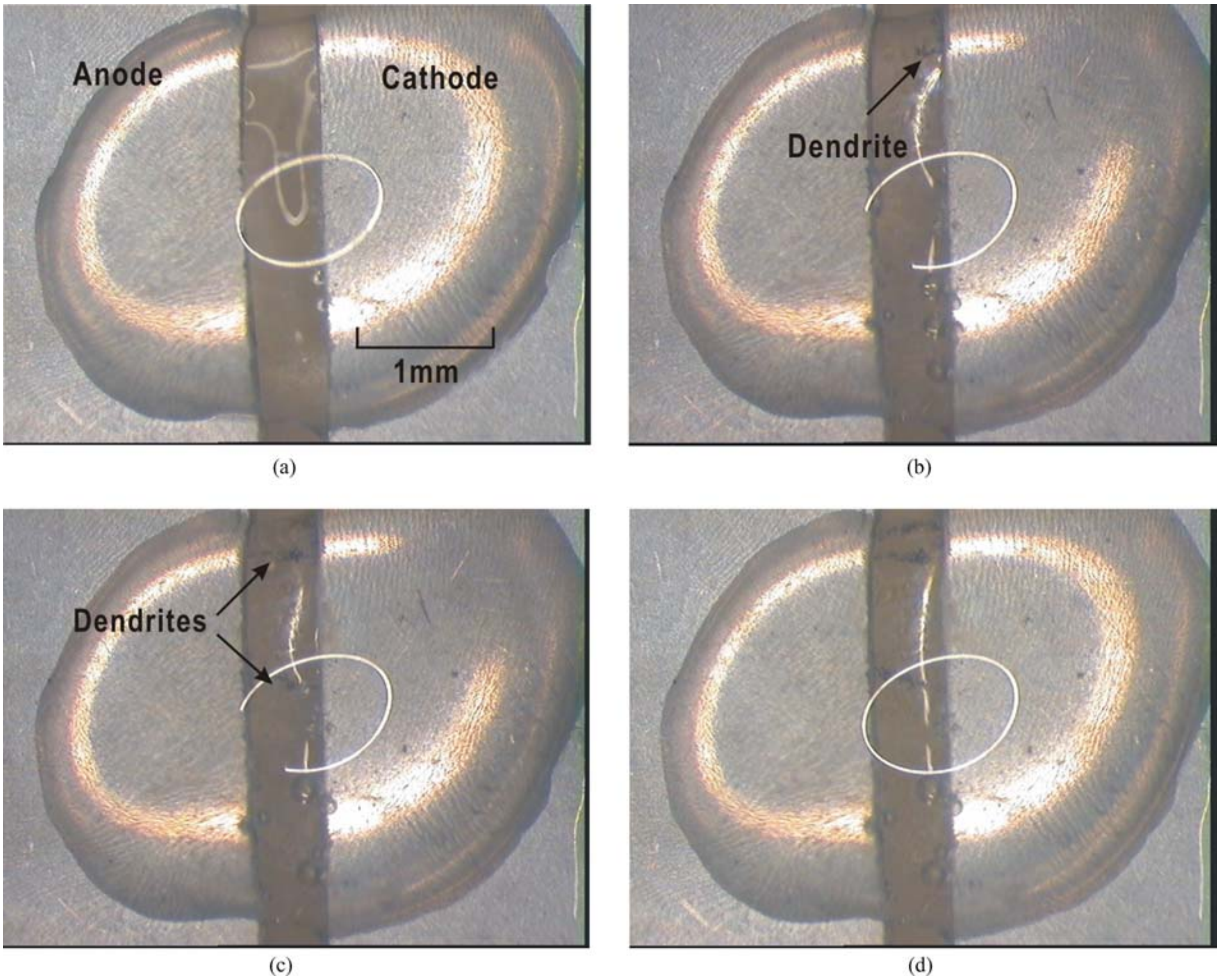

Fig. 2 In-situ optical microscopy photos of Sn-3.5Ag-0.75Cu solder under 10 voltage: (a) 0 Sec, (b) 40 Sec, (c) 50 Sec, (d) 75 Sec

dendrites, the resistances decrease and when the dendrites reach the anode, the resistance drops suddenly. The short resistance would decrease further when more dendrites grow up and reach the anode side. The resistance would be the value of the parallel connection resistance which means the short resistance would be smaller than any one among the short dendrites.

B. The compositions and microstructure of the dendrites

The compositions of the dendrites are analyzed with EDS. It is found that for different solder alloys, the migration elements are different. Fig. 5 shows the EDS results of Sn-3Ag-0.5Cu and Sn-8Zn-3Bi solder alloy respectively.

The compositions of the dendrites formed under 3 and 10 V are similar with that of 5 V. Table I summaries the compositions of the residual dendrites formed under 5 Voltage. It is clear that for Sn-37Pb and Sn-36Pb-2Ag solders, the main migration element is Pb. While for Sn-Ag and Sn-Ag-Cu solders, Sn leads the migration. For Sn-8Zn-3Bi, both Sn and Zn can migrate. The C, O elements come from air during the storage of the samples before analysis and Au is produced from sputtering process. Br element comes from the FR4 board.

The microstructures of the dendrites are shown in Fig. 6. In these photos, cathode is at the right and anode lies at the left. For the Pb bearing solders, shown in Fig. 6 (a) and (b), the migration products are longer stick-shape dendrites. While for the Sn-Ag and Sn-Ag-Cu solder, the morphologies are similar. As shown in Fig. 6 (d), one straight trunk has long branches on the vertical direction while the small branch has the same shape of the whole dendrite. Usually, one dendrite observed in OM has not a perfect trunk as Fig. 6 (d). When a dendrite grows up, the metal ions would likely get electrons and redeposit directly at the tip of the dendrite because the dendrite itself has turned to a growing cathode. However, the redeposition of the metal ions has several prerequisite steps and it is not uniform and without a constant growth speed. Thus, the dendrites are composed of small nodular dendrites which wrap and connect each other as shown in Fig. 6(c), (e) and (f). The dendrites of Sn-8Zn-3Bi solder are quite

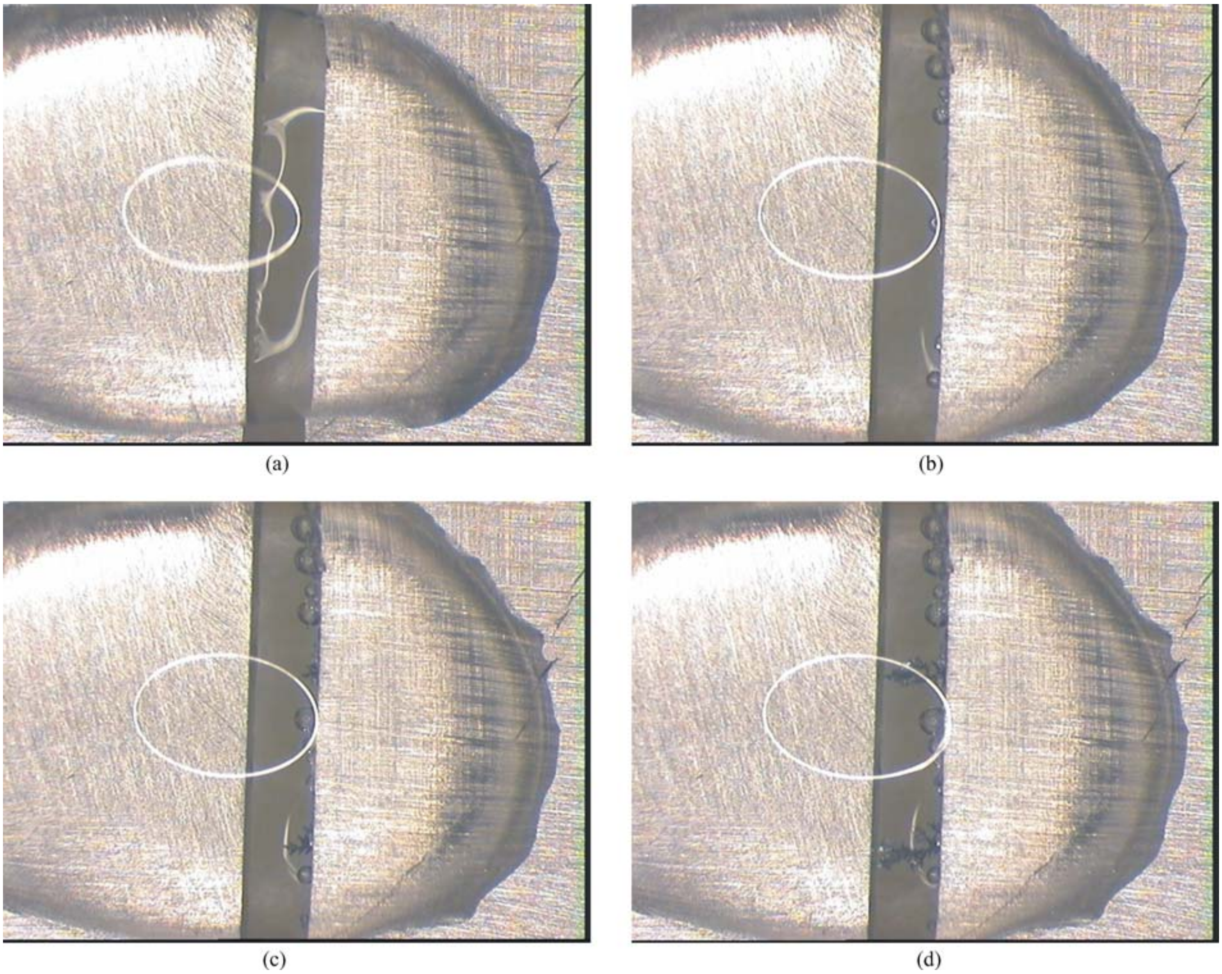

Fig. 3 In-situ optical microscopy photos of Sn-8Zn-3Bi solder under 3 voltage: (a) 0 Sec, (b) 60 Sec, (c) 90 Sec, (d) 120 Sec

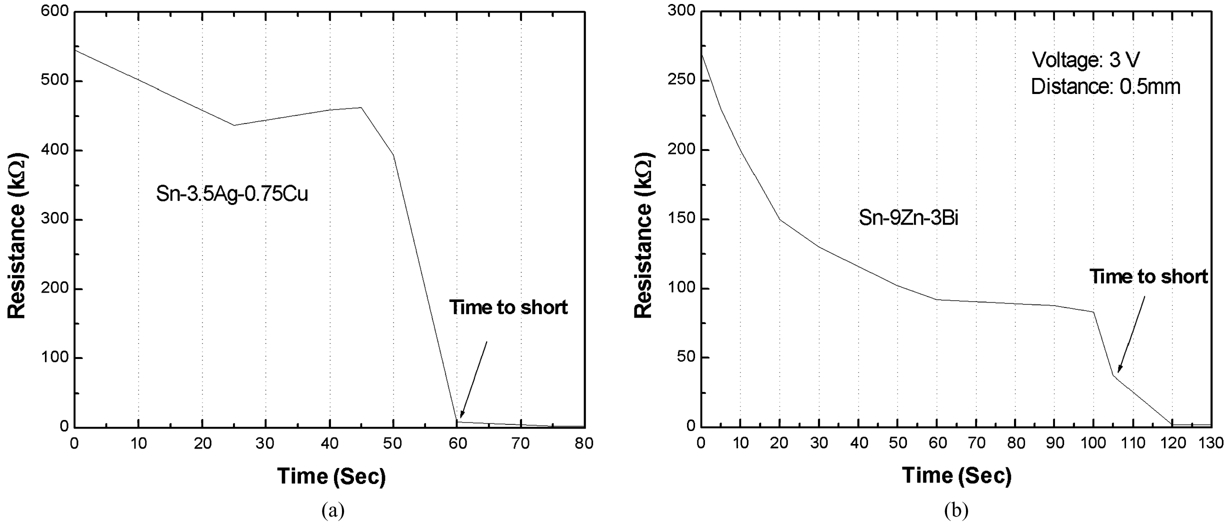

Fig. 4 Typical curves for the change of the resistance with the test time: (a) Sn-3.5Ag-0.75Cu, 10 V, (b) Sn-8Zn-3Bi, 3V

Table 1 The compositions of the residual dendrites formed under 5 voltage

Solder composition	Composition of residual dendrite (wt%)							
	Cu	Pb	Sn	Zn	Au	C	O	Br
Sn-37Pb		68.89			11.14	14.64	5.33	
Sn-36Pb-2Ag		70.14	12.81		2.63	7.94	6.48	
Sn-3.5Ag			42.93	17.90	18.30	20.87		
Sn-3Ag-0.5Cu	1.81		69.54	16.97	6.23	5.45		
Sn-3.5Ag-0.75Cu	3.51		50.41		26.27		1.83	17.98
Sn-4Ag-0.5Cu	5.84		67.07		17.55	9.54		
Sn-8Zn-3Bi			26.73	36.15	9.59	10.06	17.47	

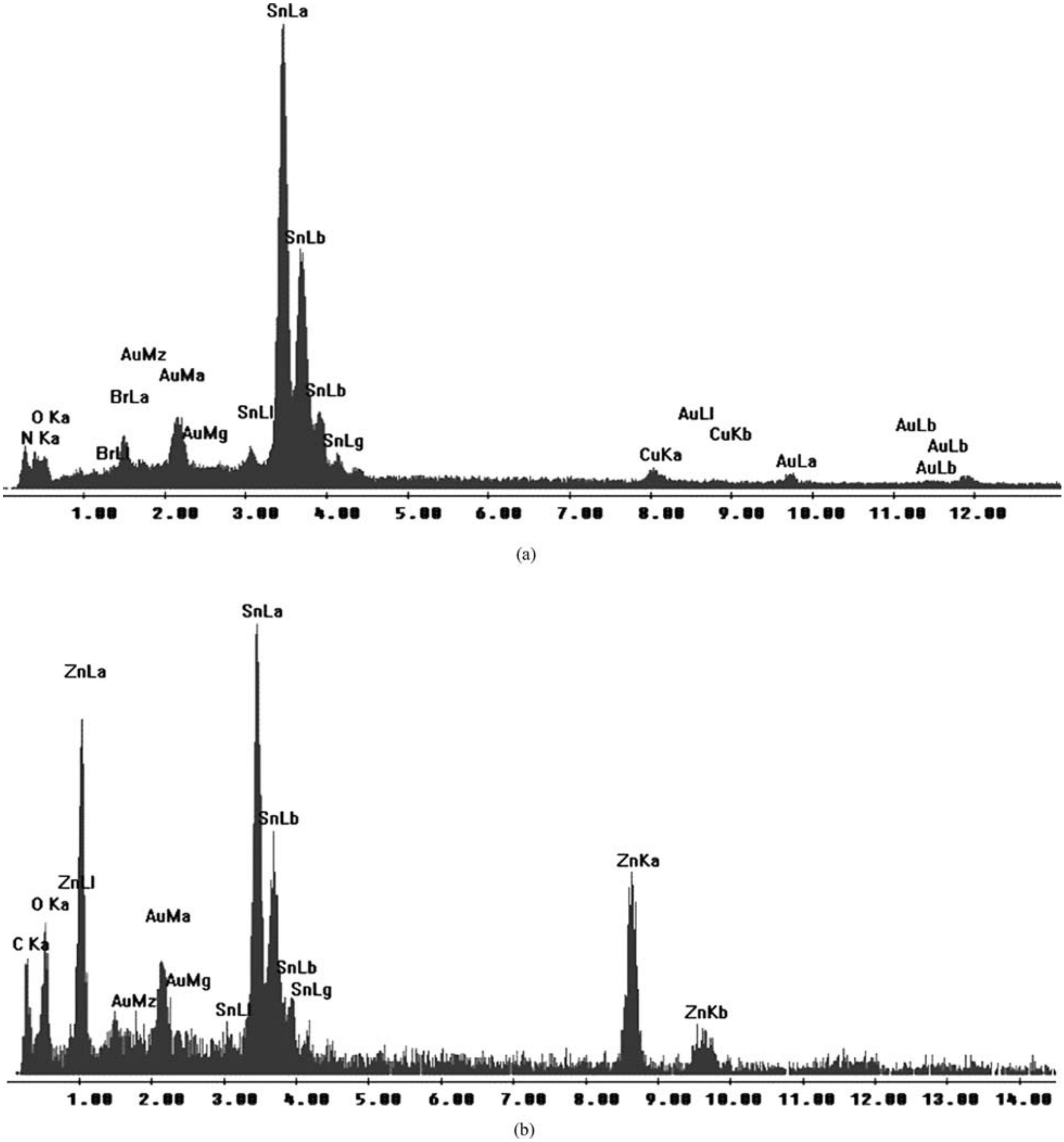

Fig. 5 EDS analysis on the compositions of the dendrites: (a) Sn-3Ag-0.5Cu, (b) Sn-8Zn-3Bi. The applied voltage is 5V

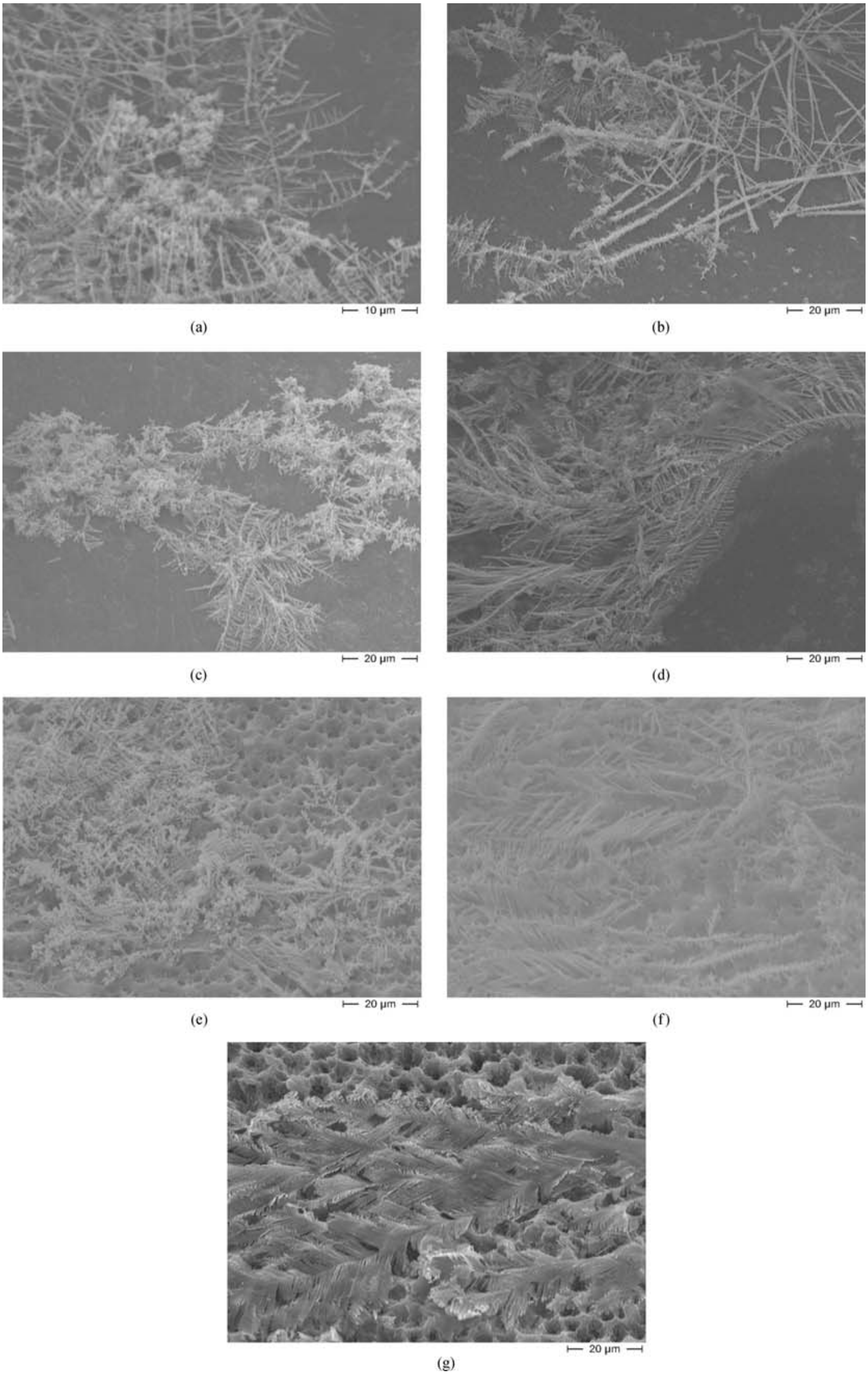

Fig. 6 Morphology of the dendrites: (a) Sn-37Pb, (b) Sn-36Pb-2Ag, (c) Sn-3.5Ag, (d) Sn-3Ag-0.5Cu, (e) Sn-3.5Ag-0.75Cu, (f) Sn-4Ag-0.5Cu, (g) Sn-8Zn-3Bi. The applied voltage is 5V

different which are like feathers. As shown in Fig. 6 (g), the small branches array themselves in order closely.

For Sn-Ag and Sn-Ag-Cu solders, the dendrites are mainly composed of Sn. It is known that silver is the metal most susceptible to migration [7]. However, in the solders of Sn-Ag and Sn-Ag-Cu, the Ag element form intermetallic compounds Ag_3Sn with Sn. Thus Ag is difficult to escape from the compounds and the migration is prevented. The same situation of Cu in the solder, they turn to Cu_6Sn_5 compounds in the solders. Therefore, to Cu containing solders, Cu content is very small in the compositions of dendrites.

C. The effect of applied voltage on the time to short and resistance

The effect of applied voltage on the time to short and short resistance was also investigated. Figure 7 displays the time to short under varying applied voltages for different solder alloys. The data show the higher the voltage is, the shorter the failure time is. Under the same voltage, Sn-37Pb and Sn-36Pb-2Ag solder alloys have smaller time to short comparing with other alloys, which means that the Pb bearing solders exhibit higher ECM susceptibility. However, the time to shorts for the solders are within several minutes. It can be conclude that the ECM would be significantly worse if water droplets exist.

Table II lists the short resistance under varying applied voltage. When the applied voltage is 10 V, the short resistances are normal several KΩ. With the decrease of the voltage, the short resistances increase gradually. The short resistance become tens of KΩunder 5 V and 3V. Because the short occurs as soon as the first dendrite touch the anode, the character of the first dendrite would determine the short resistance. To the same dendrite compositions, if the dendrite is thicker, the short resistance will be smaller than a thinner one. As a result, even for the same solder under same conditions, the short resistance values would have a large difference. Normally, the higher the voltage is applied, the larger number of metal ions would generate and the dendrites would be thicker and grow up faster. This is the reason that with the decreasing of the voltage, the short resistances increase gradually.

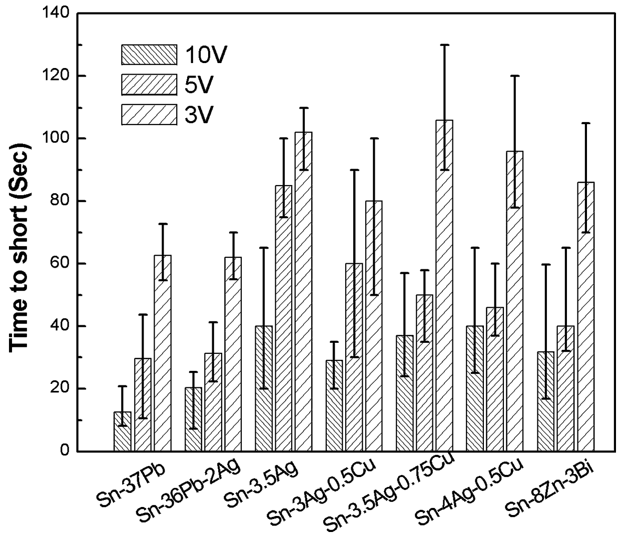

Fig. 7 Comparison on time to short under varying applied voltages for different solder alloys

Table 2 Short resistance under varying applied voltage

Solder compositions	3V (kΩ)	5V (kΩ)	10V (kΩ)
Sn-37Pb	25, 37, 47	6, 41, 4	4, 3, 2
Sn-36Pb-2Ag	10, 49, 38	35, 10, 21	5, 7, 3
Sn-3.5Ag	21, 75, 49	21, 49, 43	6, 2, 36
Sn-3Ag-0.5Cu	40, 28, 70	29, 13, 63	7, 2, 12
Sn-3.5Ag-0.75Cu	10, 48, 20	21, 8, 35	8, 4, 11
Sn-4Ag-0.5Cu	29, 18, 45	40, 4, 27	6, 3, 10
Sn-8Zn-3Bi	37, 6, 12	11, 24, 7	7, 4, 80

D. The electrochemical migration process

The theoretical decomposition voltage of water is 1.23 V. During the initial period of voltage application, $H^+$and OH^- ions from water ionization quickly collect around the electrodes and thus the current flows rapidly. According to the research of H. Katayanagi et al. [12], the PH value near the electrodes due to the electrolysis of water changed when the applied voltage was a minimum of 2V DC. At the anode, acidity with a maximum of PH=3, while at cathode side, alkalinity with a minimum of PH=10 was reported. Therefore, the following reaction formula can be hypothesized.

At cathode side:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{1}$$

At anode side:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{2}$$

Due to the electrolysis of water, metal ions graduate elute in the vicinity of the electrodes. G. Harsanyi has summarized the mechanism of the electrochemical process of metal elements. Ag, Cu, Sn, Pb and Zn belonging to the classic model have a similar ECM process [1]. Here we select Sn to discuss the process.

At cathode side, H^+come from anode side due to the electric field force would obtain electrons. It is the reason for the formation of the bubbles we have observed in Fig. 2 and Fig. 3.

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

The standard electrode electrical potential of the metal Sn dissolves in solution as Sn^{2+}at –0.136 V. Naturally, Sn ion elution occurs under present applied voltages.

At anode side, Sn dissolves forming Sn^{2+} ions:

$$Sn \rightarrow Sn^{2+} + 2e^{-} \tag{4}$$

And the higher the voltage is, the greater the amount of Sn ions elution. However, the Sn^{2+}ions cannot be transported to cathode directly. After they are generated, Sn^{2+}ions would combine with OH^{-} ions to form $Sn(OH)_2$according to the following equilibrium:

$$Sn^{2+} + 2OH^{-} \Leftrightarrow Sn(OH)_2 \tag{5}$$

Because of the relatively low solubility product of $Sn(OH)_2$, Sn^{2+} ions would escape and move toward the cathode after an incubation period. When they arrive at the cathode, electrochemical deposition occurs:

$$Sn^{2+} + 2e^{-} \rightarrow Sn \tag{6}$$

The deposition at the cathode forming dendrites which grow toward the anode and result in short when reaching it.

E. The comparison on the ECM susceptibility of the metals in solders

According to the above discussion, we can estimate the key steps for the ECM. Two steps related with the metal properties are quite important. The first is the metal dissolving at the anode. Second is the ions transport from the anode to the cathode.

We have known that the main migration elements in present solder alloys are Pb, Sn and Zn. Cu has a small susceptibility and Ag has no migration due the formation of intermetallic compounds in the solder alloys. Takemoto et al. found tin has superior ECM resistance to lead and Sn-Pb alloys [3] and this behavior corresponded well with the corrosion susceptibility of tin, lead and heir alloys in pure water investigated by Brusic [13]. It is believed that a large dissolution rate at the anode is necessary for the easy migration and which is close related with corrosion behavior of the metals. Table III lists the standard electrode electrical potential of the metals involved in present research. The bigger the potential is, the more difficult it is for the metal to dissolve.

Table 3 Standard electrode electrical potential of the metals involved in present research

Metal element	Electrical potential (V) (Ref. 5)
$Ag^{+} + e = Ag$	0.7795
$Cu^{+} + e = Cu$	0.52
$Cu^{2+} + 2e = Cu$	0.337
$Pb^{2+} + 2e = Pb$	−0.126
$Sn^{2+} + 2e = Sn$	−0.136
$Zn^{2+} + 2e = Zn$	−0.763

Table 4 Comparison on the solubility of the slightly soluble precipitate and the relative solubility of the metal ions

Compound	Solubility product constant (Ksp) under 25° in water (Ref. 13)	Ionic	solubility(S)
Ag(OH)	2.0×10^{-8}	Ag^{+}	1.4×10^{-4}
$Pb(OH)_2$	1.2×10^{-15}	Pb^{2+}	6.7×10^{-6}
$Zn(OH)_2$	1.2×10^{-17}	Zn^{2+}	1.4×10^{-6}
Cu(OH)	1.0×10^{-14}	Cu^{+}	1.0×10^{-7}
$Sn(OH)_2$	1.0×10^{-28}	Sn^{2+}	3.0×10^{-9}

The ions transport has a close relation to the solubility product of $Me(OH)_x$. If the solubility is quite small, the time for the ions transport will be quite longer. The solubility product constant (K_{SP}) reflects the ability to dissolve into ions in pure water [14]. For a given equilibrium

$$A_a B_b \Leftrightarrow aA^{n+} + bB^{m-} \tag{7}$$

The expression of K_{sp} is

$$K_{sp} = \left[A^{n+}\right]^a \left[B^{m-}\right]^b = (aS)^a \bullet (bS)^b \tag{8}$$

If we obtain the K_{sp} value, we can calculate the solubility of the ions in the water by equation (9).

$$S = \sqrt[a+b]{\frac{K_{SP}}{a^a \bullet b^b}} \tag{9}$$

Table IV gives the solubility of the slightly soluble precipitate and the relative solubility of the metal ions. It can be seen that the solubility in order is: Ag+ > Pb^{2+}> Zn^{2+}> Cu^{2+}> Sn^{2+}.

It has been recognized that the migration rates correlate better with the solubility products of the metal ion hydroxides than with the standard potentials for the same metal ions [15]. G. Harsanyi et al. also deemed that the speed of the dendritic deposition on the cathode is mainly determined by the solubility of the metal hydroxide. According to the above discuss, the main reason that Pb bearing solders such as Sn-37Pb and Sn-36Pb-2Ag have smaller time to short comparing with other lead free solder alloys is due to the higher solubility product of its hydroxides.

It should be pointed out that we could not compare the susceptibility of alloy simply by the solubility product of the metal elements. The existing form of the elements in the alloys plays a more important role. For example, in the solder alloys, Ag element forms compounds with Sn and it is immune to migration. However, for Zn element, in the Sn-Zn and Sn-Zn-Bi solder alloys, it exists as a Zn rich phase. Under this condition, Zn would migrate readily.

Conclusions

Electrochemical migration tests on several Sn-Pb and lead free solder alloys were investigated under distilled water. For different solder alloys, the migration elements are different. For Sn-37Pb and Sn-36Pb-2Ag solders, the main migration element is Pb and dendrites are stick-shape. While for Sn-Ag and Sn-Ag-Cu solders, Sn leads the migration with gracile dendrites interlaced together with each other. For Sn-8Zn-3Bi, both Sn and Zn can migrate and the relative dendrites are like feathers. It was also found that the higher the voltage is, the shorter the failure time is and the short resistances greatly depend on the character of the first dendrite reaching anode.

The mechanism of the ECM of the solder alloys were discussed. Two important steps of the ECM, metal dissolving and ions transport, have close relationship with the standard electrode electrical potential and the solubility product of $Me(OH)_x$respectively.

Comparing with lead free solder alloys, Sn-37Pb and Sn-36Pb-2Ag solder alloys have smaller time to short which means that lead free solders exhibit lower ECM susceptibility. Furthermore, in the solders, Cu has a small susceptibility and Ag has no migration due the formation of intermetallic compounds in the solder alloys. At this point, lead free solder alloys such as Sn-Ag, Sn-Ag-Cu are more reliable than Pb bearing solders.

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