Making the Lead-free Transition: The Enigma of Tin Whiskers in Connector Applications

Sudarshan Lal and Thomas D. Moyer

Component finishers have long relied on tin-lead coatings because of lead's ability to inhibit whisker formation. Presently, the industry is forging ahead with lead-free solders and finishes due to impending legislation and environmental directives from businesses. Several lead-free alternate finishes such as tin, tin-bismuth, tin-silver, tin-zinc, Pd, Pd-Ni-Au have been proposed. To date the preferred lead-free coating is pure matte tin over a nickel under-layer. However, with this coating system there remains a risk of whisker formation and the major concern is that not all of the factors relating to whisker generation are known.

This paper describes results of one aspect of our search for suitable pure tin chemistries and a definition of their process limits. This particular designed experiment investigated the critical parameters of three candidate baths and evaluated them versus the critical response variables, whisker formation. To gain a better understanding of the whisker phenomenon, we included another input variable, tin thickness, and then correlated all these input variables to numerous response variables such as coating morphology, grain size, carbon content, etc. and resulting whisker growth and density. Based on this work, (and additional related work) we have been able to select suitable chemistries and have determined their acceptable process windows.

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Introduction**:** Due to a ban of lead from electronic finishes, it is getting extremely important to evaluate alternate lead-free coatings, which are already in use in electronic applications. One of the viable options is use of pure tin {1-2}. Several commercial matte tin chemistries are available. Unfortunately, all tin chemistries are not identical especially for their processability, appearance, morphology, storage stability, solderability and whiskering tendency. It is imperative to evaluate thoroughly a given plating chemistry with special emphasis on its plating process, and deposit characteristics. This paper describes our evaluative results on three pure matte tin coatings with respect to process and tendency of whiskering. The effects of variability in process conditions and the role of grain size, crystallographic orientation, carbon content, tin thickness, and the aging environment on whiskers was investigated.

This study was undertaken to accomplish the following:

a) Evaluate and establish acceptable bath process limits by using a well structured set of designed experiments (DOE)
b) Characterize the coating properties such as appearance, morphology, grain size and orientation, deposit stress, deposit impurities, and total carbon, total hydrogen, and oxygen content, and relate them to whisker tendency.
c) Examine the effects of two different aging environments on whisker formation.

Experimental**:** Three commercial tin chemistries were selected for this investigation. Each tin bath consisted of four components: tin concentrate, methane-sulfonic acid concentrate (MSA), an additive and antioxidant. A fractional factorial DOE was carried out by varying the concentrations of tin, acid and the additive with low, optimum, and high levels of each component in presence of constant amount of anti-oxidant. The bath components were varied in the ranges given below:

Tin concentration range: 40, 80, 120 g/l
MSA concentration range: 70, 100, 130 g/l
Primary Additive: 25, 50, 75ml/l
The antioxidant additives were kept constant in each case.

The bath identifications, run orders, and conditions are shown in Table I. To maintain propriety, commercial baths are identified as Chemistry A, B, C. All tin plating was done on pure OFHC grade copper foils with 2 µm Ni under-layer, using a rotating disk electrode (RDE) @ 500 rpm in a 2L thermostated double walled beaker at 45ºC. The plated coupons for whisker study were prepared as shown in the run orders at current densities of 150 asf, 225 asf for desired plating thickness. Total carbon in the deposits at varying current densities, were determined by gas fusion technique. Macro-stress determinations were made on Be-Cu strips using a deposit stress analyzer. Microstress and grain orientations were studied by X-ray diffraction (XRD) technique. All samples were subjected to 500 thermal shock (TS) preconditioning cycles with temperature range –55ºC to 85ºC, 20 minutes cycle and 10 minutes of dwell time {3}. The preconditioning method used was thermal shock instead of sample bending. The plated foils after thermal cycling were exposed to two different conditions: a) room temperature (RT) and ambient humidity and b) 55ºC and 85% relative humidity (T, RH).

Results:

Current Density and Plating Rates: Table II summarizes the plating rates at varying current densities for different plating baths for Chemistry A. The data shows some variations in plating rates with changes in bath compositions. This implies that the bath can be operated under imbalanced chemistry conditions. However, it is against good plating practices to do so. The imbalance in chemistry may tend to change plating morphology as well as its response towards whiskering. The average plating rates were found to be linear with current density (@ 75 asf = 0.053 µm/sec, @ 150 asf = 0.104 µm/sec, and @ 225 asf = 0.149 µm/sec.).
The coating was satiny matte in appearance in current density range of 75-150 asf. The finish tends to be slightly darker at the edges @ 225 asf, which is probably due to the higher effective current density effect at the edges. This cosmetic effect (graying) was worse at 300 asf. The impact of higher current densities on organics breakdown is not known at this time. However, the bath suppliers claim there are no adverse effects on deposits when plated in aged baths provided the bath components are maintained at the desired concentrations. We tested one of the chemistries up to one metal turn over (MTO) and obtained excellent results. Thus a better control on bath chemistry especially organic additives is imperative in aging baths.

Effect of agitation: The effect of agitation (increasing rpm of RDE) was studied at current densities of 150, 300 asf. The results are summarized in Table III. At lower current density and low agitation rates, the deposit tends to be gray at the edges, which improved considerably at higher rpm > 500. The graying effect is due to limited mass transport of solution at lower rpm. This suggests that adequate agitation on the plating line will be an important factor, in addition to current density. At higher current density (300 asf), tin deposits were dark and grainy. These deposits improved at higher agitation conditions. This shows that deposits with acceptable morphology at higher current densities may not be possible under low agitation conditions. It is likely that pure tin chemistries can be operated at a speed similar to current tin-lead chemistries.

Total Carbon in Deposits: Copper foils were tin plated in different baths at varying current densities for longer times in order to produce at least 1.5-2.0 grams of tin coating. Total carbon at varying current densities for chemistries A, B, C are summarized in Tables IV, V, VI. Bath # 5 from chemistry A exhibited the highest carbon content (range 79-139 ppm) in current densities varying from 75 asf to 300 asf. In general, carbon levels tend to decrease at higher current densities, with a few exceptions. These carbon levels are typical for matte tin finishes and are significantly lower than the bright tin finishes. It is preferable to have reduced amounts of carbon in deposits for better solderability and low effective stress levels in deposits. Higher compressive stresses in deposits are known for whisker generation. In general, all chemistries produced deposits with low carbon, which should be beneficial in stress reduction.

Coating Morphology and Grain Size: The plating morphology of the tin coatings plated from chemistry A at given current densities was examined using SEM at 2000X (figure 1). It may be noted that the morphology is dictated by current density and chemical composition of the bath. Relatively smaller grains were noticed at lower thickness @ 150 asf. The topical examination by SEM provides an estimation of virtual grain size of the coatings and it was in the range of 2-5 µm. Grain size of the coatings by cross-section method appear to be larger > 10 µm (Fig. 2). SEM examinations of coatings from chemistries B and C had similar morphologies.

X-ray Diffraction Studies: X-ray diffraction (XRD) technique on tin coatings was employed for estimation of residual stress in tin coatings and to study its texture (preferred grain orientation). The popular $\mathrm{Sin}^2\psi$ method is employed in measuring the stresses in fine-grained polycrystalline materials. XRD provides a direct measurement of residual strain on a given coating by measuring the expansion or compression of lattice plane spacings in the grains of materials. The residual stress is computed from the measured residual strain. Subtle peaks of various species of different grains are obtained and the intensity of each peak is measured by the ratio of experimental intensity vs. its random orientation intensity. The residual stress and texture in samples from various baths from chemistry A are is given in Table VII.

The residual stress was found to be low in these coatings and in general was of tensile nature. Some baths (#5 and # 9 @ 150 asf) produced coatings with compressive stress but the values are close to resolution limit of 500 psi. The residual stress may vary with plating thickness and measurements are more reliable on a rigid substrate. Tin has two forms: a) gray form, which is cubic and b) synthetic tin, which is tetragonal. The preferred orientation is depicted graphically in figure 3. It is apparent that 220 orientation is the strongest in all these films plated from these baths at current densities of 150 and 225 asf. The other preferred orientations were 321 and 431.

The residual stress and preferred grain orientation for coatings obtained from chemistries B and C are given in Tables VIII and IX respectively. Coatings from chemistry B had 101,201,311 orientations depending on bath type and current density.

Whisker Studies: All eighteen tin plated coupons, plated at two current densities, from nine different baths, were examined initially using SEM. Only a few baths showed some OSEs (2-10 in number) with height < 5 µm. These samples were subjected to 500 thermal shock (TS) cycles (under specified temperatures and dwell times) and were inspected for whiskers. An area 250 µm X 250 µm was SEM examined and the number of OSEs/ whiskers counted from those images. The representative results after TS are summarized in Table X.

In general, analysis of multi-variables by using a statistical analysis JMP-ANOVA indicated that thickness was the most important factor in the formation of small whiskers and generation of OSEs. Numerous OSEs were observed at higher thicknesses (10 µm) compared to only few OSEs at lower tin thicknesses (2.5 µm). OSE density appears to depend on tin thickness. A thicker coating produced more OSEs, indicating that more material is required to produce higher density of OSEs. SEM photos in Figure 4 depict their dependence on plating thickness. These samples are in environmental chambers and the growth of these OSEs/whiskers are being monitored monthly. Whisker/ OSE examinations after 4 months of environmental exposures did not show further growth with a few exceptions. The results are summarized in Table XI.

Stress in deposits: Stress was determined with a stress monitor where the flexure beam deflection was measured after plating at time zero. The stress levels were low and tensile in nature. The variation of stress with current density is summarized in Table XII.

The deflections of stress strips tend to decrease with time when plated over copper substrate. The changes in deflections (which are proportional to changes in stress) were monitored with time, and stresses were calculated. A representative graph is shown in Figure 5. The macro- stress was tensile in nature and appeared to decrease with time (moving towards compressive stress) due to diffusion of copper in tin resulting in formation of Cu_6Sn_5 intermetallics. This behavior was not observed in presence of Ni under-layer, which retards the diffusion of copper into tin.

The variation of stress in tin coating (A) in presence of 900 ppm of zinc is shown in Figure 6. There is a rapid decrease in tensile stress in the beginning and then it decreases gradually. This indicates fast diffusion of copper into tin atoms initially forming intermetallics and IMC layer slows down further migration thus accounting for the monotonic decrease. It appears that the stress has a tendency of moving towards compression with more zinc atoms. The presence of zinc could not be confirmed by EDX. The role of zinc in stress variations is not clear yet.

Total Hydrogen in Deposits: Total hydrogen (co-deposited / adsorbed) in tin coatings from bath A at two current densities was determined in duplicate by fusion in a graphite crucible heated by an electric current. Hydrogen gas liberated from the coating was swept with pre-purified argon carrier gas and detected using thermal conductivity. (Table XIII).

Total hydrogen in the tin plated sample @ 150 asf is about 10 ppm and this increases by 34% at higher current density of 225 asf. This clearly shows that at higher current densities, electrolysis of the solution generates more hydrogen at the cathode and is incorporated in the deposit producing a more stressed film. This may contribute to higher risk for whisker formation.

Total Oxygen in Deposits: Total oxygen in tin deposits from chemistry A at two current densities was determined by combusting the sample in a graphite crucible. The oxygen released from the sample combines with carbon from the crucible to form carbon monoxide and carbon dioxide and these gases are monitored in an infrared (IR) cell. (Table XIV). The total oxygen in the deposit seems to be independent of current density. Most of the oxygen is probably due to self-limiting surface oxidation of tin coating. Auger Spectroscopy and SERA techniques may be useful in further investigations.

Effect of Impurities:
a) Nickel Ions
The effect of Ni ions as impurities was studied on plating rates and stress levels (Table XV). The coating appearance was still satin in presence of 1145 ppm of Ni^{2+} and internal stress (@ 150 asf) was tensile in nature. No appreciable effect on plating rates was noticed.

b) Zinc Ions
The effect of zinc on current efficiency and stress was also monitored in the presence of varying amounts of zinc ions. In the presence of 900 ppm zinc, a tensile stress of 414 psi was measured.

Whisker formation is a complex phenomena and several mechanisms are postulated for their appearance and growth. Galyon has recently compiled an excellent bibliography on the subject {4}. A sudden appearance of long whisker in a pure tin coating poses a serious risk in high reliability, fine pitch applications. Considering these potential risks, NEMI user group has issued guidelines {5}. OEM's and CM's should make a judicious selection of finishes based on the end use of a given product.

General Conclusions:

In general, our designed experiments showed we could operate three commercial pure matte tin baths and produce coatings with good properties with generally acceptable amount of whiskering. Acceptability of such coatings will be determined by specific customer needs. We continue to evaluate conditions that further reduce the tendency to form whiskers in pure matte tin deposits. Specifically, we learned the following:

1. The plating baths were best operated at 45ºC and in current density range 150-225 asf. The CD range may be extended depending on Sn (II) concentration and effective agitation in plating cells.
2. In the range tested, the deposits had low carbon (30-144 ppm range), 10 ppm total hydrogen and total oxygen 156-170 ppm.
3. XRD results indicated low tensile stress in deposits. The preferred grain orientation was 220 in two coatings. However, no direct correlation of texture vs. whiskering tendency was noticed.
4. Thermal shock results show that OSE formation was dependent on coating thickness. More OSEs were observed on 10 µm thick deposits.
5. Whiskers and OSE formations of varying lengths were noticed under different environments. Whiskers < 50 µm were found in some samples after three months exposure at high temperature and RH. Heat and high humidity seemed to favor OSE/whisker growth.

Acknowledgements: The authors appreciate the help of CDC, Americas Product Test Lab for whisker testing and useful comments from the technical staff of CDC, Americas.

References:

1. S. Lal et al, “Lead-free Coatings in High Speed Electronic Connectors,” Plating & Surface Finishing, Vol. 90 (9), pp. 43-51, 2003.
2. P. Elmgren et al, “Pure Tin: The Finish of Choice for Connectors,” IP/JEDEC 4th Annual International Conference on Lead Free Electronic Assemblies and Components, Frankfurt, Germany, October 2003.
3. NEMI Tin Whiskers Growth Tests, Rev. 4.5,September 2003.
4. G. T. Galyon, “Annotated Tin Whisker Bibliography and Anthology,” NEMI Tin Whisker Modeling Project, July 2003.
5. NEMI Tin Whisker User Group Report, March 2004.

Table I

Run Order & Conditions For Each of 3 Commercial Chemistries

Run Order	Bath #	Acid Conc.	Tin Conc.	Additive Conc.	Tin Thickness*	Current Density**
1	1	-1	-1	-1	2.5	225
2	1	-1	-1	-1	10	150
3	2	-1	-1	1	2.5	150
4	2	-1	-1	1	10	225
5	3	-1	1	-1	2.5	150
6	3	-1	1	-1	10	225
7	4	-1	1	1	2.5	225
8	4	-1	1	1	10	150
9	5	0	0	0	6.25	225
10	5	0	0	0	6.25	225
11	6	1	-1	-1	2.5	150
12	6	1	-1	-1	10	225
13	7	1	-1	1	2.5	225
14	7	1	-1	1	10	150
15	8	1	1	-1	2.5	225
16	8	1	1	-1	10	150
17	9	1	1	1	2.5	150
18	9	1	1	1	10	225

* Thickness in microns
** Current density in amp/sq. ft

Table II

Plating Rates (µm/s) of Various Baths

CD.,asf	Bath #1	Bath #2	Bath #3	Bath #4	Bath #5	Bath #6	Bath #7	Bath #8	Bath #9	Ave.
75	0.052	0.053	0.049	0.055	0.051	0.054	0.052	0.049	0.061	0.053
150	0.109	0.093	0.107	0.096	0.112	0.098	0.104	0.092	0.121	0.104
225	0.161	0.157	0.141	0.120	0.154	0.147	0.156	0.159	0.154	0.149

Table III

Effect of Agitation, Bath # 1 at Varying Current Densities- Chemistry A

RPM	Pl. Rate, µm/sec (150 asf)	Appearance @ 150 asf	Pl. Rate, µm/sec (300 asf)	Appearance @ 300 asf
250	0.108	Satin/sl.gray edges	0.138	Dark & grainy
500	0.106	Satin	0.190	Dark & grainy
1000	0.106	Satin	0.196	Satin
1500	0.109	Satin	0.197	Satin
2000	0.109	Satin	0.202	Satin

Table IV

Average Total Carbon (ppm) in Deposits From Chemistry A

C.D., asf	Bath # 1	Bath # 5	Bath # 9
75	33	139	56
150	49	129	30
225	57	86	30
300	37	79	41

Table V

Average Total Carbon (ppm) in Deposits From Chemistry B

C.D., asf	Bath # 1	Bath # 5	Bath # 9
75	32	36	57
150	34	33	74
225	44	65	78
300	72	130	144

Table VI

Average Total Carbon (ppm) in Deposits From Chemistry C

C.D., asf	Bath # 1	Bath # 5	Bath # 9
75	37	34	32
150	37	36	21
225	44	35	29
300	69	38	27

Table VII

Residual Stress & Texture in Tin Coatings: Chemistry A

Sample ID	Residual Stress, PSI	Preferred Orientation (h,k,l)
Bath # 1, 150 asf	700 Tensile	220,420,431
Bath # 1, 225 asf	100 Tensile	220,321,431
Bath # 5, 150 asf	-300 Tensile	220,321,431
Bath # 5, 225 asf	900 Tensile	220,321,431
Bath # 9, 150 asf	-400 Tensile	220,321,431
Bath # 9, 225 asf	900 Tensile	220,321,431

Table VIII

Residual Stress and Texture in Tin Coatings: Chemistry B

Sample ID	Residual Stress, PSI	Preferred Orientation (h,k,l)
Bath # 1, 150 asf	2000 Tensile	211,321,431
Bath # 1, 225 asf	900 Tensile	101,312,211
Bath # 5, 150 asf	00 Tensile	211,321,312
Bath # 5, 225 asf	800 Tensile	101,312,211
Bath # 9, 150 asf	-400 Compressive	301,411,321
Bath # 9, 225 asf	-300 Compressive	301,411,321

Table IX

Residual Stress and Texture in Tin Coatings: Chemistry C

Sample ID	Residual Stress, PSI	Preferred Orientation (h,k,l)
Bath # 1, 150 asf	500 Tensile	220,321,431
Bath # 1, 225 asf	600 Tensile	220,431,321
Bath # 5, 150 asf	700 Tensile	220,321,431
Bath # 5, 225 asf	300 Tensile	220,321,431
Bath # 9, 150 asf	-100 Tensile	321,431,211
Bath # 9, 225 asf	-500 Compressive	321,431,220

Table X

Whiskers Evaluation of Matte Tin Chemistry A After Thermal Shock

Bath #	CD,asf	Thickness, uinches	Sample	Ave.Whisker/OSE #	Range OSE-Whiskers
1	225	100	RH	55	5-12 um
1	225	100	RT	99	10-12 um
1	150	400	RH	447	10-20 um
1	150	400	RT	633	15-20 um
2	150	100	RH	47	5-12 um
2	150	100	RT	54	10-15 um
2	225	400	RH	567	10-15 um
2	225	400	RT	533	15-20 um
3	150	100	RH	15	10-20 um
3	150	100	RT	16	12-20 um
3	225	400	RH	427	10-18 um
3	225	400	RT	400	10-15 um
4	225	100	RH	77	10-12 um
4	225	100	RT	72	15-30 um
4	150	400	RH	487	15-20 um
4	150	400	RT	500	10-15 um
5	225	250	RH	360	15 um
5	225	250	RT	320	15 um
5	225	250	RH	280	15 um
5	225	250	RT	280	15 um
6	150	100	RH	47	5-10 um
6	150	100	RT	55	10-12 um
6	225	400	RH	840	15 um
6	225	400	RT	840	15 um
7	225	100	RH	65	15 um
7	225	100	RT	72	10 um
7	150	400	RH	720	15 um Whisker
7	150	400	RT	720	15 um
8	225	100	RH	33	5-10 um
8	225	100	RT	45	5-10 um
8	150	400	RH	660	20 um
8	150	400	RT	660	20 um
9	150	100	RH	45	5-10 um
9	150	100	RT	30	5 um
9	225	400	RH	620	15 um
9	225	400	RT	620	15 um

Table XI

Whisker Results after 4 months of Exposure @ T & RH-Chemistry A

Bath ID	CD, asf	Thickness,µin	Whisker Length, µm
# 1, RH	225	100	25/30/45/57
# 3, RH	225	400	14/18/19
# 4, RH	225	100	11/17/18
#4, RH	150	400	15/18/23
#5, RH	225	250	14/21/23
#6, RH	225	400	11/23/33
#7, RH	225	100	10/16/30
#7, RH	150	400	15/16/20
#8, RH	150	400	15/17/21
#9, RH	225	400	15/18

Table XII

Stress Variation with Current Density in Chemistry A

Current Density, asf	Stress, PSI
150	768 Tensile
225	557 Tensile
300	572 Tensile

Table XIII

Total Hydrogen in Tin Deposits (Chemistry A)

Sample ID	Current Density, asf	Total Hydrogen, ppm
A	150	9.4/10.1= Ave 9.8
B	225	12.5/13.7= Ave 13.1

Table XIV

Total Oxygen in Tin Deposits (Chemistry A)

Sample ID	Current Density, asf	Total Oxygen, ppm
A	150	124/207/180= Ave. 170
B	225	130/153/186= Ave. 156

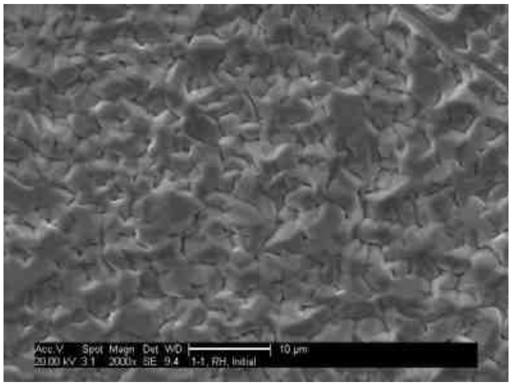
Table XV

Effect of Ni on Plating Rates and Stress

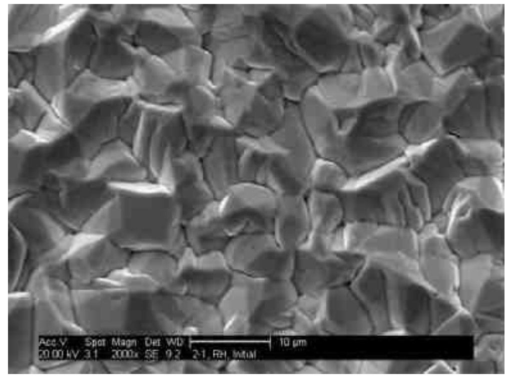
Current Density, asf	Pl. Rate, mg/sec No Ni	Pl. Rate, mg/sec 250 ppm Ni	Pl. Rate, mg/sec 468 ppm Ni	Pl. Rate, mg/sec 1145 ppm Ni
75	0.576	0.571	0.572	0.570
150	1.136	1.153	1.129	1.141
225	1.735	1.693	1.682	1.708
Stress, PSI	377.6*	467.2*	446.8*	494.1*

* Tensile

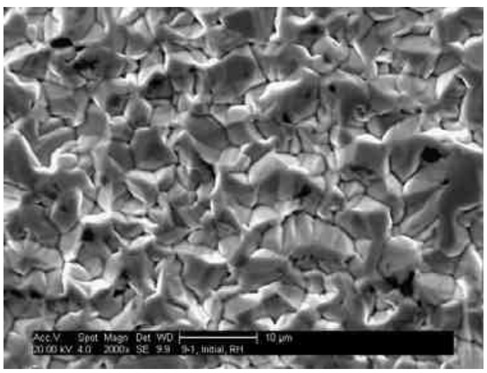
Morphology of Coatings (Chemistry A)



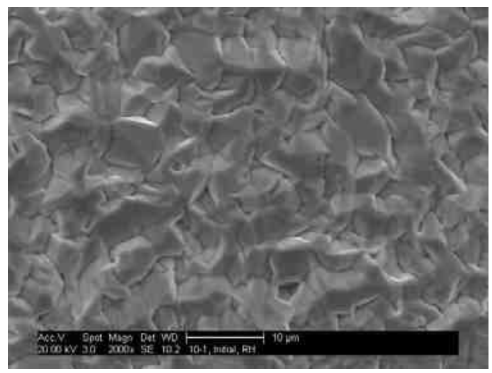
Bath #1, run # 1,100 u" @ 225 asf



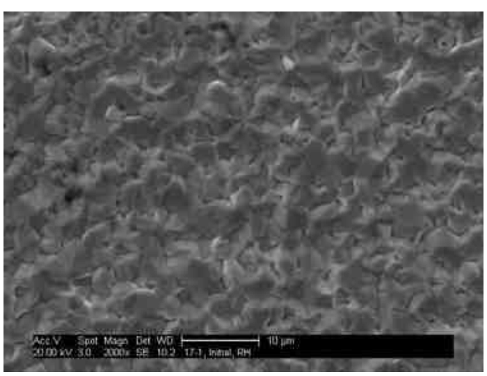
Bath # 1, run # 2, 400 u"@ 150 asf



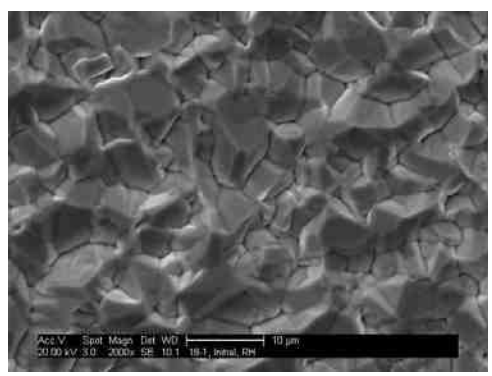
Bath #5, run # 9, 250 u" @ 225 asf



Bath # 5 , run # 10, 250 u"@ 225 asf



Bath # 9, run # 17, 100 u" @ 150 asf



Bath # 9,run # 18, 400 u" @ 225 asf

Figure 1. Tin Morphology

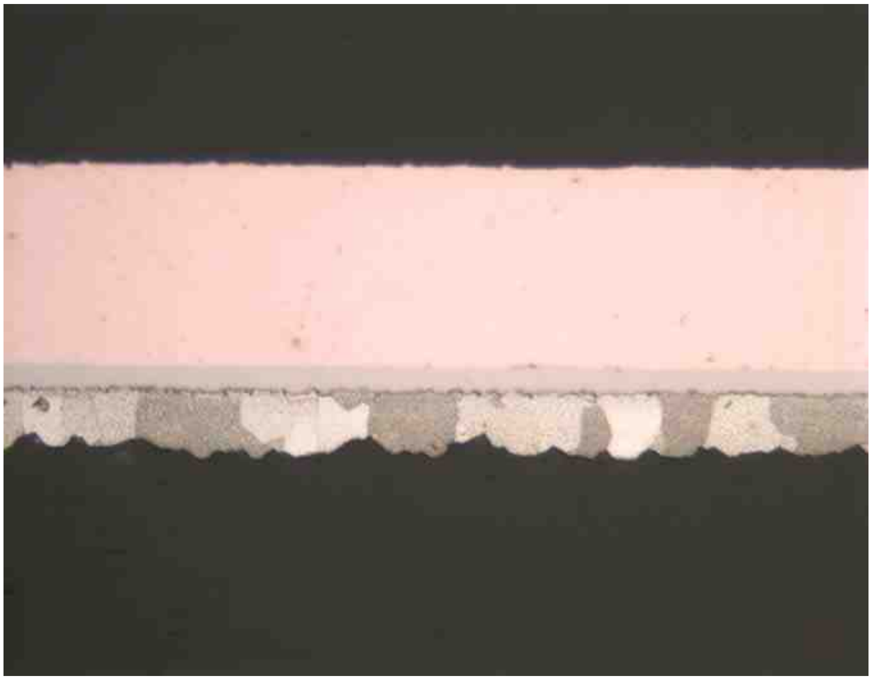


Figure 2: **Cross-section of tin coating plated @ 150 asf in bath # 5: Chemistry A**

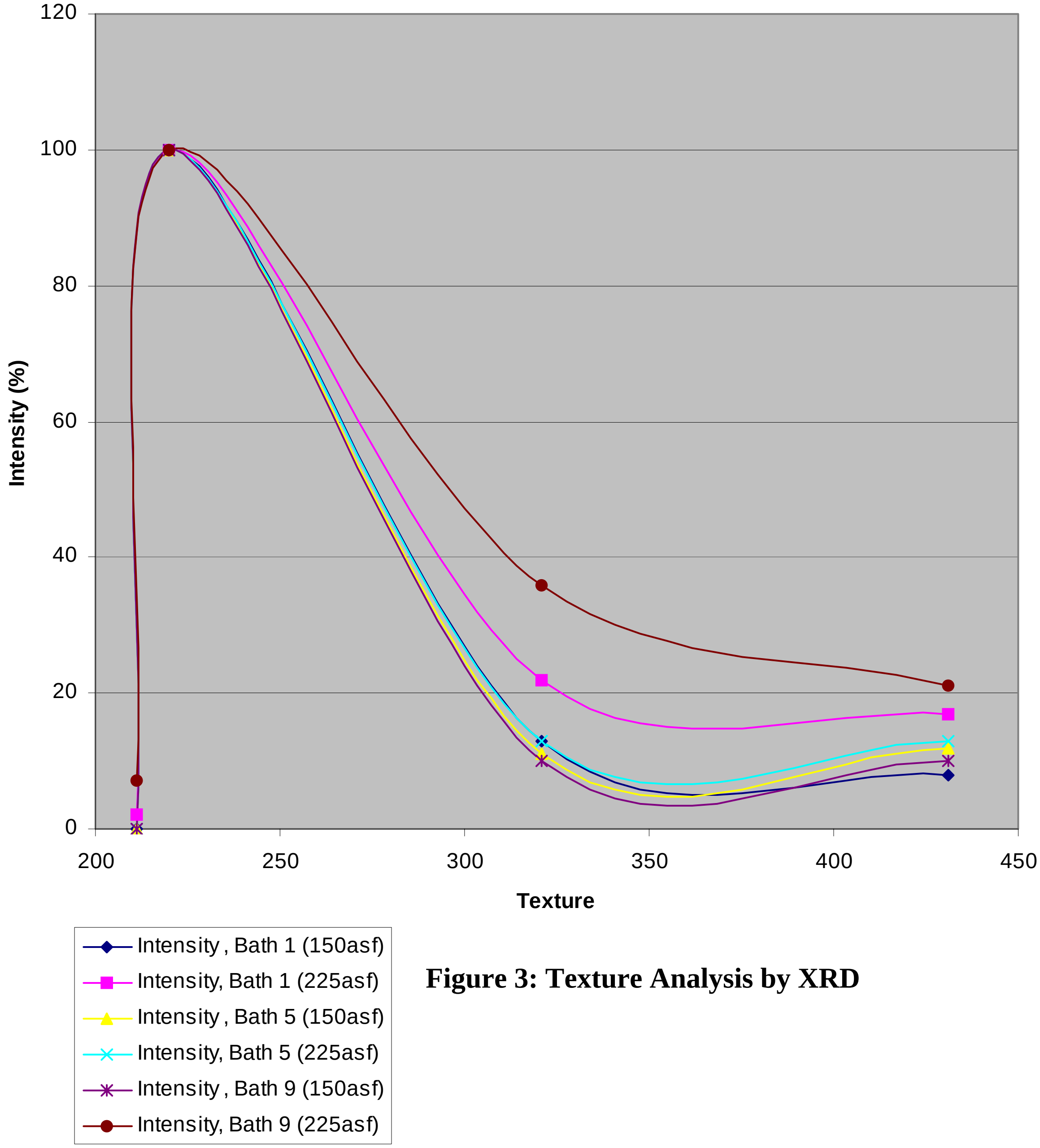
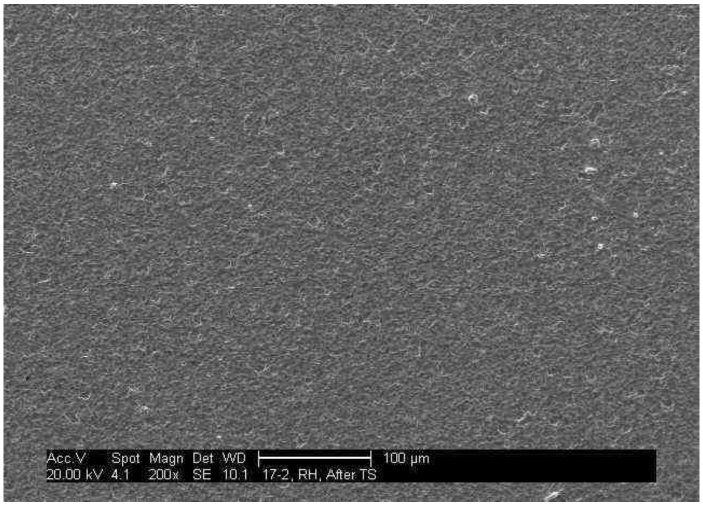
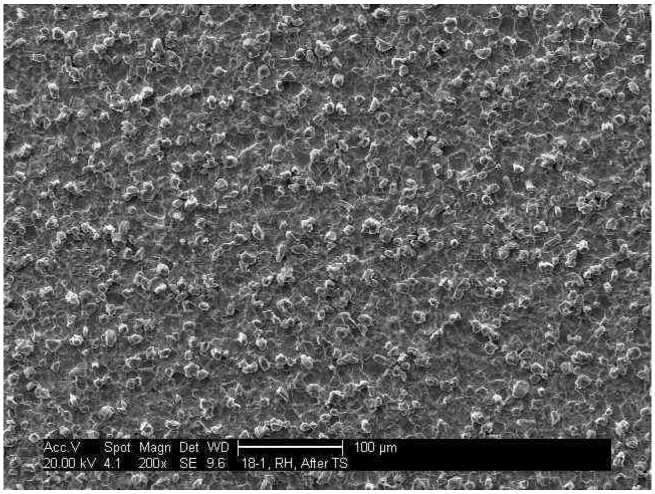


Figure 3: Texture Analysis by XRD



a) 100 µinches



b) 400 µinches

Figure 4: SEM Photos of OSEs at varying thickness after TS

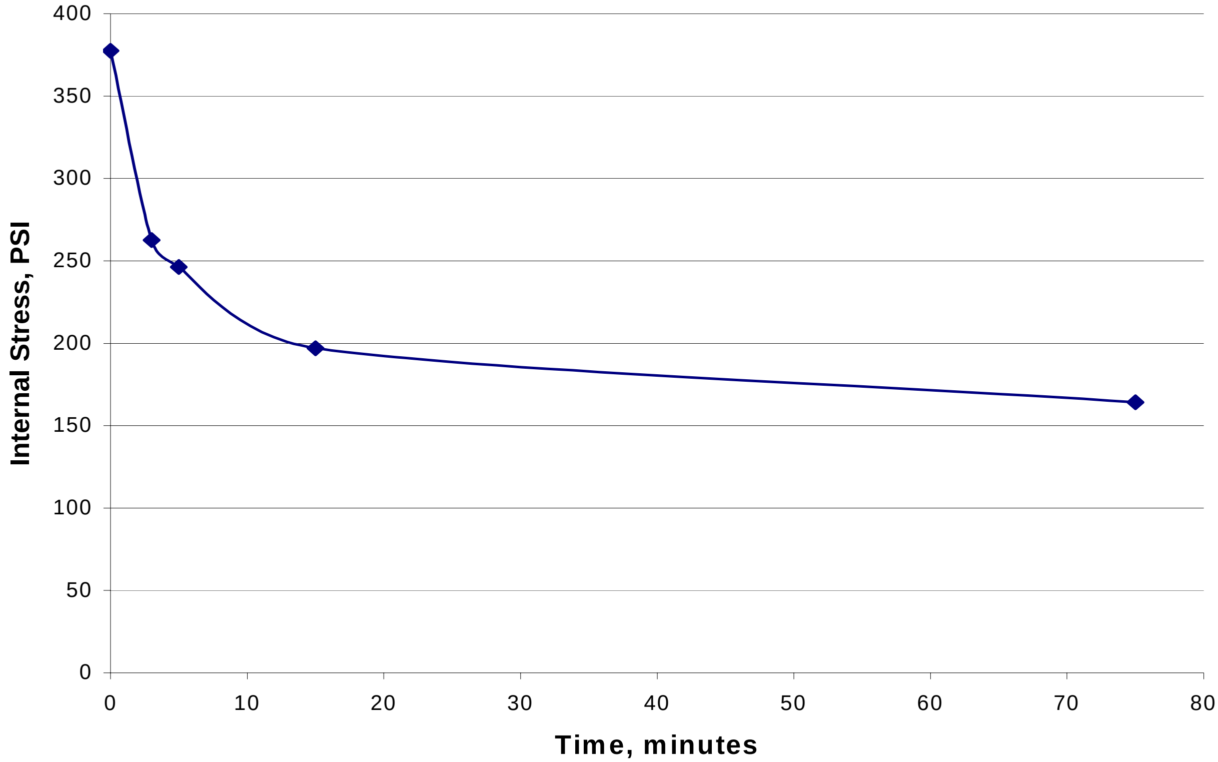


Figure 5: Stress Variation with time

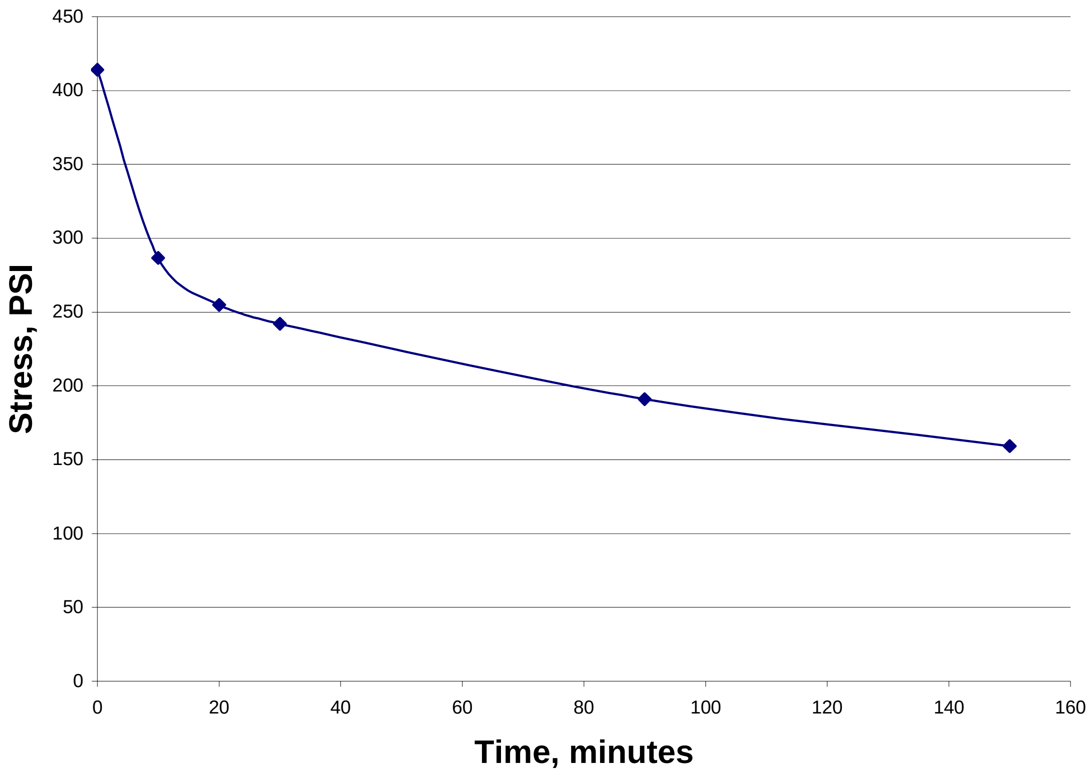


Fig. 6: Stress in Tin deposit in presence of 900 ppm zinc ions

