

New Whiskers Phenomena?

Jean Pascal Michelet: Supplier Quality Assurance, Passive Components Expert,
VALEO Créteil France _ jean-pascal.michelet@valeo.com

Jean Edmond Le Calvé: Senior Expert Passive, Power and Opto-electronic Components
VALEO GEEDS 76 rue Auguste PERRET 94000 Créteil France _ jean-edmond.le-calve@valeo.com

Introduction

Some PCBAs were submitted to a whisker test +85°C 85% RH for 200h duration and additional 2h from +85°C/85% RH -T° +25°C/50% RH 5 Cycles

The functional test pass and boards were sent to an external lab for visual inspection. Inspection failed because of Tin whiskers detected on MLCCs terminations.

As reminder a whisker is a spontaneous columnar or cylindrical filament, usually of monocrystalline metal, emanating from the surface of a finish. In automotive electronic the most common are Tin Whiskers growing on Tin plated Copper surfaces.

Our suppliers delivering components with Tin or Tin alloy finishes, if no whiskers mitigation method is used or efficiency demonstrated, should perform whisker tests according to JESD-201 standard / 22A121 method [1] [2].

As many Multi-Layer-Ceramic-Capacitors (MLCCs) got whiskers, we returned to the Bill of Material (BOM) and traceability to find out exactly the part numbers. We went back to their qualifying and the results were good.

We also checked the Process Change Notification (PCN) history to see if the suppliers submitted any PCN relative to the termination scheme and we did not find any on this topic.

Moreover, all the impacted MLCCs got a Nickel barrier between Copper electrode and Nickel plating supposed to avoid or limit the Tin whiskers growth.

Observations

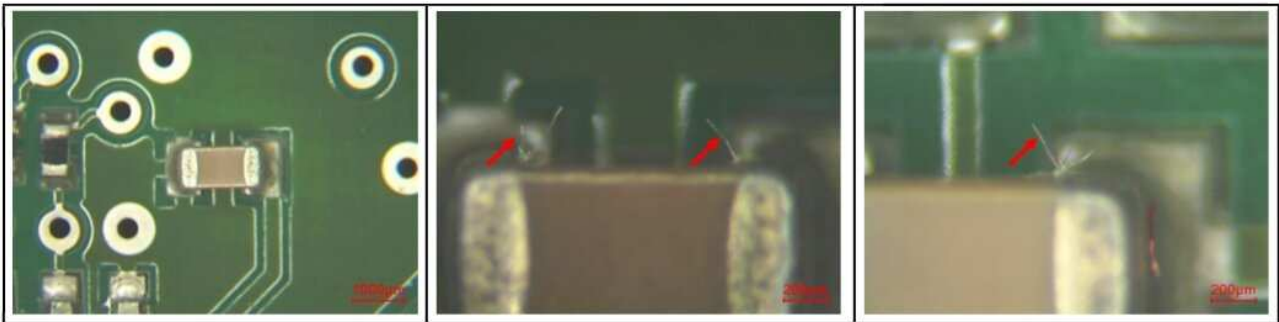


Fig1: Observations of the whiskers. Lengths are measured up to 225µm. Whiskers have tubular shapes. They are located on the sides only, never on the top (not possible to observe the bottom). Whiskers are located between the Tin plated termination and the flux rise.

The shape of these whiskers is not conventional and is not described neither by the Nasa [3] nor by Jedec [2]. Some hollow whiskers were reported [4], [5], We did not find any document on Tubular whiskers growth on Electronic components. For us it is the first observation of such structure.

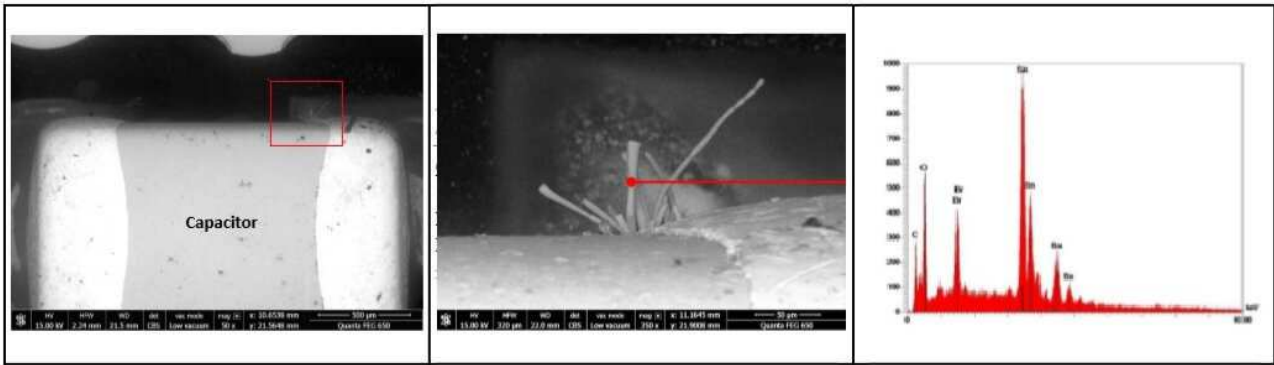


Fig2: EDX analysis evidenced Tin, Bromide, Barium and Oxygen. Barium is coming for the BaTiO₃ ceramic from X7R MLCC. Bromide origin is unknown.



Fig3: The shape of “standard” Whiskers was observed on another component terminal and compared with those found on the MLCCs.

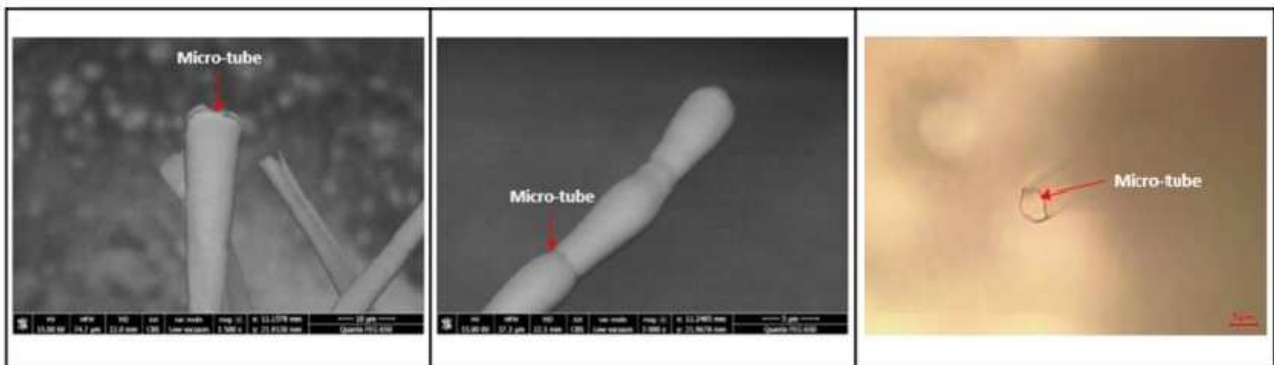


Fig4: The whiskers in question are hollow like micro-tubes. They are transparent and very brittle.

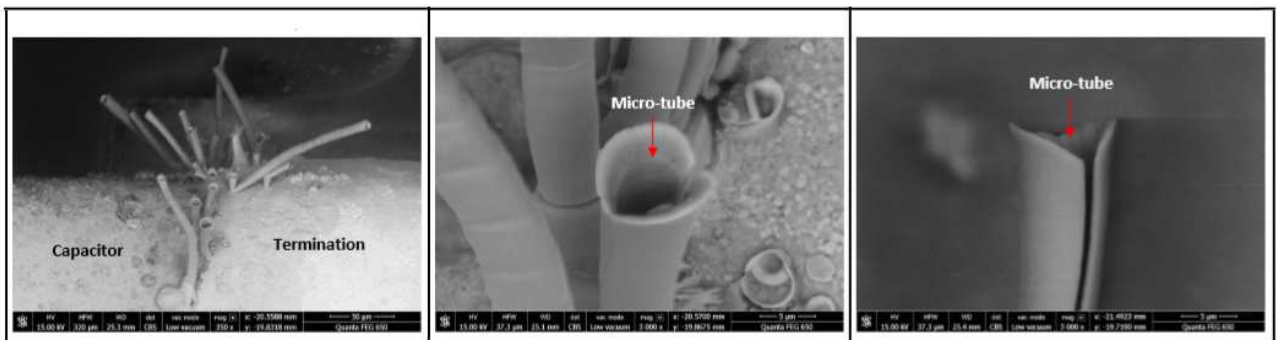


Fig5: The micro-tubes are like bamboo canes with a succession of segments. Some have their end slit on the side.

Root Cause analysis.

A cross section was done in the horizontal plane of a MLCC at the maximum flux rise where the Whiskers grow .



Fig6: The extremity of the termination evidenced Tin over Nickel and Copper. Tin is partially oxidized (grey color) like whiskers. In the section plan the tubular shape is evidenced. Whiskers growth is on the ceramic nearby or in contact with the Tin edge of Tin layer.

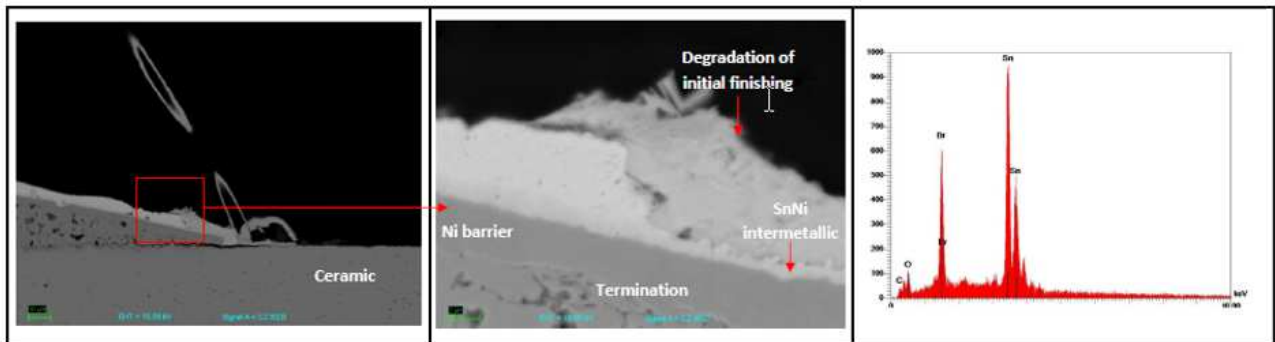


Fig7: The edge of the Tin layer is oxidized by Bromide. The crack between the ceramic and the termination is a minor polishing artefact. Bromide origin was identified as coming from the Solder Flux.

Risk analysis:

The major risk of metallic whisker is to reduce the insulation distance or worst to make a short circuit. In our case the whiskers is made of Tin, Oxygen and Bromide. The visual observation evidenced transparent tubular structure, so it is not a pure metal, but a compound of Tin oxide + Bromide.

Tin oxide is classified as wide band gap (3.6 eV) Ntype semiconductor. Considering the risk to have a conductive path, we make electrical verifications. We did several attempts to contact the Whiskers by probing but it failed because of whiskers are too brittle. We used a cross section through both MLCC termination solder and some whiskers ends to be contacted with Silver epoxy ink.

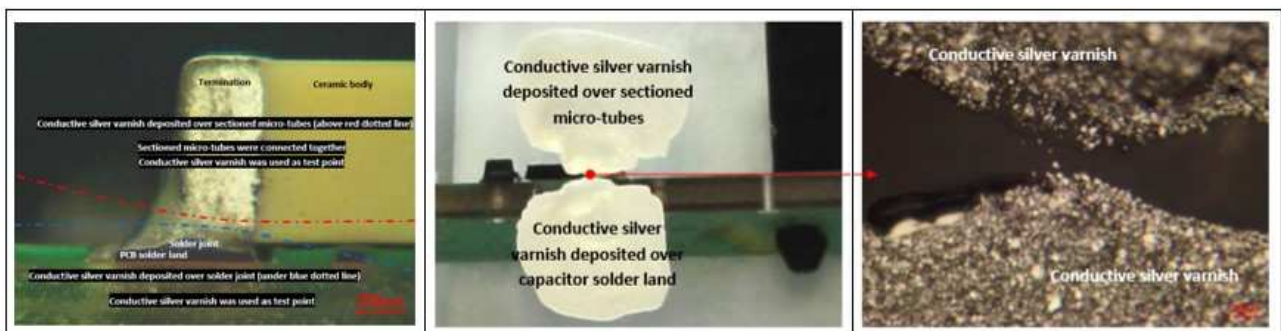


Fig8: cross section in the vertical plan contacting the MLCC solder and the whiskers ends. Both were contacted with

Silver epoxy. The realization of the microsection as much as the precise deposit of the silver lacquer are difficult to achieve.

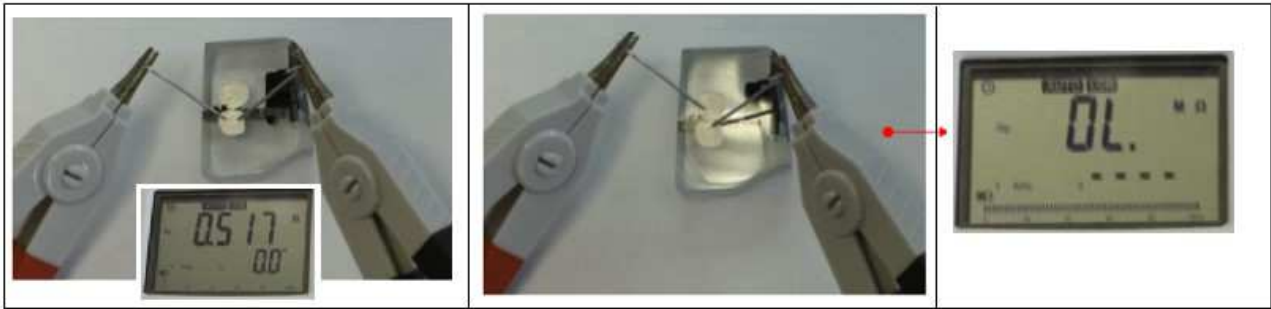


Fig9: Verification of the contact, and measure 2 probes. The whiskers are not conductive (or not contacted). A verification was done by contacting both ends of a single whiskers.

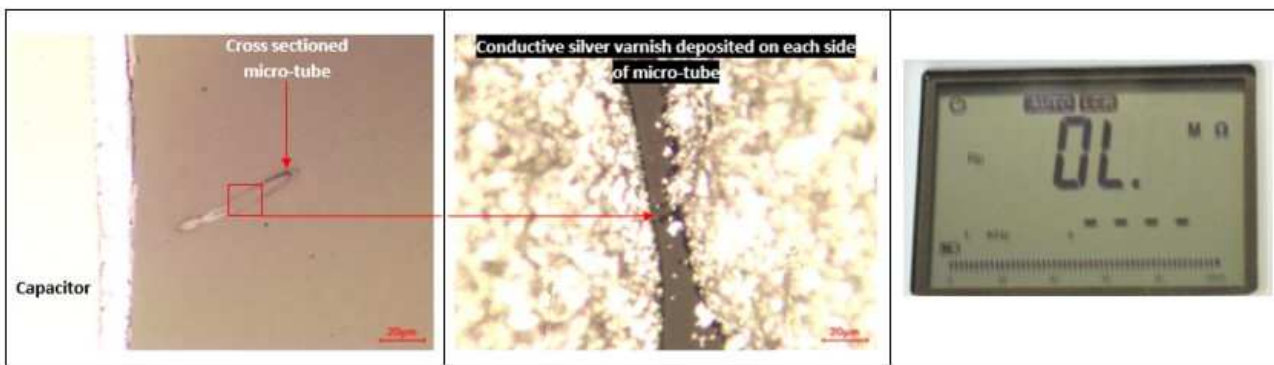


Fig10: Verification of the whiskers resistance done by contacting both ends of a single whiskers: not conductive.

Tin tubes growth hypothesis

While lowering the reflow temperature profile, more hollow whiskers were possible to be generated. This suggests that the SnO hollow whiskers growth mechanism is promoted by some still active flux residues not fully deactivated by the reflow process. Among these residues the weak organic acids (WOA) and halogen/bromine are suspected to contribute to the growth mechanism of SnO whisker.

Tin hydroxide chloride $[Sn_3O_2(OH)_2 \cdot xCl_x]$ was reported to be intermediate corrosion products on reaction from $Sn \rightarrow SnO/SnO_2$ (depending on pH and presence of chlorine halogen) [7]. A similar Tin hydroxide bromide could have been the intermediate corrosion product to give rise to the tin oxide hollow whisker encountered:

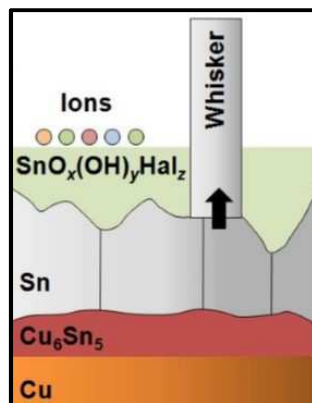


Fig11: corrosion of Tin layer with intermediate Tin hydroxide halogen [7]

This localized corrosion process in presence of halogen ion (bromine) could have been at the origin of the tube shape observed.

The transformation of Tin nanowires to amorphous oxide nanotubes has been described by HoSun Shin [8] based on a localized corrosion process in an aqueous solution involving hydrochloric acids (from halogen chlorine ion). The nano-tubes were formed by the dissolution of the tin atoms in the core of the “nanowire” while the tin oxide shell was remaining.

Conclusion

Hollow Tin Whiskers are transparent, very brittle and not conductive.

We demonstrated no risk of leakage or short circuit.

At visual inspection they can be considered as cosmetic.

Growth mechanism is suspected to come from a localized corrosion process by a Bromine acidic solution from the Solder flux residues and the moisture from the humid atmosphere of the damp heat test.

References

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- 7) Pierre Eckold, “Corrosion of Tin and its Influence on Whisker Growth”, 7th IPC–CALCE International Symposium on Tin Whiskers, November 12-13, 2013.
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Acknowledgements

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Investigation Laboratory for Electronic Devices Site Montesquieu 8 Allée Isaac Newton 33650 Martillac - France