Sn and Sn-Bi Alloy Plating Solution Development for High-speed Applications

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There have been many studies done on tin and tin alloy plating issues, ranging from simple acid sulphate and methanesulfonate electrolytes to their complicated mixtures. However, the problem of good electrolyte performance still remains in reel-to-reel high-speed applications today. There are also issues in relation to tin-bismuth alloy plating on alloy42 leadframes. Firstly, it is difficult to prevent bismuth immersion plating on the surface of tin anode and secondly, it is necessary to use a corrosion inhibitor for prevention similar displacement reaction on the surface of alloy42.

This paper summarizes the study of effects of bath composition, temperature and additives in methanesulfonate electrolyte and performance characteristics of tin and tin-bismuth electrodeposits.

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Introduction

Leadframe packages with tin-lead plating on leads protect substrate against corrosion and provide the performance characteristics of surface. Nowadays, the environmental requirement is becoming stronger in electronic industry and most semiconductor companies have to apply new environmentally friendly plating technologies. It should be noted that "Pb-free" is one but very important legislative requirement for electronic industry. Thus, all products must be "RoHS-compliant" by the July 1, 2006 according to RoHS Directive. In the practice, most of lead-frames are purchased without a coating and processed at the manufacturing site into a package. Tin based leadframe plating is applied after molding operation. Unfortunately, the predominant leadframe finish for post plating today is a tin-lead alloy. The other part of the leadframes with plated coating is Ni/Pd/Au which is purchased in a pre-plated form by the assembly manufacturer. According to last method, prior to a semiconductor package process, electrodeposited layers are formed and after finishing a leadframe has good solder wettability and protective properties[1]. More than twenty leadframe suppliers offer sophisticated technology 2-, 3- and 4-layer Ni-Pd pre-plated leadframe (PPF) worldwide, because the pre-plated Pd lead finish was found to offer advantages compared to the Sn-Pb post plating. On the other side, an advanced PPF technology using tin and tin alloys is an absolutely new process. That is why there is no sufficient practical experience in the field of application tin based PPF worldwide.

The objective of this study is to evaluate a few of nonionic surfactants as main additives for tin and tin-bismuth methansulfonic electrolytes at relatively high current densities, which may be applied in alloy42 reel-to-reel PPF manufacturing process. Meanwhile, it is interesting to test the tin-bismuth alloy with 5-10% of bismuth, because it may be effective in retarding of tin whisker growth.

1. Experimental procedure

1.1. Determination of Sn and Bi in plating on steel and brass by ICP-AES

Tin and bismuth were determined in solutions by ICP-AES on a Jobin-Yvon JY-70Plus simultaneous/sequential spectrometer operated in a sequential mode. The operating parameters of the sample introduction system were optimized for better reproducibility. The emission intensities of tin line were measured at 8 points over the whole profile of the spectral line; and the line area obtained by fitting the profile with Gaussian function was used for calculations. Due to spectral interference from iron, the bismuth line profile was registered at 5 points around the maximum, but only the intensity at maximum was used. The instrument was calibrated using standard solutions containing 0,10 and 50ppm of Sn and 0, 2 and 5ppm of Bi, prepared in 2.5% HNO_3 – 0.1% HF as a back-ground solution. In the case of Sn-Bi alloy the composition of the coating was calculated in weight % assuming the coating is composed only of Bi and Sn.

1.2. Electrolyte foaming evaluation

All experiments in this study were done in a 100ml cylinder with 50ml portion of each electrolyte at the tested temperature with air consumption of 1,5L/min. An air pump was switched off when the foam reached the top of the cylinder and the following foam sedimentation time was measured.

1.3. Electrolyte testing in Hull Cell

A Hull Cell plating unit from Jungdo Testing Instrument Co and polished steel or alloy 42 cathodes were used in plating experiments. Each tested solution of a 267 ml volume was applied for test only once. The test conditions were: anode- pure tin, current - 3A, electrolyte temperature- 30…50^{0}C, plating time - 2 or 3 min, agitation by magnetic stirrer- level 4. After plating the local current density was calculated using Hull Cell ruler, and a small part of cathode was cut off for further investigations.

1.4. X-ray photoelectron spectroscopy studies of Sn-Bi alloys

XPS measurements have been done with a Quantum 2000 Scanning ESCA Microprobe spectrometer. Spectra were excited with a monochromatized Al K_α emission. Passed energy of electron analyzer was 23eV. Depth profiling was performed using Ar^+ beam with the energy of 3keV at the angle of 45^o. A sputtering time was 30sec in intervals 6 sec. It is enough for removing surface contamination (C,O). The composition of surface layers was calculated from the area of spectra using sensitivity factors.

1.6. Grain size evaluation

The grain size was assayed qualitevely by an ink-spread test. A line of blue ink from a felt tip pen was drawn across the surface of the coating layer of interest, and the width of ink spreading is related inversely to the grain size of the deposit. SEM photographs on samples were used to verify the results founded with ink-spread test. Hitachi field emission scanning electron microscope FE-SEM S4500 was used for morphology and grain size evaluation. For coatings a diagonal line of certain length *l* was drawn on the SEM image, and the number *n* of the grains located on this line was counted. Then *l/n* gives the average grain size *d*.

1.7. X-ray diffraction and stress measurements

All of XRD and stress data reported in this work were obtained with the Philips X-port Pro MPD diffractometer, CuK_{a1} radiation was used as the X-ray source. Residual stress measurements (as ω-stress) were done with use of X-ray diffractometer. The standard software applied to <431> high-angle diffraction line was used. In addition to internal stress, deposit crystal orientation is a critical parameter that may influence whiskers growth.

2. Results and Discussion

2.1. Pure tin electrodeposition

2.1.1. Testing of oxyethylated adducts in MSA tin electrolyte

Such type of polymers is cheap and available and may be applied as a main brightener for MSA tin and tin alloy electrolytes[2]. Meanwhile, this kind of polymers is water soluble, so their aqueous solutions may be used easily. All of the tested polymers were oxyethylated adducts of same nature, but different molecular weight. Most of electroplating characteristics of MSA tin electrolyte are listed in the Table 1 and were determined in Hull Cell with tin anode operated at 3 amps during 3 min. All runs were conducted with agitation by magnetic stirrer with a fixed rate. The tin electrolyte contained Sn (as metal) -60g/l, MSA- 100g/l and antioxidant (catechol) -2g/l. An aqueous mixture of tested oxyethylated additive with known molecular weight was added to electrolyte before each experiment. Table 1 shows the comparative results obtained with use of different polymers in abovementioned tin electrolyte.

It can be seen from Table 1 that optimal electrolyte performance characteristics were obtained with polymer of 2900 molecular weight. Urgent criteria for practical application of the electrolyte are high covering power (CP) and absence of burnt deposit at high current density region. It was established in preliminary experiments that content in the electrolyte should be more then 60g/l to meet this criteria at current density more than 15 A/dm^2 (139A/ft^2). Only in this case electrolyte demonstrates high CP, without uncovered and burned areas along the whole length of Hull panel.

Table 1. *The influence of molecular weight of oxyethylated additive on the plating performance characteristics*

Performance	**Order**
Foaming in aqueous brightener composition	2000<2500<2900<8400
Foaming in tin MSA electrolyte	(2000=2500)<2900<8400
Cathodic polarization effect	2000<2500<8400<2900
Cloud point of electrolyte	(2000=2500)<2900<8400
Sn appearance on the HCD edge of panel (2mm from edge)	2000- good 2500- slightly burned 2900- excellent 8400- fair
Sn uniformity (identity) along Hull panel	2000- fair 2500- good 2900- excellent 8400- fair

The influence of cathodic polarization on covering power can be illustrated using abovementioned Hull Cell test. For instance, two cases with different values of cathodic polarization are compared. For clear understanding and data comparison the overall polarization curve is assumed to consist of two main cathodic partial reactions: $\mathbf{Sn^{2+}+2e=Sn^0}$ (j_1 or j_2) and $\mathbf{2H_30^+ + e = 2H_20 + H_2\uparrow}$ (j_{H2}).

Equal rates of hydrogen evolution in the first and second cathodic processes are considered for simplicity. Assuming that polarization of tin reduction is low in the first case, in the second case it will be of relatively higher value (see Fig.1).

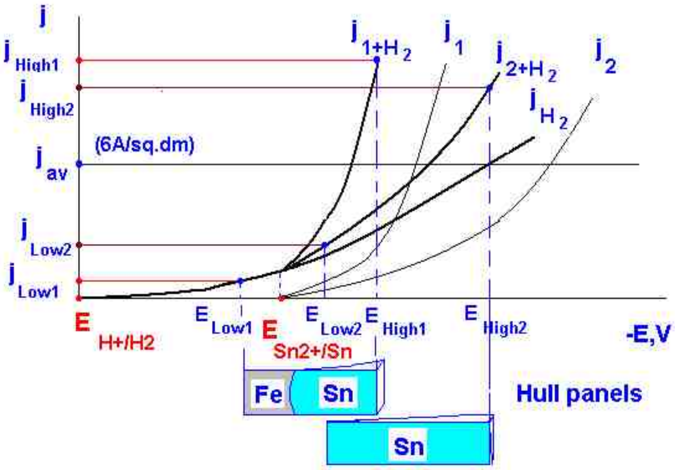


Fig.1. *Influence of cathodic polarization on covering power of Hull panel at 3A in a tin MSA electrolyte.*

According to Fig.1 obviously additives increasing mainly tin reduction polarization should be applied to increase CP (like case 2). Best case will be realized when the standard electrode potential of tin is reached at lowest current density (j_{Low2}). Consequently, the electrolyte with proper additive may produce metal deposit without any burnt and uncoated zones along the panel. In addition, such electrolyte gives the relatively low value of current density in HCD region of Hull panel ($j_{High2}<j_{High1}$) during testing. Meanwhile, throwing power is improved also. Under equal testing conditions (tin and MSA content, agitation, temperature etc.) the possibility of unburned deposit formation is higher in second case than in the first case. Comparing Hull Cell voltage values obtained at the same plating conditions, the impact of cathodic polarization can be estimated approximately, during preliminary additives assessment.

2.2.2. SEM images investigation

It is known, that grain size of tin crystals is important factor in the whisker growth prevention. The role of thickness during grain size assessment in comparative experiments is important. On the other side, grain size of 5 microns in 12 micron thick tin coating was shown[3] to be proper for whiskering mitigation.

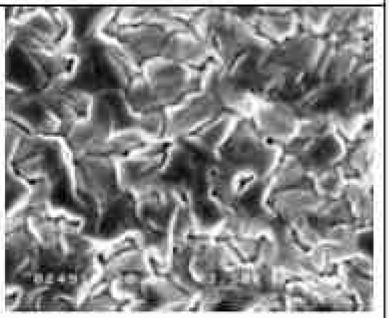
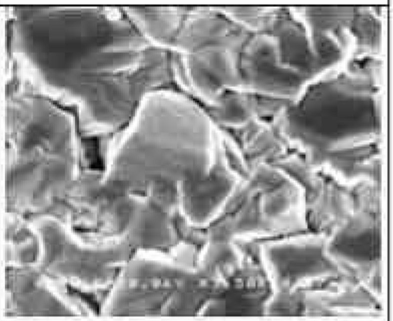
Thickness, μm /mil	Grain size, μm /mil	Domestic Sn deposits
7/0.28	3.4/0.13	
14/0.55	6.6/0.26	
21/0.83	9/0.35	

Fig.2. *Influence of coating thickness on morphology and grain size of tin electrodeposited on mild steel substrate. Magnification is 3500. Electrolyte composition, g/L:Sn-50, MSA-100, catechol-2, oxyethylated additive -10ml at* 30^0*C under agitation.*

Fig.2 shows the results on grains shape and size with variation of deposition time (thickness) obtained in tested MSA electrolyte. by It can be seen that thicker coatings generates larger grains. Increase of the thickness from 7 to 21 microns remarkably enlarges the grain size almost in three times. So, in the future to exclude this factor from consideration in comparative experiments it is necessary to evaluate whiskering only for equal deposit thicknesses. Generally, the thickness of coating defines not only the grain size but also whiskering, elongation and other coating properties. For understanding the relation between thickness and grain size of matte deposits, it is assumed that coating grows under geometrical selection[4]. So in a reality all tin deposits have grain size gradient through their thickness. Near the substrate the tin coating consists of very small grains. With further polycrystalline growth under "geometrical selection" the number of survived grains is gradually decreased with increasing thickness, consequently those grains become larger.

The influence of temperature on grains size and shape was established. In all cases a higher temperature promotes well-polygonized crystal formation (see Fig.3).

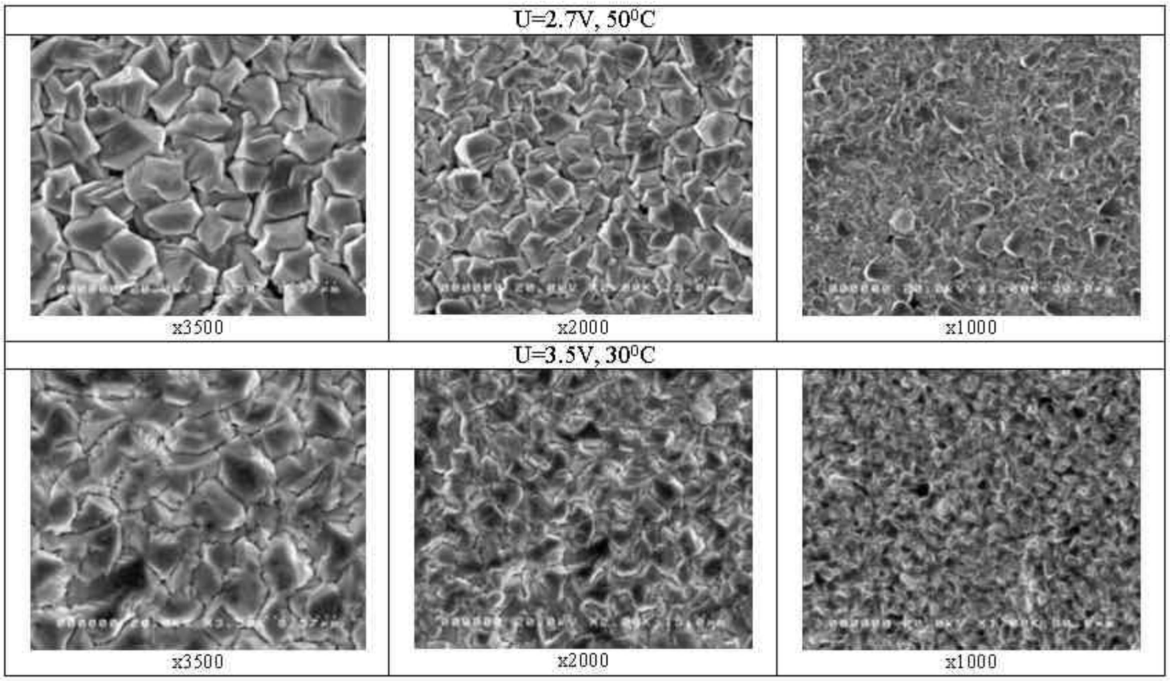
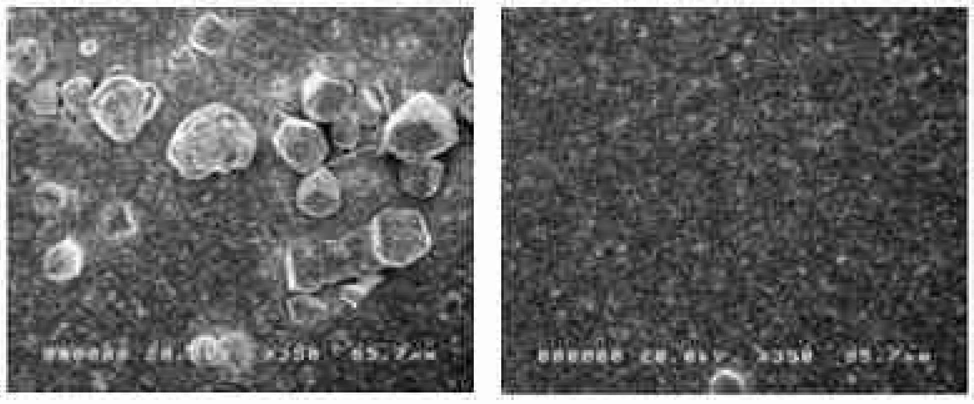


Fig.3. *Tin coatings (14µm or 0.28mil).obtained on alloy42 substrate at 15A/dm^2 (139A/ft^2) under agitation. Electrolyte composition, g/L:Sn-50, MSA-100, catechol-2, oxyethylated additive-10ml.*



without additive

with additive of 0.04g/L tetralkylammonium salt

Fig.4. *Electrodeposed tin obtained from MSA solution at 20A/dm^2 (185A/ft^2) under agitation. The thickness is 14µm (0.28mil). Eelectrolyte composition,g/L: Sn-50, MSA-100, antioxidant(catechol) -2, oxyethylated additive -10mL/L.*

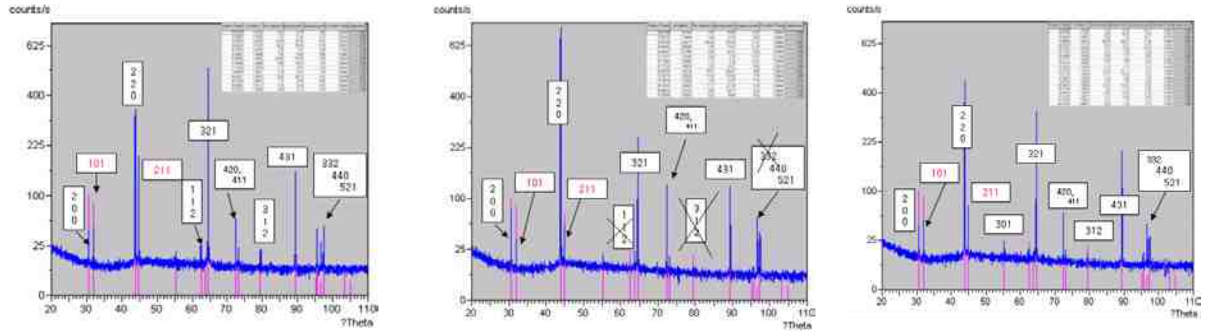
It is interesting for issue of whiskering, because such kind of crystals does hinder whiskers growth. Meanwhile, it was found that at relatively high temperature the cell voltage is decreased, very likely due to decrease of cathodic polarization and solution conductivity.

Behavior of tin MSA electrolyte at high current density is a crucial issue for PPF process. For example, it was shown, that dendrite crystal could be formed in a simple electrolyte at the current density more than 15 A/sq.dm under moderate agitation. Fortunately, it was found, that such crystal growth could be effectively inhibited by addition of the small quantities of tetraalkylammonium salts. The strong effect of small quantities of such additive on tin appearance was detected (see Fig.4).

2.2.3. XRD studies of electrodeposited tin from MSA electrolyte

It is well known that volume fractions of various orientations define deposit texture. On the other side highly textured deposits with one preferred orientation representing a large volume fraction were suggested to be less prone to whisker due to low concentration of crystalline defects[5]. It is necessary to produce tin deposits with beneficial crystal orientation at the wide range of conditions.

In this work the preferred orientation of abovementioned tin deposits was derived from the ratio of a diffraction peak of deposited film and diffraction peak of polycrystalline tin with the same orientation. This ratio is also called a "times random" and is good for our purpose, i.e., to understand what affects the orientations of electroplated tin[6]. When this number is greater than one for a particular orientation, it means that this orientation is enhanced in the deposited film, therefore it is "preferred".



7µm (0.28mil) **14µm (0.55mil)** **21µm (0.83mil)**

Fig.5. *XRD spectra for pure tin coatings. Electrolyte composition, g/l: Sn-60, MSA-100, oxyethylated additive -8ml. Coatings were obtained at 15A/dm*^{2}*(139A/ft*^{2}*), 30*^{0}*C, agitation, mild steel base.*

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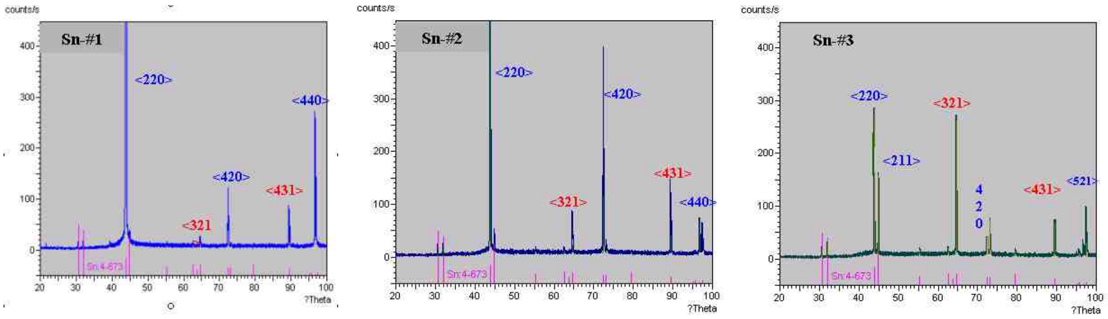
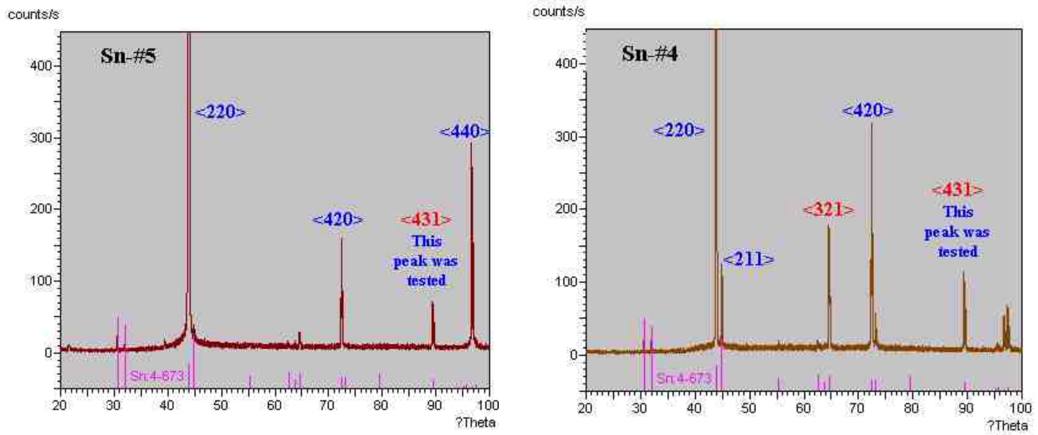


30^{0}C, Hull Cell voltage-3.4V **43^{0}C,** Hull Cell voltage -2.9V **50^{0}C,** Hull Cell voltage -2.7V

Fig.6. *XRD data of tin coatings obtained at j-10A/dm^2 (93A/ft^2). The electrolyte composition,g/l: Sn-50, MSA-100, oxyethylated additive -8ml, additive "A" -0.4g. The current through Hull panel was 3A, 2min, agitation, A42 base.*

Table 2. *The "preferred orientation(s)" data for samples ##1,2,3. More full description of plating conditions is given in Fig.6 denotation.*

Random orientation JCPDS card: Sn(4-673)		**Sample #1, 30^{0}C**		**Sample #2, 43^{0}C**		**Sample #3, 50^{0}C**	
hkl	**Expected Intensity**	**Actual Intensity**	**Times Random**	**Actual Intensity**	**Times Random**	**Actual Intensity**	**Times Random**
200	*100*						
101	*90*						
220	*34*	100	2.94	100	2.94	100	2.94
211	*74*	0	0	3.01	0.04	53.96	0.73
112	*23*						
400	*13*						
321	*20*	0.34	0.02	6.77	0.34	92.53	4.62
420	*15*	2.76	0.18	38.55	2.57	12.03	0.80
312	*20*						
431	*13*	0.88	0.07	5.86	0.45	22.07	1.70
332	*5*						
440	*2*	2.87	1.44	3.47	1.74		
521	*5*					8.75	1.75



30^{0}C, Hull Cell voltage -3.5V **50^{0}C,** Hull Cell voltage -2.7V

Fig.7. *XRD spectra of 14µm (0.28mil) Sn coatings #4 and #5. Electrolyte composition, g/l: Sn-50,MSA-100, oxyethylated additive -8ml, additive "A" -0.8g. The total current on Hull panel was 3A, 2min, agitation, A42 base*

Table 3. *The "preferred orientation(s)" data for samples ##4, and 5. More full description of conditions of their obtaining is given in Fig.7 denotation.*

Random orientation **JCPDS card: Sn(4-673)**		**Sample #4, 50^{0}C**		**Sample #5,30^{0}C**	
hkl	**Expected Intensity**	**Actual Intensity**	**Times Random**	**Actual Intensity**	**Times Random**
200	*100*				
101	*90*				
220	*34*	100	2.94	100	2.94
211	*74*	18.97	0.26	0	0
301	*17*				
112	*23*				
400	*13*				
321	*20*	27.26	1.36	0.41	0.02
420	*15*	59.80	3.99	3.53	0.24
312	*20*				
431	*13*	8.86	0.68	0.71	0.06
332	*5*				
440	*2*	4.37	2.19	2.95	1.48
521	*5*	2.94	0.59		

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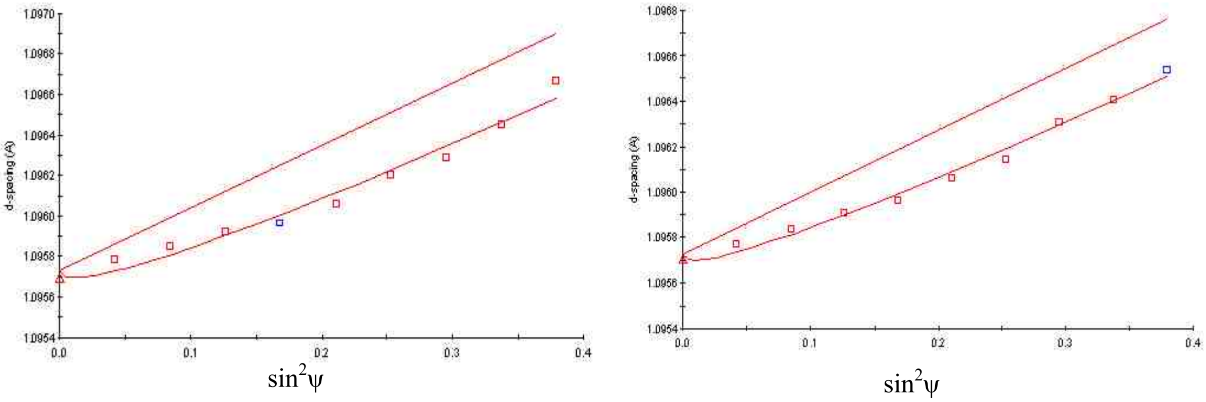
Figs.5 and 6 display the XRD patterns of tin deposits and show the effects of thickness, temperature and additive on preferred orientation. It can be seen from Fig.5 that at the presence of oxyethylated additive alone tin deposits with <220> and <321> preferred orientation are obtained. The addition of small quantities of additive “A” in the electrolyte can improve significantly the <220> preferential orientation of tin especially at 30^0 (see Fig.6).



Sn-#4: tensile stress is 103.5±11.1MPa (15000±1609 psi)

Sn-#5: tensile stress is 91.6±6.2MPa (13285±900 psi)

Fig. 8. *Measured residual stresses obtained on the base of analysis of <431> lines. More full description of conditions for samples is given in Fig.7 denotation.*

There are many factors affecting compressive stress in tin and tin alloy electrodeposits. It was established that the most important factors are grain size, shape and orientation. In this conjunction, one strategy for tin whisker mitigation may be recommended. For instance, according to our review of literature there is no absolutely exact recommendation related to whiskers-free tin and tin alloy preferred orientation. However, the most of results seem to show that <220> and <200> planes orientation are best, but <312> and < 431> orientations are detrimental for whisker-free plated tin state. In our case it was found that the <220> orientation of tin grains was strongly preferred for all samples obtained at 30^0C, but when temperature of electrolyte was increased up to 50^0C, the <321> detrimental orientation was strongly preferred (see Tables 2 and 3). On the other side, when concentration of additive “A” in the electrolyte was increased up to 0.8g/l (see Fig.8), the <220> preferred orientation has been kept for coatings obtained in “hot” electrolyte as well. In the other words it is necessary to use the additives, which promote beneficial crystal orientation at the required electrolyte temperature.

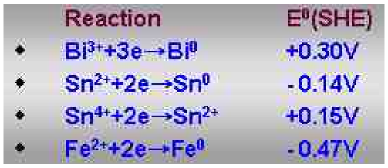
Of course, it is much easier to measure preferred orientation than stress, but qualitative type of residual stress is important. We applied a standard measuring procedure, where a residual ω-stress value is calculated from the slope of a plot (d spacing vs. $\sin^2\psi$), whereas stress direction is determined by the direction of the slope. If the slope is negative, the stress in the tin coating is compressive. If the slope is positive, the stress in the tin coating is tensile. All tin coating samples demonstrates strong tensile stress in relation to <431> planes (see Fig.8). Such behavior can be beneficial, because as a rule, tensile stress hinders the whisker formation. However, it was surprising to find that elevated temperature promotes stressed coating formation.

In conclusion, we can summarize that relatively high temperature assists the formation of large well-polygonized tin grains, which demonstrate not only orientation along <220> planes but also detrimental <321> and <431> preferred orientation. It was shown that small quantities of additive "A" are beneficial for stabilization of <220> preferred orientation of tin deposit. It was demonstrated that teraalkylammonium salts are effective additives for dendrite growth prevention at high current density.

2.2. Sn-Bi alloy electrodeposition

2.2.1. Proposed approach

Analysis of current status of pre-plated leadframe (PPF) technology revealed the necessity of formulation of the main requirements for electrolyte selection. Firstly, the list of standard electrode potentials in Fig.9 should be taken into consideration. The great difference in potentials is a real problem for alloy deposition with fixed composition over wide current density region.



	Reaction	E^0(SHE)
◆	$Bi^{3+}+3e \rightarrow Bi^0$	+0.30V
◆	$Sn^{2+}+2e \rightarrow Sn^0$	-0.14V
◆	$Sn^{4+}+2e \rightarrow Sn^{2+}$	+0.15V
◆	$Fe^{2+}+2e \rightarrow Fe^0$	-0.47V

Fig.9. *The standard electrode potentials of Bi, Sn and Fe electrodes.*

Important aspect of electrolyte development is a search and/or synthesis of proper ligand for bismuth(III) ions. Ideally, complexing agent, applied for Sn-Bi electrolyte, should react only with bismuth(III) ions, while almost not changing the reduction potential of tin.

Secondly, tin-bismuth bath formulation should be optimized on the base of the following issues consideration:

- Immersion plating of Bi on the A42 substrate at first contact of substrate with solution: **(Alloy42) $3Fe^0+2Bi^{3+} \rightarrow 3Fe^{2+}+2Bi^0\downarrow$**
- Immersion plating of Bi on the tin anodes and Sn-Bi alloy coated substrate: **$3Sn^0 + 4Bi^{3+} \rightarrow 3Sn^{4+}+ 4Bi^0\downarrow$**
- Redox reaction between Sn^{2+} and Bi^{3+} ions in the bulk of electrolyte with time: **$3Sn^{2+}+2Bi^{3+} \rightarrow 3Sn^{4+}+ 2Bi^0\downarrow$**
- Tetravalent tin ions formation with time, following their hydrolysis: **$2Sn^{2+}+O_2+4H^+ \rightarrow 2Sn^{4+}+ 2H_2O$,** where Sn^{4+} ions are quickly transform to $Sn(OH)_4\downarrow$.
- Stability of brightener and additives against oxidation and degradation in strong acid media.

Other great problem is a prevention of whiskering with aging. That is why, in ideal addressing the tin whisker growth issue a plating bath chemical formulation should be developed as robust as possible in terms of minimizing whisker growth.

Finally, we can summarize the following targets and requirements for Sn-Bi alloy electrolyte for PPF high-speed application:

- Uniform, white matte deposit with Sn-Bi alloy composition of 3-10%Bi
- Wide current density range (5-30 A/dm^2);
- Stable alloy composition vs. current density;
- No bismuth immersion on the cathode;
- Minimized bismuth immersion on tin anode;
- <220> preferred orientation;
- Grain size of 2…4µm;
- Carbon content of <500ppm;
- Layer thickness of 8…12µm;
- Good ductility;
- Good solderability.

2.2.2. Testing of oxyethylated adducts in MSA tin-bismuth electrolyte

Electrolyte composition of Sn (as metal) -60g/l, Bi (as metal) -2g/l, MSA- 100g/l, antioxidant - 2g/l, complexant-2g/l was used for the test. The testing condition was similar to abovementioned tin electrolyte. Significant effect with respect to Sn-Bi alloy plating performance characteristics was obtained with polymer (oxyethylated adduct) of 2900 molecular weight. The result is the same as for pure tin electrolyte, but the main difference of oxyethylated adducts behavior in pure tin electrolyte from that in tin-bismuth solution is higher foaming. The reason of such phenomenon in our opinion is an interaction between molecules of antioxidant, complexant and polymer with following association. Therefore, the content of oxyethylated adduct in plating solution need to be reduced in relation to that for pure tin solution. Other possible way is an application of additional defoaming agent in brightener composition for Sn-Bi plating electrolyte.

2.2.3. SEM investigation of tin-bismuth coatings

It is known far and wide that the size and shape of tin and tin alloy crystals are important factors for whisker growth mitigation. Fig.10 shows the surface of Sn-Bi deposits and two SEM images of deposits produced in conventional Japanese electrolyte. Images of deposit obtained in the latter electrolyte are given as reference. It was found that grain size of Sn-Bi alloy coatings obtained at the same conditions in all cases was smaller than that for pure tin. In most of cases deposits from both conventional foreign and domestic electrolytes demonstrated grain size around 2.3-2.6 microns only. In the other words, bismuth ions play a role of amorphisating agent during Sn-Bi alloy electrocrystallization. In this conjunction the content of brightener in Sn-Bi electrolyte may be lessened in comparison with tin one.

In preliminary studies mild steel was shown to be more corrosive and active than brass in strong acid MSA Sn-Bi electrolyte, therefore much bismuth is deposited at first seconds after cathode immersion in electrolyte before current application. It was established that Sn-Bi alloy deposits with well-defined grains were formed on the surface mild steel in comparison with brass substrate. We think it happens due to fast bismuth electroless deposition on the surface of steel during first few seconds of immersion. The addition of inhibitor to electrolyte composition for prevention of immersion bismuth plating is necessary in this case.

There are numerous ligands for bismuth stabilization in aqueous acid media. We studied the influence of only few of them. SEM images of Sn-Bi deposits obtained in electrolyte with three types of aminocarboxylic ligands are given in Fig.11, where EDTA is ethylene-diaminetetraacetic acid, DPTA is diethylenetriaminepentaacetic acid and DCHTA is 1,2 Diaminocyclohexane- N,N,N',N'-tetraacetic acid. It was found that these substances not only formed complexes with Bi(III) ions in MSA but also inhibited tin anode dissolution. However, it can be seen that rough deposit may be formed in the presence of EDTA and DCHTA in electrolyte.

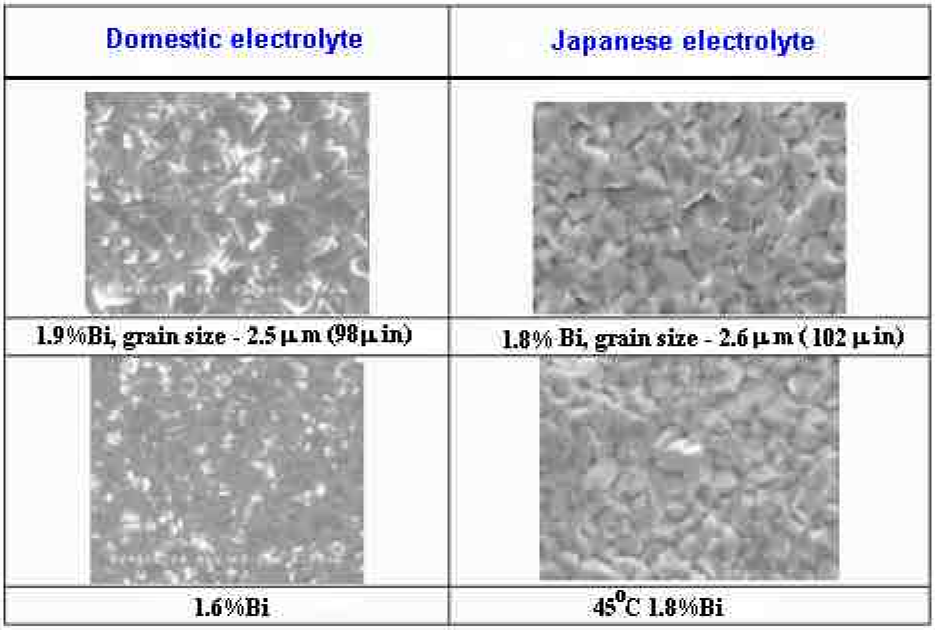


Fig.10. *Comparative typical SEM images of Sn-Bi coatings obtained from domestic and conventional Japanese electrolytes at* 50^0*C and 15 A/*dm^2 *(139 A/*ft^2*)*

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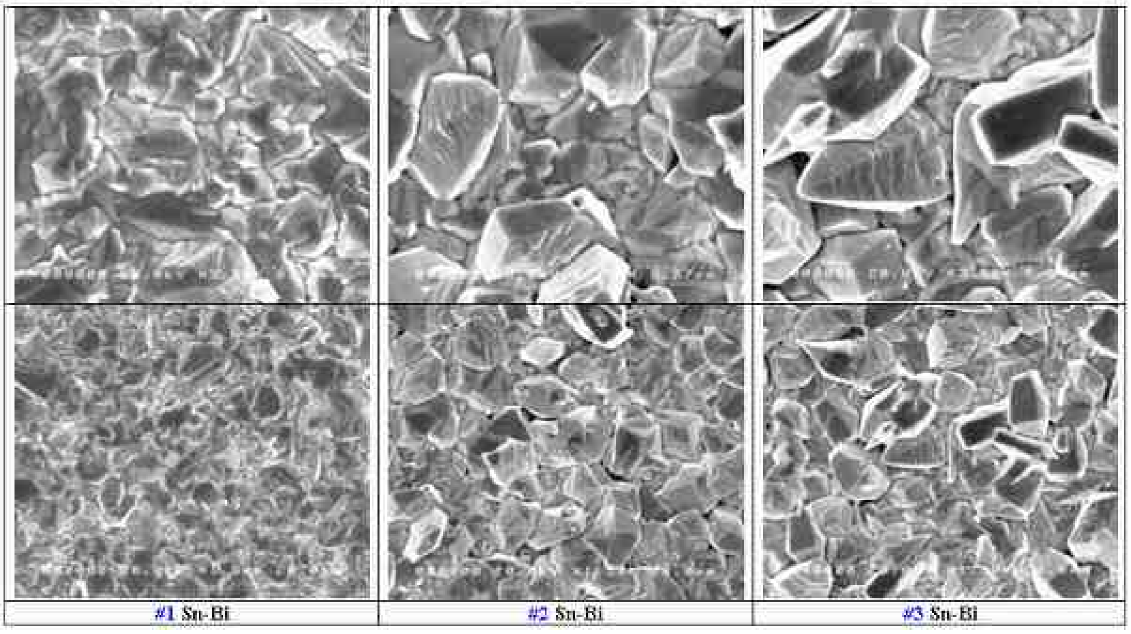

Composition g/l: Sn-60, MSA-100, Bi-2, antioxidant (tiron)-2, DEPTA-0.64, oxyethylated additive- 10.

Composition g/l: Sn-60, MSA-100, Bi-2, antioxidant (tiron)-2, EDTA-0.60, oxyethylated additive- 10.

Composition g/l: Sn-60, MSA-100, Bi-2, antioxidant (tiron)-2, DCHTA-1.2, oxyethylated additive- 10.

Fig.11. *Influence of some ligands on the morphology of Sn-Bi coatings obtained at 15 A/dm (139A/ft^2). The plating conditions were as follows: temperature- 50^{0}C, current for Hull Cell- 3A, deposition time- 2min.*

The scanning electron microscope reveals a difference between matte and dendrite deposits. At x3500 magnification, a definite structure is visible in compact matte tin-bismuth deposit (in the presence of DPTA) with crystal grain sizes from 2 to3 microns. Such deposit morphology may be proper for practical usage. On the other hand, a dendrite growth is clearly visible on the surface of deposits obtained in electrolytes with additives of EDTA and DCHTA.

2.2.4. XPS studies of tin-bismuth coatings

For XPS studies two types of thick coatings on the brass substrate were prepared. First coating was about 2% of bismuth and second one was 1% of bismuth only. XPS spectra and composition Sn-Bi coating on brass are given in Fig.12.

Depth profile of both Sn-Bi alloy coatings clearly demonstrates zinc atoms on coating surface after storage during two weeks. In both cases data show oxides of Sn and Bi on surfaces of the alloys. Meanwhile, Bi oxide is located only on the surface, but Sn oxide penetrates deeply into bulk of the coating. Also it was found that metallic zinc existed on the surface of the coatings and it was concentrated meanly near the surface. Surprisingly, its atomic concentration could reach 40% at the thickness of 7µm and copper atoms were not found on the surface. Bi content on the surface was very low; most of bismuth atoms were located in the bulk of the coatings. We suppose that the difference of bismuth content is a main reason of different zinc surface concentration. Indeed, bismuth atoms should be concentrated in a tin matrix on the grain boundaries during electrocrystallization. If we assume that transport of zinc atoms from the substrate to the coating surface is a result of diffusion along the grain boundaries, then, high quantity of bismuth atoms as main “impurities” will reduce zinc atoms diffusion. In our opinion these experimental data have some relation to the fact that alloys with high bismuth content prevent whiskers growth more effectively.

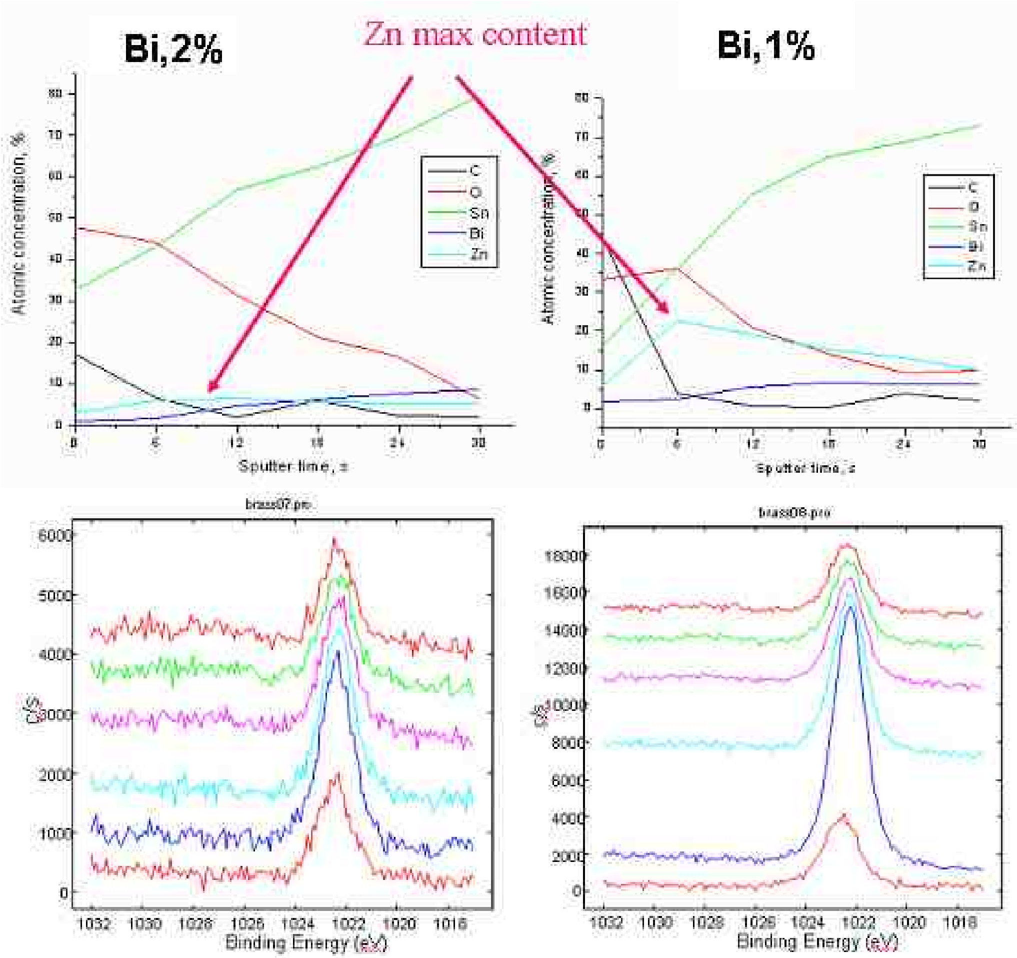

Fig.12. *Depth profile of thick (50µm or 1.97mil) Sn-Bi alloy coatings and their XPS Zn 2p spectra.*

2.2.5. Sn-Bi coating accelerating whisker performance testing

There are numerous bath formulations in technical and patent literature concerning tin-bismuth electroplating, but the quantities of main electrolyte components are not fixed clearly. In our opinion, the composition of electrolyte should include following main components: metal sources, a ligand, an antioxidizer, a brightener and an inhibitor. On the other side, bismuth content in the alloy seems to be in the range of 3-10%. Though, cracking of coating layer may occur after trimming and forming operation especially when bismuth content in the alloy is greater than 6%, however the antiwhiskering properties of such alloys will be excellent. In this conjunction, one question still remains: is it possible to plate the alloy 42 leadframes by Sn-Bi alloy coating with relatively high bismuth content and avoid their cracking after bending?

A labscale experiment flow comprise of *electroclean→ rinse →predip →rinse →plating→ rinse →neutralizer→rinse→dry*. The concept of loading was manual. The following plating conditions were used for electrolyte testing: volume- 4L beaker; anode- insoluble, current - 9A per lead frame strip, agitation - magnetic stir and by hand also, temperature- 50±1^{0}C. Two leadframes were coated in each electrolyte. Two electrolytes with different bismuth content were prepared for testing. One of them can produce deposits with 10% of Bi but second one gives only near 5% of Bi. The electrolyte composition was (g/L): Sn-60 (as metal), MSA-100, inhibitor - 0.2, anti-oxidant -1.2, ligand -1.2, brightener- 4ml/L. Bi content (as metal) in first and second electrolytes was 2.8g/L and 2,1g/L, respectively. The results were summarized in Tables 4-6 and Fig.14.

According to XRD measurements the thickness of obtained coatings is about 8.3 microns. The Bi content in all tested alloy coatings is more than 5%, therefore, expected antiwhiskering properties should be excellent, but bending properties may be poor.

It was also found that uncoated alloy 42 leadframe is almost unstressed. Measured stress values of Sn-Bi alloy coatings are greater than those for pure tin (see Fig.14). Such behavior may be expected, because bismuth atoms are interstitial atoms. A tin lattice distortion is greater at the presence of bismuth, therefore, the more bismuth in the alloy the greater tin lattice distortion is produced. XRD spectra clearly demonstrate the separate peaks of bismuth and tin phases, i.e. a two-phase system.

Table 5 shows results of thermal cycling. Indeed, the sample with 10% of bismuth reveals higher resistance to whiskers surface density. According to SEM image only few whiskers were detected after 500 cycles of testing. On the other side, it was surprising to find that the whiskers in the latter case were slightly longer compared to sample with 5% of bismuth (see Table 6). We suppose that short whiskers formation in second case may be attributed to delocalizing effect of residual stresses under the conditions leading to higher whiskers generation density.

For coating the local effect of residual stress is more dangerous, because it generates high specific stress density in local area of the surface and as a final result long whiskers are formed. Greater driving force of whisker growth in weak areas, with thin tin oxide film easy for breakthrough, results in longer whiskers formation in case of low whiskers density. In our opinion, this phenomenon is analogous to pitting depth at localized corrosion, where pitting corrosion prevention is often provided by delocalization of corrosion process. From the practical point of view it may be concluded that the maximum length of whisker is less dependent from Bi content than whiskers surface density at the equal conditions.

The images presented in Table 6 clearly show cracking of the Sn-Bi alloy plated leadframes after temperature cycling. This known phenomenon often is explained by the difference in the coefficients of thermal expansion *(cte)*. For instance, pure tin has a *cte* of $23 \cdot 10^{-6}$ /K and A42 has a *cte* of $4.3 \cdot 10^{-6}$ /K. The large difference in *cte* of tin and A42 causes excessive compressive stress in the tin based layer with the temperature rise. Of course, such coatings behavior depends on physical-chemical properties of coating material.

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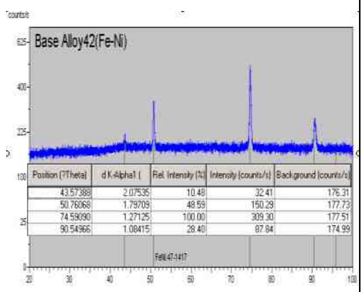
Table 4. *Results of XRF composition and thickness measurements of middle part of coated alloy42 lead frame*

First Electrolyte					**Second Electrolyte**				
Measured point	**Thickness**		**Bi, %**		**Measured point**	**Thickness**		**Bi, %**	
	Sample #1	**Sample #2**	**Sample #1**	**Sample #2**		**Sample #1**	**Sample #2**	**Sample #1**	**Sample #2**
1	8.13	7.89	10.25	9.22	1	8.24	8.09	5.07	5.55
2	8.21	8.20	9.92	8.94	2	8.38	8.39	5.15	5.45
3	8.44	7.90	9.92	9.22	3	8.06	8.54	5.15	5.27
4	8.27	8.46	9.76	8.83	4	8.18	8.92	5.14	4.86
5	8.48	8.02	9.58	8.99	5	8.11	7.80	5.18	5.43
6	8.08	8.00	10.25	9.08	6	8.03	8.37	4.99	5.06
7	8.29	8.34	10.14	8.46	7	7.93	7.69	5.38	5.56
8	8.11	8.50	10.76	8.66	8	7.58	8.32	5.37	5.28
9	9.04	8.09	9.44	9.10	9	8.91	8.71	4.84	5.28
10	8.68	8.84	9.77	8.46	10	7.90	9.14	5.43	4.69
11	8.92	8.59	9.88	8.93	11	8.90	8.82	4.83	5.16
12	9.16	8.58	9.74	8.85	12	8.53	8.86	4.98	4.99
avg.	**8.38µm (330µin)**		**9.42**		**avg.**	**8.35 µm (328µin)**		**5.17**	
std.	0.35µm (13µin)		0.62		**std.**	0.43 µm (17µin)		0.24	
max.	9.16µm (360µin)		10.76		**max.**	9.14 µm (360 µin)		5.56	
min.	7.89µm (311µin)		8.46		**min.**	7.58 µm (298 µin)		4.69	

<table>
<tr><th>Alloy42 leadframe substrate</th><th>XRD data of Sn-Bi (9.4%BI) alloy coating</th><th>XRD data of Sn-Bi(5.1%) alloy coating</th></tr>
<tr><td>


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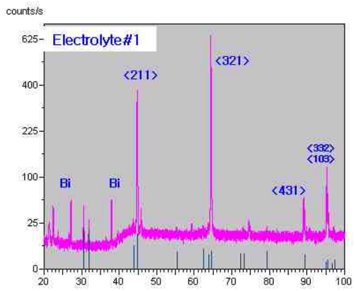

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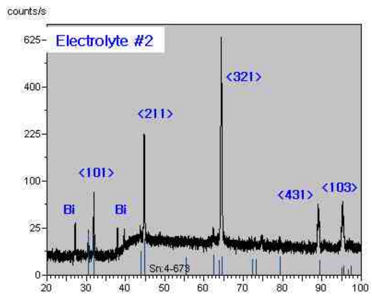

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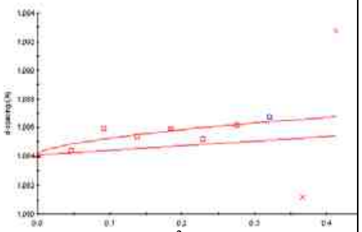
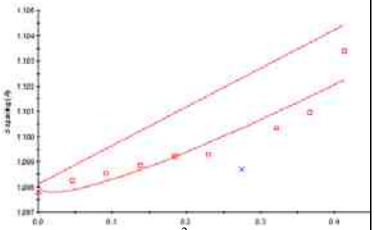
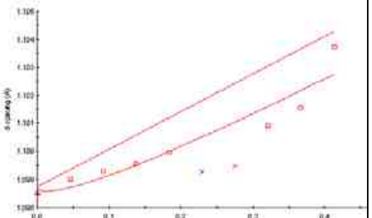

sin²ψ
Almost zero stress,
342,5± 453,7 MPa
(49674±65801psi)
</td><td>

sin²ψ
Tensile stress,
510,8 ±114,8 MPa
(74083±16650psi)
</td><td>

sin²ψ
Tensile stress,
447,4 ±108,1 MPa
(648883±15678psi)
</td></tr>
</table>

Fig.14. *XRD patterns and ω-stress values of Sn-Bi alloy coatings on alloy42 leadframe*

Finishes cracking during bending test may be due to high bismuth content and intrinsic deformation behavior. Metallurgical alloys of similar composition was shown[7] to be supersaturated solid solutions at room temperature and deformation behavior of such dilute solid solutions makes these alloys brittle. On the other hand, it is known[8] that bright tin and tin alloy coatings are relatively brittle and their columnar structure can result in cracking when connector pins are bent. In case of components for surface mounting, the area of bending is located right at the point of soldering, and cracking exposes the substrate metal. If such exposed areas are oxidized, solderability suffers markedly there. Our semi-matte coating also have columnar structure, therefore, for cracking prevention and improving their elongation property it is necessary, for example, to decrease bismuth content in the alloy and to increase the average grain size of crystals up to 3-4 microns. Proper additives and plating condition adjusting are crucial for achievement this goal.

***Table 5.** Results of leadframe coating performance evaluation.*

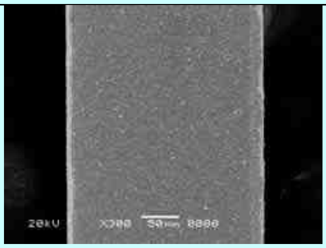
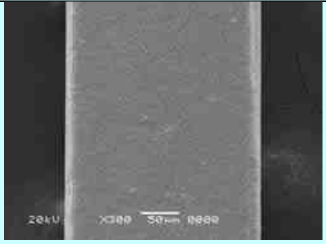
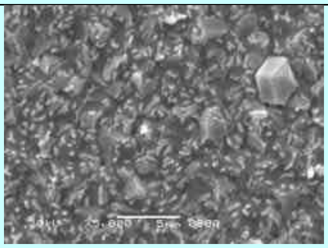
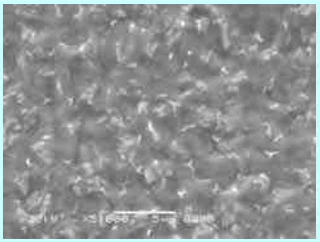
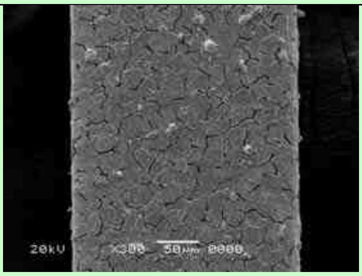
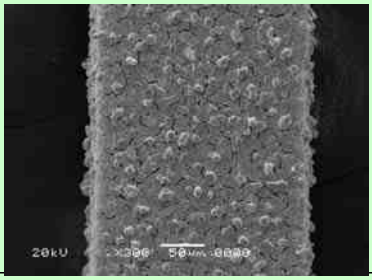
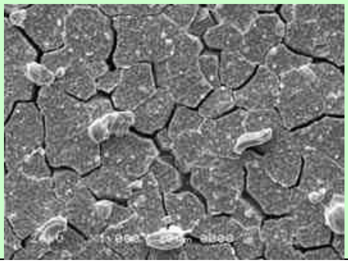
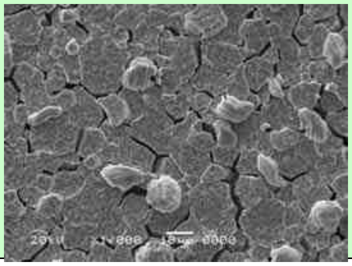
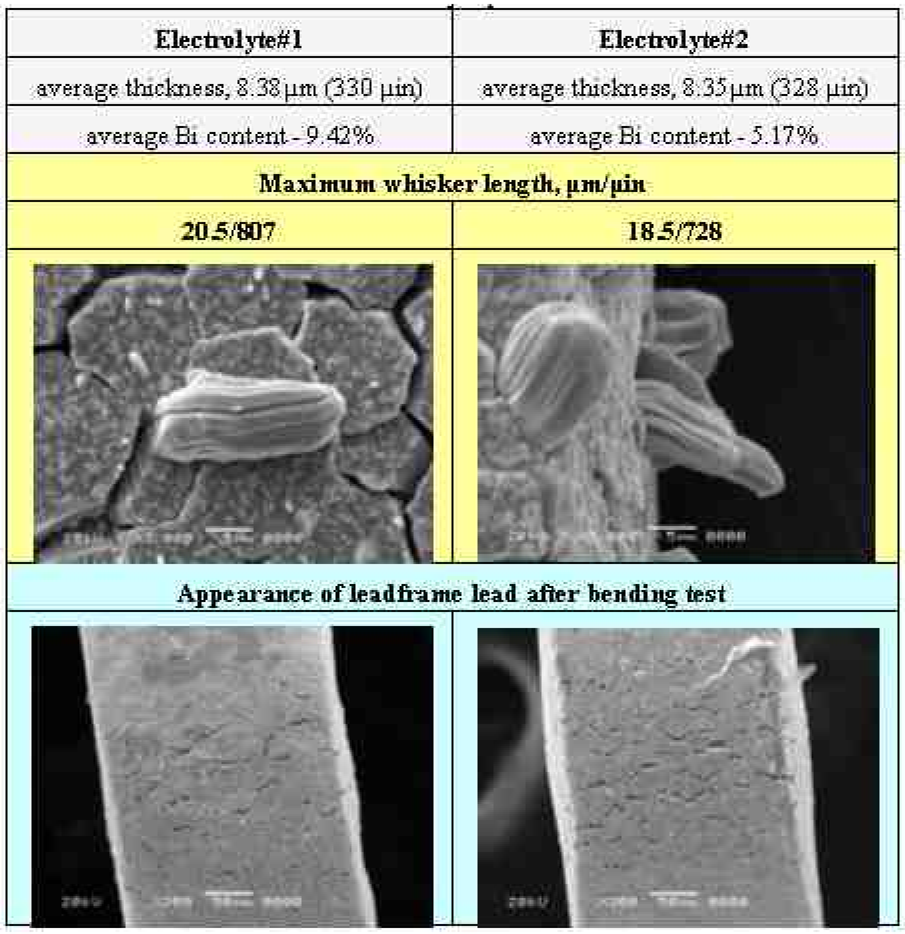
Electrolyte#1	**Electrolyte#2**
average thickness, 8.38µm (330 µin)	average thickness, 8.35µm (328 µin)
average Bi content - 9.42%	average Bi content - 5.17%
Leadframe lead after plating, x300	
	
Leadframe lead after plating, x5000	
	
Leadframe lead after thermal cycling (500 cycles, -55/+125□) x350	
	
Leadframe lead thermal cycling (500 cycles, -55/+125□) x1000	
	

Table 6. *Results of electrolyte performance evaluation.*



Electrolyte#1	Electrolyte#2
average thickness, 8.38 µm (330 µin)	average thickness, 8.35 µm (328 µin)
average Bi content - 9.42%	average Bi content - 5.17%
Maximum whisker length, µm/µin	
20.5/807	18.5/728
Appearance of leadframe lead after bending test	

Summary

From the evaluations of tin and tin-bismuth alloy coatings, the major results can be summarized as follows:

1. Performance characteristics of tin and tin-bismuth alloy electrolytes with additives of oxyethylated polymers were carried out. Highest cathodic polarization is revealed with the polymer of 2900 molecular weight as a brightener additive not only for pure tin electrolyte, but for Sn-Bi electrolyte also. Grain size of matte tin deposits depends on their thickness. Dendrite growth can be effectively inhibited by addition of small quantities of tetraalkylammonium salts.
2. All tested tin and tin-bismuth alloy samples have tensile residual stresses. Tin deposits obtained from MSA electrolyte with oxyethylated polymer especially with additive “A” demonstrate strong beneficial <220> preferred orientation, but tin-bismuth deposits consist of separate tin and bismuth phases where tin phase reveals detrimental <211> and <321> preferred orientation. Tin electrolyte with such additives may be recommended for detailed testing in the future. According to XRD studies the “room” temperature of

electrolyte is beneficial for tin crystal growth along <220> planes. However, elevated temperatures as well as bismuth addition in the tin matrix affect more the <321> preferred tin crystal growth

3. Main peculiarities of Sn-Bi alloy electrodeposition were outlined and basic components of tin-bismuth bath formulation were suggested, considering their roles. It was found that organic aromatic substances containing sulfur atoms are good inhibitors for prevention of bismuth electroless deposition on alloy 42 substrate and oxyethylated additive does increase the inhibitors action.
4. It was found by XPS that alloy coatings with relatively high bismuth content obtained on brass substrate show low surface zinc concentration. Copper atoms were not found on the surface of such coatings.
5. Testing of alloy 42 leadframes coated by Sn-Bi (5…10%) obtained from two domestic electrolytes was done. Resistance to whiskering of such coatings is sufficient for customer needs, but bending properties were unsatisfactory. The difference in whiskers length was related to delocalizing effect of residual stresses leading to tin oxide breakthrough. The analogy with pitting corrosion was suggested.

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