

Investigating and Characterizing Reduced Whisker Growth from a Bright Pure Tin Process

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Abstract

The implementation of both RoHS and WEEE Directives by the European Union (EU) mandate that electrical and electronic products put on the market within the EU shall contain restrictive amounts of lead. Bright tin-lead plating has been used for decades for electronic components and suitable alternatives have been investigated. One candidate that appears to meet most of the required criteria, such as corrosion resistance, solderability and low cost, is pure tin, however, the use of pure tin inevitably raises the specter of tin whiskers. The mechanism of tin whisker growth, despite the very significant amount of research effort devoted to investigating this phenomenon, remains incomplete. It is understood that compressive stress, introduced into the tin deposit and sometimes inherent within it, is a significant cause of whiskering. Likewise, methods of whisker growth mitigation such as the use of a nickel pre-plate are also well documented. On reviewing the literature it quickly becomes clear that there is a strong bias towards the use of matte tin plating processes. This is at least partially attributable to some basic characteristics of matte and bright processes. Matte tin electrolytes are generally less chemically “complex” than bright ones, and the resultant deposits normally contain less organic materials. Our recent research has characterized the whisker growth propensity of multiple matte and bright plating formulations utilizing recently accepted whisker test methods. We have found that the choice of organic additives used in both matte and bright tin electrolytes can have a profound effect on their respective tendency to initiate whisker growth. We will outline our whisker results in detail and examine key process and coating characteristics which may explain this preferred whisker performance.

Introduction

Tin deposits were initially introduced for use in interconnect applications in the late 1940's after repeated failures of electrical equipment that had been electroplated with cadmium. The mode of failure, short circuits, was identified as being caused by whisker growth in the cadmium deposit^[1]. It was subsequently determined that tin deposits also suffered from whisker growth^[2]. A whisker is defined as “a spontaneous columnar or cylindrical filament, usually of mono-crystalline metal, emanating from the surface of a finish”^[3]. Whiskers are conductive, typically can range up to many hundreds of microns in length, and can initiate in a timescale of seconds to years after plating; see Figure 1 below for an example.

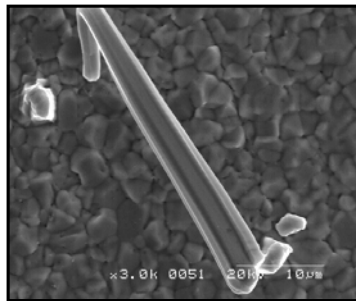


Figure 1 - Tin whisker

Large scale investigation of the phenomenon by various organizations, such as, ITRI (International Tin Research Institute), Bell Laboratories and others of note was carried out in the 1950's. As a result of this research some understanding of the mechanism by which a whisker grows, i.e., by addition of material to the base of the whisker rather than to the tip^[4], was gained. A variety of theories were proposed as to the driving force causing whisker growth in tin deposits, most notably R.M. Fisher et al^[5] published a paper in which the influence of compressive stress in the tin deposit was suggested as the major cause of whisker growth. Around this time many of the whisker mitigation strategies still used in the industry today were also developed. Importantly, Arnold et al^[6] described the use of alloying tin deposits with lead (3-10% by weight) as a means to mitigate the growth of tin whiskers.

The use of tin lead alloys in the production of electrical interconnections has remained the dominant strategy since this time as not only is whisker growth retarded, but other important characteristics such as good solderability and corrosion resistance coupled with low cost are also retained. In the case of bright tin lead deposits, an attractive aesthetic appearance is also achieved.

Following the introduction of the RoHS (Restriction on certain Hazardous Substances) and the WEEE (Waste Electronic and Electrical Equipment) Directives, however, the use of lead containing alloys is no longer a viable option.

Many possible candidates have been proposed over the years as possible alternatives or replacements for tin lead deposits, including tin-copper, tin-bismuth and tin-silver alloys, as well as finishes based on precious metals such as, gold and gold flashed palladium nickel deposits, however, all suffer from some performance, application or simply economic, shortcomings

Pure tin deposits retain many of the desirable performance characteristics required to be successfully used as a material for the production of electrical interconnects. It is a low cost option and is compatible with existing processing procedures and associated equipment. Pure tin electrolytes can also be modified to produce a matte or bright (reflective) deposit depending on the organic compounds added to the electrolyte. On searching through the literature it soon becomes apparent that there is a very large volume of work, since the 1950's, detailing whisker studies in pure tin deposits. It also becomes apparent that there is a strong bias in the industry towards the use of matte tin over bright tin deposits in terms of whisker mitigation characteristics, which has been driven by this body of work^[7].

In this paper we present results of a whisker study wherein matte tin deposits are directly compared with bright tin deposits produced from a new generation of plating electrolytes. It will be shown that deposits can be produced from these electrolytes that are both bright, aesthetically pleasing, and whisker mitigated, frequently equaling, and in many cases, outperforming matte tin deposits tested under identical conditions.

Test Methods and Experimental

Flat, phosphor bronze, test coupons, see Figure 2 below, were plated at a current density of 100 A/ft² with matte tin using commercially available, high speed electrolytes to an average tin thickness of 3-4 microns.

A second set of flat test coupons were plated with bright tin, at a current density of 100 A/ft² using commercially available, high speed electrolytes also to an average tin thickness of 3-4 microns.

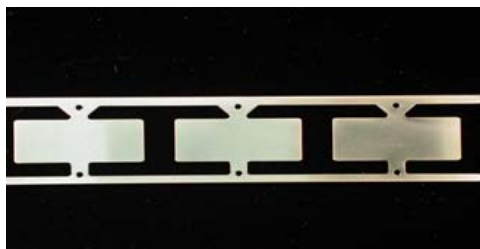


Figure 2 - Test coupons plated

The use of a nickel pre-plate has long been established as an effective whisker mitigation practice^[8,9] and the mechanism by which it is effective has been elucidated by Y. Zhang , Chen Xu et al^[10,11, 12]. During this study, half of all the coupons plated with tin had been previously processed through a standard sulphamate nickel electrolyte, the resulting nickel deposit thickness was 1.5 microns average.

Half of the total number of sample coupons processed, both with and without a nickel pre-plate, were then bent around a mandrel (1 mm diameter) using a three point bend fixture thereby inducing compressive stress into the deposits. The coupons were bent a full 180°C and allowed to spring back. The tin remains stressed due to the elastic spring back differences between the tin deposit and the phosphor bronze substrate.

All the coupons processed, both flat and bent, were then subjected to accelerated whisker test regimes as prescribed by JEDEC/IPC^[13];

- Heat and humidity testing for 4000 hrs at 60°C and 90 % relative humidity
- Thermal cycling between -40 and +85°C for 1000 cycles, 3 cycles per hour
- Uncontrolled humidity for 4000 hrs at 60°C

On completion of the above test cycles a representative sample of the various matte and bright tin deposits, with and without a nickel pre-plate, both flat and bent were evaluated using a Scanning Electron Microscope (SEM) for whisker growth. On the bent coupons the outside radius of the bend, in particular, was evaluated as this is an area where the tin is in compression after forming.

Other information gathered included x-ray diffraction data which was generated using a Rigaku Multiflex 2kW spectrometer to determine the crystal plane orientations of the tin deposits in this study. Scan parameters used were as follows;

- 10 – 100° 2 θ
- step size 0.02°
- scan rate 1.3 – 1.5 s/channel

Carbon content (%C) of the tin deposits was also investigated and was determined as per MIL 38510.

Results and Discussion

Figures 3A below illustrates a typical deposit produced from a matte plating electrolyte. The matte deposit, illustrated here at a 5000X magnification, clearly shows a well defined grain structure, with a grain size in the range of 1-4 microns. Matte deposits are typically highly ductile, slight softer than bright deposits with a carbon content in the range of 0.001% to 0.05% C.

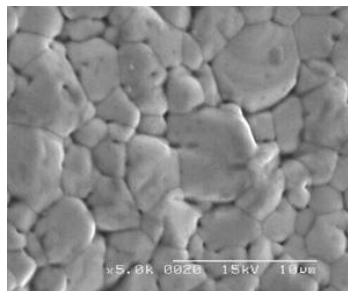


Figure 3A - Matte tin deposit

Figure 3B illustrates, at the much higher magnification of 30,000X, the typical featureless structure of a bright tin deposit. These types of deposits tend to be aesthetically pleasing but are less ductile than matte deposits and can crack if severely deformed. They are also slightly harder than matte deposits and typically have a carbon content in the range of 0.2 to 1.0 % C.

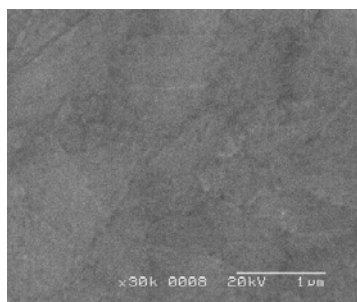


Figure 3B - Bright tin deposit

To be commercially acceptable bright tin deposits need to be haze and pit free and, amongst other important characteristics; discoloration should be minimal after steam age (95 to 99°C for 8 hrs) and IR reflow testing. Figure 4 below clearly demonstrates what is considered to be an unacceptable level of deposit discoloration after a bright tin deposit has been subjected to steam age testing.



Figure 4 - Deposit discoloration after component has been subjected to steam age testing

Significant research efforts have been carried out to identify, eliminate and replace the various organic compounds that induce or at least, significantly contribute to the discoloration of the tin deposit. It has been found that this discoloration is often associated with a high level of occluded organic material (%C) in the deposit and that selection of base and top brighteners used is critical. By choosing a preferred combination of organic components it has been found that the carbon content of a bright deposit can be greatly reduced, from the typical range of 0.2 to 1%, to << 0.1%, whilst still obtaining a highly reflective, haze and pit free deposit. Figure 5 below details the %C content obtained for one such preferred combination of brightener compounds versus two more traditional bright tin processes, plated at a variety of current densities. As mentioned above, a typical matte tin deposit usually has a carbon content in the range of 0.001% to 0.05% C.

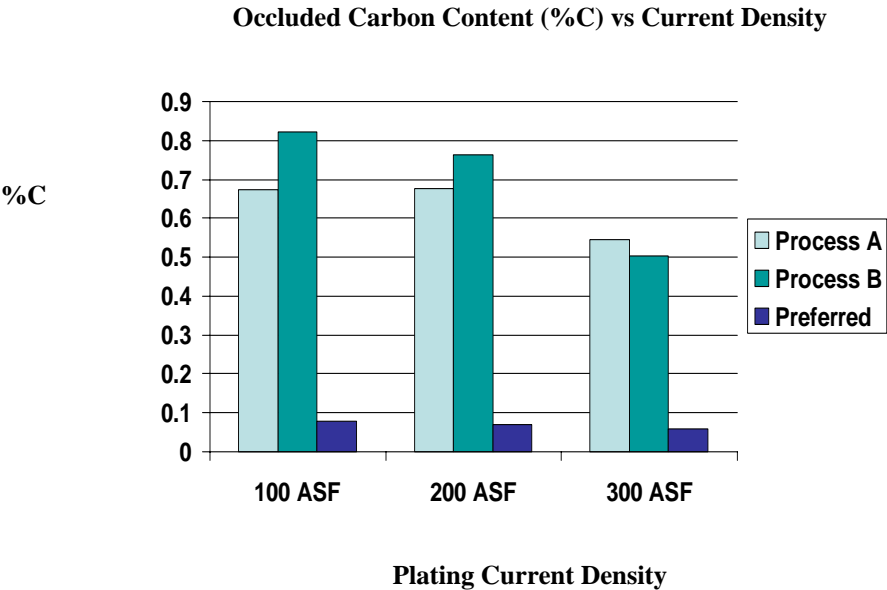
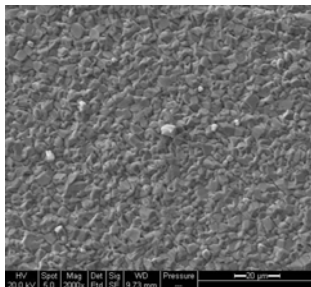


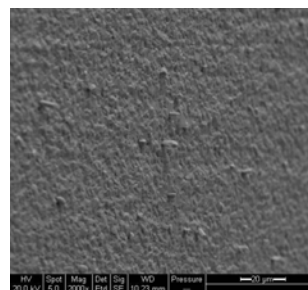
Figure 5 - A comparison of three bright tin processes

As part of qualifying any newly developed electrolyte, whisker testing of the resulting deposit using the procedures now prescribed by iNEMI and JEDEC/IPC^[13] are also routinely carried out. During such a study, where both flat and bent plated coupons, prepared as detailed above, were evaluated. Perhaps surprisingly, it was found that one of the bright tin processes in the study consistently equaled, and in some cases, exceeded the performance of matte tin processes being tested simultaneously for a tendency to whisker growth.

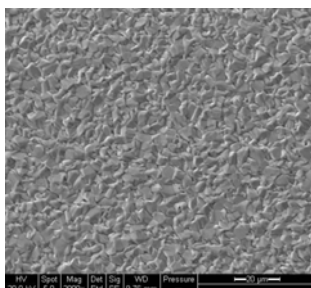
Repeatedly, during the accelerated whisker testing carried out, it was found that of the three test environments, the combination of exposure to both heat and humidity (4000 hrs at 60°C and 90% relative humidity) proved to be the most severe and thus, the most likely to initiate whisker growth, producing a higher population density and longer whiskers. Figures 6A and 6B below details the results obtained for a preferred matte and a preferred bright tin deposit, respectively, for both flat and bent samples, with and without a nickel pre-plate.



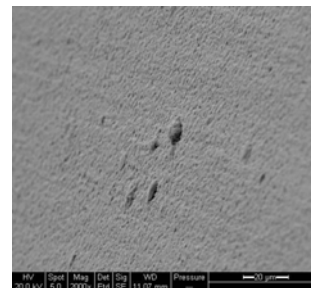
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate

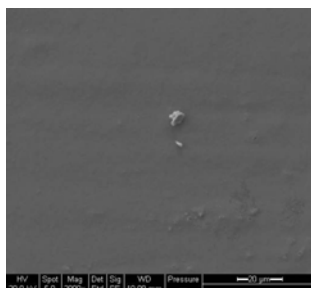


(ii) Flat, with Ni pre-plate

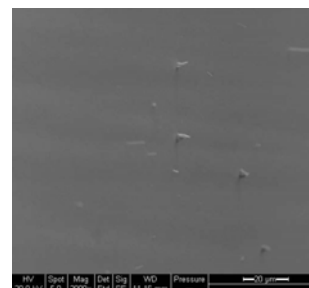


(iv) Bent, with Ni pre-plate

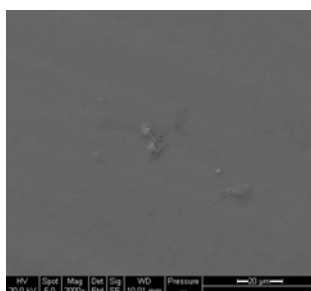
Figure 6A - Matte tin deposit subjected to 4000 hrs @ 60°C and 90% RH at 1000X magnification.



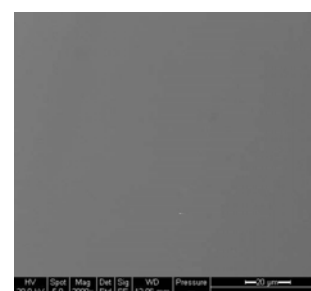
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate



(ii) Flat, with Ni pre-plate



(iv) Bent, with Ni pre-plate

Figure 6B - Bright tin deposit subjected to 4000 hrs @ 60°C and 90% RH at 1000X magnification

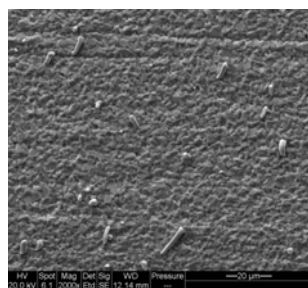
As can be seen in Figure 6A (i) above, slight whisker growth is evident in the preferred matte deposit in the absence of a nickel pre-plate. The maximum whisker length was measured in the range of 7-8 microns. On the flat test coupons, whisker growth is completely mitigated by the presence of a nickel pre-plate, see Figure 6 (ii). This was not the case for the bent samples, where some very slight whisker growth is in evidence, see Figure 6A (iv). Figure 6A (iii) illustrates however, that on samples subjected to a degree of mechanical stress (bent) and with no nickel pre-plate a maximum whisker length of no greater than 8-10 microns was recorded after 4000 hrs of exposure to heat and humidity.

Figure 6B details the results obtained for a preferred bright tin process after heat and humidity exposure. No whisker growth is evident in Figure 6B, with the exception being, perhaps unsurprisingly, a sample that had been bent and not pre-plated with nickel prior to testing. Again, however the maximum whisker length measured in this case was in the range of 10–12 microns. Test samples that had a nickel pre-plate showed no whisker growth, even after 4000 hrs exposure to this aggressive environment.

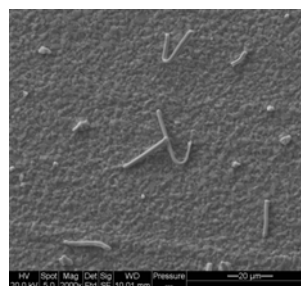
By comparison, Figures 7A and 7B details typical results that were obtained in this study for “non-preferred” matte and bright tin processes, respectively, i.e., where the choice of organic components used to formulate the electrolyte additive system were not optimum.

For “non-preferred” matte tin processes a very significant degree of whisker growth was frequently observed, in the absence of a nickel pre-plate, on both flat and bent coupons. Whisker lengths in the range of 40-50 microns were frequently recorded coupled with a population density often in excess of 1200 whiskers per mm² of deposit area. Figure 7A (iv) illustrates that even with a nickel pre-plate, bent coupons tested generated whiskers, many in the range of 25-30 microns in length.

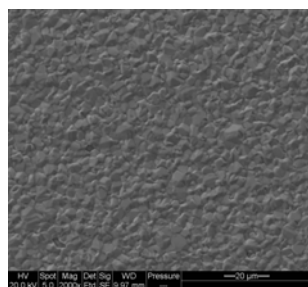
For “non-preferred” bright tin processes tested, whisker growth in the absence of a nickel pre-plate was severe, with whisker lengths often in excess of 100 microns being routinely recorded.



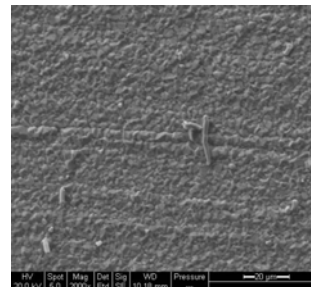
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate



(ii) Flat, with Ni pre-plate



(iv) Bent, with Ni pre-plate

Figure 7A - “Non-preferred Matte tin deposit subjected to 4000 hrs @ 60°C and 90% RH at 1000X magnification

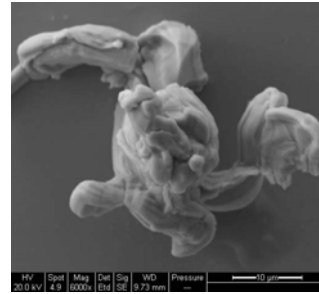
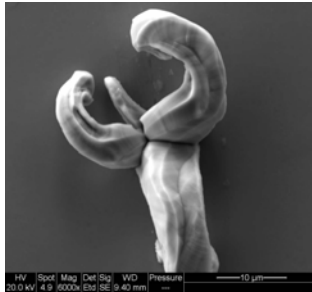
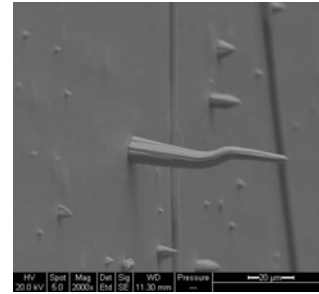
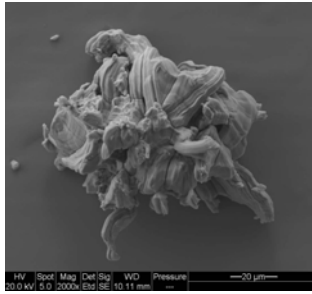
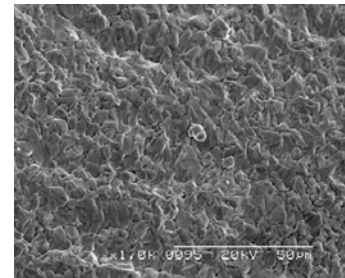


Figure 7B - “Non-preferred” bright tin deposit subjected to 4000 hrs @ 60°C and 90% RH at 1000X and 3000X magnifications, in the absence of a nickel pre-plate

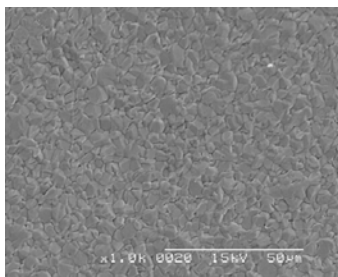
Figures 8A and 8B below details the results obtained for both the preferred matte and bright tin deposits, respectively, for flat and bent samples, with and without a nickel pre-plate after thermal cycling between -40 and +85°C for 1000 cycles at a rate of 3 cycles per hour.



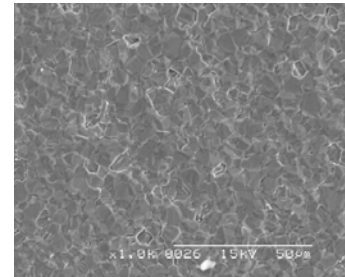
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate



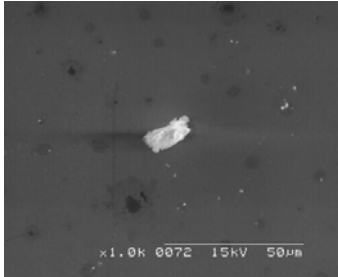
(ii) Flat, with Ni pre-plate



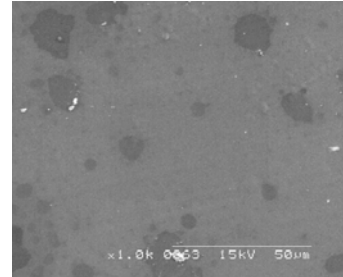
(iv) Bent, with Ni pre-plate

Figure 8A - Matte tin deposit subjected to 1000 thermal cycles between -40 and +85°C, at a rate of 3 cycles per hour at 1000X magnification.

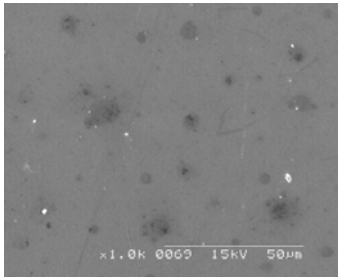
As can be seen from the images in Figures 8A and 8B, both matte and bright deposits have a reduced tendency to produce whiskers in this environment when compared to the more severe heat and humidity exposure test results that are illustrated above in Figures 6A and 6B. In fact, the only whiskers evident are those detailed in Figure 8A (i) and (iii) on both flat and bent matte tin samples without a nickel pre-plate. The average maximum whisker length measured was in the range of 8-10 microns. It should be noted that no whiskers were in evidence after 1000 cycles on any of the preferred bright tin samples.



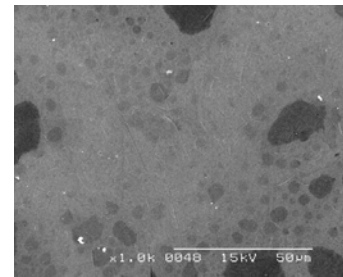
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate



(ii) Flat, with Ni pre-plate

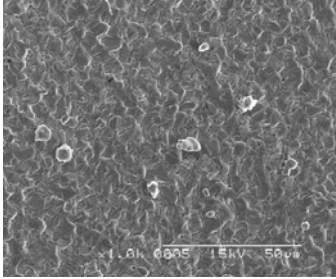


(iv) Bent, with Ni pre-plate

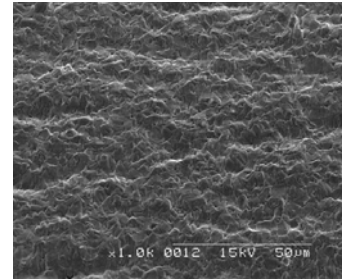
Figure 8B - Bright tin deposit subjected to 1000 thermal cycles between -40 and +85°C, at a rate of 3 cycles per hour at 1000X magnification.

Figures 9A and 9B below details the results obtained for both the preferred matte and bright tin deposits, respectively, for both flat and bent samples, with and without a nickel pre-plate after exposure to an environment of uncontrolled humidity for 4000 hrs at 60°C.

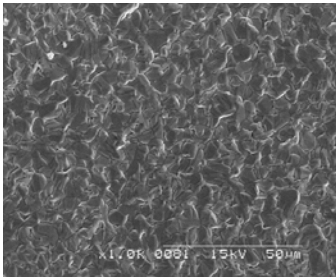
As can be seen from these images both matte and bright deposits again have a further reduced tendency to produce whiskers in this test environment. Whisker growth is evident on Figure 9A (i), flat tin samples without a nickel pre-plate but, perhaps a little surprisingly, not on the bent sample detailed in Figure 9A (iii). The average maximum whisker length noted was in the range of 6-8 microns. No significant whisker growth was observed on any of the bright tin samples subjected to this test environment.



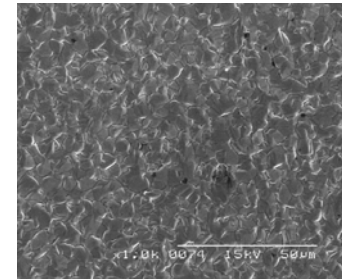
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate

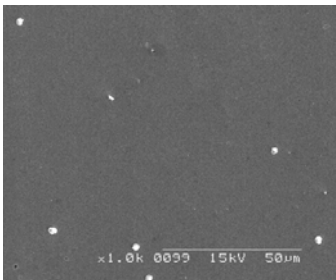


(ii) Flat, with Ni pre-plate

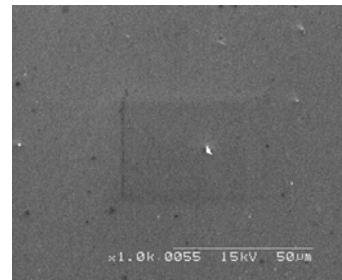


(iv) Bent, with Ni pre-plate

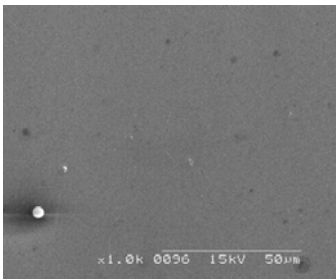
Figure 9A - Matte tin deposit subjected to uncontrolled humidity for 4000 hrs at 60°C, at 1000X magnification.



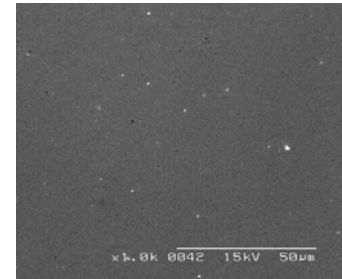
(i) Flat, without Ni pre-plate



(iii) Bent, without Ni pre-plate



(ii) Flat, with Ni pre-plate



(iv) Bent, with Ni pre-plate

Figure 9B - Bright tin deposit subjected to uncontrolled humidity for 4000 hrs at 60°C, at 1000X magnification.

The results outlined above clearly indicate that in some cases a bright tin electrolyte can be formulated to produce deposits that can outperform matte tin deposits in the iNEMI and JEDEC/IPC^[13] accelerated whiskering test environments.

This may appear to be a surprising and counter-intuitive result, especially considering the large amount of literature published to date that has detailed the contrary findings and recommended the use of matte tin for reduced tendency to produce tin whiskers. However, what must be reinforced is that no claim is being made here for the general performance of all bright tin deposits; in fact, as stated above, during this study some of the “non-preferred” bright tin processes evaluated proved to perform very poorly, see Figures 7A and B above where this is illustrated very clearly.

What is being brought to the industry’s attention is that bright tin electrolytes can be formulated to produce whisker mitigated deposits. This is not the first time that this has been proposed, similar findings have been reported by K. Whitlaw et al^[14] and by R. Hilty^[15].

A single definitive mechanism to explain this result is simply not possible at this time. There is a general agreement in the industry that compressive stress is the major driving force behind whisker formation, however, there are many contributing factors, some still poorly understood, that can induce stress to varying degrees in a tin deposit.

A primary cause of stress when tin is plated onto a copper substrate is the irregular growth of the Cu₆Sn₅ intermetallic compound as discussed in detail by A. Egli et al^[16], however, there is no evidence to suggest that intermetallic growth proceeds at significantly different rates, or is more or less regular in either bright or matte tin deposits.

M. Barsoum and E. Hoffman et al^[17] have proposed that oxide formation on a tin surface is also a means of introducing compressive stress into a tin deposit and it has been demonstrated by Schetty et al^[18] that some bright tin processes form thinner oxide films than others. This may infer that thinner oxide film formation may result in lower induced deposit stress, which in turn ultimately reduces the propensity for whisker formation and growth. This warrants further investigation and may be one contributing factor that may help explain the results presented here. K.N. Tu^[19] has also suggested that impurities and defects in tin oxide films contribute to whisker growth.

Other factors such as, deposit corrosion^[20], differences in coefficient of thermal expansion^[21] between the substrate and tin plate, as plated deposit stresses and impurities in the bulk tin deposit^[7,22] have all been detailed as sources by which stress is induced in a tin deposit. The role of mechanical stresses, introduced, for example, by the post plate forming of components, has also been described, at length, as a means of inducing stress in a tin deposit, ultimately causing whisker growth. All these factors, however, affect all matte and bright tin deposits significantly, so no clear route to an explanation of the results presented here is evident.

It has been suggested that the higher hardness, and thus higher yield strength, of a bright tin deposit may enable grains subjected to compressive stress to resist recrystallisation somewhat, thereby retarding whisker growth, however, this does not explain the significant differences found between a poorly performing bright tin deposit and one that exhibits significant whisker mitigating behaviour. Also, as Hilty^[15] points out, samples subjected to accelerated whisker testing are frequently mechanically deformed, many to such a degree that there is clear evidence of plastic deformation of the tin deposit. This clearly overcomes the yield strength of the deposit under test and therefore reduces the importance of this as a potential variable.

There is a volume of recent literature, most notably by A. Egli and K. Whitlaw et al^[23, 24] and Schetty et al^[25, 26], that details the possible link between preferred crystal plane orientation in both matte and bright tin deposits and subsequent whisker growth. Crystal plane orientation can be readily determined by x-ray diffraction techniques (XRD).

Figure 10 below details the (XRD) pattern for the preferred matte tin process presented in this paper over a nickel pre-plate. Although a number of orientations are evident, a strong preference for the (220) orientation is clearly demonstrated.

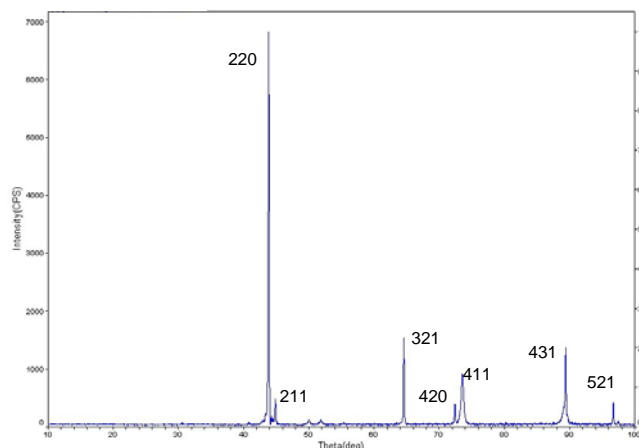


Figure 10 - X-ray diffraction pattern for the preferred matte tin deposit

Figure 11 details the XRD pattern obtained for the preferred, whisker mitigated bright tin process presented here over nickel. The two major peaks evident are for the (101) and (112) orientations, orientations such as (200), (220) are very significantly repressed.

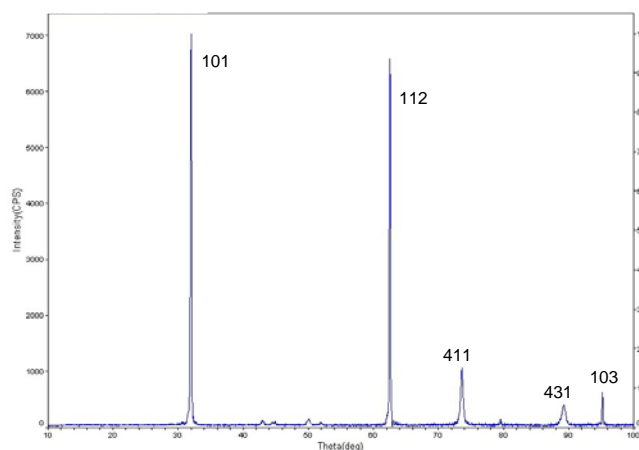


Figure 11 - X-ray diffraction pattern for the preferred bright tin deposit

Increased, localized stresses between adjacent crystal planes with low angles of incidence relative to each other are proposed as likely sites for whisker initiation. Crystal planes at angles between 5-22° are often considered critical sites, i.e., most susceptible to producing whisker growth. Examples of such “detrimental” orientation combinations include; (211)-(321), (211)-(411) and (220)-(431). Further work is clearly warranted in this area and may provide some fundamental insight as to the role of preferred crystal plane orientations and the phenomenon of whisker mitigation in bright tin deposits.

Conclusions

With the correct choice of organic additive systems both matte and bright pure tin deposits can be produced that demonstrate a much reduced tendency toward whisker formation and growth. Bright tin deposits can be produced that are at least equal to matte tin deposits, in terms of whisker mitigation. This is contrary to general consensus in the industry. All the factors that contribute to this improved performance remain unclear and further work is required. Bright tin may offer an aesthetically pleasing alternative to matte tin. Bright tin should not remain overlooked and be disregarded as a possible RoHS and WEEE compliant replacement for bright tin-lead.

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