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Ann Hopper
Technological University Dublin, ann.hopper@tudublin.ie

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Ann P. Hopper

Dublin Institute of Technology, ann.hopper@dit.ie

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Dr Ann Hopper, *Dublin Institute of Technology*

Abstract.

The miniaturisation of electronic components coupled with requirements for high temperature lead free soldering has forced the improvement of the termination finish of surface mount components to meet the critical demands of the electronic industry. In the present work the processing parameters necessary to plate miniature multilayer varistors (MLV's) have been explored. The tooling selected was a 'Rotary flow-thru' plater" which achieved high volume plating with <0.5% rejects. The anode selection proved critical and Nickel S rounds only were suitable with the chosen parameters. A very tight plating distribution with Nickel thickness average 2.2μm (σ 0.28 μm) and tin thickness average 3.5μm (σ 0.31 μm) was achievable in production size quantities. An evaluation of product by examining solder fillet heights and tombstoning in mass board mounting trials concluded that the nickel tin finish is effective for high speed soldering applications.

Keywords: nickel and tin plating, nickel anodes, solderability, tombstoning, Rotary flow Thru' plater.

Introduction

Metal oxide varistors (MOV's) are discrete electro-ceramic components that come in two basic architectures; chip and disc. Their key function is the ability to detect and absorb transient overvoltages without suffering damage to their own structure. When exposed to a high voltage the varistors' impedance varies from a near open circuit to a highly conductive state, thus clamping the transient voltage to a harmless level and protecting downside electronic components in expensive electronic devices. Their physical size determines how much energy they can absorb but below a rated value they can withstand multiple transient events. Multilayer chip varistors (MLV's) are physically small and are used in digital electronic circuits. Their sizes range from 4.5 x 3 mm down to 1.0 x 0.5mm, the latter classified as 0402 in accordance with the US EIA standard classification. They have significant applications in the mobile phone markets, laptop and consumer electronics where they absorb electrostatic discharge (ESD) and transient voltages. ESD occurs where there is a transfer of electrons within a body or between bodies, e.g. walking across a nylon carpet and touching a metal handle you get a shock. The high population density of components in electronic circuits has led to an increase in the need for protection against ESD. The small size MLV's are an ideal, low cost ESD suppression option capable of clamping the voltages in these rapid events. As well as mobile phones (where there can be up to 28 MLV's per phone), other critical growth areas are USB ports, flat screen displays and netbooks. Automotive electronic assemblies also continue to be a major use of MLV's.[1]
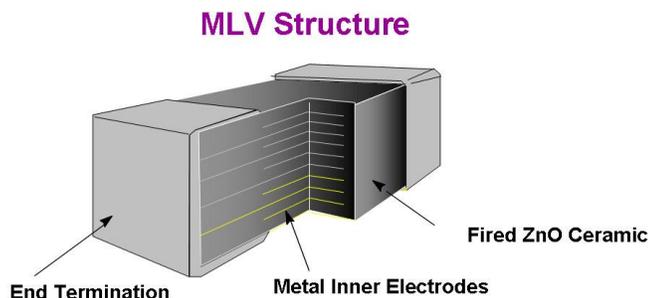

Figure 1 Internal structure of MLV (courtesy of Littelfuse Inc)

Figure 1 shows the internal structure of a MLV. The layers of ceramic are interweaved with internal electrodes. The ceramic is made of zinc oxide doped with specific additives such as bismuth trioxide, antimony trioxide, manganese dioxide and cobalt oxide; the concentration depending on the electrical properties required of the varistors (nominal voltage, breakdown voltage, leakage current etc.) The internal electrodes are made from silver palladium. The ceramic is produced by thick film technology followed by sintering and then dicing the components into the required sizes. The external electrodes or end terminations were originally made from expensive silver/platinum or silver palladium alloys to provide contact for board mounting. This is applied in the form of a metal loaded paste. The paste contains Ag/Pt or Ag/Pd powder or flake, glass frit and a vehicle make up of binders and solvents. After application, the devices are fired at $>650^0$C when the metal powder/flake grains sinter and the glass frit both binds the metal grains together and bonds the termination to the ceramic by diffusion. The standard for other discrete components (Capacitors, inductors etc.) was thick film silver finished with nickel barrier and tin plating. Plating the terminations of MLV's proved challenging due to the semiconducting nature of the ceramic material, an issue not affecting other discrete component devices.[2,3]

Components with non- plated terminations were susceptible to "tombstoning" or "drawbridging" when mounted onto circuit boards. The issue of tombstoning affects two ended terminations such as MLV's and MLCC's and is most prevalent in the smaller sizes such as 0402 and 0201. The self centering force of the solder which helps to re-aligning slightly misplaced devices is also the force which contributes to the tombstoning effect. Tombstoning is a phenomenon where, in the presence of moving forces, the chips tend to dislocated during reflow and either twist, misalign or tip up on one end as can be seen in Fig. 2. It is caused by an imbalance in the wetting forces between the chip's two terminations and the solder pads. The consequences are that the device detaches from the printed circuit board at one end leaving the opposite end bonded to the circuit board, leading to electrical disconnections or intermittent contact. The majority of attributable causes relate to reflow conditions and board design. In practice it has been found that the slower solder wetting speeds of the Ag/Pt or Ag/Pd termination compared to the plated termination exacerbated the problem.[4]
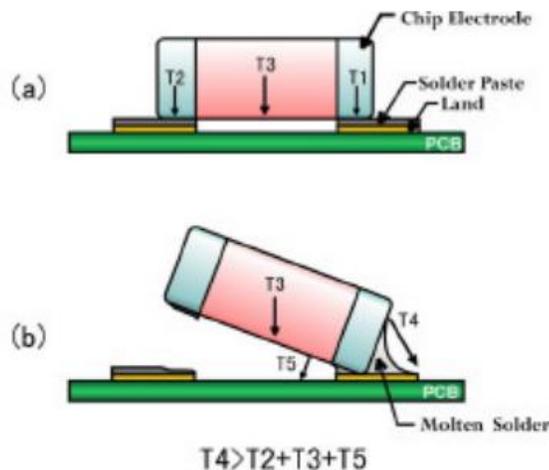

$$T4>T2+T3+T5$$

Figure 2 Forces causing tombstoned device (courtesy of A. Takaki, Senju Advanced soldering Technology) [5]

A novel technique of selectively coating the exposed ceramic in the MLV with an insulating glass prior to plating the terminations with nickel and tin overcame the problem of selective plating.[6] Barrel plating with media proved successful for larger chip sizes > 3 x 5 mm but was ineffective with the miniature 0402's due to termination damage, electrolyte starvation, wide variation in plate thickness and there were also issues of separation of products after plating.

A review of plating technology developments revealed a "Rotary Flow Thru" (RFT) plater as an option. The aim of the present work was to determine the processing parameters required to efficiently plate 0402's in the RFT. Subsequent to this, the selection of nickel anodes and the optimisation of the RFT processing parameters was based on solderability, % rejects and plating thickness distribution.

Patented in 1999 by Griego Electroplating Technology , the Rotary Flow Thru plater was an new approach to electroplating small articles and powders. A schematic of this machine can be seen in Figure 3 below. At the core of the system is a rotating dome that holds the product to be plated, different solutions are pumped into this dome at various stages in the process. It rotates, as chosen, at either high or low speed and the dome changes direction to achieve a tumbling action. It is designed for miniature electronic components and small metal parts down to 50μm. The dome has a titanium cathode contact ring at the perimeter on top of which is a plastic ring with very fine slots in it. This allows the plating solution to transfer out of the dome back into the holding tanks but the pores or slots are fine enough for the plated parts to stay retained by the ring. The anodes are metal chunks held in titanium baskets which are transferred into the neck of the dome when the metal is to be plated. The plating solutions are held in two tanks and when required, these solutions are pumped into the dome through the anode. The catch basin of the RFT system is designed to rotate the position of the outlet over a return drain manifold so that a multiple-step process can be carried out without physical transfer of the plating cell or its contents, i.e. when plating nickel the manifold allows the nickel to pump down through the anode, into the dome and back into the tank again. This eliminates the need for transporters for barrels, large open tanks and extraction systems, allowing a foot print as small as $4m^2$ as opposed to a barrel plating shop that would be on average, $25m^2$. It also means that the tool can be at end of line in the production process allowing for lean manufacturing guidelines to be achieved.

During normal operation when electroplating MLV's , the first step after the product is loaded into the dome is a balancing rinse so only DI water is pumped into the dome and the dome spins and the water is allowed to go to drain. The next step is nickel plate, the nickel anode is loaded into the opening of the dome and the nickel solution is pumped through the anodes and into the cell. Temperature control of both plating solutions was achieved by thermostatically controlled heating elements in the plating solution reservoirs. The Nickel was controlled to $55^0C \pm 2^0C$ and the tin solution to $22\,^0C \pm 2^0C$. With reference to Figure 3 below, the dome rotates at sufficient speed for the centrifugal force to keep the parts on the cathode ring, only at this point does the rectifier switch on and plating start. The system uses no media and contact is made only with the parts on the ring. To improve the distribution the rotating dome stops, the product fall back off the ring and then, for the next cycle, the ring starts up again at high speed and the process repeats itself. [7]
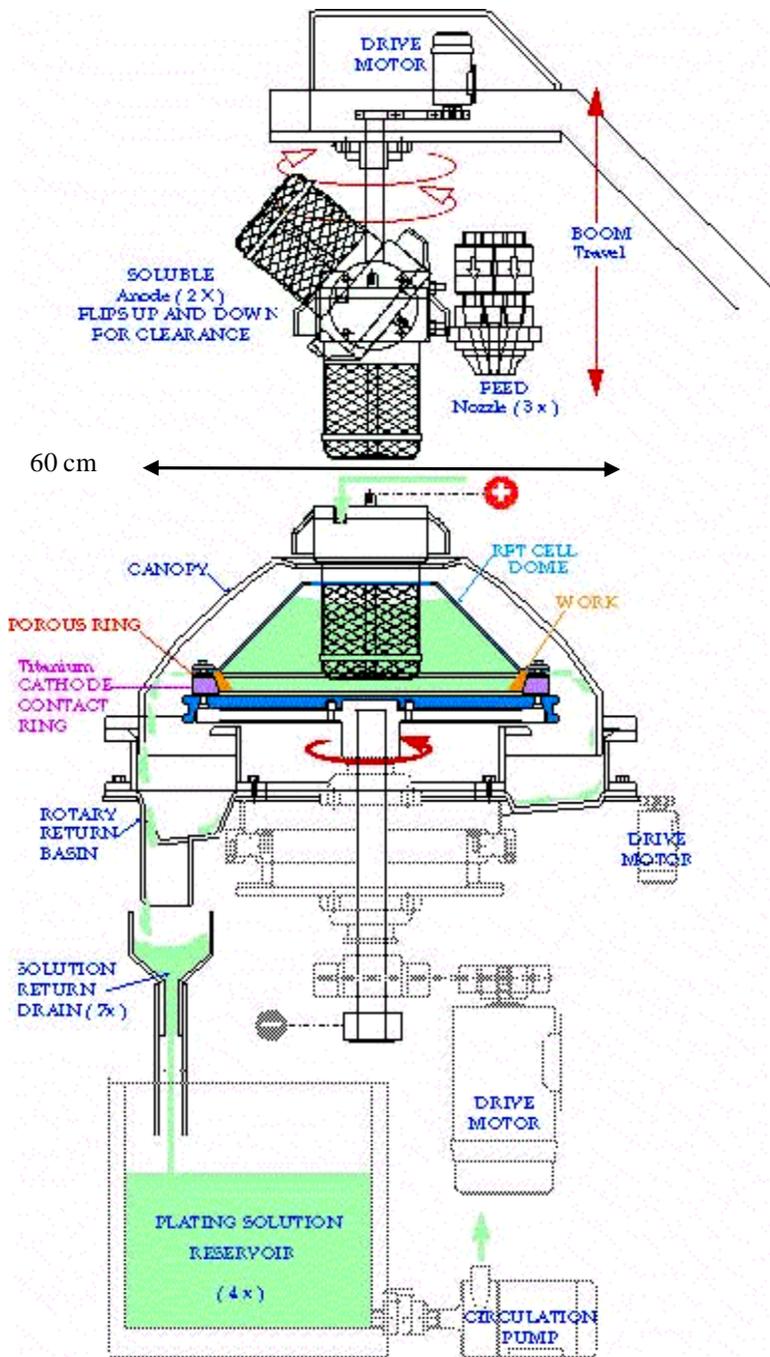
Figure 3 Schematic of Rotary Flow Thru' Plater

Nickel Chemistry Selection

Stress is an important parameter in the plating of a nickel barrier layer for ceramic components. The nickel layer should have zero to slightly tensile stress so that the plate would contract around the end termination, improving adhesion to the body. Excess stress would cause the ceramic to crack and excess compressive stress could cause the plating to expand and peel away from the termination during subsequent soldering operation.

Lowenhein examined the influence of the anion species on residual stress and found Watts solution values had values of 125MPA and the lowest value was with a sulphamate solution at 3.5MPa.[8] According to Kushner, the stress that develops at the initial deposition stage is controlled by atomic mismatch between coating and substrate. As the layer builds up the influence of the substrate is reduced. The stress is initially at a higher level and it reduces to a steady state value as the thickness increases above 12.5 μm [9.] The MLV end termination is a thick film matrix of silver and glass and for a 2μm Nickel deposit, this initial stress is critical. Y. Tsura, et al examined the effects of the three halides chloride, bromide and iodide on the internal stress in films deposited from a sulphamate bath. The concentration of the halide was varied from (0.01M to 0.5M). Part of the conclusion was: In chloride and bromide solutions the internal stress initially rose to a maximum value and then decreased before it started to increase again. At lower thickness the effect of halides was more dramatic as the stress is much higher, residual stress quoted were 300MPa for a 2.5μm thickness with 0.5M NiCl solution.[10]

Ideally an electrolyte with little or no additives would be the aim for high speed processing of electronic components. As the purpose of the deposit is to act as a barrier for the board mounting soldering step, the aim is to avoid or minimise the sulphur loading of the deposit which might give rise to grain boundary embrittlement of the nickel deposit above 200^0C.[11] Also, the incorporation of impurities derived from additives may reduce the local conductivity. Hence, very lows levels of additives were used. The anodes in the RFT are held in a titanium basket 300 mm in diameter and 700 mm in length. Anode chunks, pellets or squares are recommended as is the use of polypropylene anode bags. Both DeBari and Hart investigated the effect of sulphur on the electrochemical activity of nickel anodes and found that the sulphur nickel anodes dissolved smoothly at a uniform rate and independently of the chloride content of the bath.[12,13] Hart found that with non-activated nickel there is a critical current density appearing around + 50mV HNE above which the nickel becomes passive. The presence of about 0.025% sulphur in the nickel however prevents passivation until much higher potential values are reached, from + 800 to + 1,200 mV NHE The critical current density before passivation occurs is therefore up to three orders of magnitude higher than it is with non-activated nickel[13,14.]. This allows for uniform dissolution to occur in chloride free baths and with pH up to 5.5.[12] The objective is to use the most pure anode material to reduce additives to the nickel plate. This work concludes with an evaluation of the process parameters on a large scale board mount experiment to evaluate the effect on tombstoning.

Experimental

Selection of Nickel Anodes
Based on literature review a nickel chemistry of nickel sulphamate (0.7M), nickel chloride (0.14M), boric acid 0.5M and saccharin 5 cm^3/dm^3 and wetting agent Schlotter Solution M at 0.2 cm^3/dm^3 was used for the following experiments.
Three types of anode were tested: Nickel S rounds containing 250ppm sulphur (supplier Inco); Nickel D crowns are sulphur depolarised electrolytic nickel with 20 ppm carbon and 200 ppm sulphur (supplier Falconbridge) and Electrolytic Nickel squares 99.9% Ni (supplier Inco).
The anode basket was loaded with 11 kgs of each of the anode types and the solution was made up as above. Metal shot media with a diameter range from 0.85 to 1 mm were used with a surface area of 45dm^2, the current density was 6.6Am^{-2} and the temperature set at 50^oC.

Optimise RFT plating efficiency
The RFT was set up to give the maximum cathode efficiency. The relationship between the rotation and the rectifier can be seen in Figure 4 below. The rectifier parameters were set up as in Table 1. An AC inverter on the system varied the rotation speed of the cell. The Hi and Lo times are the amount of time in seconds that the cell rotated at high and low speeds. The cell could be spun in a clockwise or anti-clockwise direction and this could be varied throughout the run. An "on delay" allowed the parts to climb onto the ring before the rectifier switched on and the "off-delay" switched the rectifier off before the cell stopped. For example, the plating could take place for 2.6 seconds from a total cycle time of 3.8 seconds giving 68% "on time" per cycle.
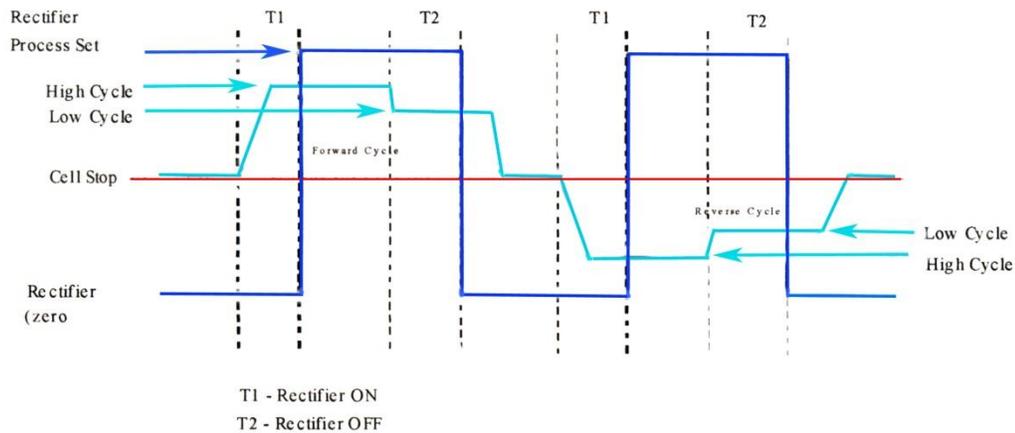
T1 - Rectifier ON
T2 - Rectifier OFF

Figure 4 RFT Cell Rotation and Rectifier current relationship

	Hi Time	Lo Time	Stop	Rotation	On Delay	Off Delay	Time rectifier on	% on time per cycle
Seconds	2	1	0.8	0	0.2	0.8	2.6	68
Freq (Hz)	23	20						

Table -1 Parameters for RFT set up

Plate glass coated 0402's

A batch of 60,000 MLV 0402's with a platable surface area of 0.079 m^2 was prepared with a protective glass finish on the ceramic. The Nickel electrolyte was made up as above. The tin electrolyte was made up in accordance with Lea Ronal Solderon LG solution with tin content = 15 g L^{-1} specific gravity of 1.15 g cm^{-3}; and the pH was adjusted with methyl sulphonic acid to pH 4.0.
The Nickel was plated at 40 Am^{-2} (3A for 50 A.mins)   and the tin at 25 Am^{-2} (2 A for 25 A.mins).
The cathode spin speed was set by loading 15 cm^3 of parts and stepping through the cycle to ensure that the parts all went onto the ring in a monolayer and fell off again. The acceleration and deceleration speeds are also controlled so that the units drop off the ring and are tumbled between cycles. The deposit thickness was measured with a XVDM Fischerscope XRF (sample size 30 pcs). This instrument uses a SD (Silicon Drift) detector with an energy dispersive x-ray analyser to determine the deposit thickness of single and multiple coatings.

Large scale board mount operation

A further experiment to verify these settings and determine the impact of Ni/Sn plated 0402's on tombstoning was run by plating 8 batches (480,000 units) and the overall data were:

Plate material	Average thickness	Standard deviation
Nickel	2.2 μm	0.20 μm
Tin	3.5 μm	0.31 μm

Table 2 Plate thickness of large scale 0402's.

To compare the Ni/Sn plated termination with the prior Ag/Pt and Ag/Pd terminations, a total of 11,200 pieces were board mounted on 7 circuit boards and reflowed by Infra-Red (IR) heating . This required approximately 3730 pieces from each termination type. To block any potential influences of within board reflow variability, during the pick and place operation the unit was selected randomly. 5 of the boards were reflowed under standard reflow condition. The oven was profiled to have a ramp rate of 40^{0}C/minute to

liquidus temperature and 40 seconds above liquidus. The second oven profile was a fast ramp rate of 55^0C/ minute to liquidus temperature and 35 seconds above liquidus.

Results & Discussion
Effect of anode selection

Anode Material	Nickel S Rounds	Nickel D Crowns	Nickel Squares
%Carbon	0.003	0.002	0.002
% Sulphur	0.025	0.02	0.0002
CCE (%)	90.2	85.4	52.4
Volts	7.7	11.2	16
Reduction in solution Ni content (g/l)	0	-1.3	-13.4

Table 3 Results of different anode materials on cathode efficiency.

Effect of RFT process parameters

In this experiment the CCE for the S rounds was the highest at 90.2%, and the squares are the lowest recorded at 52.4% efficiency (see Table 3). The voltage was highest for the non- activated nickel squares, as the run progressed the voltage gradually increased and the solution became cloudy.

Both the nickel D crowns and the nickel squares anode materials became passive and nickel metal no longer dissolved into the solution, oxygen evolution produced the cloudy effect at the anode and the efficiency decreased. The reduction in the metal content of the bath confirmed this; when the anode no longer oxidized, the reaction started using up the metal available in solution. It was concluded that for the RFT plater and the low current densities appropriate for plating varistors, nickel S rounds were the preferred anode material. There was little difference in the analysis of the nickel S rounds and nickel D crowns to explain the difference in results

Run No.	A	B	C	D
nickel thichness μm	1.3	1.3	1.8	1.86
%COV	9.70%	7.30%	17.20%	4.8%
tin thickness μm	3.42	3.5	3.57	3.68
% COV	5.7%	4.6%	10.2%	3.1%
Hi Time	2	1	3	1.5
Lo Time	1	1	1	1
Stop	0.8	0.8	1	0.8
Rotation	8	0	4	0
% on time time/cycle	68	57	72	64
% Rejects	20%	2.5%	12.0%	2.5%
Solderability	Pass	Pass	Pass	Pass
Comments	edges corners missing		corners missing	

Table 4 Results of plating 0402 MLV's.

Table 4 shows the results of the RFT optimisation parameters. The effect of any reversing of the rotation from a forward direction caused damage to the corners of the end termination. A setting of zero was optimum. Figure 5 is a cross section of a sample from Run D showing a uniform nickel and tin layer on the glass loaded silver termination.

The co-efficient of variation (COV) expresses the variation as a percentage of the mean. The lowest COV was achieved for both nickel and tin plate when the rectifier % on time of 64% for Run D, increasing the on time beyond this point increased the COV to 17% for nickel and 10% for tin as can be seen in Run C.

The resistance of the cell at 2.6V for 3 Amps for nickel and 2.6V for 2 amps for tin was very high. It was expected that this was mostly the cell resistance so that as the product load increased the voltage would not increase substantially

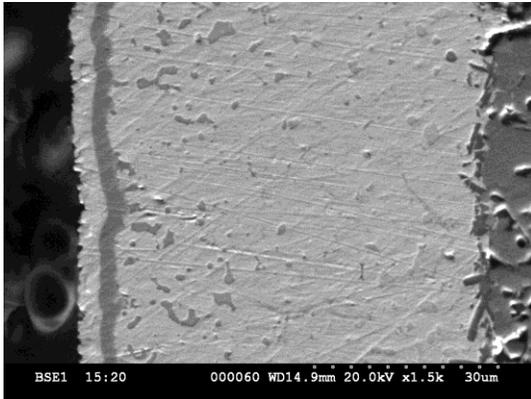BSE1 15:20   000060 WD14.9mm 20.0kV x1.5k   30um

Figure 5 Cross section of plated 0402. The outer white layer is tin, next grey layer is nickel followed by the white silver termination bonded to the dark grey ceramic of the MLV.

Effect on tombstoning & evaluation of the solder fillet

In the mass surface mount reflow experiment the criteria for rejects were devices that misaligned or tombstoned. Misaligned is where the device has moved from the horizontal during the reflow process and is an indication that the solder wetting forces are inadequate. Figure 6 is an example of a misaligned device. Under the fast ramp rate for IR reflow used for boards 6 & 7 the Nickel/Tin plated termination was significantly less likely to tombstone than Ag/Pt and Ag/Pd terminated devices. Table 5 shows that there were no statistically significant differences between termination types regarding the levels of tombstoning under the standard reflow profile conditions. This is not unexpected as in general it is difficult to determine the root cause of tombstoning, which is normally found in very low levels (<0.1%).[15]

Board No.	Ag/Pt	Ag/Pd	Ni/Sn
1	0	0	0
2	2	0	0
3	4	0	0
4	0	3	0
5	0	4	0
6	28	42	0
7	214	149	0

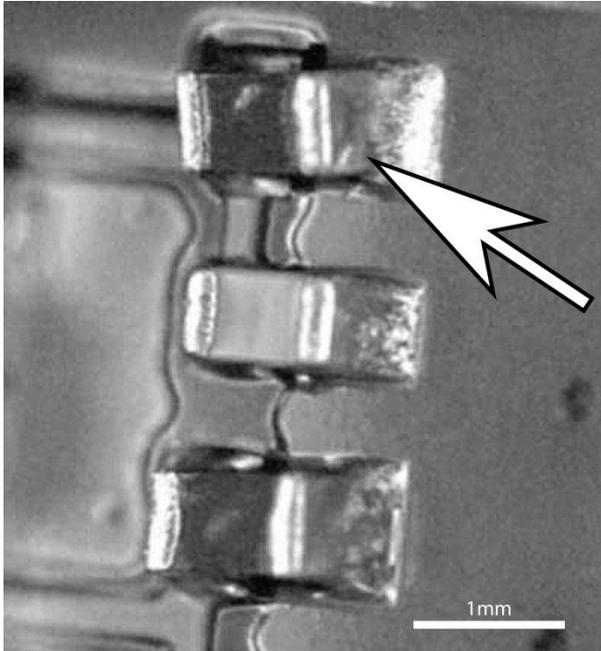**Table 5 Quantity Tombstoned / Misaligned devices (ss 530 devices per board)**

Figure 6. Image of three 0402 electronic components, , the top device highlighted with an arrow is misaligned on the circuit board.

A requirement for good solderability was that the solder fillet height was >50% of the height of the unit.[15,16] In Figure 7 can be seen the fillet height in the Ni/Sn parts compared to the other two devices. In cross section the differences are more obvious, Figure 8 highlights this showing the cross section of a Ag/Pt terminated devices having a low fillet height with leaching of the termination into the solder and Figure 9 is the cross section of a Nickel plated device with the solder fillet covering the whole of the termination area.
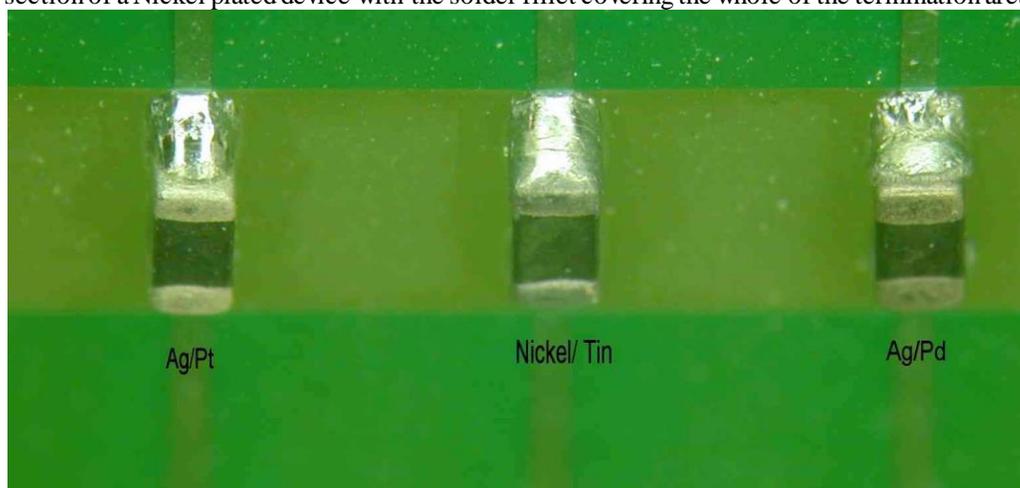

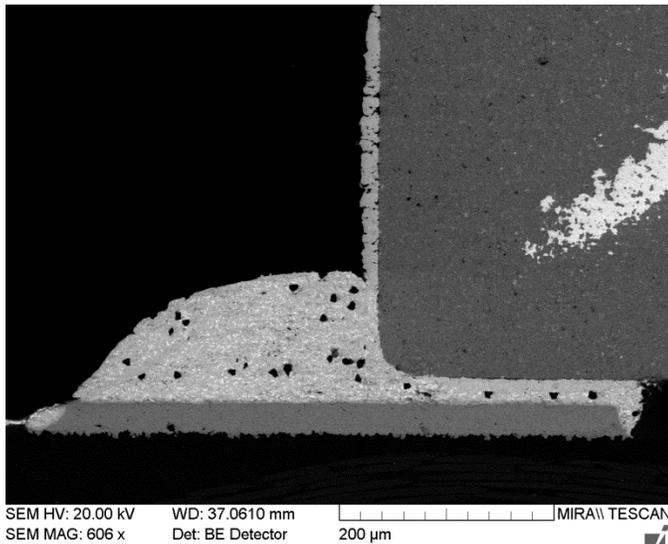**Figure-7 Solder fillet height for three termination types.**

Figure 8 SEM image with back scatter detector of AgPt solder fillet height in cross section showing <40% fillet height. This image the solder pad loaded with solder, the dark grey ceramic chip and the thin porous layer of the Ag/Pt termination is visibly leaching into the solder paste.
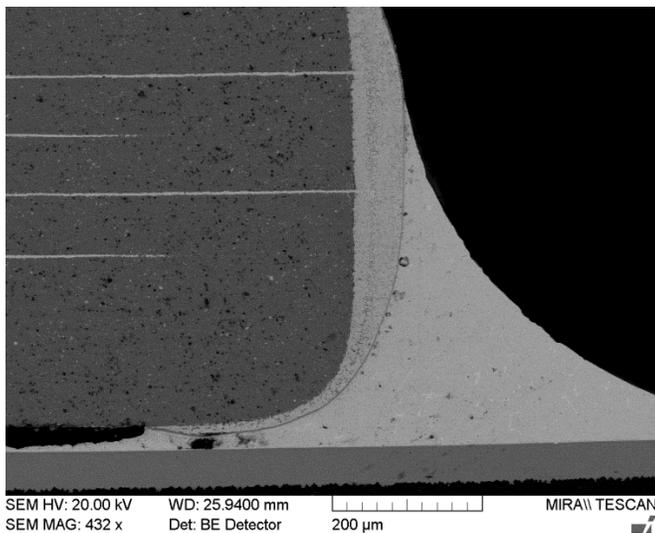

Figure 9. SEM image with back scatter detector of nickel/tin plated termination in cross section showing good fillet height of >50%.

Conclusion

Successful plating chemistry and optimal process parameters for plating 0402 MLV's were established without the use of media using the RFT plater. Anode selection was critical and only Nickel S rounds were suitable. The soldering performance of the nickel /tin plated termination shows a significant improvement versus silver based termination. Both the fillet height (> 50%) and resistance to tombstoning/misaligned is superior on Nickel /Tin plated terminated devices.

Under extreme soldering conditions Nickel /Tin plated terminated devices exhibited zero tombstoning compared to a high level on the silver based terminations. The large number of devices processed in this

experiment (11,200pcs) confirms the robustness of the Nickel /Tin plated termination for IR reflow applications.

Acknowledgements

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