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Whisker-Impenetrable Metal Cap Process for Electronic Assemblies

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Abstract

A process is described for depositing a nickel (or other whisker-impenetrable metal) cap over all lead-free tin and high-percentage tin alloys, but not on any insulating surfaces (component bodies, solder mask, etc.) of an electronic assembly. Reasons are given for expecting that this cap layer will prevent the growth of tin whiskers *permanently*. The process is contrasted with other whisker prevention approaches and with earlier, so-called "mitigation," measures available to electronics OEMs that at best reduce whisker growth risk.

Introduction

The widespread use of Pb-free Sn[2] as a termination finish on components in electronic equipment poses a significant risk of a whisker-caused short circuit. This risk is well known among engineers, although many in the larger electronics manufacturing community remain virtually unaware.[3] The whisker problem is of particular concern for high-reliability electronic assemblies because of their high cost and long design life,.

The options available to original equipment manufacturers for combating whisker growth have been limited. While an OEM is free to specify the termination (i.e., land) finish to be used on the boards) it designs, in most cases it does not have a choice of finish on the components, and the subassemblies, it needs to build its equipment. Most of those needed components and assemblies are now Pb-free commercial-off-the-shelf, and most of those have Pb-free Sn[4].

Some customers prohibit the use of exposed Pb-free Sn. Where that is the case, the manufacturer has had to adopt a process of component-by-component finish replacement (i.e., reballing Pb-free BGAs, producing a Sn-Pb termination finish by electroplating or dipping in Sn-Pb solder). Finish replacement is labor-intensive and not without risk. It involves:

- Scrubbing the bill of material to identify each component with Pb-free Sn
- Testing for Pb-free Sn at receiving (since the right component doesn't always get ordered – or delivered)
- Accepting the risk that virtually undetectable damage may occur during the process and its associated handling

For assemblies with mostly Pb-free Sn components and for COTS assemblies, finish replacement is impractical.

Where the customer does not prohibit Sn, most high-reliability OEMs use what has come to be called "mitigation." The most common whisker risk mitigation approach is to apply a suitable polymer as a conformal coating to the assembled, soldered, and tested assembly. However, with

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[1] Co-founders, LDF Coatings, LLC.

[2] For consistency in this paper, the chemical symbols are used to refer to the metals, as follows: Au, gold; Cu, copper; Ni, nickel; Pb, lead; Pd, palladium; Sn, tin.

[3] nepp.nasa.gov/whisker

[4] Pb-free BGAs have solder balls made of a solder that is mostly tin.

the exception described below, all classes of coating (acrylic, silicone, paraxylylene, epoxy, urethane) have been found incapable of preventing whisker penetration from the underlying Sn, in part because it has proved practically impossible to get a thick enough coating on all surfaces.[5]

Ideal OEM whisker-prevention process For an OEM, the ideal process would:

- Suppress whisker growth totally and permanently (i.e., for as long as the equipment is intended for use)
- Have data to support that claim (with no known way to accelerate whisker growth, this may be difficult to *prove*)
- Pose a negligible risk to an assembly's function, reliability, and marking legibility
- Be applicable to *any* entire assembly (made or bought) after it has been soldered and tested
- Be performed between cleaning and conformal coating (thus imposing no additional cost for masking areas required to remain uncoated)
- Cover all Sn and high-Sn alloys (no shadowing or skips)
- Be inherently safe (i.e., not require chemicals not already in use in the electronics manufacturing industry)
- Be quick (handling time ≤ 5 minutes per assembly, so no bottleneck)
- Allow easy compliance verification
- Have a small equipment footprint
- Require only simple training of operators and process engineers

Compared to using a component-by-component remedy, it would have:

- Negligible labor cost
- Negligible material cost (including disposal/recycling)
- Negligible equipment fixed and maintenance costs

Three real whisker-prevention processes compared

Recently, three processes, each claiming to prevent, not just "mitigate," whisker risk for tested assemblies, have been announced. Each applies what is intended to be a permanently impenetrable coating.[6]

- "ALD-Cap" conformal ceramic – Sundew Technologies
- "Whisker-Tough" conformal polymer – Smith & Co.
- Selective metal cap – LDF Coatings, LLC

The first two will be discussed briefly and the third in more detail.

ALD-Cap

By sequentially injecting specially selected chemically reactive gases into a proprietary vacuum chamber, a thin layer (~ 200 nm) of ceramic is deposited layer by layer ("atomic layer deposition") onto suitably prepared surfaces inside. Because the composition of each layer can be dif-

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[5] Although no cases have been reported of a whisker that penetrated a conformal coating causing a short circuit (it would also have to contact a metal), it is possible. It could meet another penetrating whisker, penetrate (from above) the coating to reach the underlying metal surface, or break off and reach an area required to remain uncoated. These events have unknown probabilities, but taken together they suggest that conformal coating alone is mitigation, not prevention.

[6] The prospects for any approach *other* than coating, e.g., surface treatment, are gloomy.

ferent (and even include polymers to make it more flexible), an ALD coating can be tailored to have the desired combination of properties.

Vacuum deposition ensures total coverage, even of balls under BGAs. The coating is too thin to interfere with rework soldering, and if Sn-Pb solder is used to rework the connections, no recoating is needed. Provided the adhesion to the underlying Sn is adequate, the ALD coatings that have been reported on appear to be equal to the task – there has been no penetation for over 2½ years.[7] Two advantages of the ceramic coating are:

- They are insulators (hence, with adequate adhesion to insulating surfaces, no polymer coating is needed to prevent dendritic growth in humid operating conditions)
- Their physical properties are unlikely to change with temperature, humidity, or time.

"Whisker Tough" conformal coating

As discussed in the Introduction, Sn whiskers have been shown to penetrate all types of polymer conformal coatings. Recently a polyurethane-based conformal coating has been announced that, in addition to functioning as other conformal coatings to protect the assembly at high humidity, is claimed to be whisker-impenetrable. Its properties:

- Applied as a thixotropic liquid, thus ensuring an adequate cured coating thickness (at least 25 μm) on all surfaces
- Cured coating has high adhesion and tear strengths
- Coating, instead of preventing whisker *growth*, prevents whisker *penetration.* A growing whisker lifts it away from the substrate and stretches it (like a tent and pole) until the coating re-directs the whisker back toward the surface from which it is growing.
- Coating is ompletely transparent, simplifying inspection
- Coating contains a fluorescent dye – under UV illumination any area of non-coverage is non-fluorescent

Its application features:

- Pot life ≥ 3 hrs (and by replacing drag-out is extendable indefinitely). Hence the marginal costs are negligible, and may actually be lower
- A specially designed dip tank allows virtual elimination of particle contamination
- Cure conditions: overnight bake with temperature ramp followed by 2 hours at 85°C
- The amounts of operator and process engineer training required are reasonable
- Proper composition and cure are easily verified by measuring modulus of cured coating
- Coating removal for rework is comparable to the process for removing conventional urethane coatings

Unlike ceramic and most industrial metal films, however, the physical properties of polymer films change over time, temperature, and humidity. Manufacturers rarely report these changes, nor have they yet been reported for "Whisker Tough" coatings. Thus it is not yet known whether they are whisker-impenetrable under all conditions for decades.

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[7] The minimum ALD thickness needed for impenetrability has not been announced.

LDF Coatings LLC selective metal cap over all Sn

Both the ALD and "Whisker-Tough" processes involve applying an insulating coating to the entire assembly. A third possibility would be a whisker-impenetrable metal coating applied to an entire assembly *selectively*, i.e., in such a way as to coat all the Sn but no insulating surface.

Impenetrability Researchers in Japan[8] were interested to see if a metal coating could be put over the Sn plating of a component termination so as to meet two objectives: 1) not interfere with solderability, and 2) prevent whisker penetration, even during growth between the metal and the Sn of the intermetallic compound layer.

Kim *et al*. electroplated Ni, Au, and Pd over 6 μm (240 μin.) of Sn. They found that very thin Ni (50 nm) deposited in islands and severely reduced the solderability – what solderability remained was due to uncoated Sn regions. Ni thick enough to form a continuous layer (200 nm) wiped out solderability.[9] It is important to note that while Ni over a component's Sn termination finish renders it unsuitable *before* soldering, *after* soldering loss of solderability is of no concern.[10]

As for impenetrability, the researchers found that 200 nm of each of the metals investigated was sufficient. For *over five years* there has been no penetration of a 200 nm Ni cap layer. [11] In contrast, two other researchers have reported metals that are *quickly* penetrated by Sn whiskers: Pb over Sn[12], and Cu over Sn – a 600-nm layer was penetrated in *three days*.[13]

The differences in the whisker penetration properties of Ni, Pd, and Au compared to Pb and Cu are dramatic. They strongly suggest that for as long as a metal coating remains intact, its physical properties determine whether a Sn whisker can, or cannot, penetrate – *ever*.

Not yet known is what effect the growth of intermetallic compound has on a metal coating's (or the IMC's) impenetrability. It is however significant that Au, which reacts with Sn much more quickly than does Ni, has also proved to remain impenetrable for years.[14] Presumably, a coating thick enough to retain a thickness of 200 nm or more after, say, thirty years, during which time the remainder had reacted, would still be impenetrable, *whether or not the underlying IMC was itself impenetrable*.

Selective application Given that Ni, Au, and Pd have been found to be impenetrable, can any of these metals be applied to coat all Sn and no insulating surface?[15] Some candidate processes can be eliminated:

- ✗ Physical vapor deposition (e.g., by sputtering), because it would coat everything.

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[8] Kim, Keun-Soo *et al*., ISIR, Osaka University, presentation to 2008 TMS conference. Also private communication, 2010.

[9] It might seem obvious that this would have been the result, but the native oxide layer on tin, which is not chemically attacked by ordinary rosin flux, does break up in its presence simply due to the expansion during melting of the underlying tin. Of course, the oxide layer is seldom thicker than 3 nm and not as strong as Ni.

[10] In fact, since component terminations are subject to very little deformation after testing, even the coating's ductility is of minor concern.

[11] The other metals were started later, but there has been no penetration reported for them, either.

[12] Ed Li, AEM, private communication 2005.

[13] Eric Chason, Brown University, J. Mater. Res., Vol. 24, No. 12, Dec 2009, 3583-3589. Also private communication, 2010.

[14] The thickness of an IMC *increases* as $t^{1/2}$ while its growth rate *decreases* as $t^{1/2}$.

[15] It is is a matter of indifference whether other metals are coated (some are not – see Note 16).

- ✖ Electrochemical deposition, because it would require making an electrical connection to each metalized area of the assembly (there are far too many for this to be practical).
- ✖ Some metals can be deposited on some substrates by a so-called “immersion” process, but there are only a few combinations of substrate and depositing metal, and even for those the resulting thickness is not great enough.

That leaves electroless deposition as the only remaining candidate process, but this process indeed does have the requisite characteristics. It is autocatalytic, meaning that it must start on a conductive surface[16], and the deposit itself catalyzes further deposition. Of the three impenetrable metals discussed above, *all* can be deposited electrolessly on Sn, so all appear to be suitable for the intended purpose. Ni has the added benefit of being inexpensive.[17]

Experiments and results The theory of applying a metal cap layer over Sn is straightforward enough, but the notion of immersing in a hot and highly conductive solution a functioning and tested assembly, especially one that may be worth several thousand dollars, is enough to make anyone at least a little nervous. What if something goes wrong? As with any remedy, taking this step must be shown to be safe and effective.

To that end, six inexpensive PC video cards (assemblies) were masked with tape or removable plating mask (to protect metal areas intended to remain uncoated), and electrolessly plated with Ni. The thickness needed to impart permanent impenetrability was estimated to be 1 μm, which for the bath and conditions used required an immersion time of less than five minutes.

A masked assembly was conventionally cleaned, immersed for the chosen time, conventionally aqueous rinsed[18], dried, placed in a card slot of a PC, and found to function. This demonstrated concept feasibility. The process was repeated for longer times, with the same results. The accumulated immersion time was one hour, enough to give a thickness of about 25 μm (1 mil). This demonstrated a wide process acceptability window.

The remaining assemblies were similarly given the electroless Ni cap. Each electrical test was successful and no coating of insulating surfaces was observed, implying the remedy’s safety. All Sn surfaces were observed to be coated. Based on the data of Kim *et al.*, this demonstrated the remedy’s effectiveness.

Demonstration that the process is safe and effective means that the concept has been reduced to practice.[19] The process has since been applied to a number of production assemblies, with no failures observed. Further evidence of safety and effectiveness is expected as the remedy is applied to more assemblies.

Comparing the Electroless Selective Metal Cap Process to the Ideal

Electroless deposition of a metal cap layer on the Sn of a functioning electronic assembly closely matches the list for an ideal whisker-prevention process.

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[16] Unless special measures are taken (undesired in this case), metals will not deposit electrolessly on insulating surfaces, including metals that have a thick and tenacious native oxide.

[17] While less noble than the other metals, Ni forms a strong protective oxide and is regarded as quite corrosion-resistant. The physical properties of all three, like those of ceramics, are unlikely to change even over decades.

[18] Thorough cleaning under components with very small standoff height (e.g., a micro-BGA) could be assured by the use of steam, which is a well-established practice at companies that specialize in removing and measuring residues on electronic assemblies (e.g., Foresite, Kokomo, IN).

[19] A provisional patent has been applied for.

- Applied to entire assembly between cleaning and conformal coating
- Eliminates BOM scrubbing and testing components for Pb-free Sn at receiving
- Remedies termination finish whiskering problem with COTS assemblies
  - No additional masking cost
  - Can add components later if necessary
- All Sn covered (no shadowing)
  - Hot aqueous immersion penetrates small clearances
- *Permanently* suppresses whisker growth
  - None seen in > 5 yrs for 200 nm Ni
- Easy rinsing of assembly for next process step
  - Water and steam then dry
- Inherent practical compliance verification
  - Bubble evolution indicates deposition is occurring
  - Cu (if present) looks different coated and uncoated
  - X-ray fluorescence measurement useable as a referee
- No interference with rework
  - Ni coating too thin to affect melting of underlying solder
- Insulating surfaces unaffected
- Risk of damage to assembly function, reliability, and legibility appears negligible
- Fixed and maintenance costs negligible
- Small equipment footprint
- Inherently safe
  - No chemicals not already used in electronics industry
  - Electroless Ni use has long history, widespread use
- Simple work force training
  - Broad process window
- Quick, so no bottlenecks
  - Required time < 5 minutes per assembly

Conclusion

Electroless Ni has been applied selectively as a cap layer to all Sn surfaces of a number of functioning electronic assemblies (i.e., without coating insulating surfaces) without impairing their function, reliability, or marking legibility. Based on previously published data extending over more than five years, it appears that this cap layer will permanently prevent the penetration of Sn whiskers, and hence, will prevent whisker-caused short circuits.

Au and Pd, which also can be deposited electrolessly and have been found to remain impenetrable, would likely serve as remedies as well, and possibly other metals that have yet to be investigated for this purpose.

The penetrability of Pb and Cu layers is dramatically different. This difference may indicate that Sn-whisker penetrability is a physical attribute of the metals themselves. Alternately, there may be a great difference in how thick a layer of a particular metal on Sn must be to render it whisker-impenetrable.[20] This possibility remains unexplored.

The electroless cap layer process appears to be a safe and effective remedy, and closely matches the attributes of an ideal process for OEMs to apply to the assemblies they buy and build. The cap layer deposits selectively (i.e., on tin but not on insulating surfaces). Because the layer appears to remain impenetrable and (apart from growth of an intermetallic layer) its properties are invariant with temperature, humidity and time, the process is superior to conventional “mitigation” practices, and compares favorably with the two other processes (ceramic and polymer coating) that have been announced as remedies.

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[20] As a thought experiment, it seems hard to imagine a Sn whisker penetrating say a cm. of *any* overlying metal layer.