Lead (Pb) – Free Plating for Electronics and Avoidance of Whisker Formation

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Abstract

Lead (Pb), commonly used in plating of electronic components, is required to be phased out due to the hazards it poses. Possible alternative technologies and materials are discussed. Whisker formation, avoidance of which was an important reason for the use of lead as an alloying element, is examined. Whisker formation is dependent on stress in the electrodeposit, and strategies for its avoidance are discussed. Alloys of tin with bismuth, copper or silver may be difficult to control on an ongoing production basis and are also known to be liable for whisker formation. Pure matte tin, when plated appropriately with respect to substrate, current density and other operating conditions, has fewer problems and can be used profitably in existing plating installations.

INTRODUCTION

Lead alloys, particular Sn/Pb alloys, are ubiquitous in the electronics industry. The advantages they offer include low melting point, freedom from whiskers, insusceptibility to tin – pest, slowing down of inter metallic phase formation or copper dissolution, technical reliability, and cost – effectiveness. From a metal finishing point of view, the requirements from modern Sn/Pb plating baths include electrodeposition over the entire alloy range, the possibility to use in rack, barrel as well as high – speed, high current density reel to reel plating lines, and conformance of the electrodeposits to (soldering) specifications such as Mil-STD-883E and DIN IEC 68.

The hazards posed by lead, though recognized for decades, are in recent years also stimulating legislation restricting its use. Many countries, for example have either severely restricted the sale of lead – acid batteries for automobiles or have made it mandatory for manufacturers to accept the old batteries back for recycling either at the time of sale of a new one or at the time of scrapping. Although the legislative situation seems to be a bit confusing sometimes, there is a clear tendency to phase out the use of lead. The European Community and Japan are the most active countries in lead-free legislation.

In the European Community, the two directives **WEEE** (Waste from Electrical and Electronic Equipment) and **RoHS** (Restriction of Use of certain Hazardous Substances in Electrical Equipment) had been signed on January 27th 2003 and put into force with their publication in the Eurpean official gazette on February 13th 2003. Whereas the **WEEE** is concerning recycling and take back legislation, the **RoHS** directive restricts directly the use of lead in electronic components. It states in article 4: "Member States shall ensure that, from **1 July 2006**, new electrical and electronic equipment put on the market does notcontain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethersPBDE)." [1, 2, 3].

Although there is no specific legislation, except a proposed take back legislation for electronic components by the Ministry of International Trade and Industry (MITI), in Japan calling for the reduction or elimination of lead in electronics, several Japanese OEMs have taken upon themselves to be as proactive in this market as possible. The Japanese Electronic Industry Association (JEIPA) has suggested the eradication of the use of lead in electronic products completely, a suggestion which has been scheduled for implementation in the near future. Major Manufacturers planned to eliminate lead solder completely already by 2000/2001 [1, 2, 3].

Since not only the lead containing solder, but also the electroplated lead containing solderable component finishes are concerned, there is the need to develop alternative electrolytes which can be used in place of lead containing alloy electrolytes.

The proposed solutions should be evaluated on the basis of criteria such as solderability, risk of whisker formation, high speed operation, ease of control, possibility of using existing plating and effluent treatment equipment, economy and acceptability as a non – toxic and reliable material by the relevant bodies.

POSSIBLE LEAD – FREE ALTERNATIVES

1. Other Technologies

This point refers to alternative technologies like galvanic ("electroless") nickel-phosphorus with goldflash or the palladium nickel technology for leadframes or to the electrodeposition of PdNi (80/20) alloy. Presently all these technologies can be regarded as technological and economical niche solutions, which are relatively far away from the original tin / lead technology.

2. Pb-Substitution Alloys

These kind of alternatives are very much in discussion at the moment. They are all based on the asumption, that the lead in the electrolytes has to be substituted by another metal like silver, copper or bismuth. At this time there is no Pb-substitution electrolyte in the market, which can be operated under production conditions comparable to tin/lead. The main reason is the relatively high electrochemical potential for the deposition of silver (+0.799 V v/s NHE), copper (+0.340 V v/s NHE) and bismuth (+0.317 V v/s NHE) compared to the electrodeposition of tin (-0.137 V v/s NHE) and lead (-0.125 V v/s NHE) [4]. (See Fig. 1). In fact, the closeness of the electrodeposition potentials of tin and lead helped immensely in the development of commercial processes for tin/lead electrodeposition over wide alloy composition ranges and for varied applications. The wide potential gap between tin and the other alloying materials such as bismuth, silver and copper introduces problems such as the need for frequent replenishment, cementation on the anodes, the need for specialized strippers, the need to alter the existing plating lines and effluent treatment plants at huge costs, complexity of control, etc. To a certain extent, the EU-legislation is taking this into account, since the latest draft of the ROHS contains an exemption for lead in high melting temperature type solders (i.e. tin-lead solder alloys containing more than 85% lead) [1, 2,]. Pb-substitution electrodeposits are ecologically controversial as well, since bismuth is a byproduct of lead mining and leaching tests carried out on Pb-substitution alloys show that they have to be classified as hazardous waste [5].

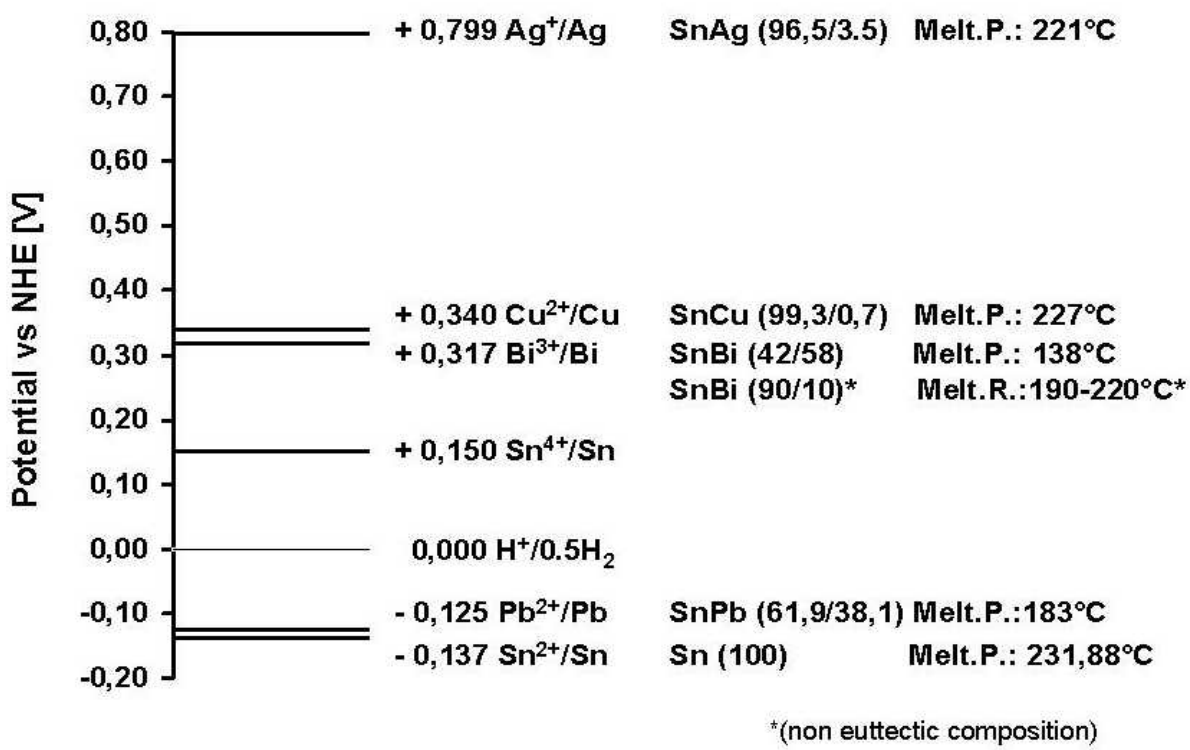

Fig. 1 Aqueous redox potentials of solder metals versus NHE and eutectic melting points of their tin alloys.

3. Pure Tin

Instead of substituting the lead it is much more convenient just to drop the use of lead wherever possible and to deposit pure tin. Although the lead has been historically introduced in tin electroplating only for solderability and specification reasons, most people today are sceptical about pure tin plating since they fear enhanced whisker formation in the absence of lead or Pb-substituting metals [6]. Some of the above mentioned Pb-substitution alloys also exhibit considerable whisker growth and hence do not offer any advantage over pure tin [6]. Pure tin electrolytes have been and are being used to plate electronic and electrical devices. Reviewing the literature, there is no systematic investigation on a broader scale proving sufficiently the benefit of lead (bismuth, silver, copper) codeposition. At the moment, there are no specified whisker tests available. Therefore we started our ongoing research program to examine the conditions and tendency of whisker formation of pure tin deposits.

WHISKER FORMATION

Whiskers are elongated hair-like single crystals of pure metallic white β-tin that grow more than several mm in length and from 0.3 to 10 µm in diameter (typically ~ 1 µm). [7, 8, 9, 10, 11]. They grow spontaneously without an applied electric field or moisture and also independent of atmospheric pressure from the electroplated tin deposit. They may start to grow soon after plating or may take years to initiate. Growth occurs from the generally thicker base of the whisker in the direction of the low index faces. Sudden reorientation during the growth process leads to well defined kinks or bends of the whisker. Since whiskers are mono crystals the often observed striations in growth direction are terraces formed by the crystal planes. Due to their length and their ability to conduct current, they are able to short circuit electrical components. Prevention of whisker formation is thus an important goal of interconnection technology. Depending on the diameter and length of the whisker, a current of up to 50 mA is needed to fuse a whisker open [11].

Apart from the real single crystal whiskers there are often whisker-like tin protrusions on the electrodeposited surface which are referred to as warts, nodules or hillocks. Very often these nodules are starting points for the hair-like whiskers (Fig.3, Fig.5). Whiskers appear to grow more readily at temperatures approaching 50 ^{o}C, [12] and their growth seems to cease at temperatures higher than 140 ^{o}C and lower than – 40 ^{o}C [9].

MECHANISTIC IDEAS ON WHISKER FORMATION

Whisker formation is a relaxation process of the stressed, electroplated tin. Compressive stress is the driving force of whisker growth. Since whisker growth happens at ambient temperature on polycrystalline tin deposits, grain boundary diffusion is the only way for transporting tin material to the growing whisker [8]. Sn atoms are being transported to areas of low compressive stress, whereas the diffusion of the vacancies they leave behind happens in the opposite direction. Whisker formation can be regarded as a kind of hindered recrystallization of the electrodeposited layer at ambient temperature to achieve energetical equilibrium. Reflowed electrodeposits of tin hardly exhibit whisker growth at

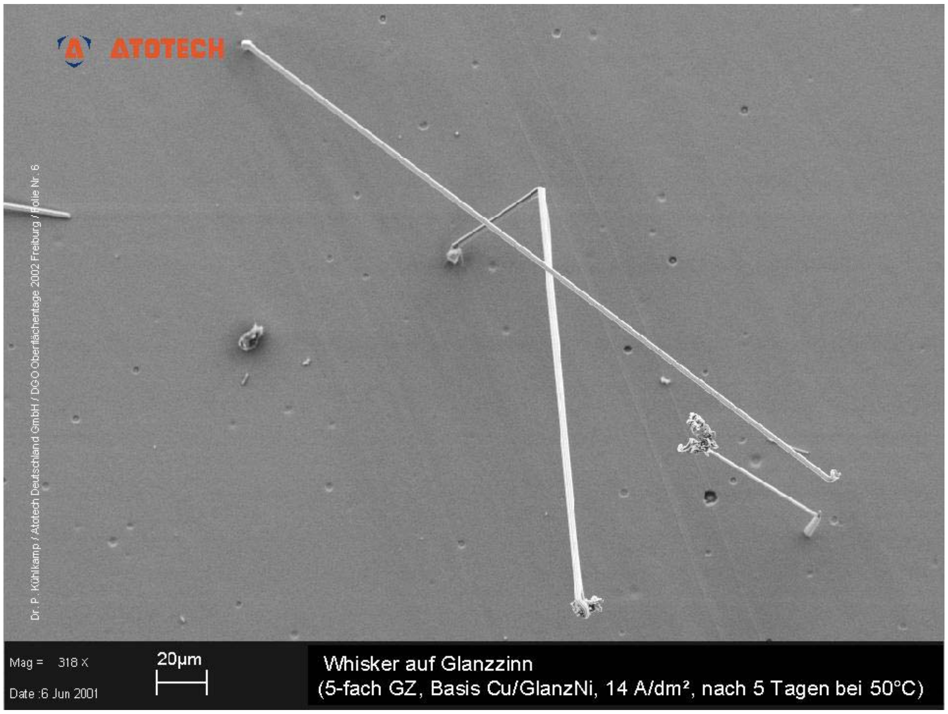

Fig. 2 Whisker on bright tin deposit, organic brightener concentration in plating bath increased five – fold, 14 A/ dm^2 after 5 days at 50 ^oC. Base: Cu / bright nickel.

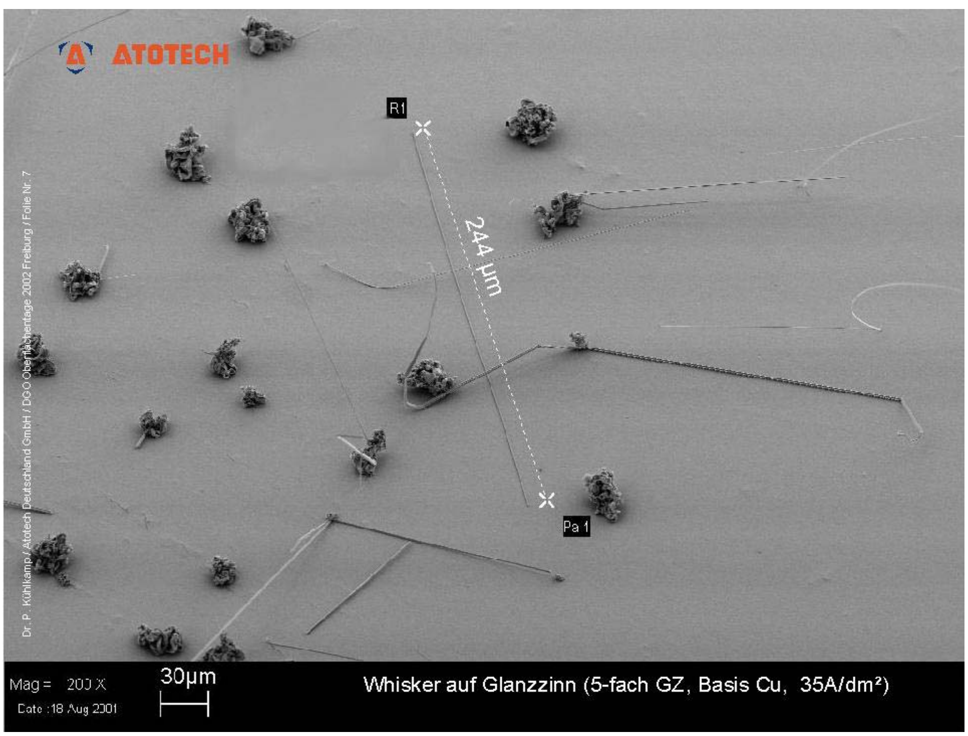

Fig. 3 Whisker of bright tin deposit, organic brightener concentration in plating bath increased five – fold, 35 A/ dm^2 Base: Cu

all, since they had the chance for recrystallization in which the internal stress and the dislocations had been eased out whereas the grain size increased up to a few mm size.

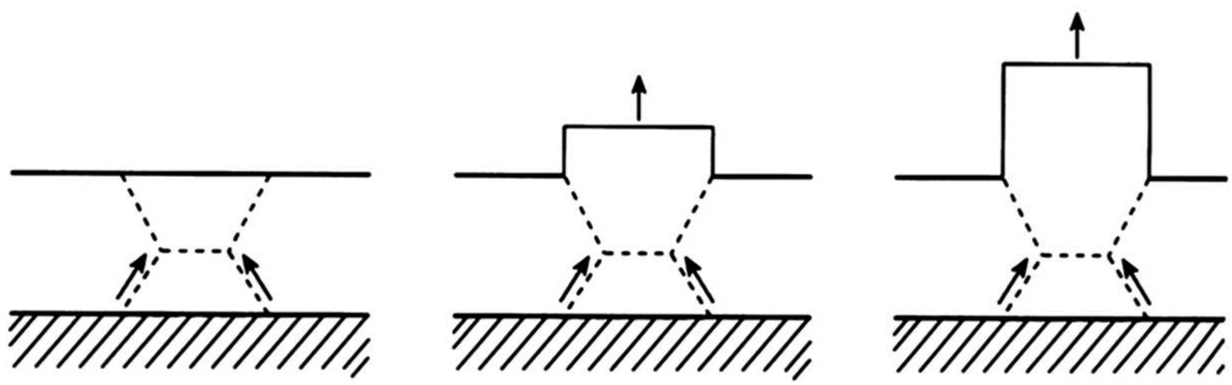

Fig. 4 Schematic mechanism of whisker growth in a polycrystalline deposit by grain boundary diffusion [8]

CAUSES OF WHISKER FORMATION

Whiskers are known to be caused by compressive stress in the electroplated deposit [7-15], which can have various origins:

- Unsuitable highly stressed base material
- Too much codeposition of organics
- Too much hydrogen codeposition
- Too high current density
- Too low layer thickness
- Formation of intermetallic compounds
- Stamping processes like 'trim & form' or mechanical damages like scratches or nicks in the plating introduced by handling

Very often, two or more of these influences in combination are necessary to cause whisker growth. Seldom is the electrolyte itself the only reason for whisker formation.

WHISKER EXAMINATION BY SEM

Our research included the examination of some of the various above mentioned causes of whisker formation. All samples had been prepared from either matte or bright tin electrolytes based on methanesulphonic acid. The following Field-SEM pictures had been made approximately after four weeks of dry storage at 50°C.

1. Bright tin

Bright tin is much more susceptible to whiskering than matte tin deposits. Especially the deposits from 1st generation bright tin electrolytes had a penchant for producing whiskers due to their high content of unsuitable brightening agents like wood tar. Electrodeposits from a today's state of the art bright tin electrolyte did not exhibit any hair-like whisker growth. Only a layer deposited at 2 A/dm² showed tiny a few hundred nm high columnar protrusions (200-500nm high, 1-2µm diameter). Experiments have been performed deliberately inducing a five – fold increase in the concentration of additives used for brightening tin (Fig. 2 and Fig.3) Electrodeposits from such an electrolyte showed a markedly higher tendency to form whiskers. Further on, the influence of current densities can easily be shown when comparing aged layers deposited at 14 A/dm ^{2} and 35 A /dm ^{2} (Fig.5).

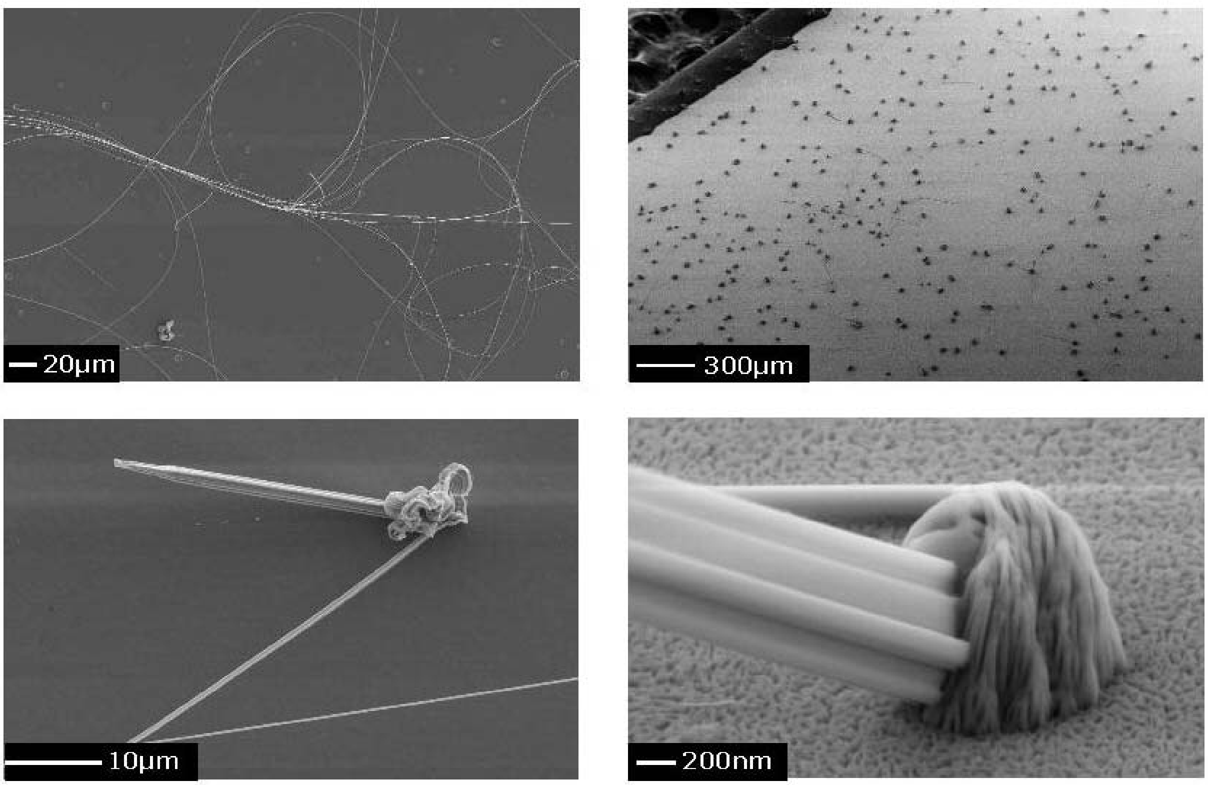

Fig. 5 Whisker of bright tin deposits, organic brightener concentration in plating bath increased five – fold, left: 14 A/dm², Base bright Ni; right: 35 A/dm^2, Base: Cu

Brass is very prone to induce whisker formation, and as per ISO 2093, it is not permitted to plate tin directly onto brass for electronic applications, an intermediate electrodeposit is recommended. SEM examination of an electrodeposit of bright tin on brass substrate from an electrolyte with a five – fold increase in organic brightener concentration at 35 A / dm^2 showed, in first instance, after four weeks, hillock-shaped growths (Fig. 6).

When examined again eight weeks later, (twelve weeks after plating) a whisker in the process of growth could be observed.

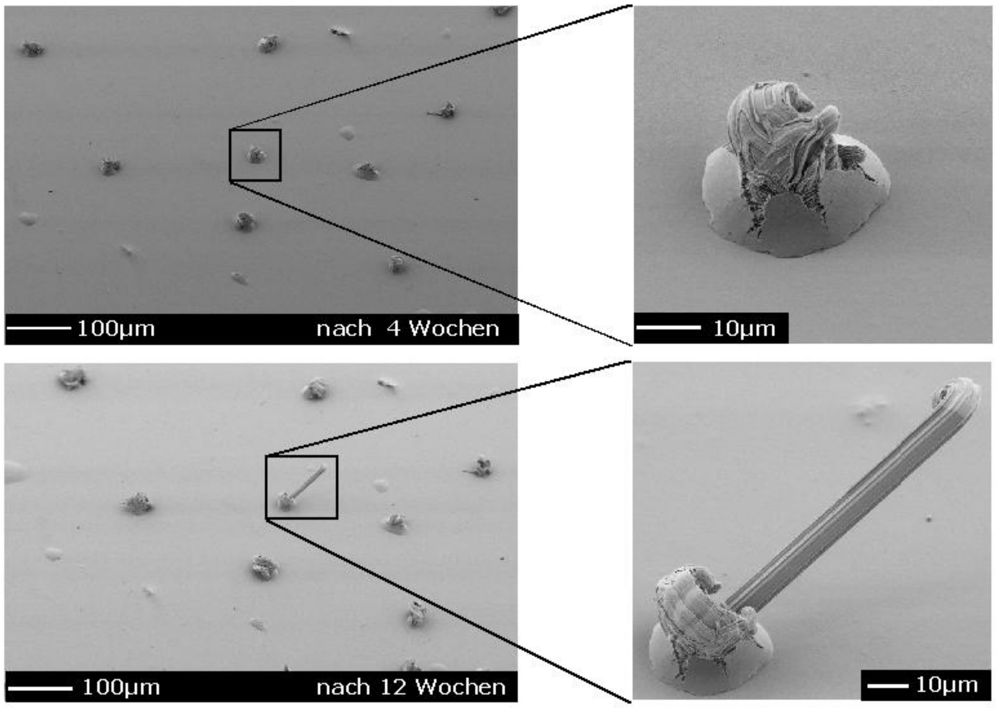

Fig. 6 Examination of whisker growth from tin electrodeposited on brass at 35 A/dm^2 from a bath overdosed five – fold with organic brightener; top: four weeks after plating, and bottom: twelve weeks after plating

Nevertheless, it must be stated that the risk of whisker formation though reduced is not fully excluded by alloying tin. Figure 7 shows a SEM of whisker growing on a tin / lead 90/10 electrodeposit on brass. EDAX analysis of the growth clearly shows the presence of lead, zinc and copper besides tin.

.2. Matte tin

Due to the experiences with the bright tin electrolytes almost 50 years ago, tin is still perceived to be a whisker – prone material. Modern matte – tin electrolytes are, however, much less prone to whisker growth. Figure 8 displays regular polygonal deposits from a modern matte tin electrolyte plated at different current densities (4 A/dm^2 and 50 A/dm^2) on brass. From all matte tin deposits only the sample plated at 50 A/dm^2 on brass exhibited whiskers. Again the picture demonstrates the influence of two causes in combination –base material plus current density. The freeze fractures below show the influence of the current density on the grain size. With decreasing grain size the main pathway for material transport -the grain boundary surface- increases.

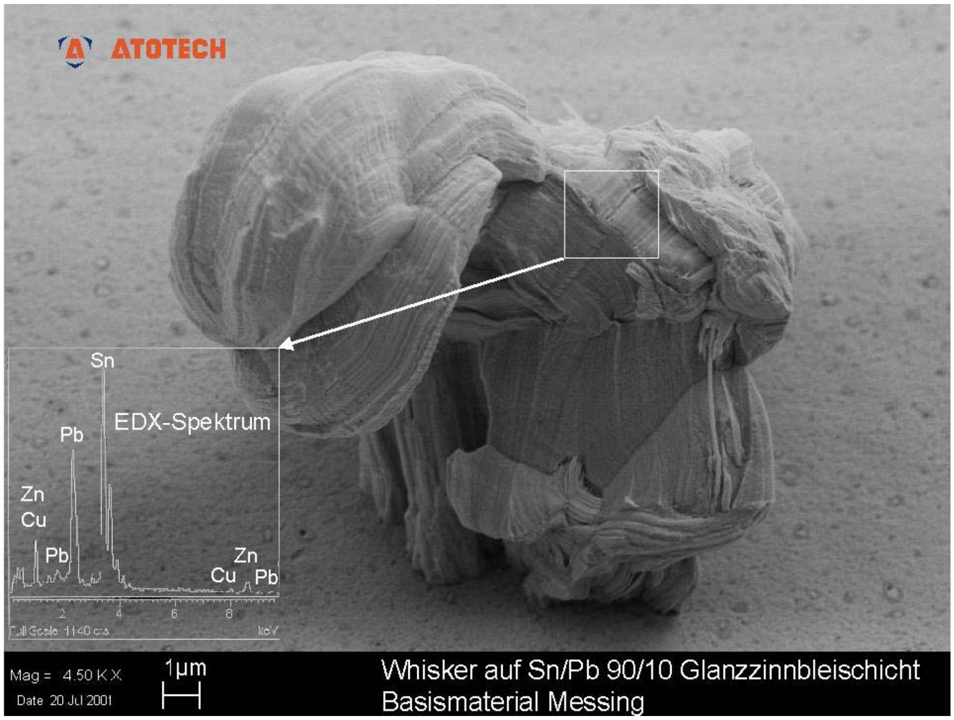

Fig. 7 Whisker growing from tin–lead alloy electrodeposited on brass. EDAX of the indicated spot shown in inset.

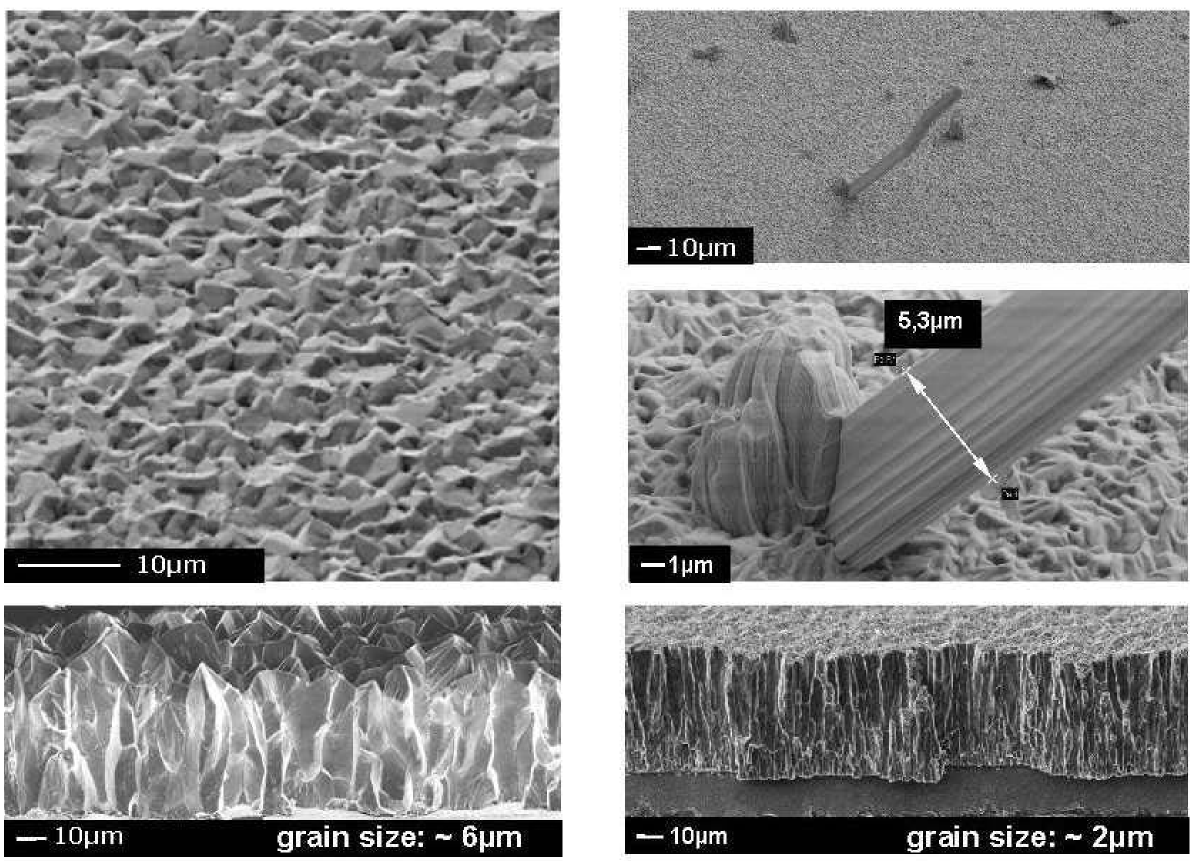

Fig. 8 Matte tin deposits on brass at 4 A/dm² (left) and at 50 A/dm² (right).

3. Influence of base material and applied mechanical stress

Not only brass, but also the particle hardened alloys like C151, C194 and C7025 used in semiconductor industry are highly stressed base materials which promote whisker formation when directly plated with tin in IC-Lead (Leadframe) plating. (see Fig. 9). In fact the producers of these high performance alloys advertise the excellent resistance to stress relaxation of these alloys. Their high strength to provide good contact force and excellent electrical and thermal conductivity make these alloys an attractive choice for integrated circuit leadframes. Copper, nickel and alloy 42 show the least propensity to induce whisker formation. Sulphamate nickel or copper are recommended as intermediate electrodeposits for substrates prone to induce whisker formation.

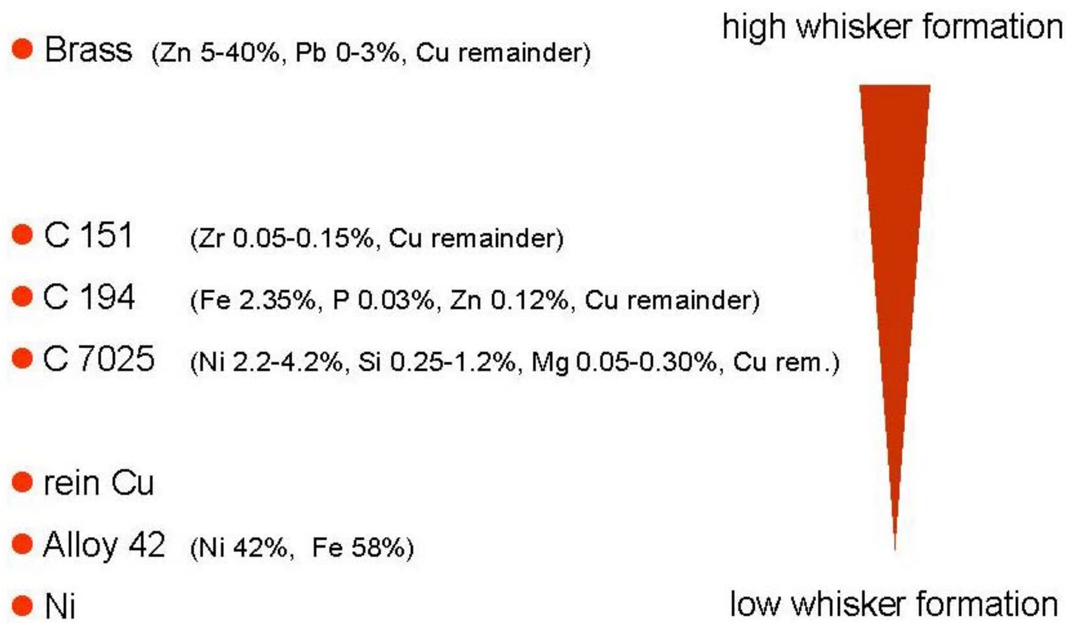

Fig. 9. Approximate tendency of whisker formation dependent on base material

The material C 151 is a precipitation hardened alloy of copper with zirconium (0.5 - 0.15%). An SEM examination done of the etched surface reveals the Zr-rich particles which prevent the stress relaxation and hence are responsible for the strength of this material (Fig. 10). Unalloyed hardened copper will try to reach it lowest state of energy by reducing its internal dislocations by diffusion and glide mechanisms and hence lose its hardness and strength. In precipitation hardened alloys these stress relieving mechanisms are blocked by the included particles.

Today most plating on IC-Leads is done with Sn/Pb (85/15). Examination of the surface of a PLCC (pin plastic J- lead chip carrier) made of C 151 plated with pure tin shows needle like whiskers along the punched edges which suffered deformation by the stamping process. (Fig 11). Again the whisker formation originates from two causes, unsuitable base material plus additional mechanical stress before plating. The small size of the whiskers should hardly pose a hazard concerning short circuits.

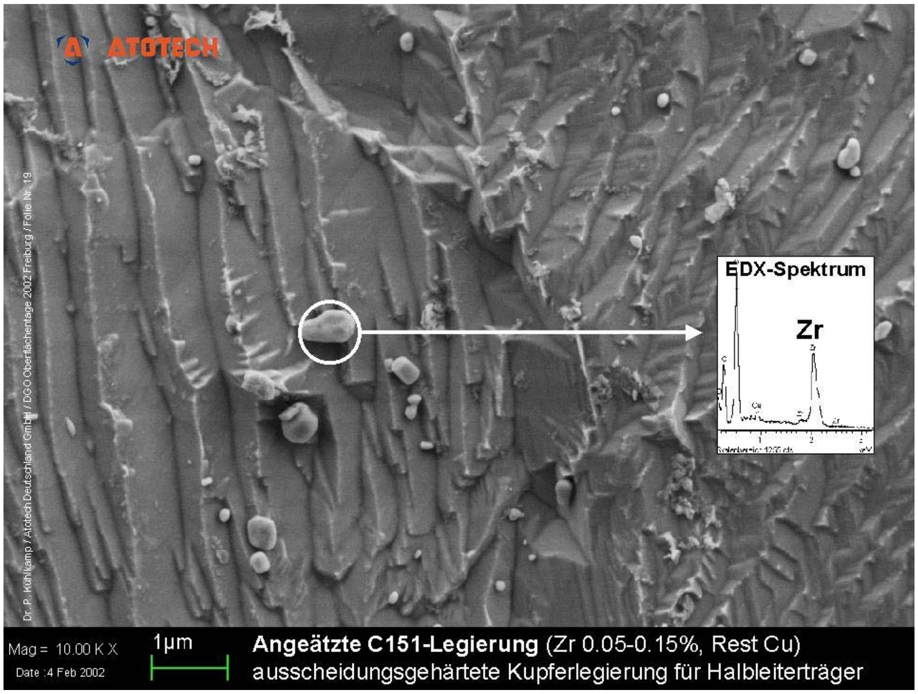

Fig. 10. Examination of the surface of C151 material. EDAX confirms that the particles on the surface contain Zr.

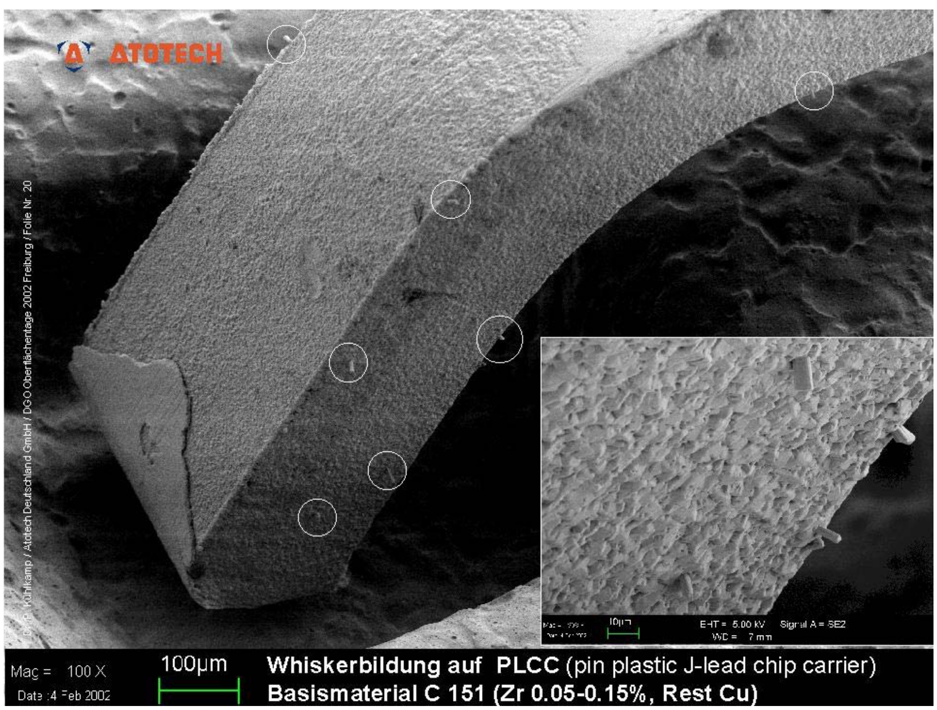

Fig. 11. Examination of the surface of PLCC (Pin Plastic J-lead Chip Carrier) basis C151 material plated with tin. Note whisker growths along the punched edges.

Not only mechanical stress applied before plating can lead to whisker formation, the stamping processes performed after plating can also lead to whisker formation. Fig. 12 shows a small whisker in the area of the squeezed tin after trim & form processing of an IC (lead frame) strip.

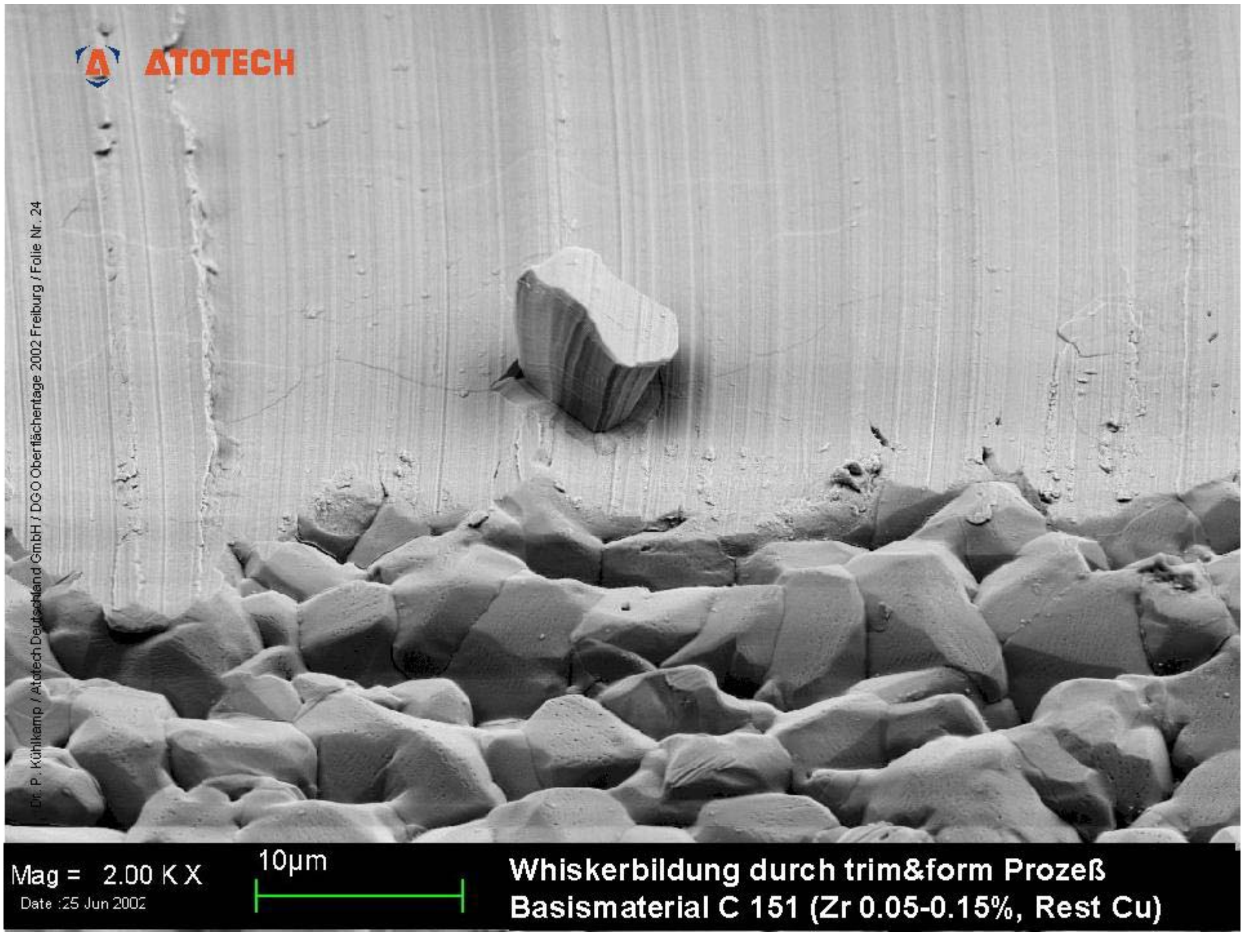

Fig. 12. Examination of a PLCC (Pin Plastic J-lead Chip Carrier) lead (basis C151) plated with tin after the 'trim & form' process.

STRATEGIES TO PREVENT WHISKER FORMATION

The preceding SEM pictures served as bad but instructive examples for whisker formation. Concluding from them, the measures listed in Table 1 have to be taken to prevent whisker growth.

Since all cases of whisker formation are somehow linked to compressive stress of various origins - sometimes in combination - the main goal should be to provide low stress deposits. Following the above mentioned standard practices a minimization of the whisker risk can be accomplished to a large degree.

One step to low stress plating can be the use of matte tin deposits which exhibit relatively large undistorted polygonal grains close to their energetical equilibrium.

Table 1. Strategies for avoiding whisker formation

• Avoidance of overdosing of plating bath with organic brighteners • Preference to deposit more matte electrodeposits with larger grain size • Preference to deposit sufficiently thick electrodeposits (> 8 µm) • Avoidance of direct electrodeposition on stressed alloys including phosphor – bronze, zirconium hardened copper or brass. As per ISO 2093, a barrier layer of sulphamate nickel or pure copper should be used • Operation of electrolytes within the recommended optimal operating ranges • Avoidance, as far as possible, of mechanically stressing before and after plating , such as bending, compression or damage by scratches, indentations, etc. • Use of reflow melted coatings. The tin surface of the plated electrical or electronic parts is reflowed anyway during the SMT soldering process. • Annealing treatment of tin coatings after deposition at approximately 200°C to release internal stresses

MATTE TIN AS A LEAD – FREE ALTERNATIVE

Although there is no drop in solution for tin / lead electrolytes, pure matte tin is the nearest match. The electrodeposition of pure tin had been practice in semiconductor industry already [6] and is standard, trouble-free practice in connector plating. Of all alternatives it is the most well known and well studied system. The main disadvantage faced is the perceived propensity of pure tin for whisker formation, although the situation for Pb-substitution alloys (Sn/Bi, Sn/Cu, Sn/Ag) is much more uncertain in this respect. Due to the various possible stimuli for whisker growth, there can be no “magic tin electrolyte” –whether alloyed or not- providing “absolutely whisker free” deposits.

Apart from this matter pure tin technology has only advantages when compared with Pb-substitution electrolytes:

- Pure tin electrolytes can be used in existing plating lines without major modification.
- Pure tin electrolytes enable high speed applications.
- Pure tin electrolytes and deposits are easy to control.
- Pure tin electrolytes are the most cost effective lead-free solution.
- Pure tin electrolytes do not require a modification of existing waste water plants.
- Pure tin technology does no require the development of new (hazardous) strippers.
- Pure tin deposits are compatible with all tin-based soldering technology.

Again, whisker formation can be prevented by following the rules listed in Table 1.

CONCLUSIONS

Environmental considerations have prompted the issuance of lead (Pb) – free directives, and hence Pb – free plating is an important area of research and study for all connected with plating of electronic components. Proposed alternatives like tin-silver, tin – copper and tin – bismuth as well as pure tin are under study. The large difference between the electrodeposition potentials of tin and elements like copper, silver and bismuth creates process problems for continuous production, such as the need for frequent replenishment of concentrates, cementation of anodes, current density limitations, effluent treatment issues, need for modification of processes, etc. Besides, there is no guarantee that any coating containing tin (including tin/lead) is completely whisker - free. Whisker formation is dependent on stress. The stress can be either from the substrate, the component manufacturing process, or the electroplating chemistry or process.

Matte tin is a promising lead free alternative. The advantages it offers include that it is a well - studied process, with ease of process control and capability of being used in rack, barrel and high speed reel–to–reel modes in existing plating lines, using existing plants for effluent treatment and at reasonable cost. Strategies for whisker avoidance include operation of plating baths within supplier – specified operating conditions, including current density, etc., avoidance of overdosing with organic additives, deposition of sufficiently thick electrodeposits, use of appropriate intermediate layers such as sulphamate nickel or copper when plating on stressed substrates and prevention of mechanical stresses after plating if possible. Thus the prevention of whiskers is rather a quality management issue in the application of existing technology than choosing a specific new electrolyte.

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