An Investigation into Methods for Minimising Tin Whisker Growth

Keith Whitlaw & Jeff Crosby, Shipley Europe Ltd., Coventry, England

Abstract

Previous work has shown that pure tin and tin alloy plating processes do not produce coatings with the same resistance to whiskering as tin/lead alloy electrodeposits. In the earlier study nickel barrier layers, deposit annealing and thick coatings were all shown to be beneficial in reducing whiskering.

A pure tin deposit which possesses specific X-ray diffraction patterns (i.e. the absence of small angles between adjacent crystal planes) has also been shown to have minimum whisker formation tendencies.

This paper presents the results of further laboratory trials examining the effect of deposit thickness of a new tin deposit on whiskering. The influence of pre-treatment (etch depth, etch rate and etch type), post treatment annealing (time/temperature) and the use of undercoats (nickel and copper) are reported.

Recommendations for minimising whisker formation are presented.

For more information, contact:
Keith Whitlaw
Shipley Ronal Division
Shipley Europe Limited
Herald Way
Coventry, CV3 2RQ
United Kingdom

Introduction

Work reported last year[1] detailed an investigation of 22 different finishes (tin and a range of tin alloys) on 7 different substrates (Olin 194, brass, Alloy 42, nickel undercoat, copper undercoat etc). Samples were stored at 52°C and 98% relative humidity for 3 months and a whisker assessment made at monthly intervals. The conclusions of this study were that no drop-in replacement for 90/10 tin lead exists. The use of a nickel barrier layer reduces whiskering as does deposit annealing after plating. Thicker coatings are also helpful in reducing the tendency to whiskering.

In this paper we will investigate the effect of countermeasures against tin whisker growth on a new pure tin process[2] that has been specifically designed to produce a crystal orientation that minimises tin whisker growth.

It has been established from examination of the X-ray diffraction patterns of numerous tin coatings that there is a correlation between the angles between the crystal planes and the tendency for the deposit to grow whiskers. It is beyond the scope of this paper to go deeply into the theory behind this concept, but this is covered in an excellent paper published last year[3]. It has been found that coatings with large angles between the crystal planes have a low tendency to grow whiskers whereas deposits with small interplanar angles are more prone to whisker growth. The smaller angles equate to narrower grain boundaries and because there are fewer pathways for tin to diffuse there is greater compressive stress build up and this stress is relieved by subsequent whisker growth. With larger angles between adjacent planes the stress is more readily dissipated and does not build. It is the minimisation of compressive stress build up that is the key to producing whisker free tin deposits. It has been found empirically that angles smaller than 22° are deemed to be critical (in fact there is a critical range of 5-22°). In practice electrodeposits contain a variety of crystal orientations and to predict whisker performance it is important to calculate the percentage of critical angles as compared to the total possible number of angles.

The predominant orientations of the deposits from new tin process are 101, 211, 112, and 312. This combination of orientations has 8% of angles in the critical range. A typical pure tin process with a high tendency for whiskering may have a texture of 431, 321, and 211 orientations and this combination has 65% of angles smaller than 22°.

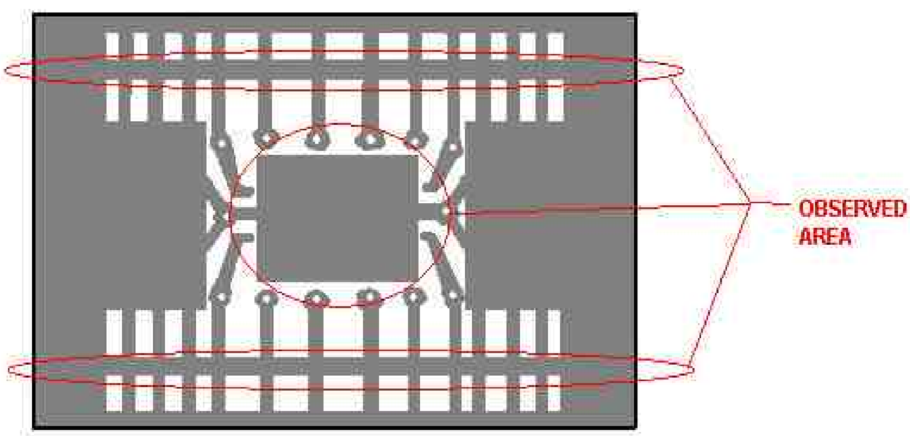
In the current study we will also compare the performance of stamped and etched lead frames since the cut edges of a stamped lead frame have been determined to be the most important area for whiskers to grow. We will also use ambient temperature storage to determine whisker growth since this has been shown to grow the longest whiskers as compared to any form of elevated temperature storage. It is postulated that at higher than room temperature annealing starts to take place reducing the length of the growing whisker.

Experimental Methods

The substrates were commercially produced lead-frames in Olin 194, brass or Alloy 42 and manufactured either by an etching process or by a mechanical stamping process. The same low-whiskering tin plating processes[2] was used for all samples and, unless otherwise indicated, the tin deposit thickness was 3µm. The lead-frame samples were plated at a cathode current density of 10 A/dm² in a 1 litre volume of the working bath using reciprocal agitation. Average deposit thicknesses were confirmed by accurate measurement of weight gain during plating onto test pieces of known surface area. The same pre-treatment was used in most cases and consisted of cathodic alkaline clean (proprietary formulation), rinse, dip in 10% sulphuric acid, rinse, and electroplate. For experiments designed to investigate the influence of etching of Olin 194 substrates on whiskering behaviour the etching step was introduced after the cathodic alkaline clean in the pretreatment sequence. The etchant was a proprietary persulphate-based formulation used under conditions giving either low (ca. 0.5 µm/minute) or high (ca. 5 µm/minute) etch rates. For samples with barrier layers, the nickel layer was provided from a proprietary sulphamate-based process[4] and the copper layer either from a proprietary bright acid copper process[5] or from a proprietary satin acid copper process[6]. For samples subjected to post-plate annealing the annealing condition was either 150°C for 1 hour or 180°C for 3 minutes.

Samples were examined by optical microscopy (200X) to assess whisker formation in the deposits. All samples were examined in the 'as-plated' condition and then at weekly intervals. Samples were stored under ambient conditions. Each sample at each examination was viewed over a fixed area of the lead frame as indicated in Figure 1 and <u>all</u> whiskers or incipient whiskers observed in this area were counted, the total number of these features giving the Whisker Grade. 'Incipient whisker' means a feature which is not present in the as-plated condition but which appears with time and, typically, grows into a whisker. The method accurately measures whisker population density but does not directly assess whisker length. In practice, low Whisker Grades (<100) tend to correlate to short whisker lengths (<10µm).

Figure 1 – Inspection Area on Lead Frame



Results

All results are summarised in Figures 2 – 10.

Figure 2

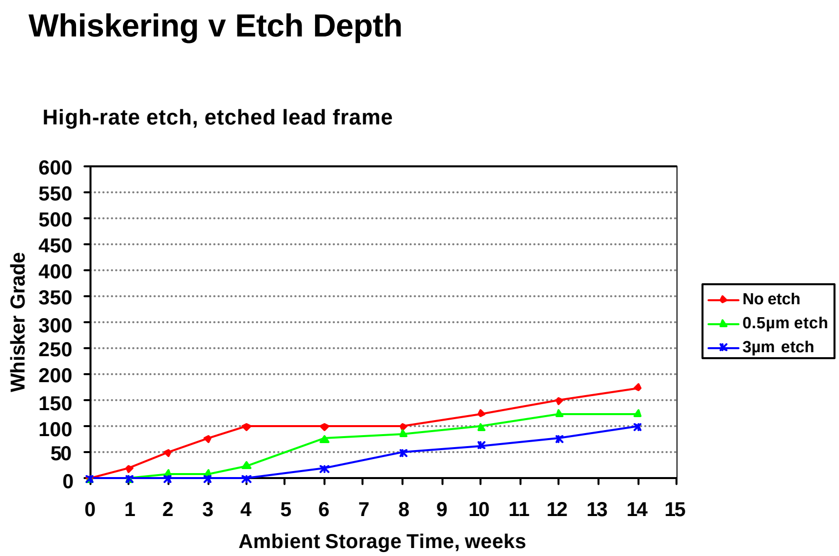
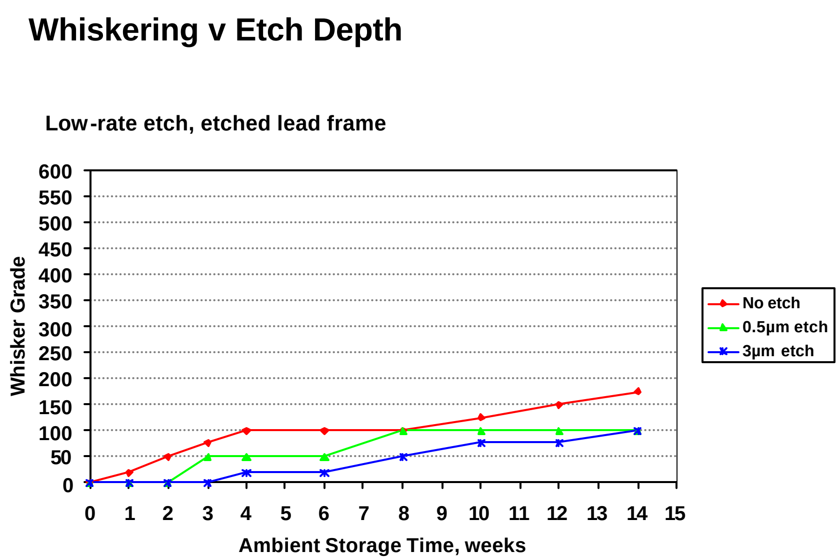


Figure 3



Figures 2 and 3 show that etch rate is relatively unimportant and that increasing etch depth reduces whiskering.

Figure 4

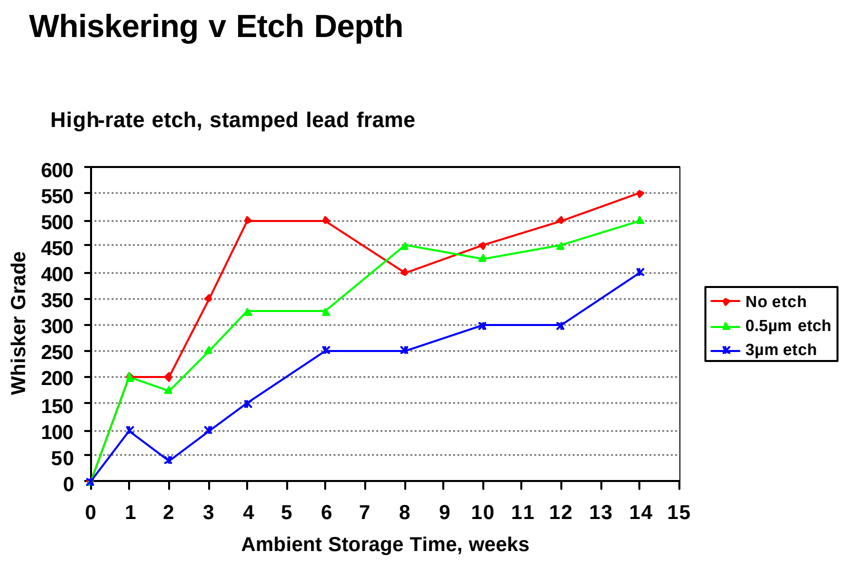
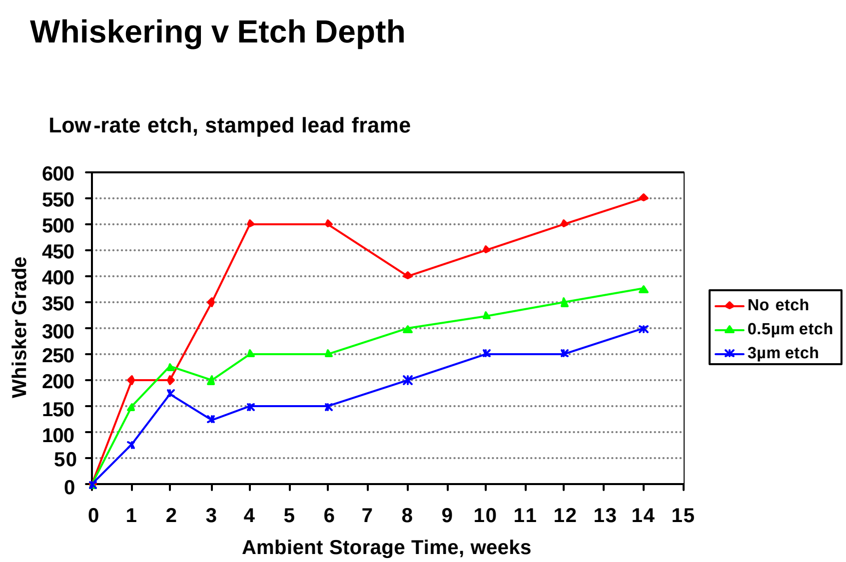


Figure 5



Similar trends are observed as in Figure 2 and 3; the absolute values of the Whisker Grades are much higher, indicating the severity with stamped lead frames.

Figure 6

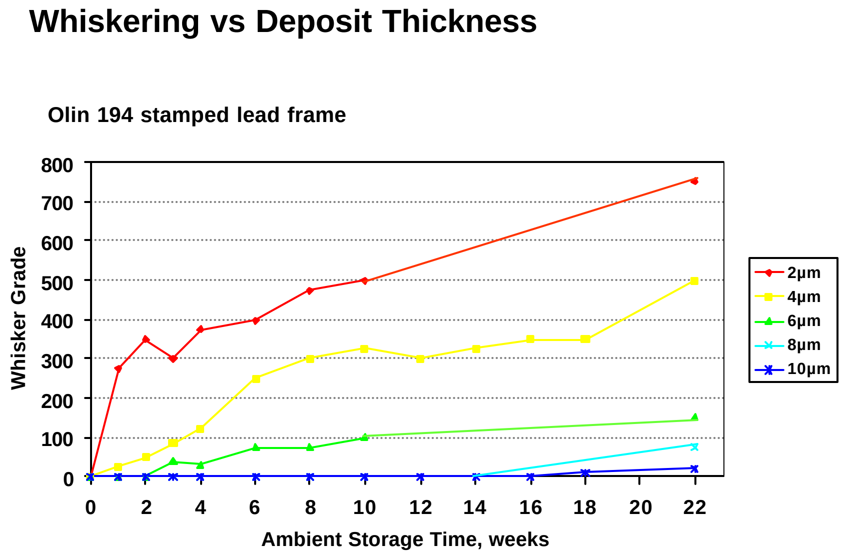
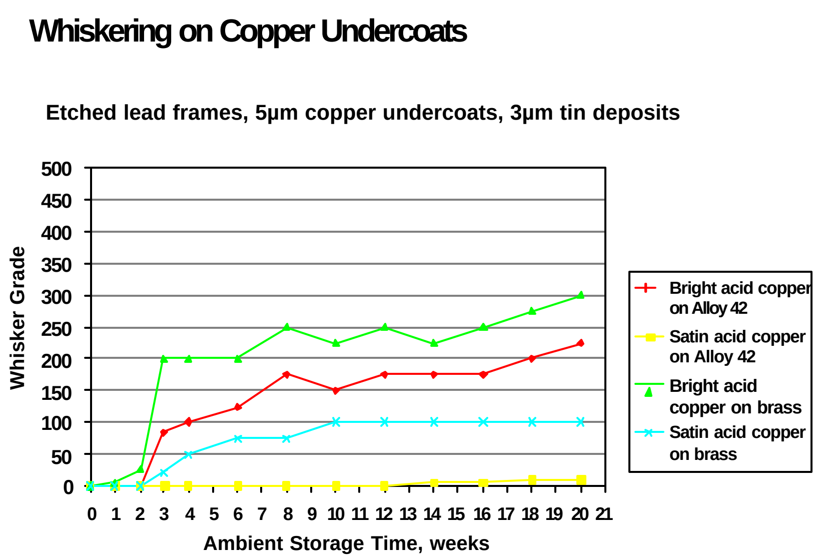


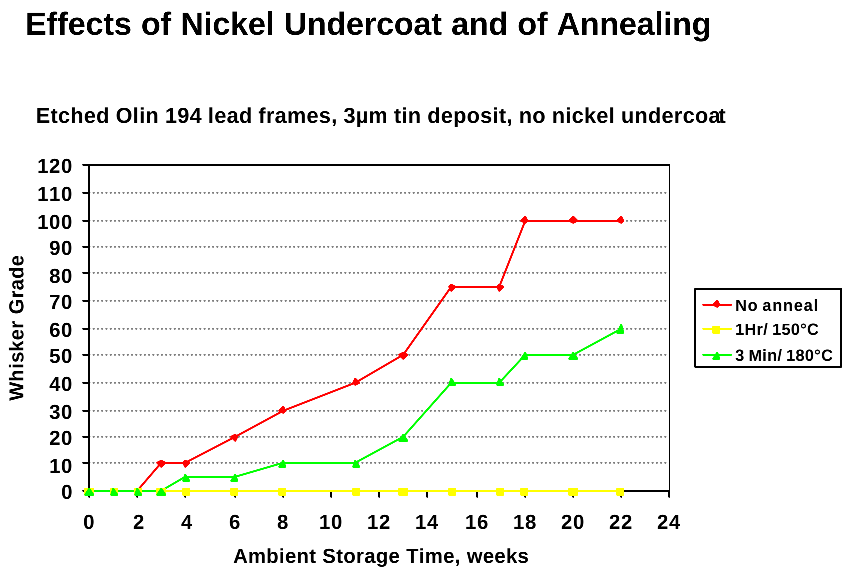
Figure 6 illustrates the effect of increasing deposit thickness in reducing whisker formation.

Figure 7



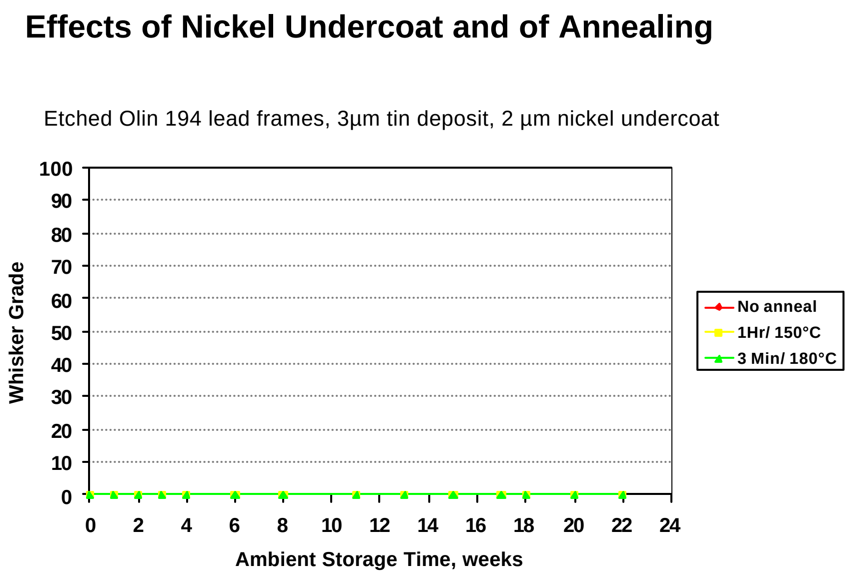
The propietary satin acid copper has a 220 orientation whereas the propietary bright acid copper has a 111 orientation. On Alloy 42 the use of satin acid copper produces very low whiskering. With both copper undercoats the results are worse on the brass substrate as compared to Alloy 42, demonstrating the effect of zinc diffusion from the brass substrate.

Figure 8



Annealing is shown to be beneficial in eliminating whiskers, although the shorter time/higher temperature annealing cycle is less effective.

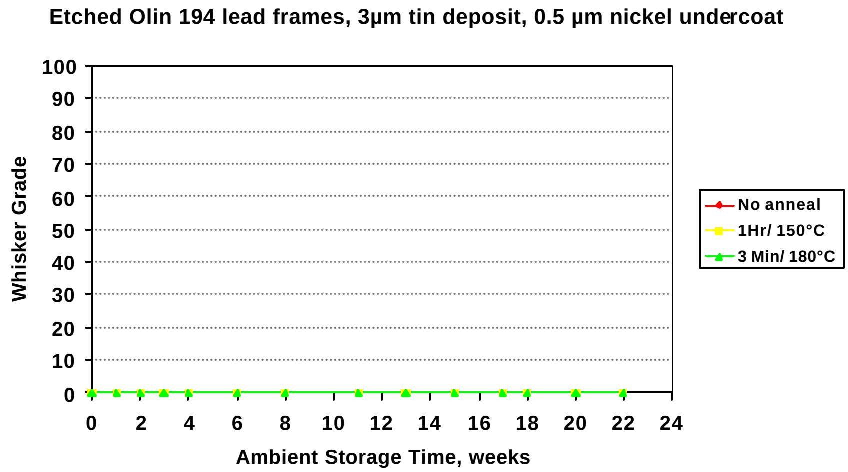
Figure 9



Nickel undercoat completely prevents whiskering and annealing is not necessary when using nickel.

Figure 10

Effects of Nickel Undercoat and of Annealing



Even a low nickel thickness (Figure 10 – 0.5μm cf Figure 9 – 2μm) is completely effective and lower thickness is better for ductility and to prevent cracking during the trim and form process.

Discussion

The recommended etch depth of 3.5 μm for Olin 194 substrates may not be suitable for all copper alloy substrates e.g. CA-7025 will produce a black smut with this degree of etching and zirconium based alloys e.g. Olin 151 will produce tin filaments during plating. Fortunately these two alloys have a lower propensity to produce whiskers and do not require heavy etching.

The etchant that is used in the pre-treatment process is based on persulphate. Different types of etchant based on various persulphate salts give broadly similar results. Specifically formulated proprietary etchants are available that are optimised to produce ideal results over a wide range of alloy substrates.

The nickel process[4] used in this study is a special high ductility formulation that is designed to withstand the bending of the trim and form process without cracking. Many nickel processes will not be sufficiently ductile to meet this requirement and therefore are unsuitable for lead frame applications.

It should be noted that the baking process of one hour at 150°C will slightly reduce the solderability shelf life of the tin deposits by forming an initially thicker copper/tin intermetallic compound layer than would occur by natural ageing.

Some companies use thermally cured marking ink for components and if this is applied after plating the curing process will anneal the tin deposit and a separate annealing step is not required. This is obviously not the case with laser marking.

Countermeasures such as nickel (or copper) undercoating or post plating annealing are additional, resource consuming, non-value adding processes that are not ideal but are necessary to guarantee whisker freedom. A tin plating process is still under development where the as deposited crystal structure is such that whiskers will not grow from thin deposits without the need for special pre-treatment, undercoats or post treatment. A drop in replacement for tin/lead without additional treatment remains the goal.

Conclusions

Stamped lead frames show more defects than those produced by etching and the majority of defects occur at the stamped edge of the frame. This is clearly as a result of the additional stress introduced by the stamping process.

Increasing etch depth in the pre-treatment process reduces the tendency for whisker formation. The removal of the surface layer damaged by the rolling process leaves a uniform surface that produces a homogenous layer of copper/tin intermetallic compound which results in minimum compressive stress formation on ageing.

Etch rate and etch type were not highly significant factors. Achieving the minimum etch depth is the critical factor; how this is achieved is of secondary importance.

The use of a nickel underlayer (0.5 µm) was completely effective in preventing whisker formation.

The use of post-plate annealing (one hour at 150°C) was also completely effecting in preventing whisker growth. Higher temperatures for shorter times could also be used but this may not always be totally effective.

When using copper undercoats, the type of process used is critical to success. To obtain whisker free deposits the copper undercoat must have a 220 crystal orientation[7]. Bright copper deposits with a 111 orientation can actually increase propensity for whiskering.

Recommendations

An etch depth of 3.5 µm is recommended as part of the pre-treatment for Olin 194 substrates.

A tin coating thickness of >10 µm is recommended to minimise whisker risk.

A copper or nickel barrier layer can be used to prevent whiskering but this means that modification to existing plating lines would be required to retrofit a plating cell for the undercoat process.

A deposit annealing procedure should be used if equipment modification to accommodate an undercoat is not practicable. Unfortunately this is a slow batch process so relatively large ovens will be required to maintain a high rate of productivity. It may be possible to fit a continuous on-line oven to the end of the plating line but care must be taken to ensure that the time/temperature combination is adequate to produce sufficient annealing to guarantee whisker freedom.

Acknowledgements

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References

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7. Patent applied for.

