Some Examples of "Whiskers" from Tin-Based Alloys

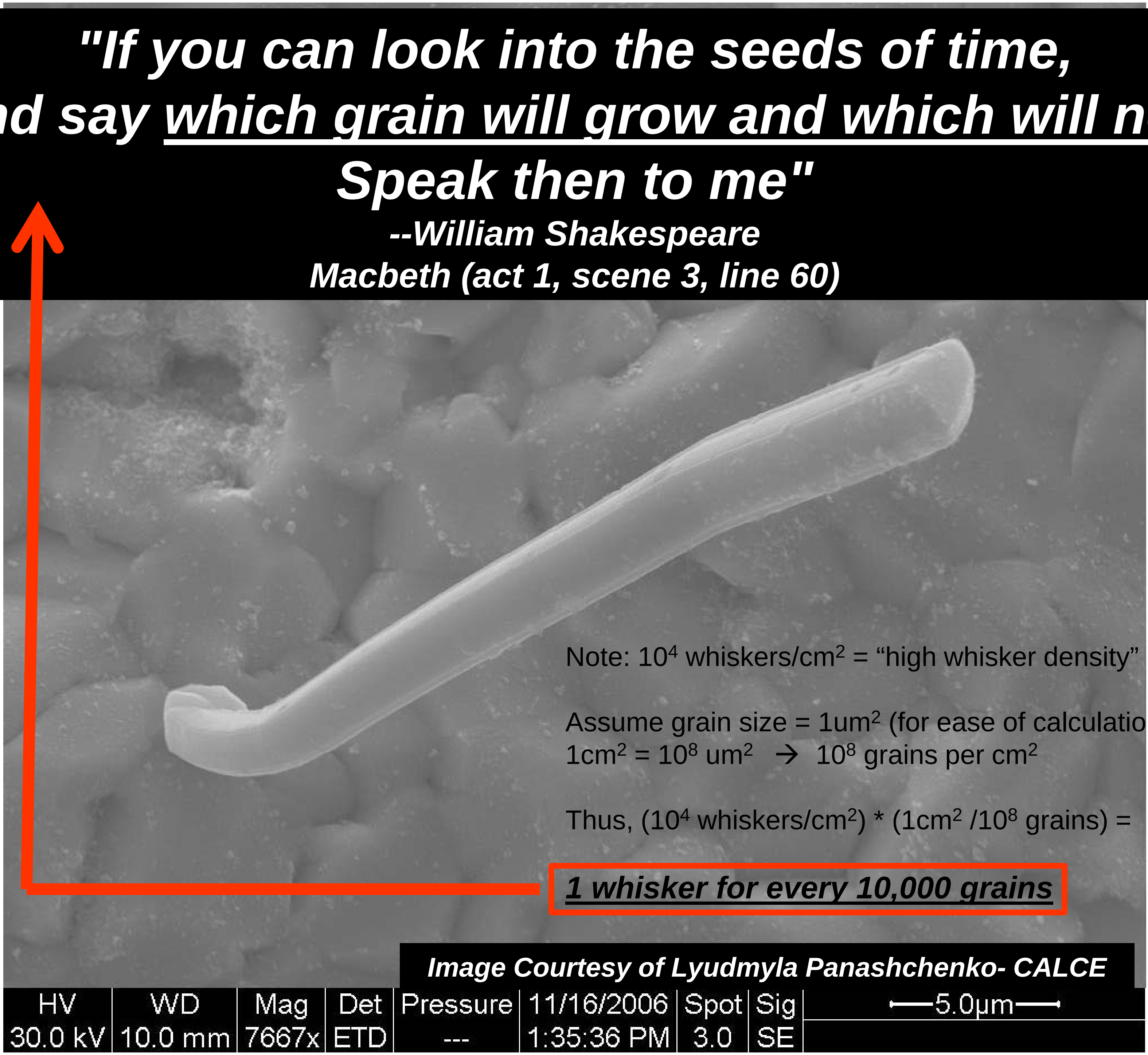
Alternate Title:

"Sometimes	*Tin*	*Whiskers"*
Adverb	*Noun*	*Verb*

-- Quote attributed to Lyudmyla Panashchenko

Compiled by
Jay Brusse/Perot Systems
July 2009

> ***"If you can look into the seeds of time,***
> ***And say <u>which grain will grow and which will not</u>,***
> ***Speak then to me"***
>
> ***--William Shakespeare***
> ***Macbeth (act 1, scene 3, line 60)***



Note: 10^4 whiskers/cm^2 = “high whisker density”

Assume grain size = 1um^2 (for ease of calculation)
1cm^2 = 10^8 um^2 → 10^8 grains per cm^2

Thus, (10^4 whiskers/cm^2) * (1cm^2 /10^8 grains) =

<u>1 whisker for every 10,000 grains</u>

Image Courtesy of Lyudmyla Panashchenko- CALCE

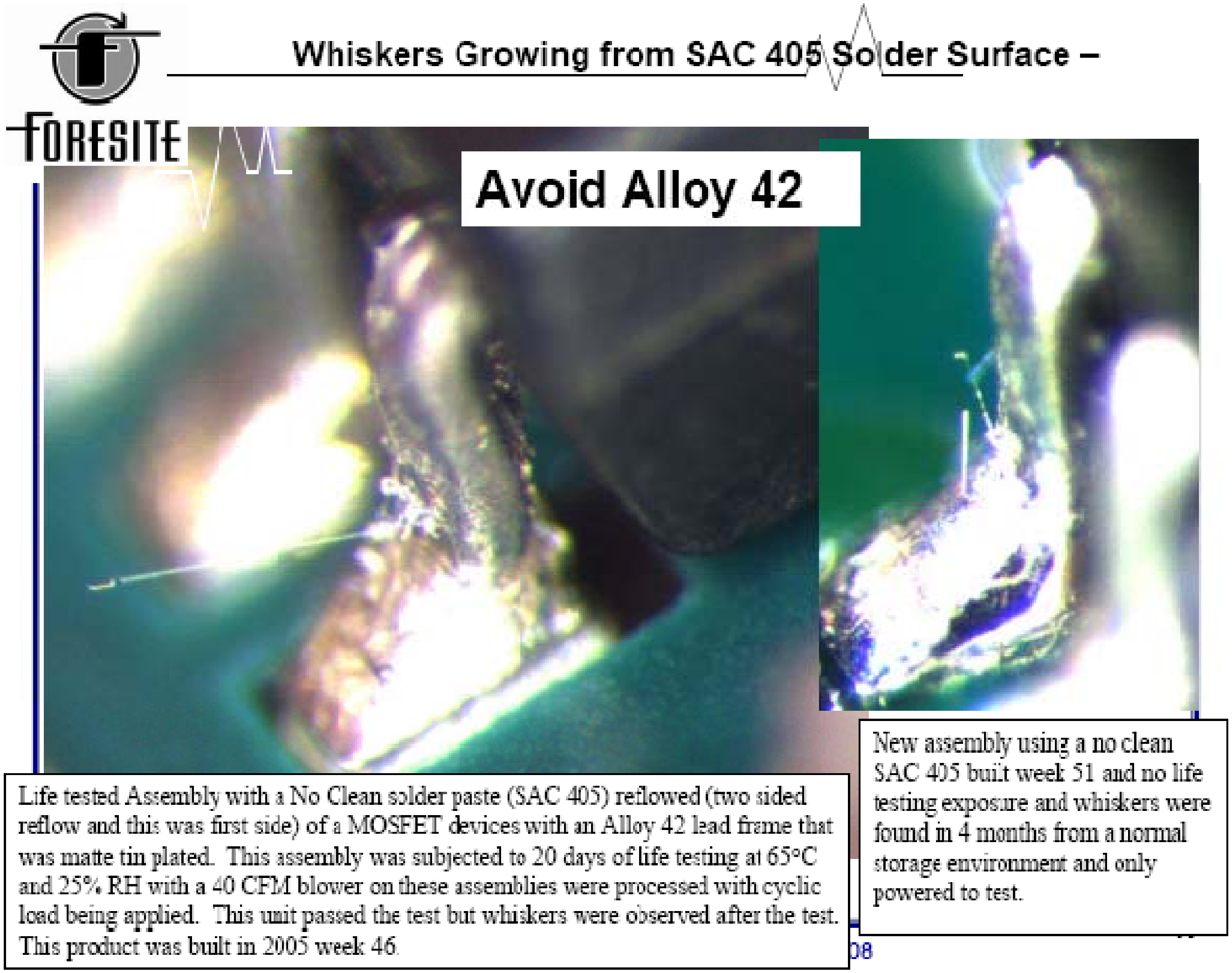
Background

- This listing is NOT all-encompassing
  - Exhaustive literature search was NOT performed
  - Many more examples are known, but due to time constraints were not compiled herein
  - Permission to distribute some known examples has often been denied
    - For example, In 2006/2007 Munson & Handwerker reported a case of tin whisker induced shorting where whiskers grew out of SAC305 (or maybe SAC405) solder joints. The Mfr of the assembly later requested distribution of photographs be curtailed.
    - Later in 2008, Handwerker publicly presented images from this experience

- Purpose:
  - Show that tin whiskers can/have been documented on a variety of Sn-based alloys
  - To facilitate discussions about whether or not to prohibit various Sn alloy coatings

- Purpose is **NOT**:
  - To imply that whisker growth mechanism is understood
  - To imply that the alloys shown herein are always prone to whisker formation

Whiskers from Sn-Ag-X Based Alloys



Whiskers Growing from SAC 405 Solder Surface –

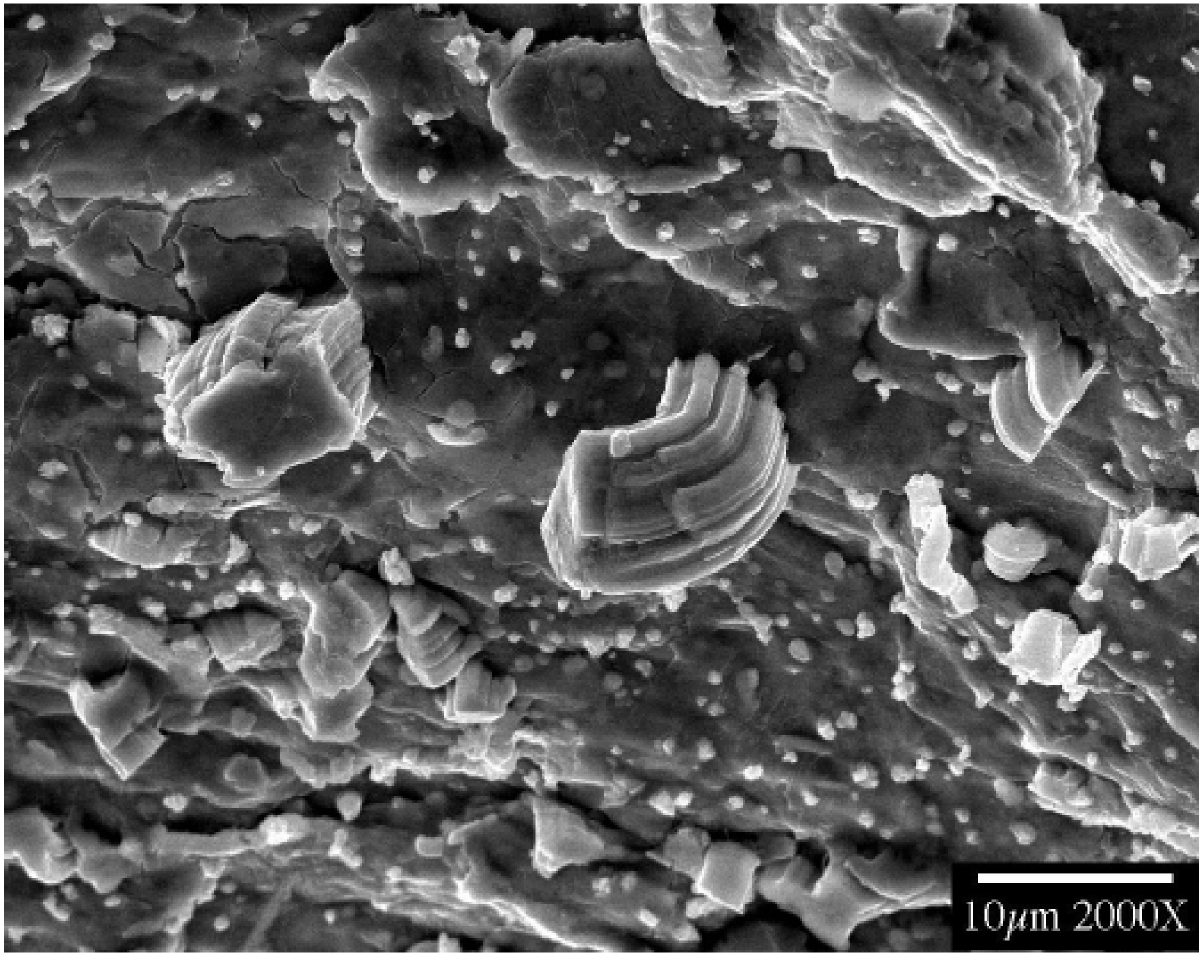
Avoid Alloy 42

Life tested Assembly with a No Clean solder paste (SAC 405) reflowed (two sided reflow and this was first side) of a MOSFET devices with an Alloy 42 lead frame that was matte tin plated. This assembly was subjected to 20 days of life testing at 65°C and 25% RH with a 40 CFM blower on these assemblies were processed with cyclic load being applied. This unit passed the test but whiskers were observed after the test. This product was built in 2005 week 46.

New assembly using a no clean SAC 405 built week 51 and no life testing exposure and whiskers were found in 4 months from a normal storage environment and only powered to test.

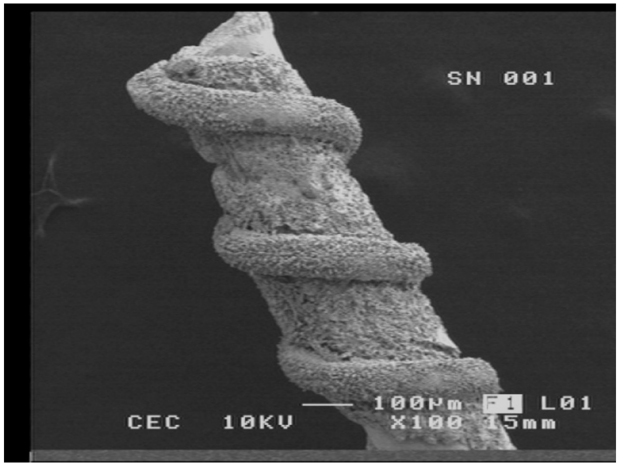
Tin Whiskers on hot dipped SAC305 surface mount resistor termination after 500 hrs @85C/85%RH + 500 T-cycles -55C to +125C

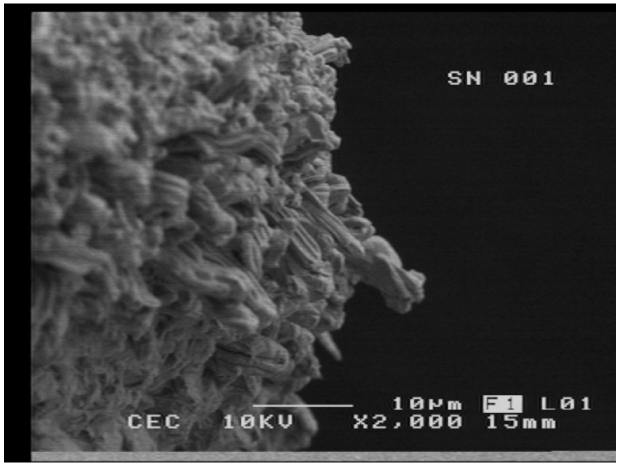
Peter Bush/SUNY Buffalo



Whiskers from SnAg Eutectic Solder

Anonymous





- small diameter pure copper transformer wire is wrapped around a cupronickel pin and then soldered in place using SN 96 eutectic tin-silver solder.
- unit was exposed to unusually high temperatures over an extended period of time as a result of system failure unrelated to these whiskers

Whiskers from SnAg Eutectic Solder

Tin Whiskers Formation on an Electronic Product: A Case Study

Nausha Asrar · Oliver Vancauwenberghe ·
Sebastien Prangere

Submitted: 31 January 2007 / Published online: 20 June 2007

Background

During qualification testing, a printed circuit board (PCB) of an electronic device from a drilling tool failed. The circuit board did not fail during the 120 h aging at 180°C. However, during the subsequent thermal cycles, in the temperature range of –40 to 180°C, it failed after 10 cycles (each cycle was of 2 h). During the inspection numerous white whiskers were observed over the Sn96 solder joint surfaces of components. In addition, fracture of the wire-bonds of a PCB-mounted chip were observed, which caused the failure of the circuit board. In this paper likely causes of tin whisker formation are discussed.

- Product being tested for “Down Hole Oil” Application. Uses Sn96 High Temp Solder

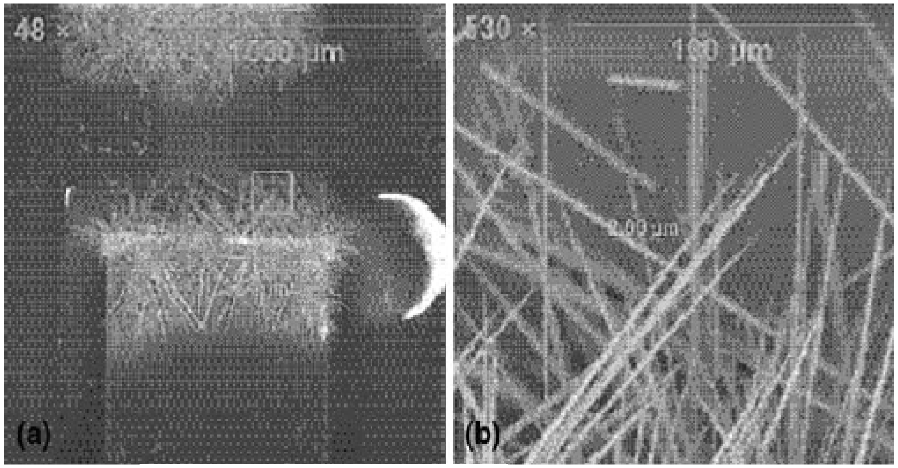


Fig. 4 (a) SEM picture showing the length of the tin whisker (0.344 mm, formed in 140 h). (b) Thickness of the tin whisker (0.002 mm)

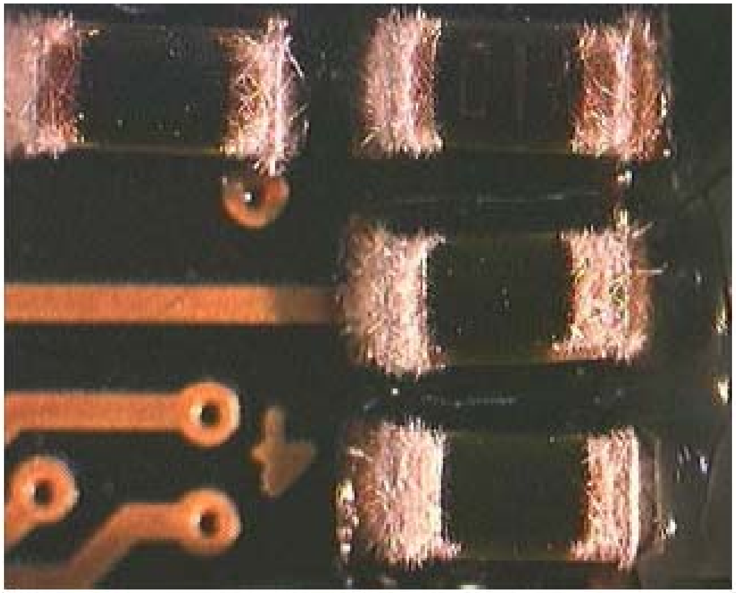
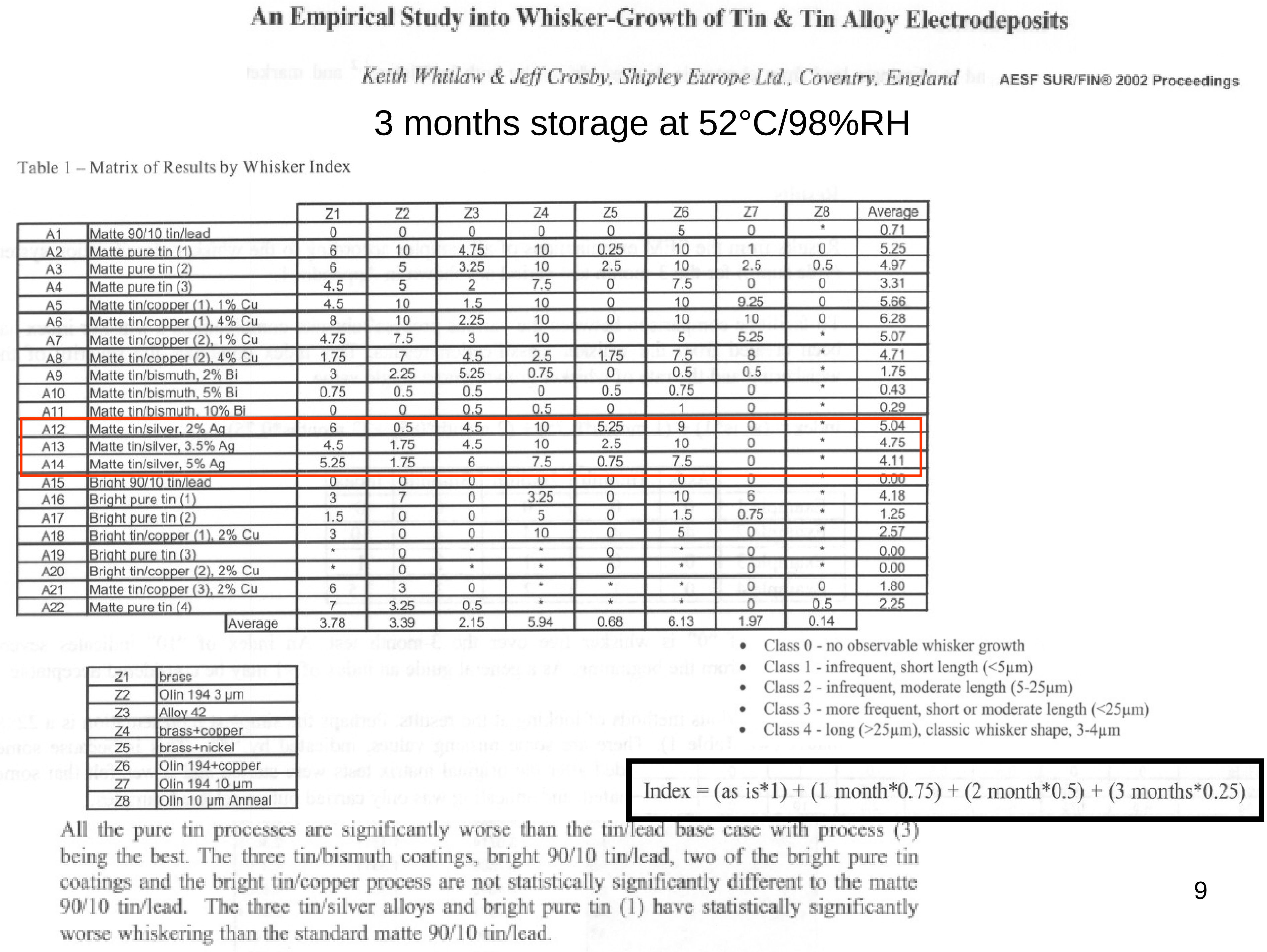


Fig. 3 Close-up showing tin whiskers on the solder joints. 40×



An Empirical Study into Whisker-Growth of Tin & Tin Alloy Electrodeposits

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

AESF SUR/FIN® 2002 Proceedings

3 months storage at 52°C/98%RH

Table 1 – Matrix of Results by Whisker Index

		Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Average
A1	Matte 90/10 tin/lead	0	0	0	0	0	5	0	*	0.71
A2	Matte pure tin (1)	6	10	4.75	10	0.25	10	1	0	5.25
A3	Matte pure tin (2)	6	5	3.25	10	2.5	10	2.5	0.5	4.97
A4	Matte pure tin (3)	4.5	5	2	7.5	0	7.5	0	0	3.31
A5	Matte tin/copper (1), 1% Cu	4.5	10	1.5	10	0	10	9.25	0	5.66
A6	Matte tin/copper (1), 4% Cu	8	10	2.25	10	0	10	10	0	6.28
A7	Matte tin/copper (2), 1% Cu	4.75	7.5	3	10	0	5	5.25	*	5.07
A8	Matte tin/copper (2), 4% Cu	1.75	7	4.5	2.5	1.75	7.5	8	*	4.71
A9	Matte tin/bismuth, 2% Bi	3	2.25	5.25	0.75	0	0.5	0.5	*	1.75
A10	Matte tin/bismuth, 5% Bi	0.75	0.5	0.5	0	0.5	0.75	0	*	0.43
A11	Matte tin/bismuth, 10% Bi	0	0	0.5	0.5	0	1	0	*	0.29
A12	Matte tin/silver, 2% Ag	6	0.5	4.5	10	5.25	9	0	*	5.04
A13	Matte tin/silver, 3.5% Ag	4.5	1.75	4.5	10	2.5	10	0	*	4.75
A14	Matte tin/silver, 5% Ag	5.25	1.75	6	7.5	0.75	7.5	0	*	4.11
A15	Bright 90/10 tin/lead	0	0	0	0	0	0	0	*	0.00
A16	Bright pure tin (1)	3	7	0	3.25	0	10	6	*	4.18
A17	Bright pure tin (2)	1.5	0	0	5	0	1.5	0.75	*	1.25
A18	Bright tin/copper (1), 2% Cu	3	0	0	10	0	5	0	*	2.57
A19	Bright pure tin (3)	*	0	*	*	0	*	0	*	0.00
A20	Bright tin/copper (2), 2% Cu	*	0	*	*	0	*	0	*	0.00
A21	Matte tin/copper (3), 2% Cu	6	3	0	*	*	*	0	0	1.80
A22	Matte pure tin (4)	7	3.25	0.5	*	*	*	0	0.5	2.25
	Average	3.78	3.39	2.15	5.94	0.68	6.13	1.97	0.14	

Z1	brass
Z2	Olin 194 3 µm
Z3	Alloy 42
Z4	brass+copper
Z5	brass+nickel
Z6	Olin 194+copper
Z7	Olin 194 10 µm
Z8	Olin 10 µm Anneal

- Class 0 - no observable whisker growth
- Class 1 - infrequent, short length (<5µm)
- Class 2 - infrequent, moderate length (5-25µm)
- Class 3 - more frequent, short or moderate length (<25µm)
- Class 4 - long (>25µm), classic whisker shape, 3-4µm

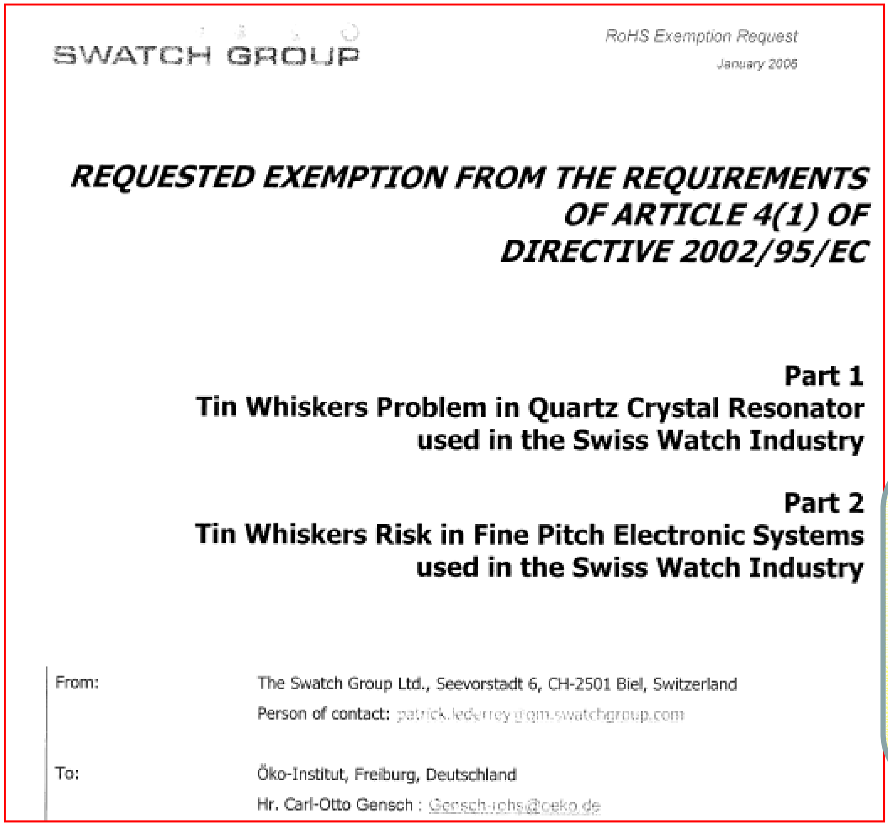
Index = (as is*1) + (1 month*0.75) + (2 month*0.5) + (3 months*0.25)

All the pure tin processes are significantly worse than the tin/lead base case with process (3) being the best. The three tin/bismuth coatings, bright 90/10 tin/lead, two of the bright pure tin coatings and the bright tin/copper process are not statistically significantly different to the matte 90/10 tin/lead. The three tin/silver alloys and bright pure tin (1) have statistically significantly worse whiskering than the standard matte 90/10 tin/lead.

Whiskers from Sn-Cu Alloy Systems

SWATCH Petition to EU TAC for RoHS Exemption

January 2006



SWATCH GROUP

RoHS Exemption Request

January 2006

REQUESTED EXEMPTION FROM THE REQUIREMENTS OF ARTICLE 4(1) OF DIRECTIVE 2002/95/EC

Part 1

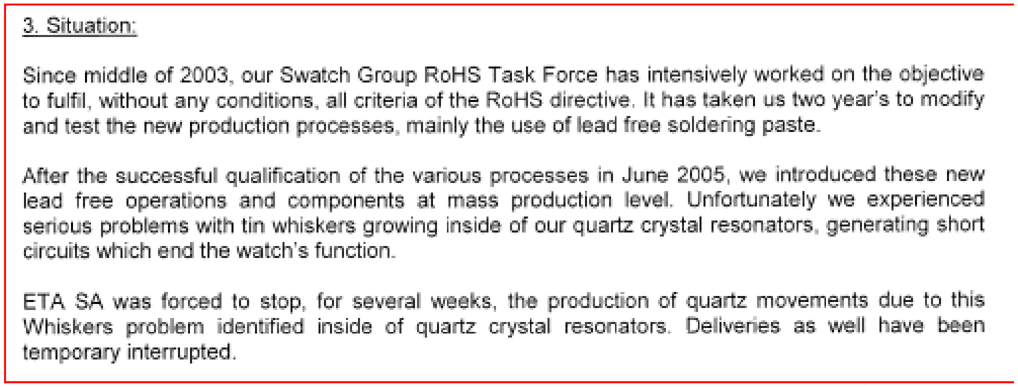
Tin Whiskers Problem in Quartz Crystal Resonator used in the Swiss Watch Industry

Part 2

Tin Whiskers Risk in Fine Pitch Electronic Systems used in the Swiss Watch Industry

From: The Swatch Group Ltd., Seevorstadt 6, CH-2501 Biel, Switzerland
Person of contact: patrick.lederrey@gm.swatchgroup.com

To: Öko-Institut, Freiburg, Deutschland
Hr. Carl-Otto Gensch : Gensch-ichs@oeko.de

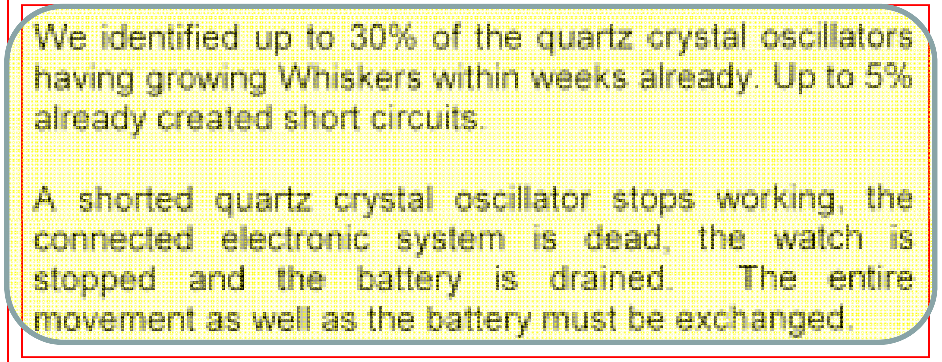


3. Situation:

Since middle of 2003, our Swatch Group RoHS Task Force has intensively worked on the objective to fulfil, without any conditions, all criteria of the RoHS directive. It has taken us two year's to modify and test the new production processes, mainly the use of lead free soldering paste.

After the successful qualification of the various processes in June 2005, we introduced these new lead free operations and components at mass production level. Unfortunately we experienced serious problems with tin whiskers growing inside of our quartz crystal resonators, generating short circuits which end the watch's function.

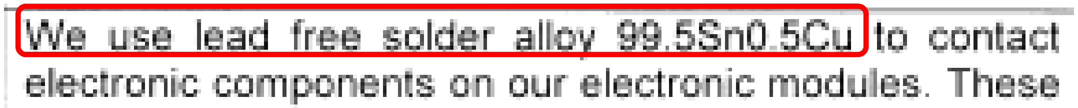
ETA SA was forced to stop, for several weeks, the production of quartz movements due to this Whiskers problem identified inside of quartz crystal resonators. Deliveries as well have been temporary interrupted.



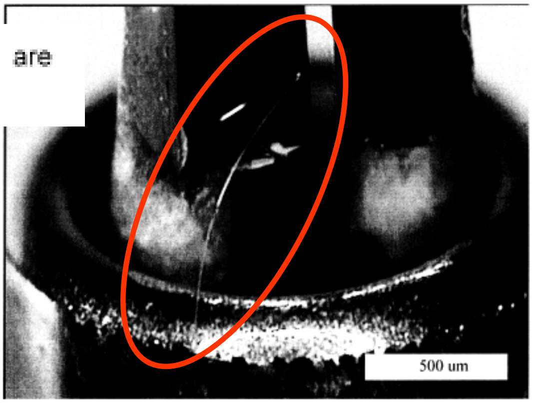
We identified up to 30% of the quartz crystal oscillators having growing Whiskers within weeks already. Up to 5% already created short circuits.

A shorted quartz crystal oscillator stops working, the connected electronic system is dead, the watch is stopped and the battery is drained. The entire movement as well as the battery must be exchanged.

We present you some Whisker examples, at different stages of growth. The parts analysed are taken out of the production we had to stop.



We use lead free solder alloy 99.5Sn0.5Cu to contact electronic components on our electronic modules. These



Tin Whiskers on SnCu electrodeposit

Whisker Formation on Electroplated Sn-Cu

Proc. 2002 AESF SUR/FIN Conference

M. E. Williams, C. E. Johnson, K.-W. Moon, G. R. Stafford, C. A. Handwerker,
and W. J. Boettinger
Metallurgy Division, MSEL/ NIST/ Gaithersburg/ MD 20899-8555/ USA

Table 1. Summary of Measurements

Cu^{2+} in electrolyte (mol/L)	Cu in deposit (mass %) EDS	Cu in deposit (mass %) ICP	Sn surface grain size (µm)	Defect Density after 1 year (mm^{-2})	Longest Whisker Observed (µm)
0	0	0.04 ± 0.01	0.64±0.05	0	-
0.00050	0.29±0.33	0.05 ± 0.02	0.60±0.05	1.6 ± 0.9	15
0.00275	0.67±0.38	0.25 ± 0.2*	0.57±0.06	5.1 ± 1.8	37
0.00500	1.49±0.42	0.67 ± 0.2*	0.58±0.10	48 ± 9	400
0.00750	1.42±0.45	0.67 ± 0.04	0.55±0.09	32 ± 11	400
0.01500	2.93±1.15	1.42 ± 0.06	0.31±0.03	42 ± 12	1600
0.02500	3.28±0.92	1.61 ± 0.49*	0.19±0.02	32 ± 11	1050

*Not analyzed; values estimated from linear fit of EDS to ICP values of other samples.

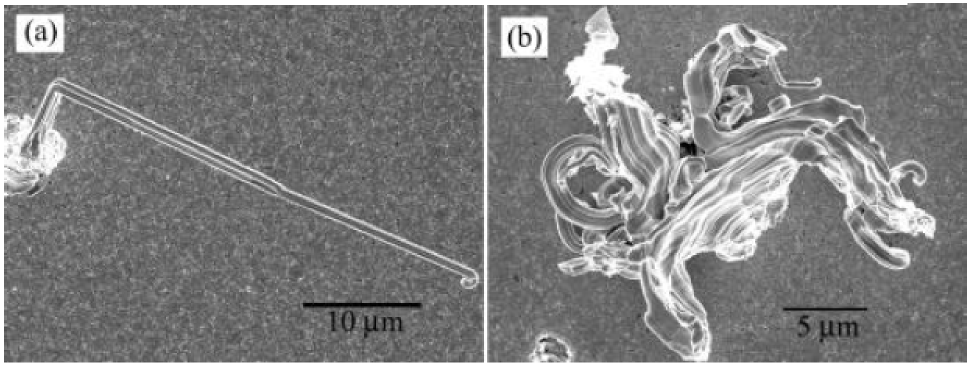


Figure 1: Types of defects on the Sn deposit; (a) a filament type Sn whisker and (b) a Sn eruption with small length whisker.

Whiskers from Sn Alloys with Rare Earth Elements

(Cerium, Lanthanum, Erbium, Yttrium)

Sn-6.6Lu alloy with Sn Whiskers

Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Scripta Materialia 56 (2007) 45–48

Scripta MATERIALIA

www.actamat-journals.com

Rapid growth of tin whiskers on the surface of Sn–6.6Lu alloy

T.H. Chuang,* H.J. Lin and C.C. Chi

Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Received 6 June 2006; revised 18 August 2006; accepted 26 August 2006
Available online 5 October 2006

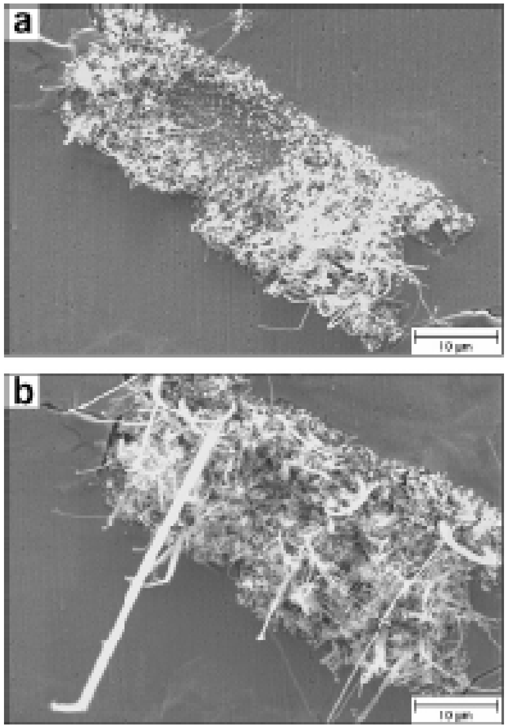
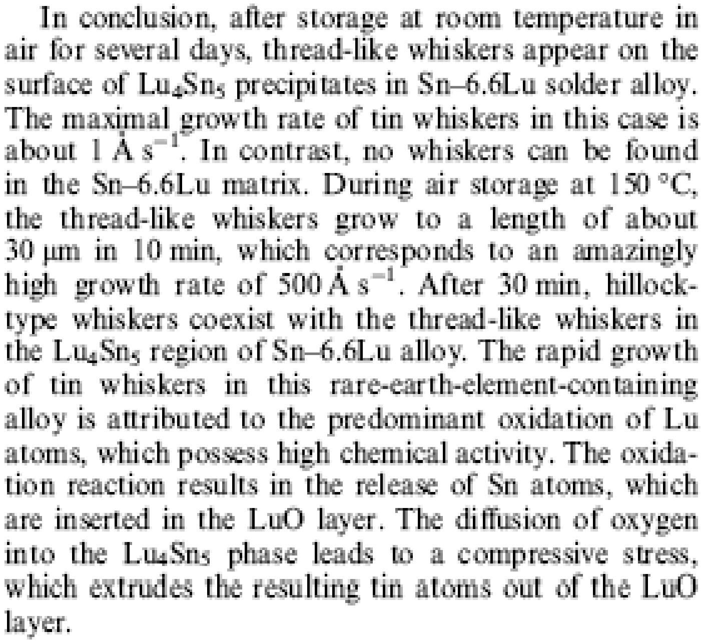


Figure 2. Thread-like tin whiskers formed on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after air storage at room temperature for long periods: (a) 48 h, (b) 240 h.



In conclusion, after storage at room temperature in air for several days, thread-like whiskers appear on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu solder alloy. The maximal growth rate of tin whiskers in this case is about 1 Å s^{-1}. In contrast, no whiskers can be found in the Sn–6.6Lu matrix. During air storage at 150 °C, the thread-like whiskers grow to a length of about 30 μm in 10 min, which corresponds to an amazingly high growth rate of 500 Å s^{-1}. After 30 min, hillock-type whiskers coexist with the thread-like whiskers in the Lu_4Sn_5 region of Sn–6.6Lu alloy. The rapid growth of tin whiskers in this rare-earth-element-containing alloy is attributed to the predominant oxidation of Lu atoms, which possess high chemical activity. The oxidation reaction results in the release of Sn atoms, which are inserted in the LuO layer. The diffusion of oxygen into the Lu_4Sn_5 phase leads to a compressive stress, which extrudes the resulting tin atoms out of the LuO layer.

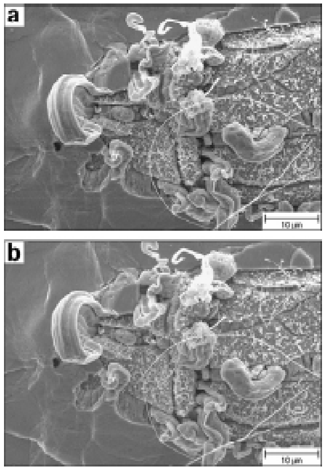


Figure 4. Hillock-type tin whiskers formed on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after air storage at 150 °C for long periods: (a) 112 h, (b) 224 h.

Whiskers in Sn3Ag0.5Cu1.0Ce Solder Balls

Rapid whisker growth on the surface of Sn–3Ag–0.5Cu–1.0Ce solder joints

Tung-Han Chuang

Institute of Materials Science and Engineering, National Taiwan University, 106 Taipei, Taiwan

Received 16 June 2006; revised 1 August 2006; accepted 12 August 2006
Available online 15 September 2006

T.-H. Chuang / Scripta Materialia 55 (2006) 983–986

In spite of the many beneficial effects obtained from the addition of rare earth elements to solder alloys, rapid growth of tin-whiskers has been found in Sn–3Ag–0.5Cu–1.0Ce solder joints. The morphology of the whiskers changes from fiber-shaped to hillock-shaped when the storage temperature increases from 25 to 150 °C. The driving force for the whisker growth is the compressive stress resulting from the volume expansion of the oxidized $CeSn_3$ phase, which is constrained by the surrounding solder matrix.

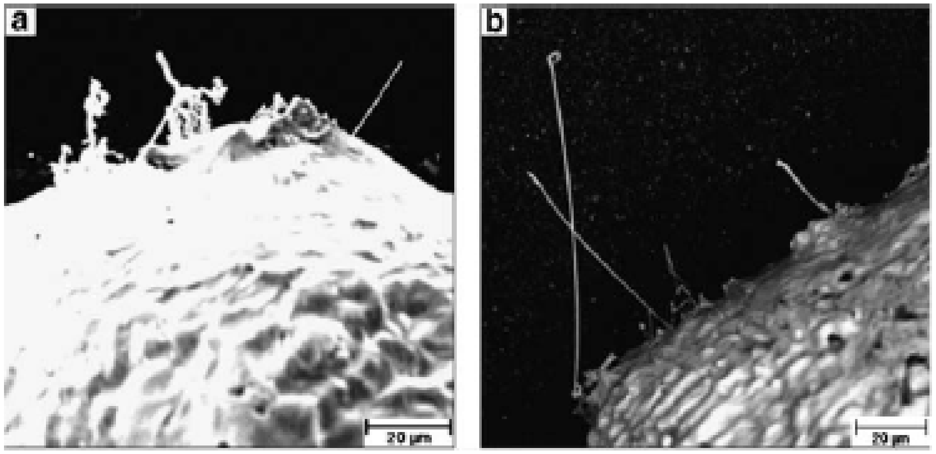
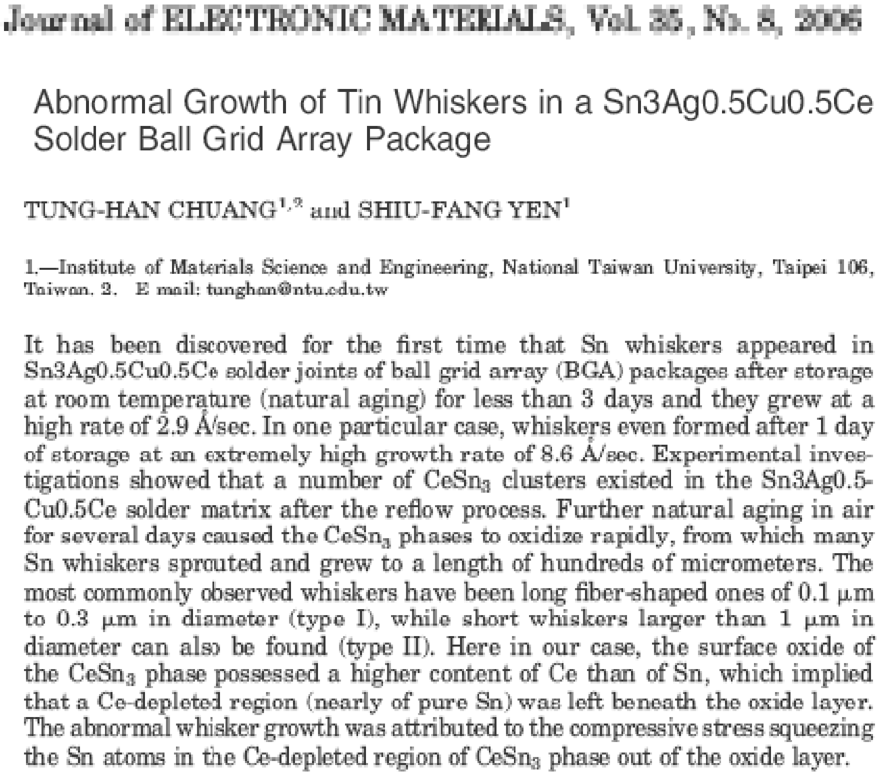


Figure 1. Whiskers formed on the surface of a Sn–3Ag–0.5Cu–1.0Ce solder joint after storage at room temperature for 10 days.

Whiskers in Sn3Ag0.5Cu0.5Ce Solder Balls



Journal of ELECTRONIC MATERIALS, Vol. 35, No. 8, 2006

Abnormal Growth of Tin Whiskers in a Sn3Ag0.5Cu0.5Ce Solder Ball Grid Array Package

TUNG-HAN CHUANG[1,2] and SHIU-FANG YEN[1]

1.—Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan. 2. E mail: tunghan@ntu.edu.tw

It has been discovered for the first time that Sn whiskers appeared in Sn3Ag0.5Cu0.5Ce solder joints of ball grid array (BGA) packages after storage at room temperature (natural aging) for less than 3 days and they grew at a high rate of 2.9 Å/sec. In one particular case, whiskers even formed after 1 day of storage at an extremely high growth rate of 8.6 Å/sec. Experimental investigations showed that a number of $CeSn_3$ clusters existed in the Sn3Ag0.5-Cu0.5Ce solder matrix after the reflow process. Further natural aging in air for several days caused the $CeSn_3$ phases to oxidize rapidly, from which many Sn whiskers sprouted and grew to a length of hundreds of micrometers. The most commonly observed whiskers have been long fiber-shaped ones of 0.1 μm to 0.3 μm in diameter (type I), while short whiskers larger than 1 μm in diameter can also be found (type II). Here in our case, the surface oxide of the $CeSn_3$ phase possessed a higher content of Ce than of Sn, which implied that a Ce-depleted region (nearly of pure Sn) was left beneath the oxide layer. The abnormal whisker growth was attributed to the compressive stress squeezing the Sn atoms in the Ce-depleted region of $CeSn_3$ phase out of the oxide layer.

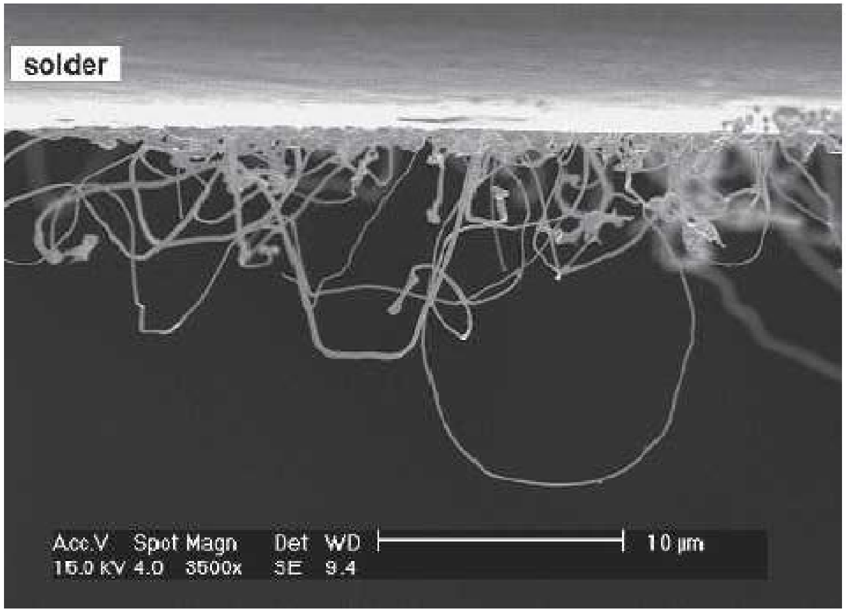
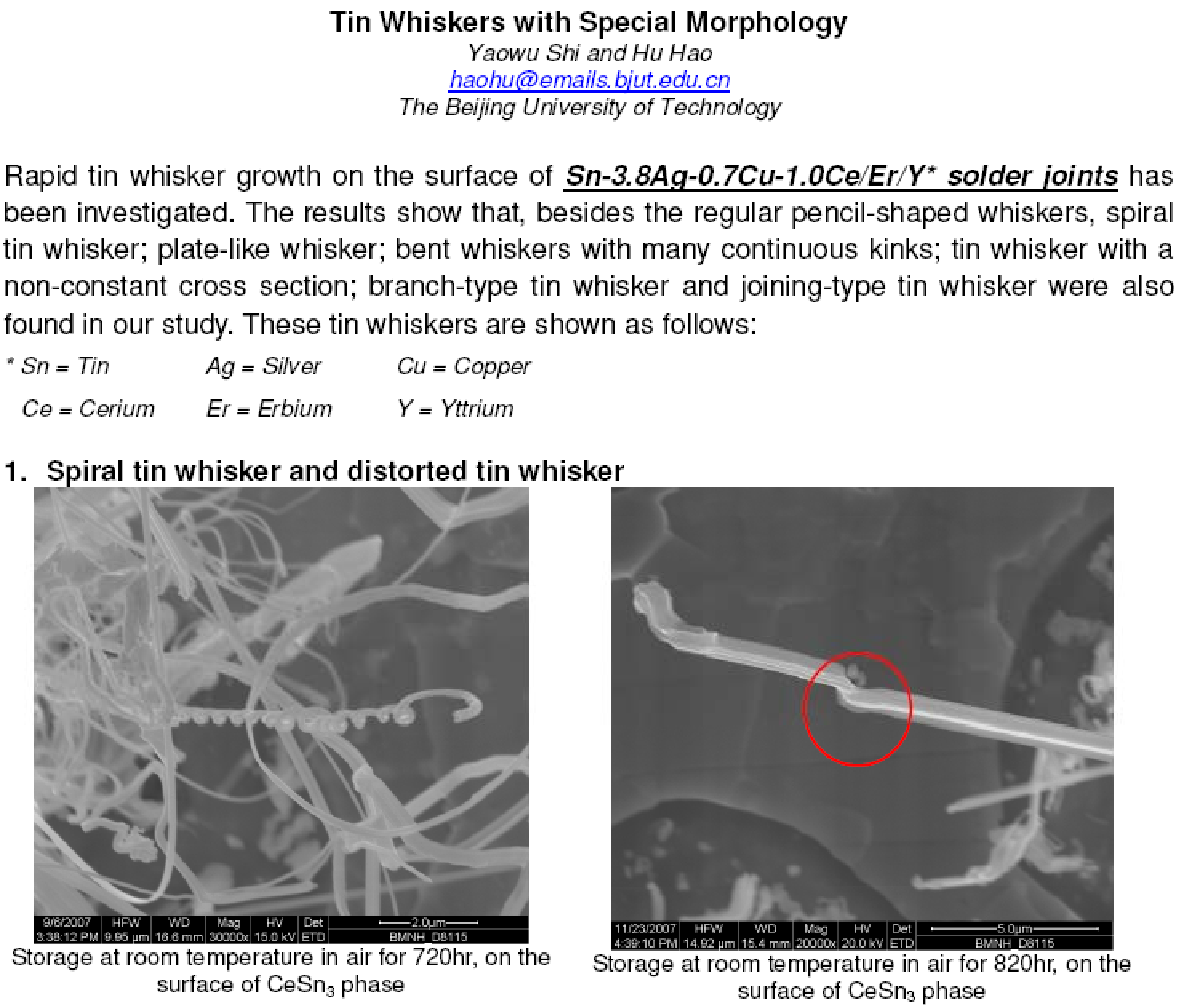


Fig. 5. A particular case occurred in a Sn3Ag0.5Cu0.5Ce solder joint: the Sn whiskers grew at an extremely high rate of 8.6 Å/sec after storage at room temperature for 1 day.

http://nepp.nasa.gov/whisker/other_whisker/SAC/index.htm



Tin Whiskers with Special Morphology

Yaowu Shi and Hu Hao
haohu@emails.bjut.edu.cn
The Beijing University of Technology

Rapid tin whisker growth on the surface of ***Sn-3.8Ag-0.7Cu-1.0Ce/Er/Y* solder joints*** has been investigated. The results show that, besides the regular pencil-shaped whiskers, spiral tin whisker; plate-like whisker; bent whiskers with many continuous kinks; tin whisker with a non-constant cross section; branch-type tin whisker and joining-type tin whisker were also found in our study. These tin whiskers are shown as follows:

** Sn = Tin* *Ag = Silver* *Cu = Copper*
Ce = Cerium *Er = Erbium* *Y = Yttrium*

1. Spiral tin whisker and distorted tin whisker

Storage at room temperature in air for 720hr, on the surface of $CeSn_3$ phase

Storage at room temperature in air for 820hr, on the surface of $CeSn_3$ phase

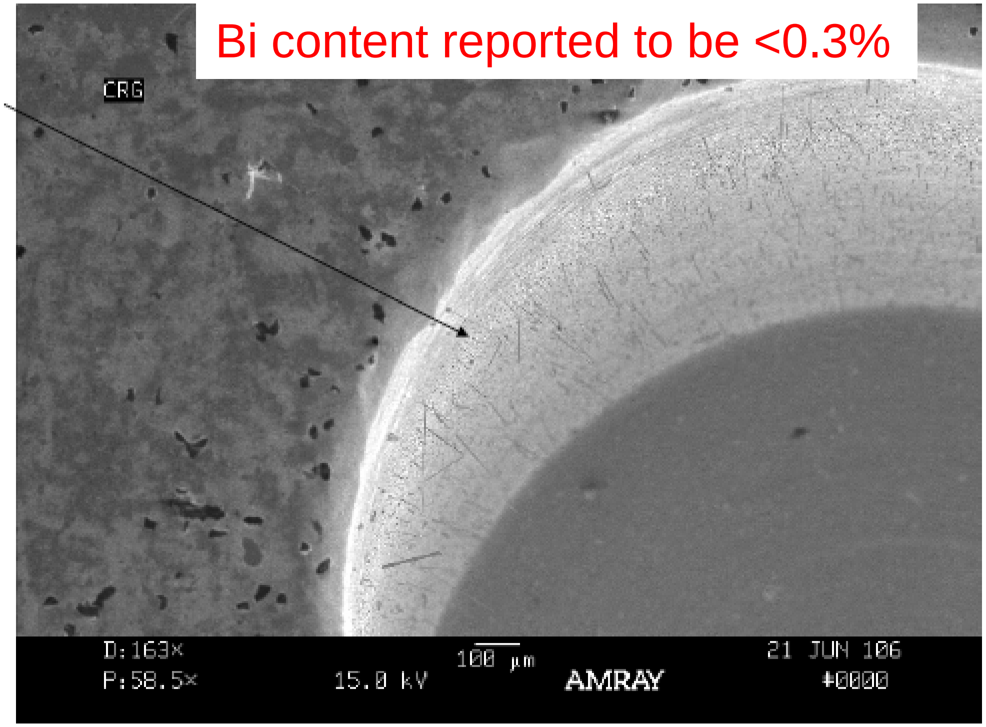
Whiskers from Sn-Bi based Alloy Systems

The Use of Tin/Bismuth Plating for Tin Whisker Mitigation on Fabricated Mechanical Parts

David Hillman, Sue Margheim, Eric Straw
Rockwell Collins

CALCE Part Reprocessing, Tin Whisker Mitigation,
and Assembly Rework/Repair Symposium
November 2008

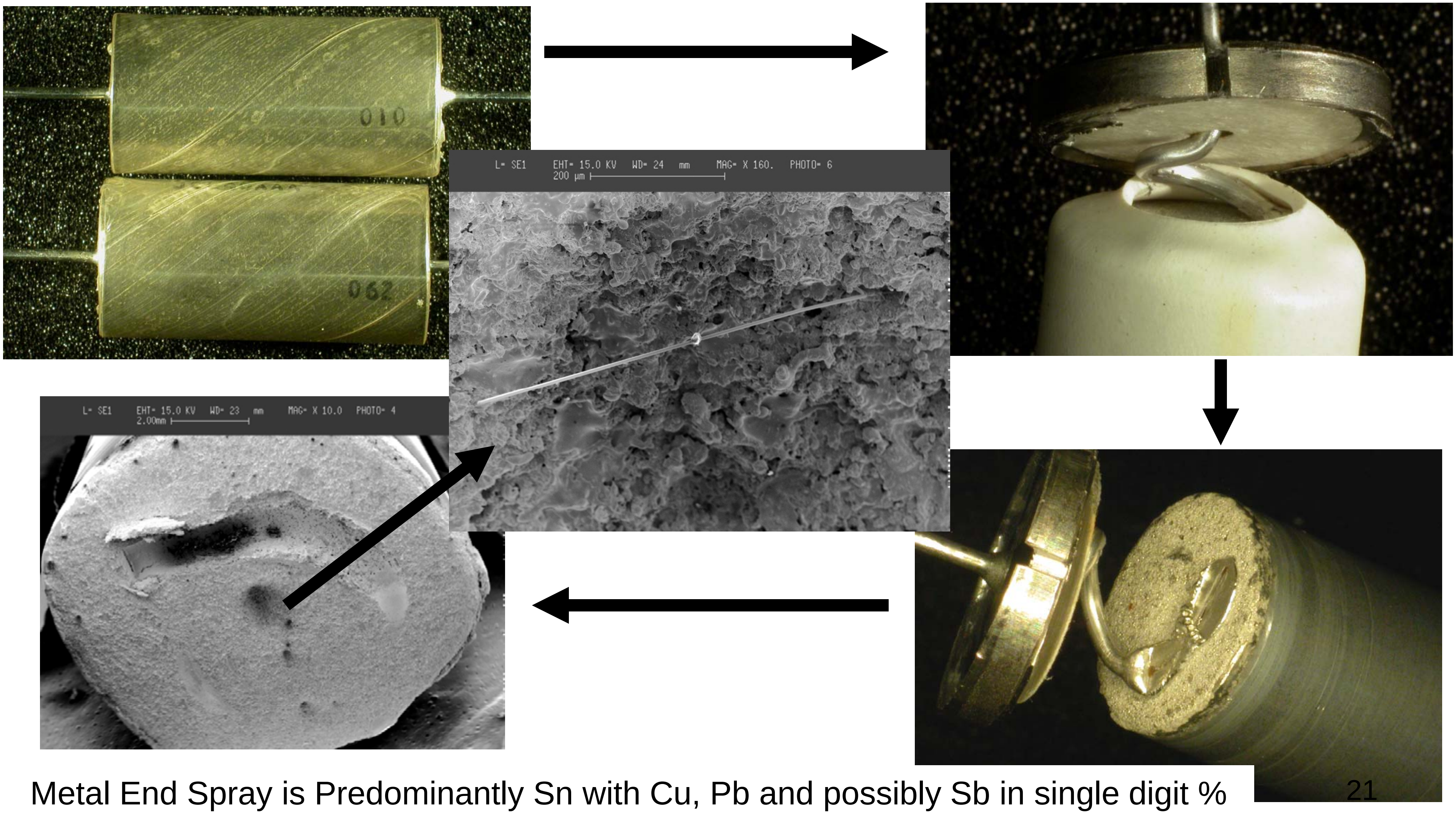
- **Test Vehicle**
  - **Aluminum sheet: 5000 series**
  - **Electrolytic Copper underplate: approximately 0.001 inch thick**
  - **Three Plating Chemistries Selected**
    - **SnBi - 0.3% to 3.0% Bi deposit content**



Bi content reported to be <0.3%

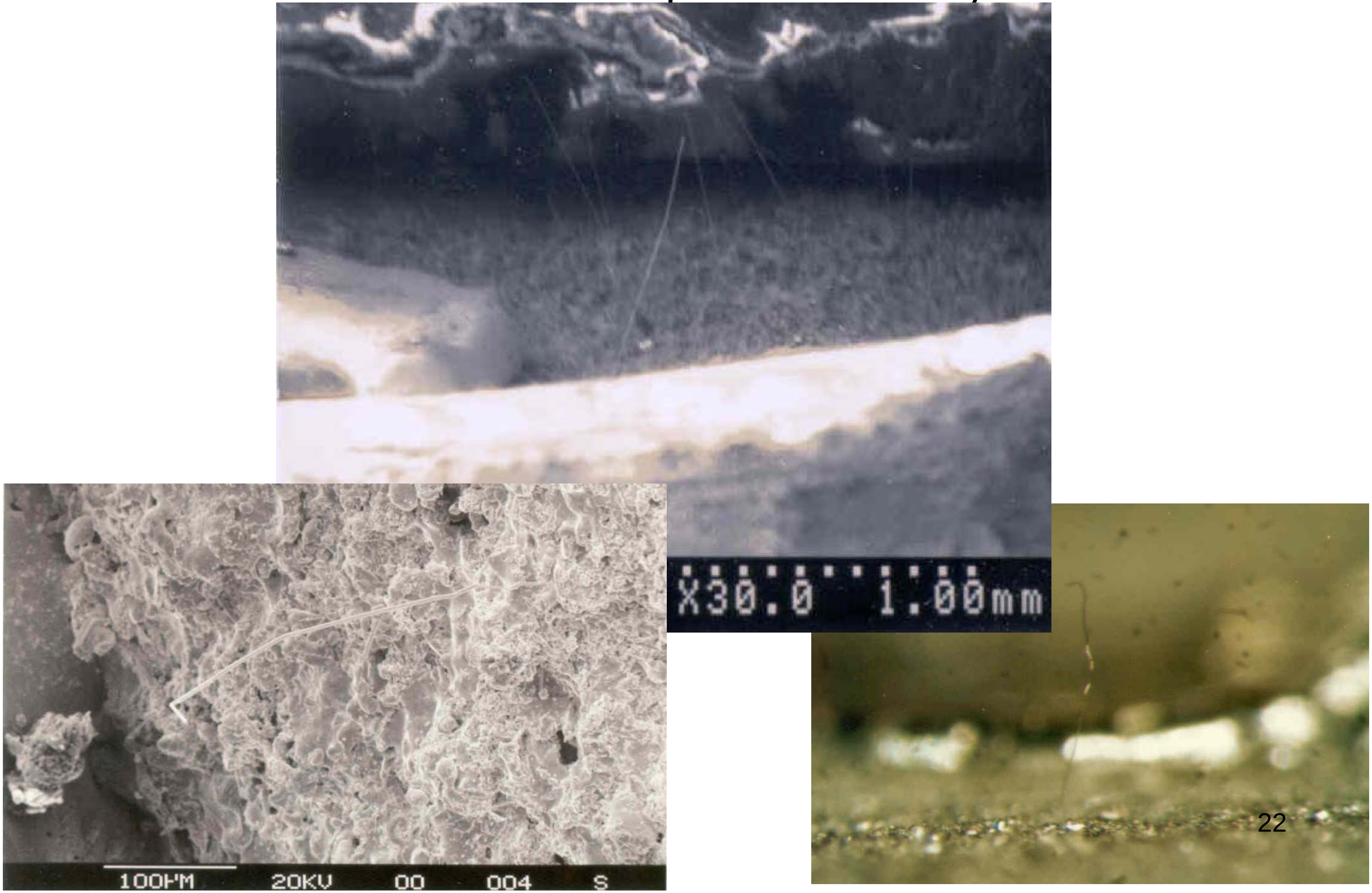
Whiskers from Sn-Sb based Alloy Systems

Metallized Film Capacitor –
Disassembly of ~3.5 year old capacitor
0.5-mm Long Tin Whisker on Metal End Spray
Source: NASA Goddard Space Flight Center Code 562



Metal End Spray is Predominantly Sn with Cu, Pb and possibly Sb in single digit %

Tin Whiskers on Sn-Sb based Metal End Spray of a Plastic Film Capacitor -- Anonymous

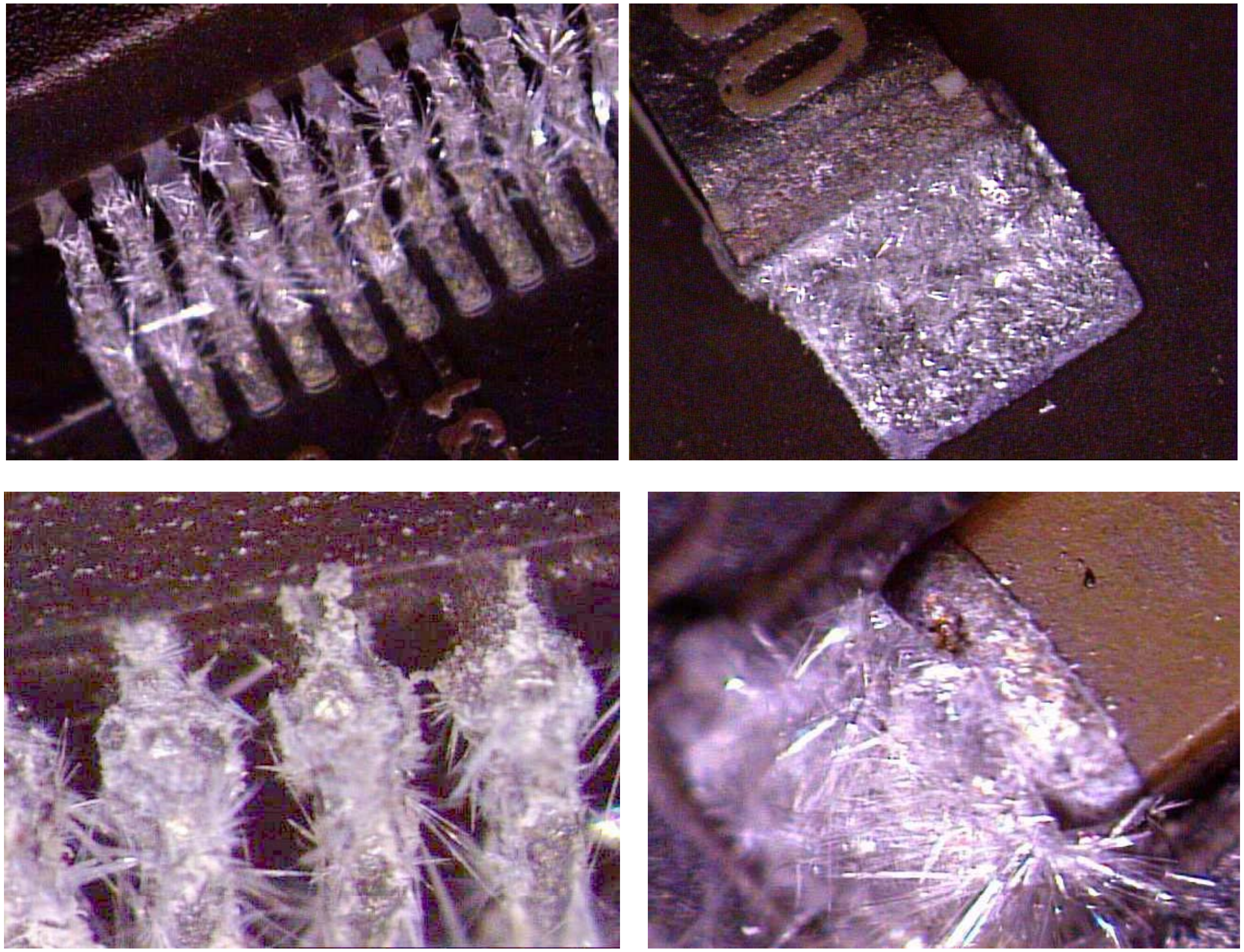


“Whiskers” or some other crystalline formations? on Sn95Sb5 solder joints after 200°C Storage Test

Source: Phil Hinton 2002

The solder used was Sn95Sb5 (MP 235oC), the unit was place in an oven at 200oC and held for 200 hours. The components were supposedly nickel tin plated gull wing, discrete resistors, capacitors of the 1206 size, connectors etc. The boards were polyimide with a final finish of electrolytic nickel (200microinches), palladium (8 microinches) and gold (6 microinches). The “whiskers” grew from the leads, and from the solder in large continuous patches that looked like a a field of crabgrass. Even the solder on the Ni/Pd/Au lands on the board grew whiskers.

Also in the test were assemblies soldered with Pb85Sb10Sn5. This solder did not grow whiskers, but the leads did.

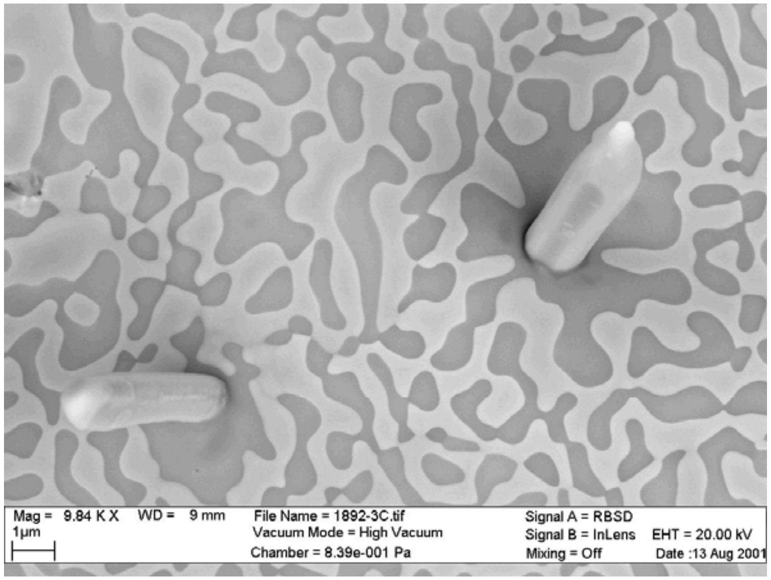


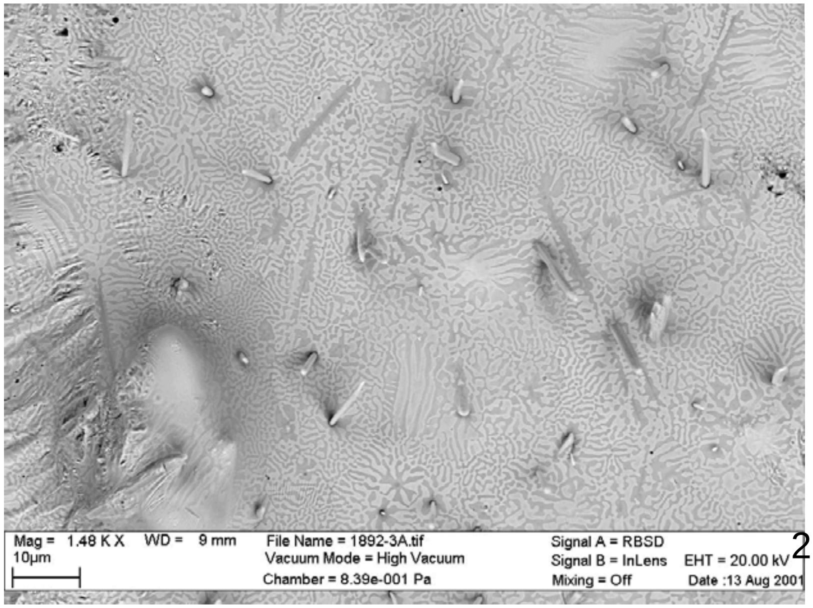
Whiskers from Au-Sn Alloy Systems

Au-Sn Whiskers

Anonymous

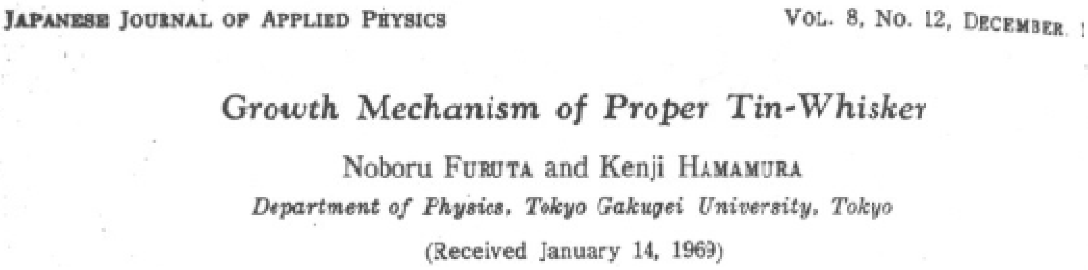
- These alloy whiskers growing from AuSn solder. Some whiskers were pulled off the surface with carbon tape in order to confirm the composition without the solder in the background. The whisker composition is Au, Ni, Cu and Sn. In the SEM images, the dark surface area is Sn rich and the light areas are Au rich.





Whiskers from Sn-Al Alloy Systems

Tin whiskers on Sn50Al50



Japanese Journal of Applied Physics Vol. 8, No. 12, December.

Growth Mechanism of Proper Tin-Whisker

Noboru Furuta and Kenji Hamamura
Department of Physics, Tokyo Gakugei University, Tokyo

(Received January 14, 1969)

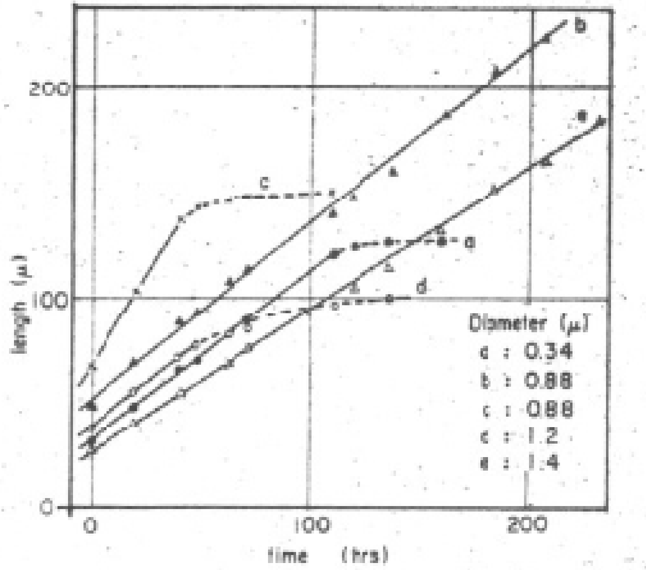


Fig. 4. Rates of growth of the straight whiskers shown in Fig. 3.

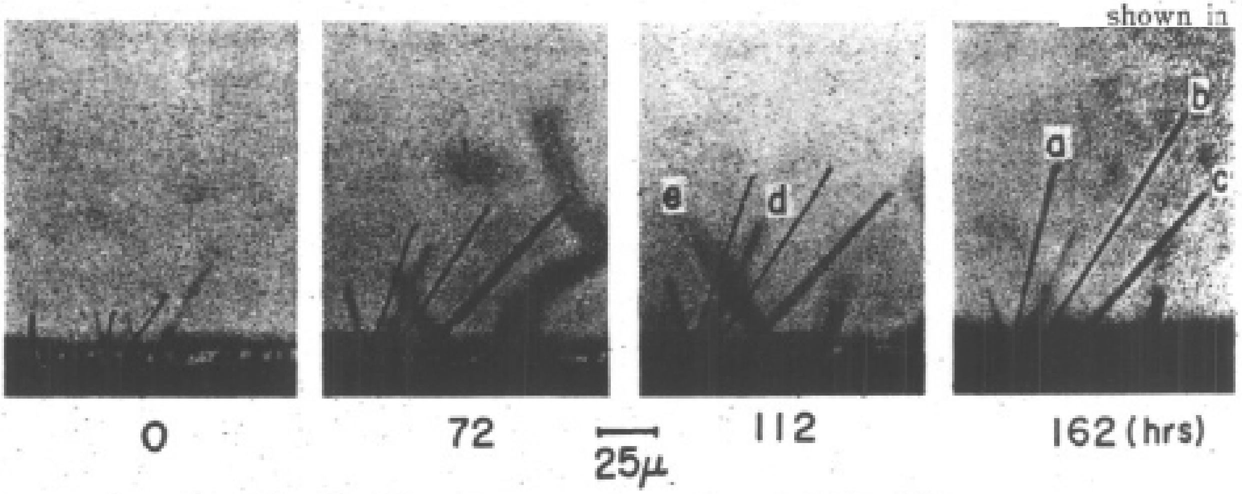


Fig. 3. Time-sequence of growing straight whiskers.

Whiskers from Sn-Mn Alloy Systems

Tin Whiskers on Sn-Mn Electrodeposits

(~40%Mn by weight)

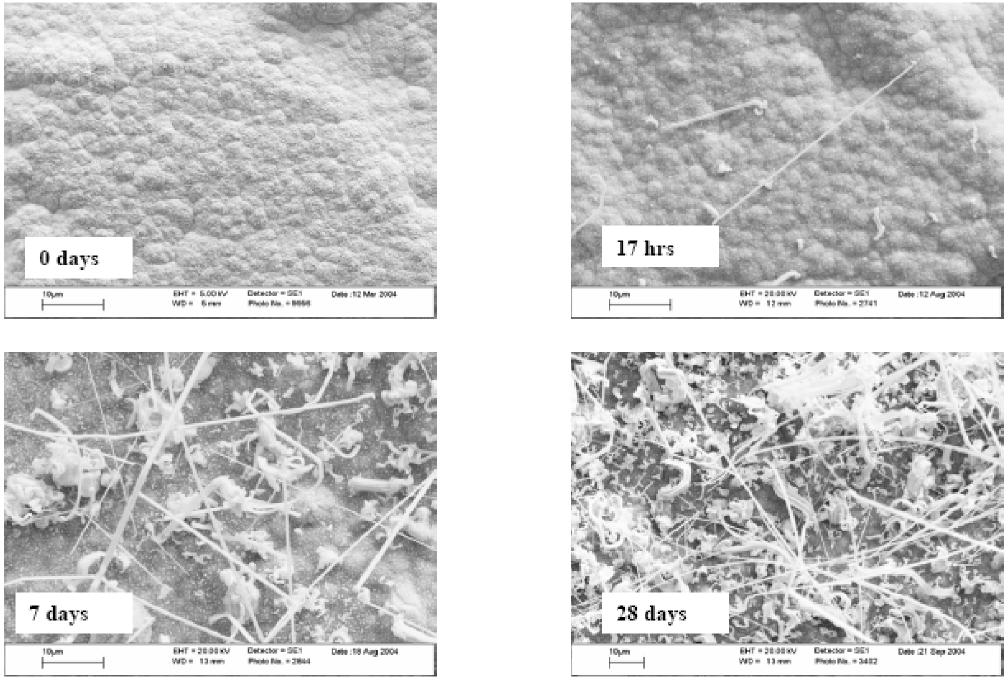
Observations of the Spontaneous Growth of Tin Whiskers on Tin-Manganese Alloy Electrodeposits

Keming Chen and Geoffrey D. Wilcox
Institute of Polymer Technology and Materials Engineering, Loughborough University,
Loughborough, Leicestershire, LE11 3TU, United Kingdom

(Received 18 November 2004; published 17 February 2005)

The spontaneous growth of tin whiskers on electrodeposited tin-manganese alloy coatings has been observed. This growth is distinct from any previously reported whisker growth on either pure tin or other tin-based alloy electrodeposits. It has an extremely short incubation period of a few hours only, followed by a spectacularly rapid and profuse growth. During the whole period of whisker growth, the tin-manganese electrodeposits were found to be in a tensile residual stress state. This rules out the commonly accepted explanation of a compressive stress as the driving force for tin whisker growth.

DOI: 10.1103/PhysRevLett.94.066104 PACS numbers: 68.70.+w, 61.10.–i, 81.15.Pq



Whiskers from Sn-Pb Alloy Systems

SnPb Whiskers Formed on Sn63Pb37 Reflowed Die Attach

NASA Goddard Space Flight Center Code 562

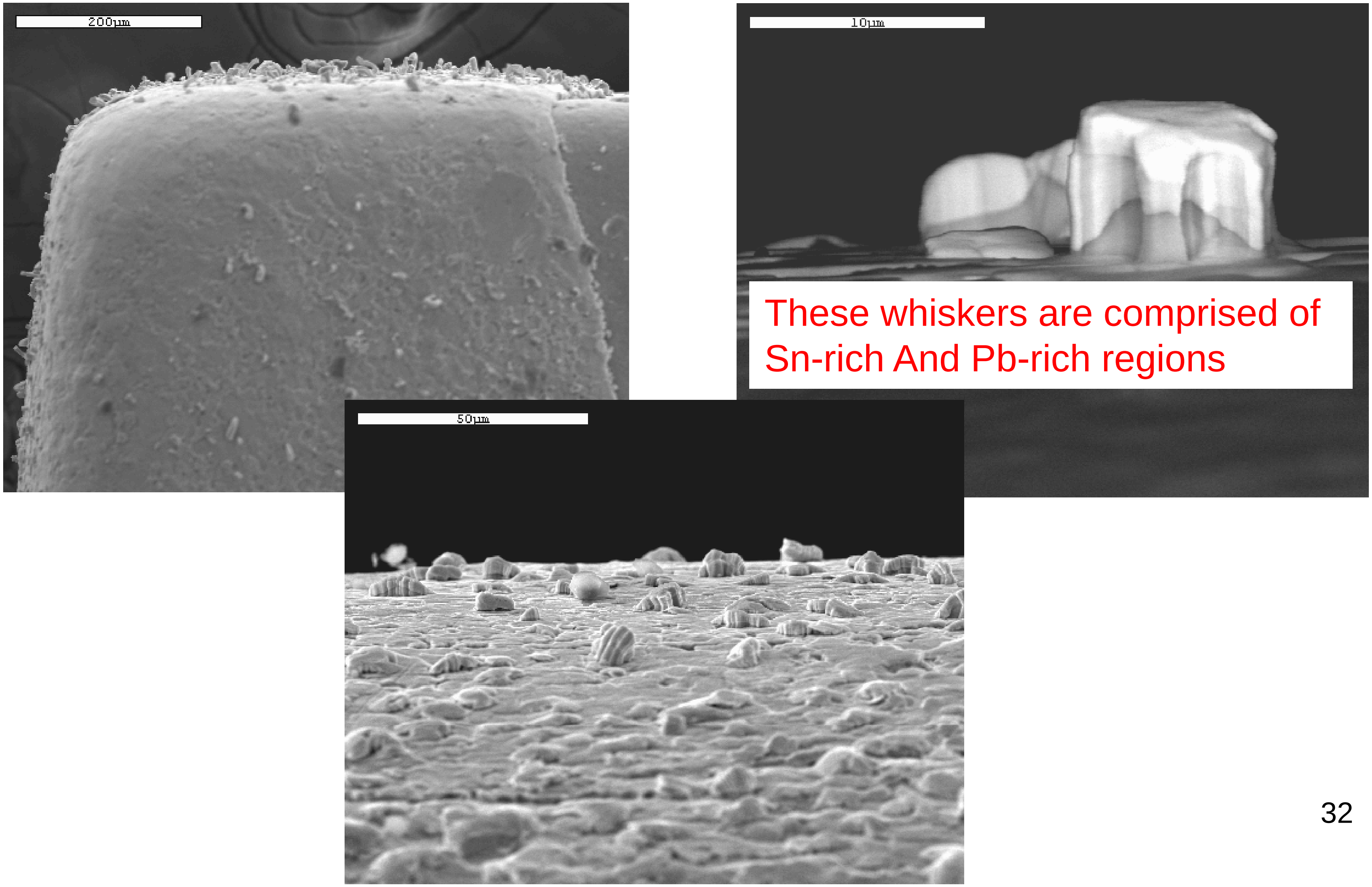
- GaAs Laser Diode Array attached to Cu-W heatsink using Sn63Pb37 solder
- Current densities during operation ~10^5 Amps/sq.cm
- Shunting distance < 5 microns

These whiskers are comprised of Sn-rich And Pb-rich regions

http://nepp.nasa.gov/whisker/reference/tech_papers/Leidecker2003-SnPb-whiskers-on-laser-diode-array.pdf

Sn-Pb Whiskers from Sn-Pb Coated Ceramic Chip Capacitor Terminations after Extensive T-Cycle

Source: R. Wagner/Kemet



These whiskers are comprised of Sn-rich And Pb-rich regions