Sample Preparation for Mitigating Tin Whiskers in Alternative Lead-Free Alloys

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ABSTRACT. As lead-free alloys shift into high reliability electronics, the issue of tin whisker growth remains a primary concern among those in the industry. Current research shows that there is no perfect alloy for all cases of electronic usage. Industry leaders and researchers continue to study and search for a lead free alloy that is able to withstand harsh environments while maintaining high reliability.

INTRODUCTION. This study looks at one of the many concerns regarding lead-free solder in high reliability electronics. The work in this paper has been accumulated over time with some of the initial work released in 2010. Since most of the tin whisker issues in modern electronics have been tin plating related, testing has been geared toward this type of whisker growth. While some did, most of the established tin whisker testing revealed alloys that did not grow whiskers.

TEST METHOD. A simple test was developed to test solder. A copper wire of approximately 0.03" standard house wiring is fluxed and coated by hot dipping with solder. The solder coating is approximately 300 um thick. The wire is allowed to cool. After all samples are prepared, 10 of each alloy are then placed in an arbor press and bent into a U. The bent samples are then placed in a chamber at 60°C /87RH (initial runs were prepared using two other conditions, however it was determined this condition would be used for all future testing). The U shaped wire was then placed in a holder that stands them up.

Figure 1. Bent Samples

EXPLANATION. Lead-free alloys grow whiskers at different rates. S(Sn) A(Au) C(Cu) is consistently the worst, however Sn63 is a control that does not grow whiskers. This initial test was run with nine lead-free alloys. Subsequent research was done where 30 different alloys were tested.

TEST RESULTS. Tin whiskers always grow in the same region of the bend as shown below in Figure 2.

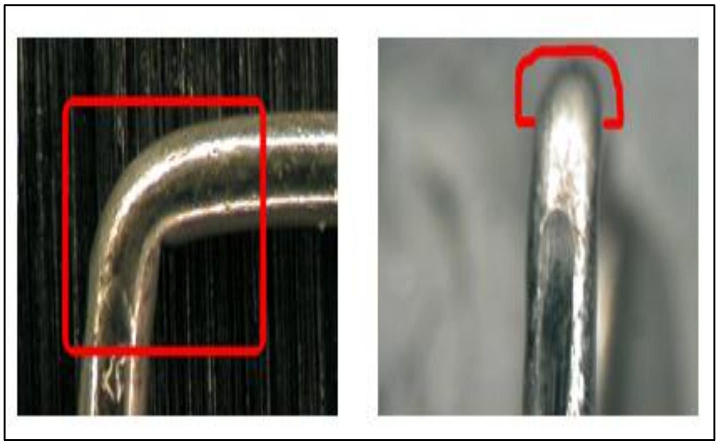

Figure 2. The Bend

Figure 3. Typical Whisker Growth

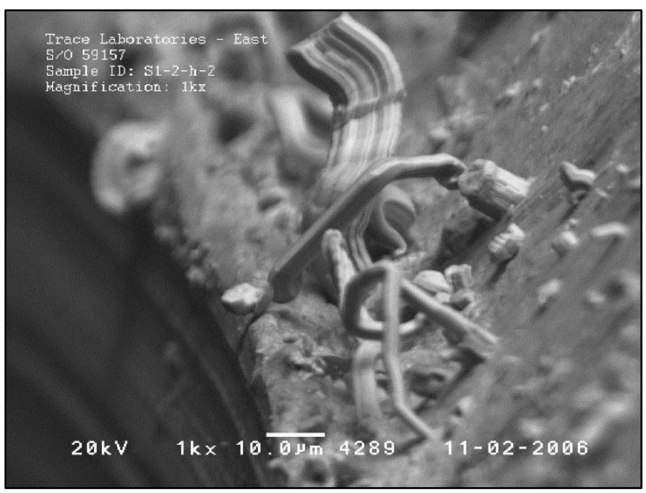

Figure 4. Typical SAC305 Whiskers

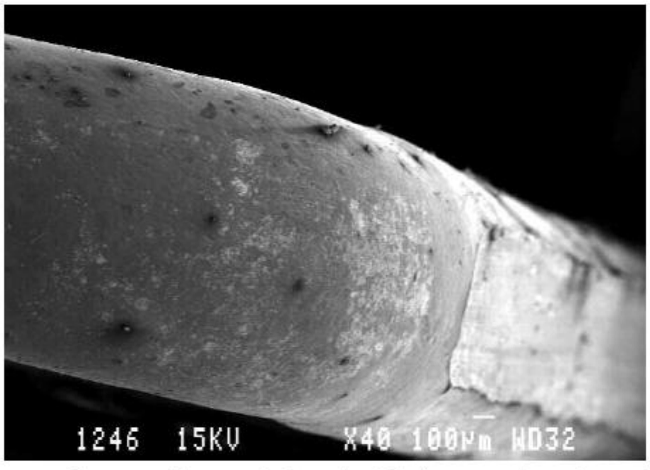

Figure 5. Sn63

If a leaded device is solder coated and bent, or scratched, there is a possibility of whisker growth from standard lead-free alloys. Shown in figure 6, is a typical gull wing device illustrating the potential growth zone at the bend.

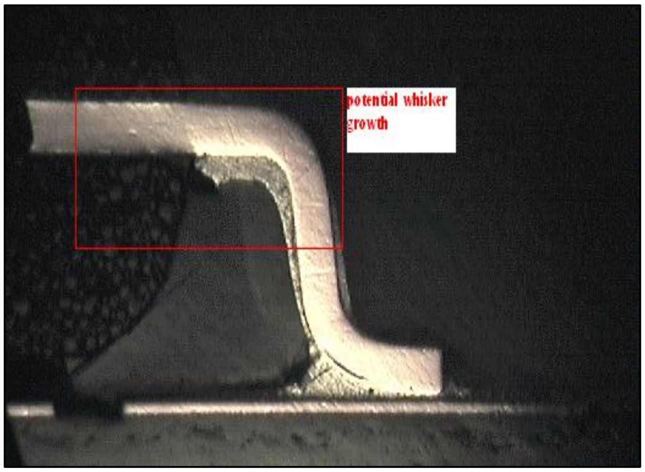

Figure 6. Potential Whisker Growth

Developmental Alloys #41, #60, & #61 all mitigate whisker growth as evidenced in Figures 7, 8 & 9.

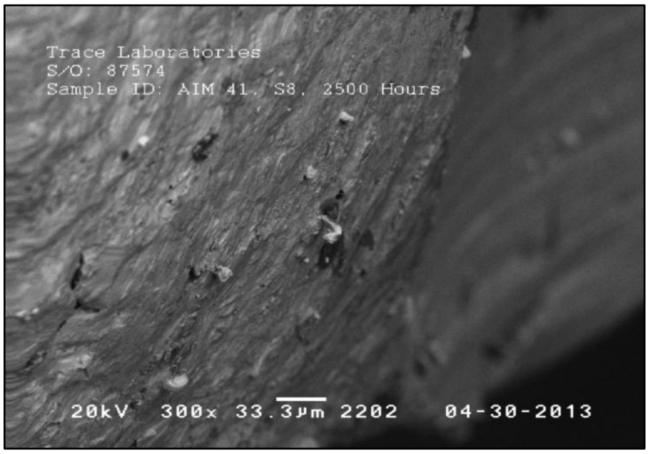

Figure 7. #41

Figure 8. #60

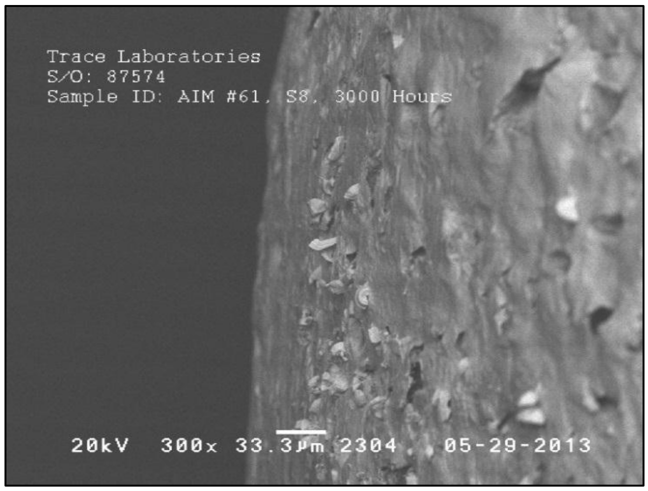

Figure 9. #61

Recent work has shown that the above alloys contain micro additions, and in conjunction with other low percentage elements, do mitigate whisker growth. These alloys were studied for grain size and shape, DAC (Should this be DSC), dip wetting (wetting balance), spread testing, tensile, hardness, and percent elongation.

The following pictures examine the grain structure of the different alloys.

Alloy #41 exhibits a very different grain structure with only 500 ppm of an addition. Alloy #60 is with 2000ppm of an element and Alloy #61 that has two additions, one at 600ppm and one at 2000ppm. (Can any indications be given on the type of alloying additions used).

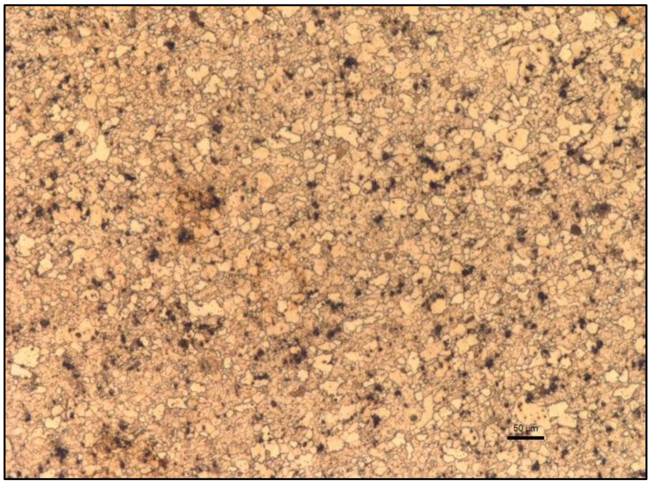

Figure 10. Alloy #41

Figure 11.Alloy #60

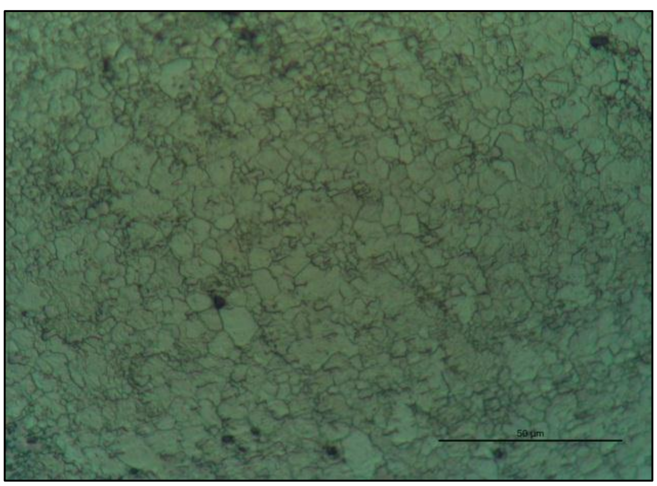

Figure 12. Alloy# 61

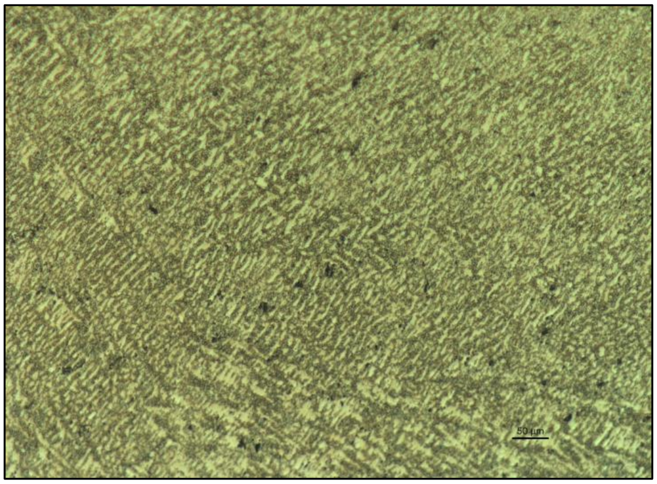

Figure 13.SAC305

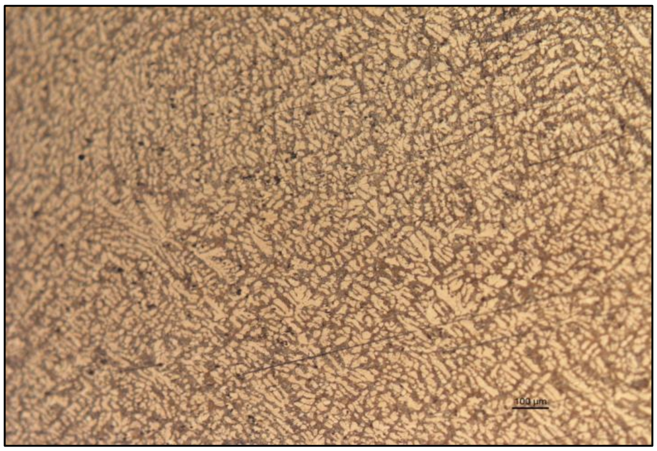

Figure 14. Sn/0.7Cu

The below chart is of several alloys that have been developed. Some have been tested for whisker growth and some are still in testing. From the properties, one can see that hardness, tensile, and percent elongation all have been affected by these additions.

Summary results

Alloy	T[illegible](°C) (Heating)	Pasty range (°C)	Wetting Time, ta (s) (300C)	Wetting force (mN) (300C)	Hardness (HV10)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
#41	226	11	0.82	3.15	7.5	24.1	40.3
#60	201	24	0.6	3.63	15	77	26
#61	216	17	0.64	4.54	16	28.1	37.2
#69-2	204	21	0.56	4.77	25	82	21.5
#71	206	20	0.74	4.82	21	-	-
#81	204	20	0.79	4.8	-	-	-
SAC0607	217	18.5	0.49	4.66	15	35.1	39
SAC305	217	13	0.57	4.88	17.7	35	46.7
#82	205	20	0.58	4.8	-	-	-
#84	227	12	0.67	4.4	15	-	-
#69-6	210	18	0.58	4.63	14	-	-
#69-7	210	21	0.64	4.41	20	64	21.3
#69-8	210	20	0.55	4.17	19	63	23.5

Figure 15. Alloy Chart (Can this figure be separated into 2 tables to make it easier to read)

As previously mentioned, there is no “one” alloy that offers an absolute solution. Some of the alloys that had the best whisker mitigation had some of the worst wetting. This can be seen in the wetting balance coupon inspection.

Alloys #41, #60, and #61 all had poor coverage on the coupon as shown below in figures 16, 17, & 18.

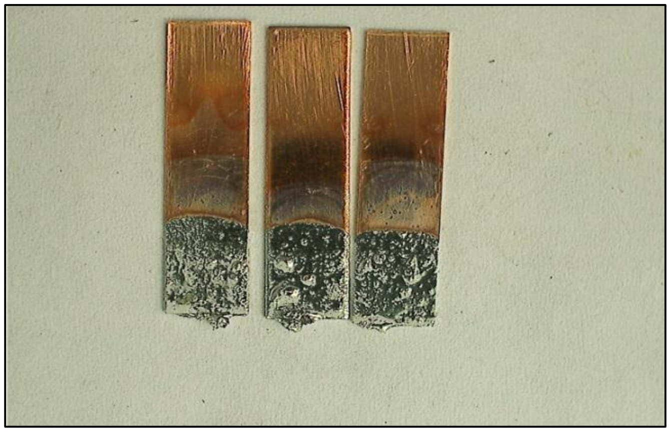

Figure 16. Alloy #41

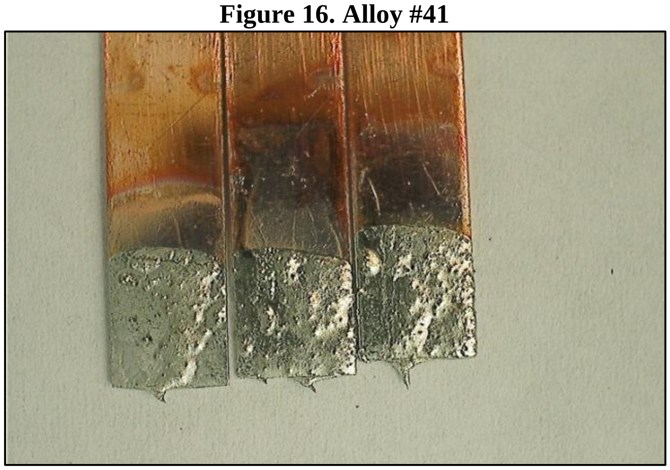

Figure 17. Alloy # 60

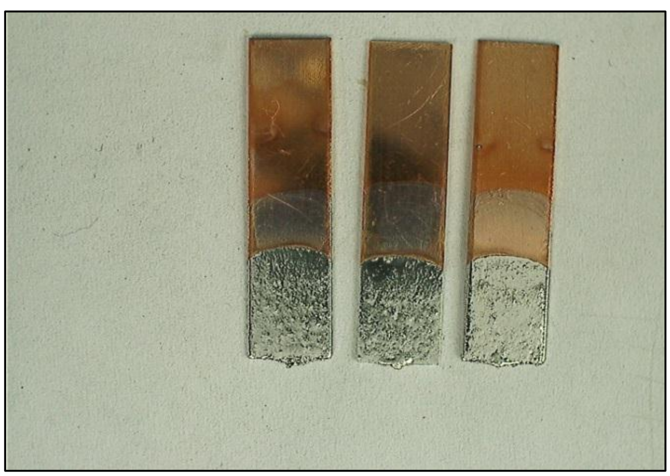

Figure 18. Alloy #61

MODIFIED ALLOY. Alloy #81 is a modified alloy with lower levels of one of the materials contained in the others. It appears to exhibit better wetting.

Figure 19. Alloy # 81

CONCLUSION. Based on the above work, further research is necessary. As evidenced in this paper, it is likely that tin whiskers can be mitigated by alloy additions and acceptable physical properties can be achieved for high reliability alloys.

ACKNOWLEDGEMENTS

The experimental work done reported in this study was conducted by Trace Labs with Dr. Mehran Maalekian at AIM.

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LAS VEGAS, NEVADA

Lead Free Tin Whisker Growth

Nine Alloy Study

Karl Seelig, VP Technology
Mehran Maalekian PhD, Research & Development

Test Background

Lead Free Tin Whisker Growth

- Typically, this has been studied for plated surfaces
- AIM and Nihon Superior developed a test to compare lead free alloys, **9 alloys** were tested
- A copper wire was hot coated then bent into a U 1” on each leg and ½” on the cross member. Solder thickness was from 300-500 uin.
- These were humidity tested and thermal cycled

Alloys Tested

The submitted solder-coated samples were serialized / identified as follows:

- S1 – "Castin"
- S2 – "K-100"
- S3 – "SAC305"
- S4 – "SACX"
- S5 – "Sn63 (Control)"
- S6 – "Sn100C"
- S7 – "Sn0.7Cu0.3Ag0.05Ni"
- S8 – "Solder Coat"

Test Description

- Copper wire .093 diameter is “hot tin” coated with each alloy
- Alloys thickness=300-500uin
- Cut to length
- Formed into U using Arbor Press

Samples

TRACE Laboratories

TRACE LABORATORIES-EAST

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5 North Park Drive
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Telephone: 410/584-9099
Fax: 410/584-9117
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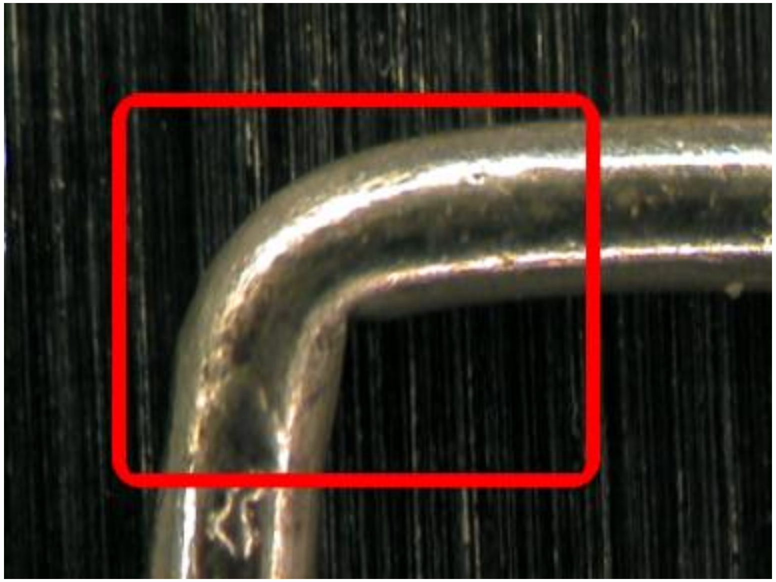
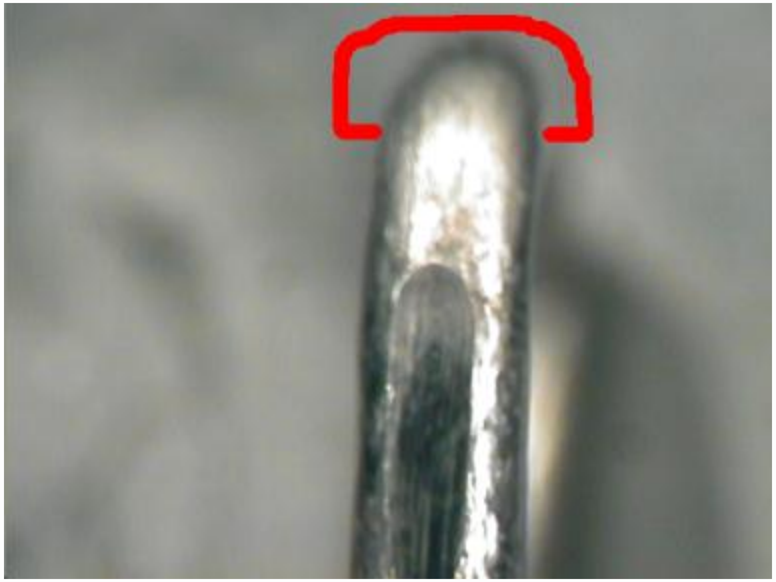
P.O. Box 370736
Denver, CO 80237
USA
Telephone: 303/683-4806
Fax: 303/683-4972
Email: tracelab@connext.net
www.tracelabs.com

CERTIFICATED

Photograph #1: Representative Overview of Submitted Solder-Coated Samples

Whisker Growth Region





Thermal Cycling

- -40 +85C, 3 cycles per hour, 10 minute soak times
- Inspected at 500 cycles and 1000 cycles
- No whisker found

Ambient Temperature/Humidity Soak

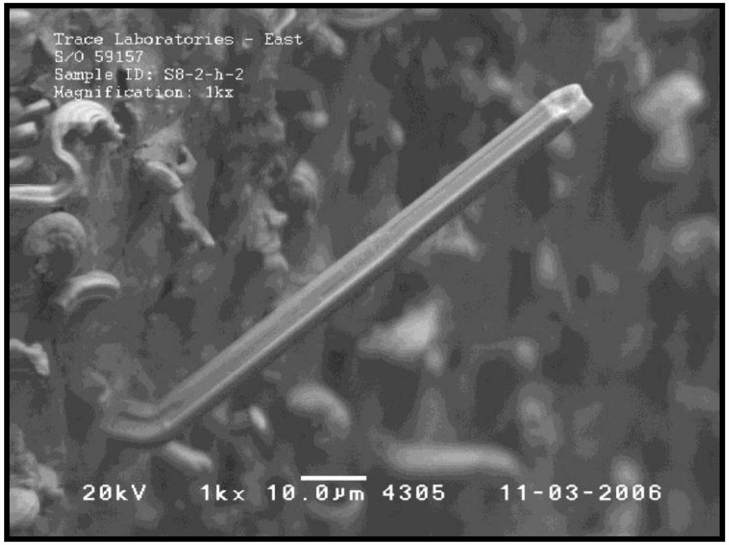
- 30C at 60RH
- Inspected at 1000, 2000, and 3000 hours
- At 3000 hours, all samples began to show evidence of whisker growth

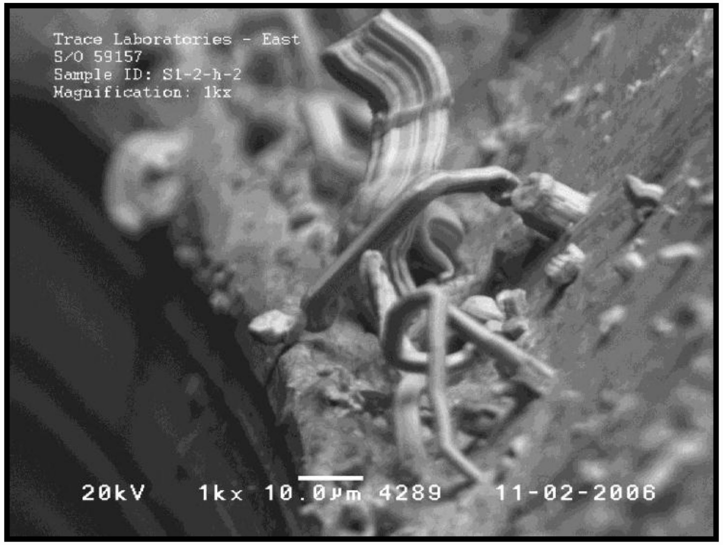
High Temperature/Humidity Soak

- 60C, 87Rh soak
- 1000,2000,3000 hours
- At 1000 hours, some specimens showed signs of whiskers
- By 3000 cycles, all samples showed signs of whiskers

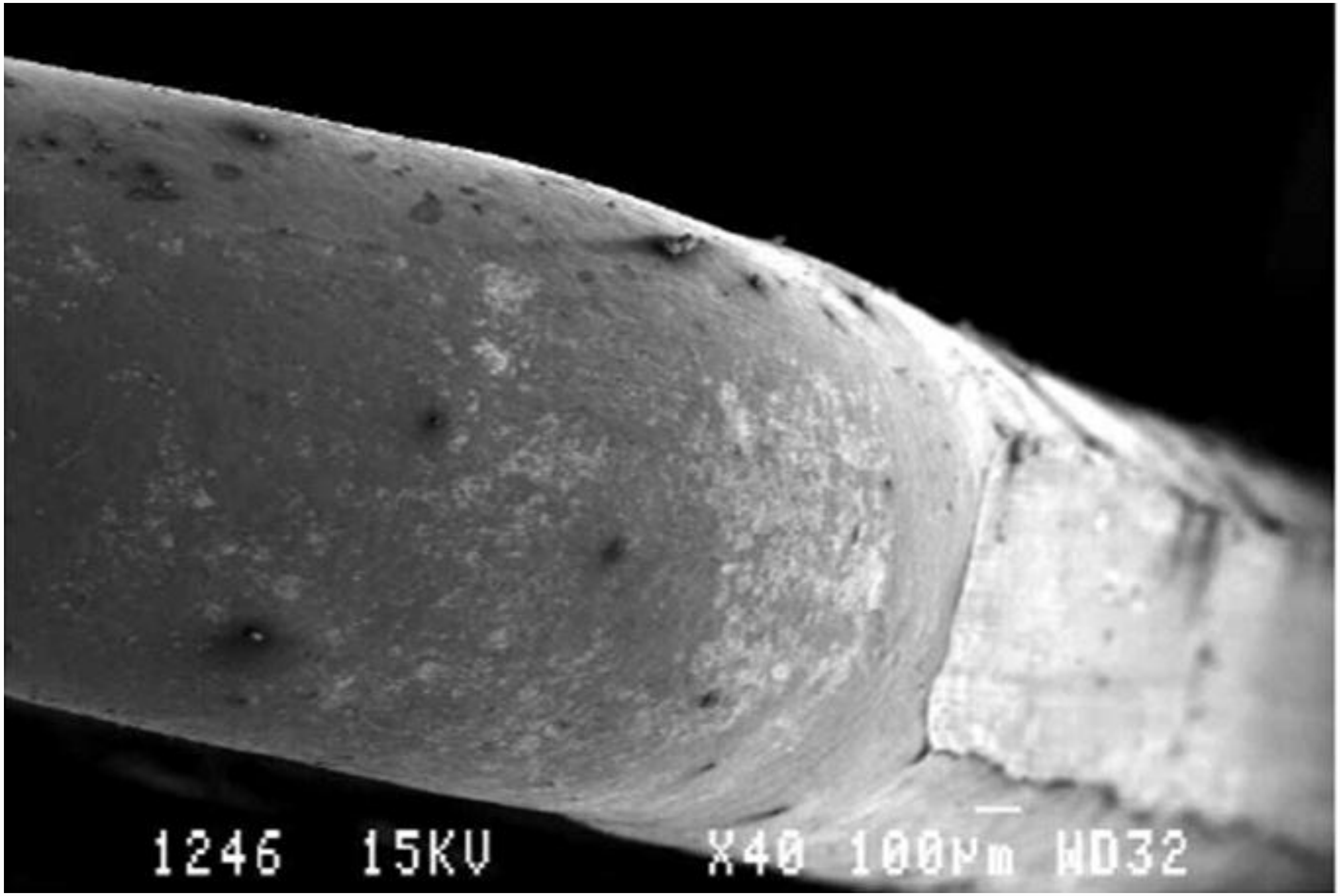
Tin Whisker on Wire Bend

Typical Tin Whisker





Sn63



Whisker Revelations

✓Whiskers are not only a problem with plated surfaces

✓Alloys of high tin still grow whiskers, none greater than 115um with the shortest being 50um. Density classifications were low <10, medium10-40, high >45

✓Whiskers grew from the tension side not the compression side as originally thought

✓High temperature storage with humidity grew the most whiskers

✓Thermal cycling did not seem to cause whisker growth

✓Whiskers grew on bare copper and exhibited Kirkendall voids

Tin Whisker Study-Second Round
(3 Alloys)

- This section of the report shows detailed information on three alloys AIM performed tin whisker growth testing on as well as summary results on other alloys investigated

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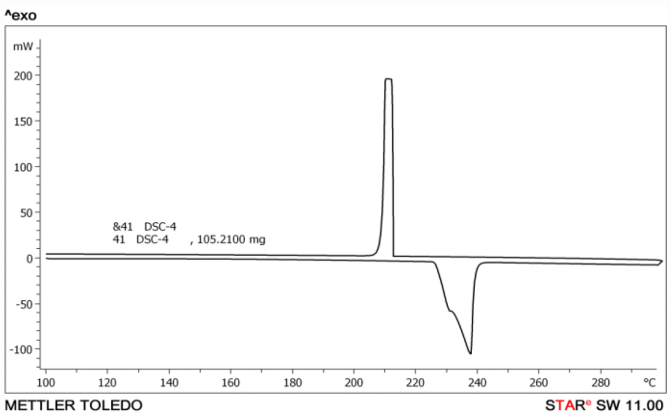
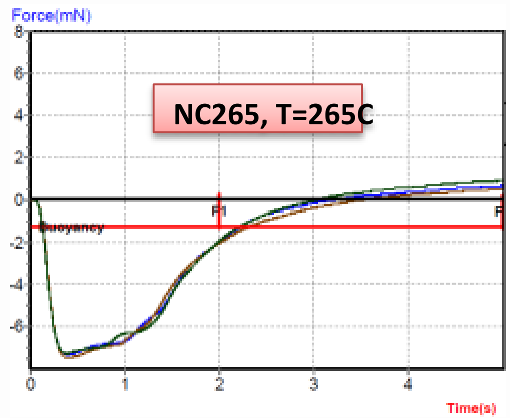
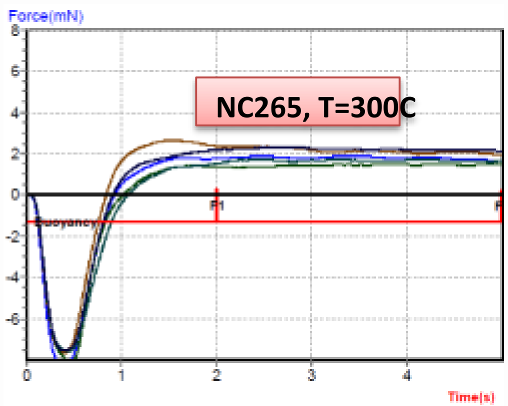
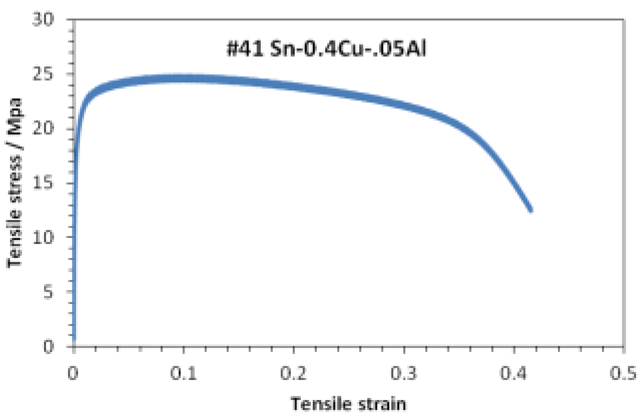
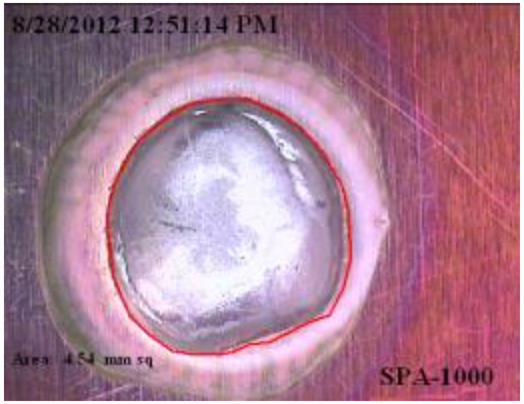
#41 (Sn-0.4Cu-0.05Al)

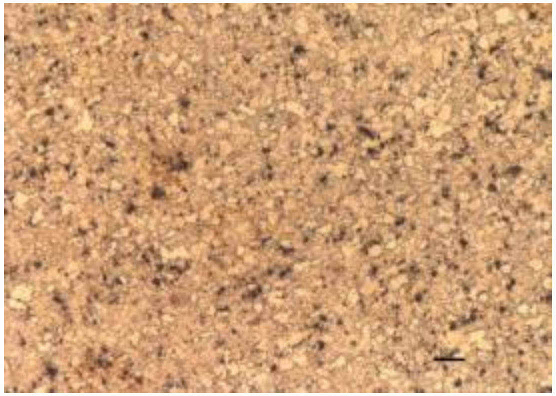






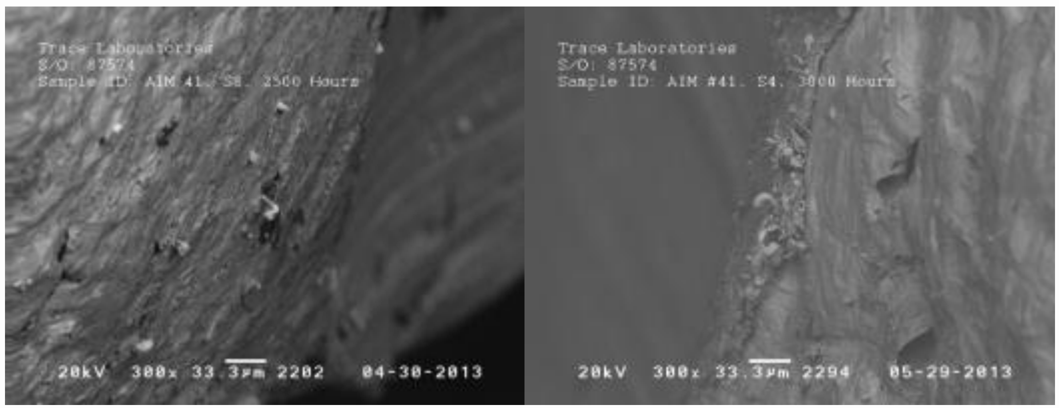






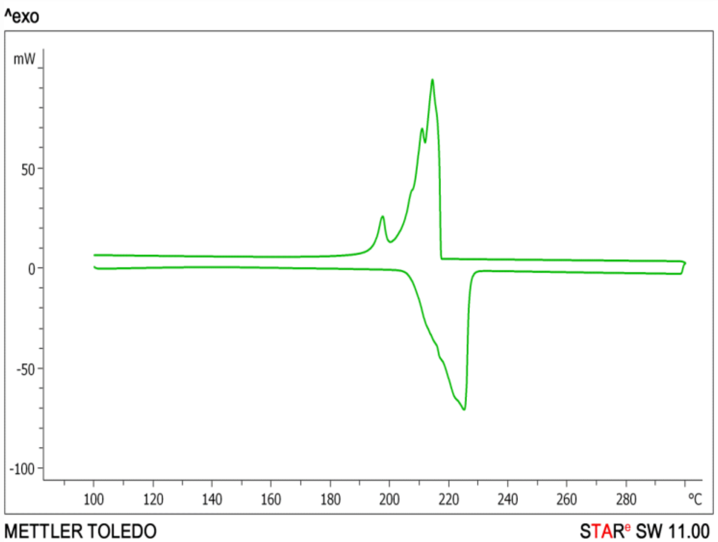
#41 (Sn-0.4Cu-0.05Al)

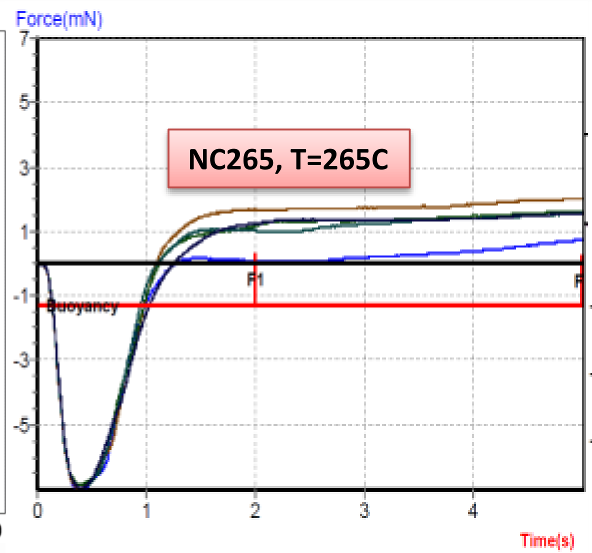
Alloy	T_{onset}(°C) (Heating)	Pasty range (°C)	T_{onset}(°C) (Cooling)	Undercooling (°C)	Wetting Time, ta (s) (300C)	Wetting force (mN) (300C)	Hardness (HV10)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
#41	226	11	213	13	0.82	3.15	7.5	24.1	40.3

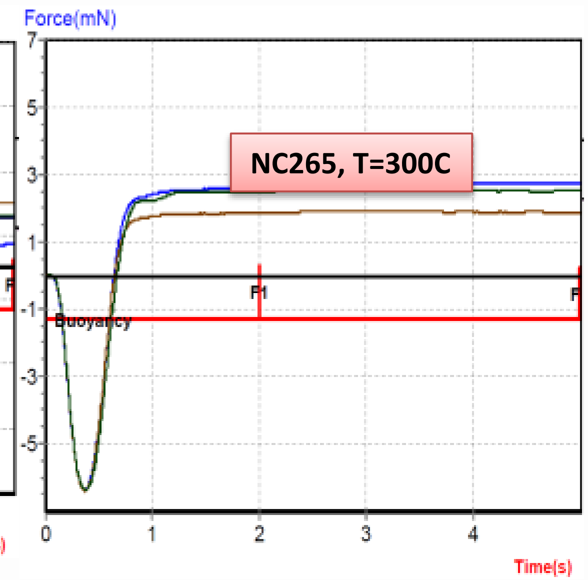


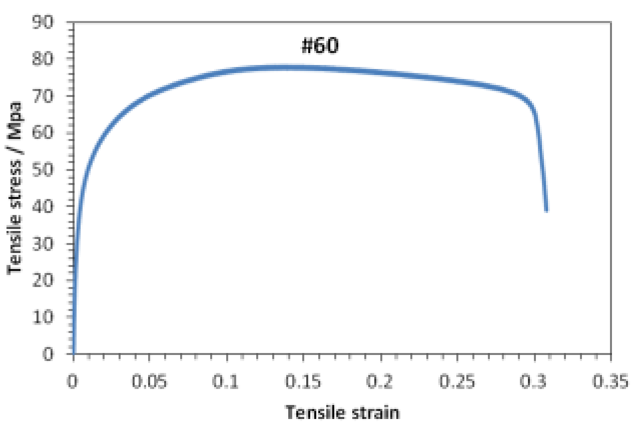
- This alloy is soft with low hardness, low tensile strength and large elongation.
- The grain structure is equiaxed.
- Wetting test pass at 300C, but fails at 265C for NC265.
- Some dross forms during melting.
- Tin whisker growth is observed after 2500hr held at 60C and 85% humidity.
- Al addition mitigates tin whisker growth, refines grain structure, and deteriorates wetting properties as compared to Sn-Cu alloy.

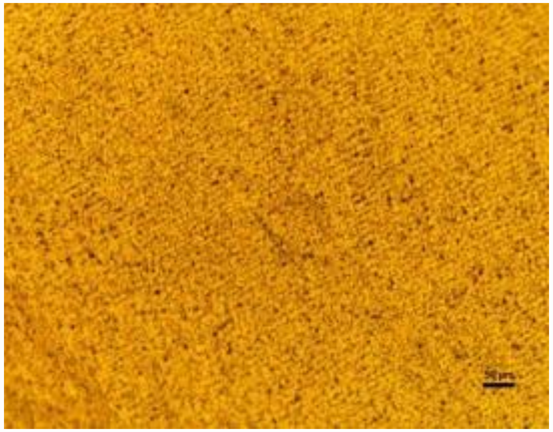
#60 (Sn-0.5Cu-0.2Zn-3.3Bi-0.5Ag)





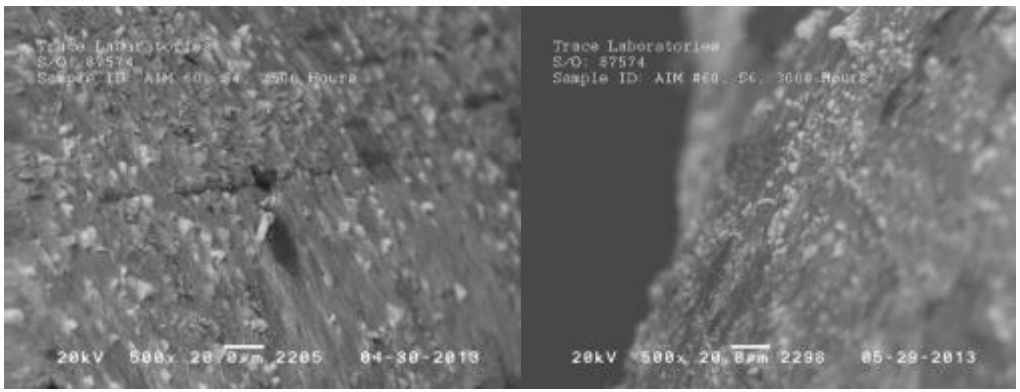






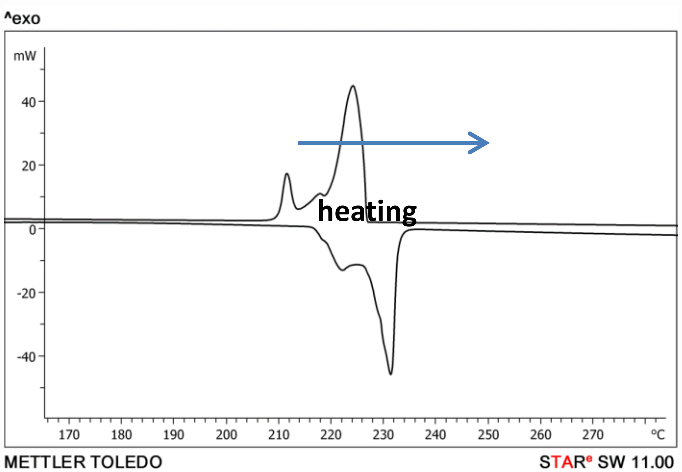
#60 (Sn-0.5Cu-0.2Zn-3.3Bi-0.5Ag)

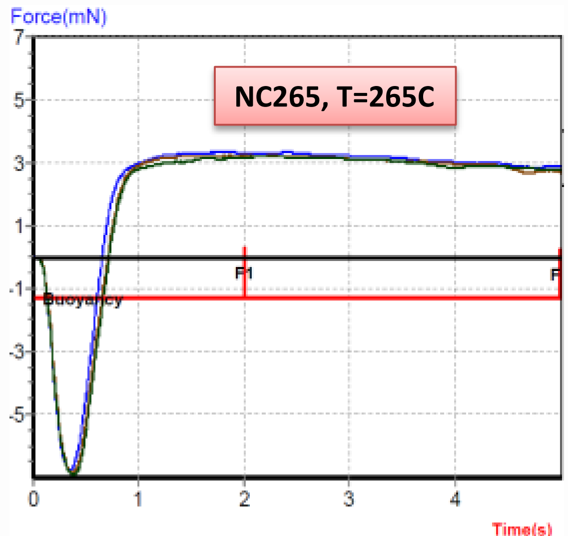
Alloy	T_{onset}(°C) (Heating)	Pasty range (°C)	T_{onset}(°C) (Cooling)	Undercooling (°C)	Wetting Time, ta (s) (300C)	Wetting force (mN) (300C)	Hardness (HV10)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
#60	201	24	217	No	0.6	3.63	15	77	26

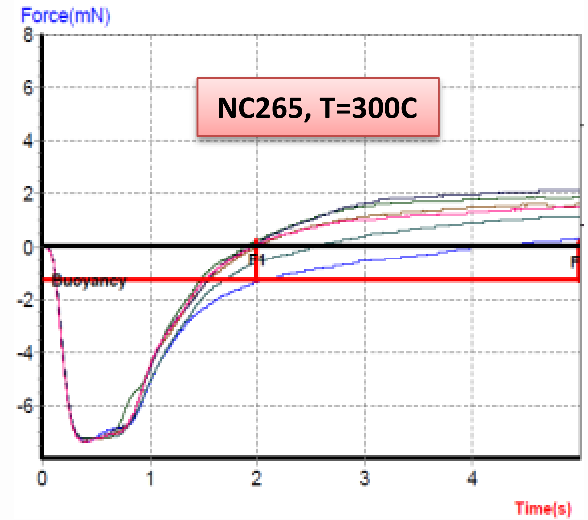


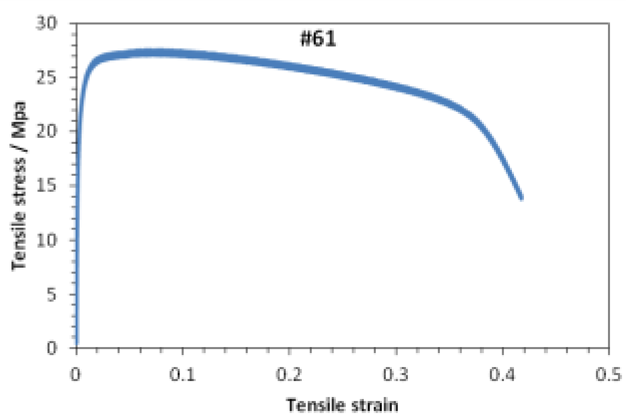
- The solidus temperature is low but pasty range is about 24°C. DSC result does not show undercooling which is odd.
- This alloy has high tensile strength, good elongation and hardness.
- The grain structure is dendritic.
- Wetting test pass at 265°C for NC265.
- Some dross forms during melting.
- Tin whisker growth is observed after 2500hr held at 60°C and 85% humidity.
- Zn and Bi addition mitigates tin whisker growth, increases the strength, lowers melting point and deteriorates wetting properties as compared to Sn-Cu-Ag alloy.

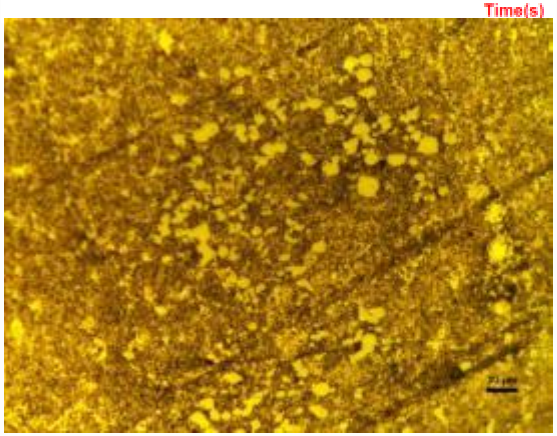
#61 (Sn-0.5Cu-0.5Ag-0.06Al-0.2Ge)

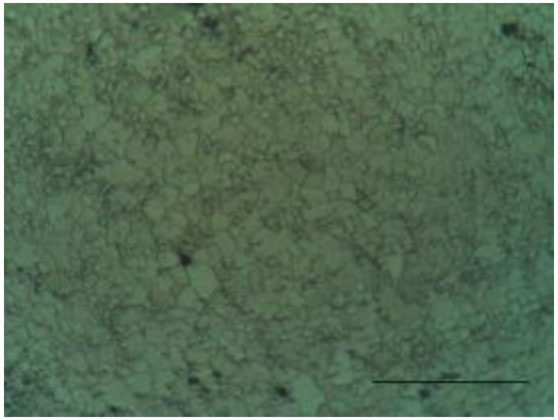












#61 (Sn-0.5Cu-0.5Ag-0.06Al-0.2Ge)

Alloy	T_{onset}(°C) (Heating)	Pasty range (°C)	T_{onset}(°C) (Cooling)	Undercooling (°C)	Wetting Time, ta (s) (300C)	Wetting force (mN) (300C)	Hardness (HV10)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
#61	216	17	227	No	0.64	4.54	16	28.1	37.2

- The solidus temperature is as low as SAC305 but pasty range is 17C. DSC result does not show undercooling which is odd.
- This alloy has low tensile strength, good elongation and hardness.
- Wetting test pass at 300C for NC265.
- Some dross forms during melting.
- Tin whisker growth is observed after 3000hr held at 60C and 85% humidity.
- Al and/or Ge addition mitigates tin whisker growth, increases the strength, lowers melting point, and deteriorates wetting properties as compared to Sn-Cu-Ag alloy.

Max Whisker Size Observed After 3000hr

SAC305

#41 (Sn-0.4Cu-0.05Al)

#60 (Sn-0.5Cu-0.2Zn-3.3Bi-0.5Ag)

#61 (Sn-0.5Cu-0.5Ag-0.06Al-0.2Ge)

Summary Results

Alloy	T_{onset}(°C) (Heating)	Pasty range (°C)	Wetting Time, ta (s) (300C)	Wetting force (mN) (300C)	Hardness (HV10)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
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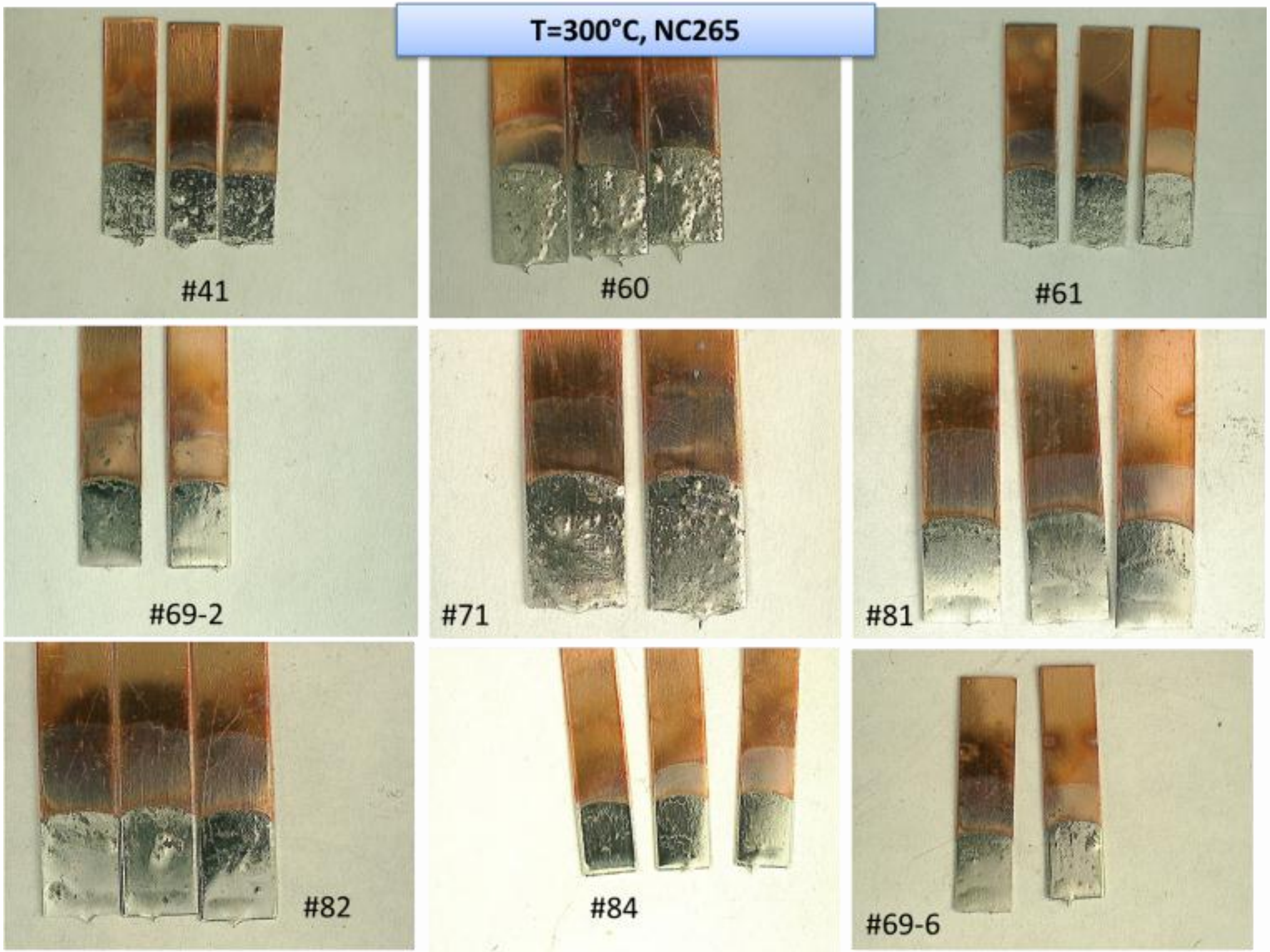
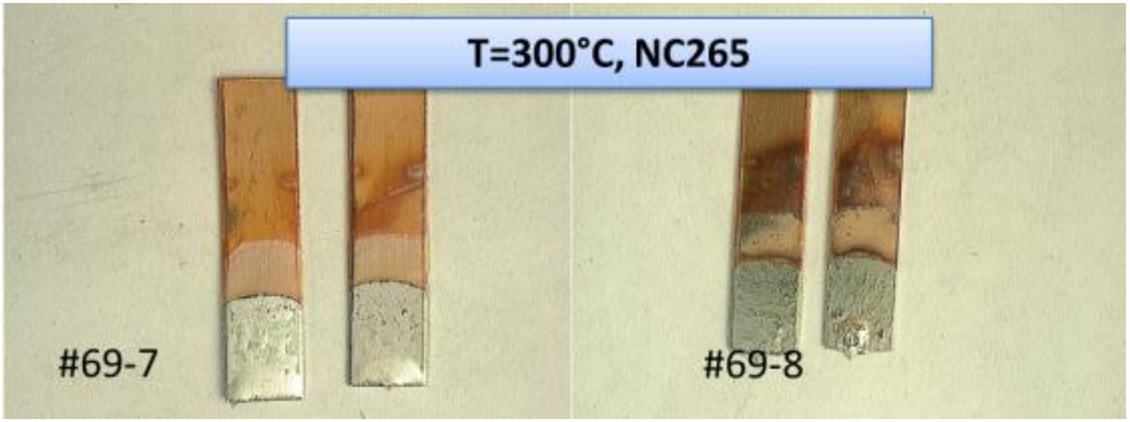
#69-2 (Sn-0.6Ag-0.7Cu-3Bi)	204	21	0.56	4.77	25	82	21.5
#71 (Sn-0.6Ag-0.7Cu-3Bi-0.04Al)	206	20	0.74	4.82	21	-	-
#81 (Sn-0.6Ag-0.7Cu-3Bi-0.06Ni)	204	20	0.79	4.8	-	-	-
SAC0607	217	18.5	0.49	4.66	15	35.1	39
SAC305	217	13	0.57	4.88	17.7	35	46.7
#82 (Sn-0.6Ag-0.7Cu-3Bi-0.056Ni-0.004Al)	205	20	0.58	4.8	-	-	-
#84 (Sn-0.5Cu-0.3Ni-0.3Sb-0.09Fe-0.09Mn)	227	12	0.67	4.4	15	-	-
#69-6 (Sn-0.6Ag-0.7Cu-1.2Bi-0.002Al)	210	18	0.58	4.63	14	-	-
#69-7 (Sn-0.6Ag-0.7Cu-1.2Bi-0.7Sb)	210	21	0.64	4.41	20	64	21.3
#69-8 (Sn-0.6Ag-0.7Cu-1.4Bi-0.07Al-0.1Sb)	210	20	0.55	4.17	19	63	23.5

T=300°C, NC265




T=300°C, NC265
#69-7
#69-8

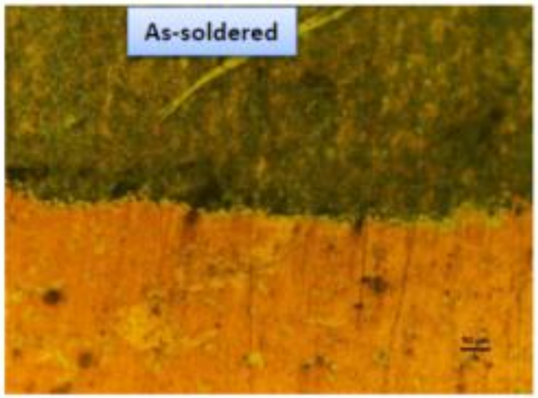
Third Round of Alloy Testing

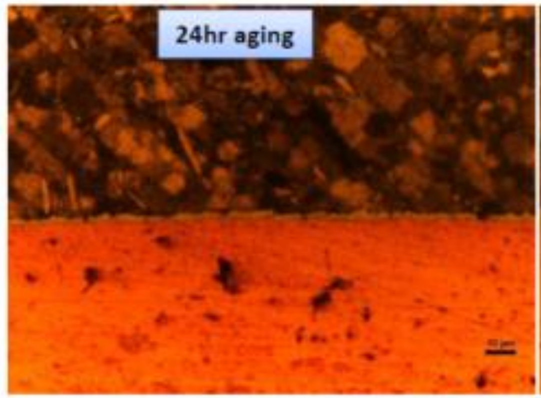
Alloy	Note
87(Sn-0.7Cu-2Bi-0.026Al)	
88(Sn-0.6Cu-2Bi-0.052Ni)	
89 (Sn-0.6Cu-2.8Bi-0.049Ni-0.049Fe)	
90 (Sn-0.66Cu-2.1Bi-0.074Zn)	
91 (Sn-0.66Cu-0.53Ag-2Bi-0.038Al)	
92 (Sn-0.5Cu-0.5Ag-2Bi-0.7Sb)	
93 (Sn-0.7Cu-0.07Ni-0.2Sb)	**Reference**
69-2 (Sn-0.6Ag-0.7Cu-3Bi)	**Reference**
SAC305	**Reference**
Sn100C	**Reference**
63Sn-37Pb	**Reference**

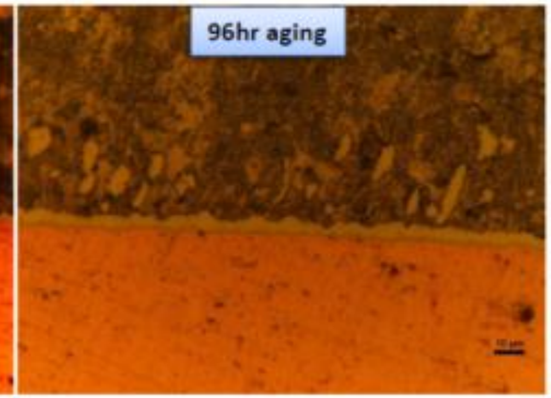
SAC 305

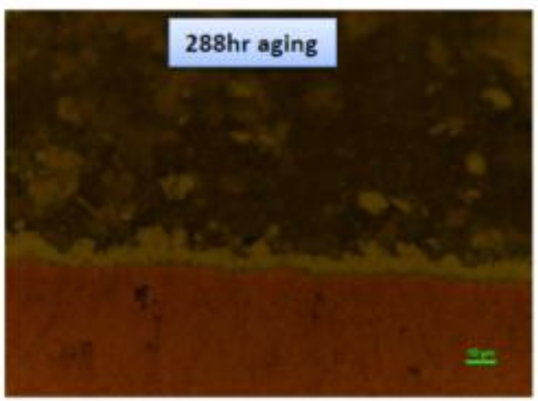
Kinetics of IMC growth at 150°C

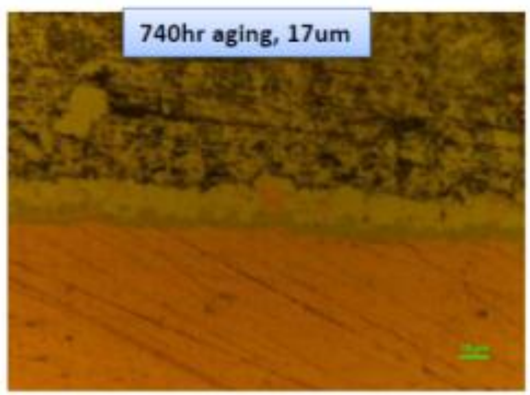
Spread test was done at 260°C for 40s using NC258

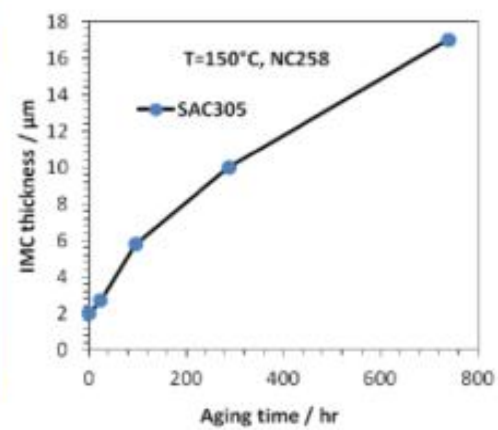








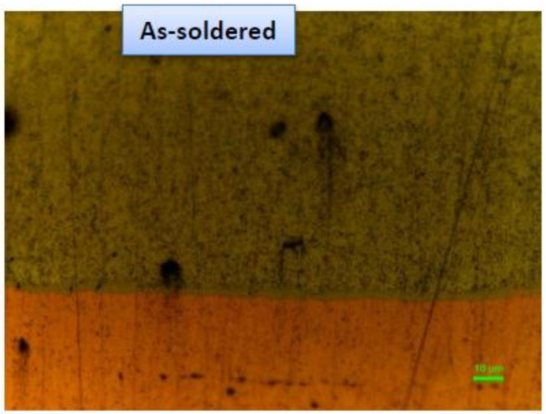


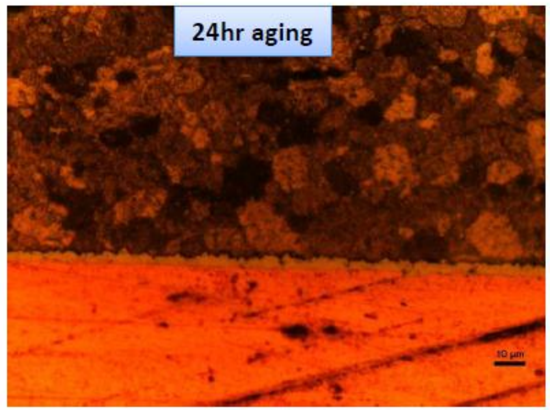


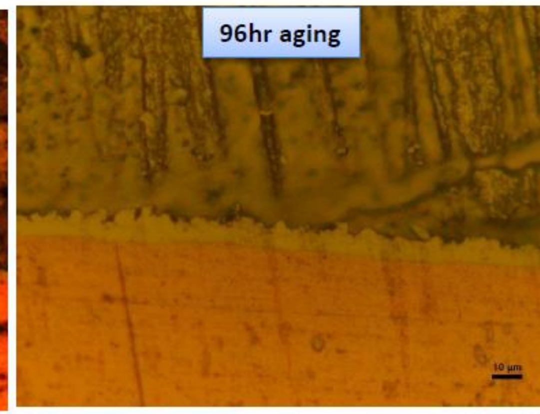
Sn100C

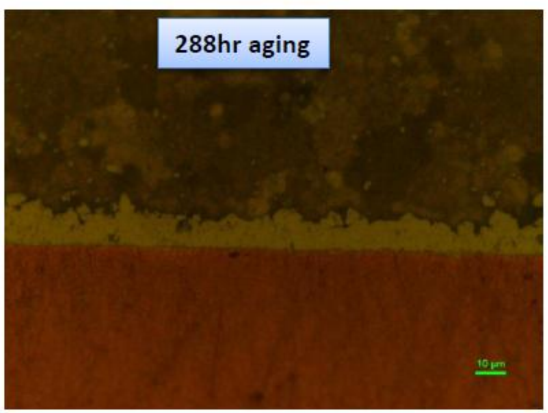
Kinetics of IMC growth at 150°C

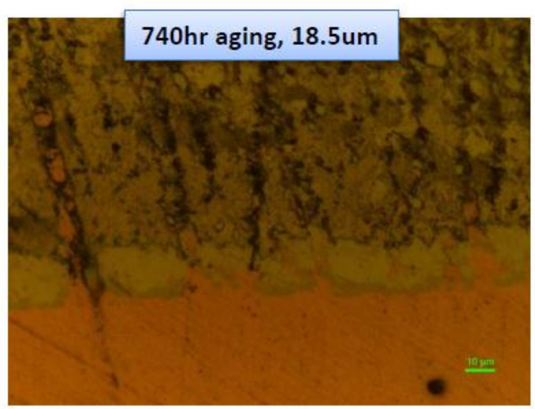
Spread test was done at 260°C for 40s using NC258

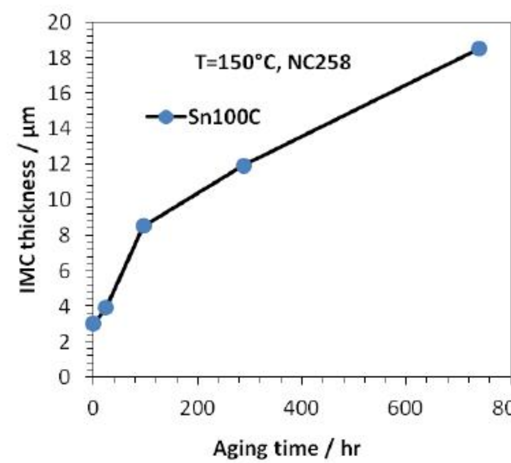








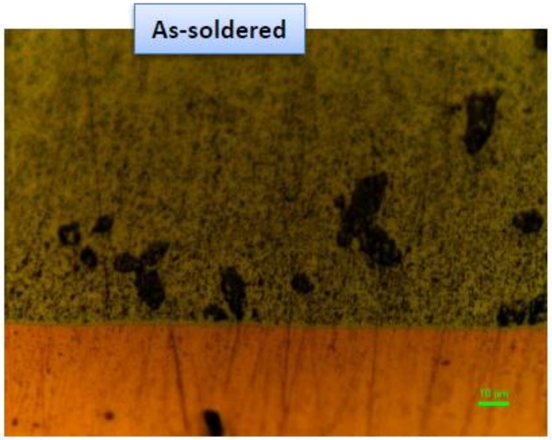


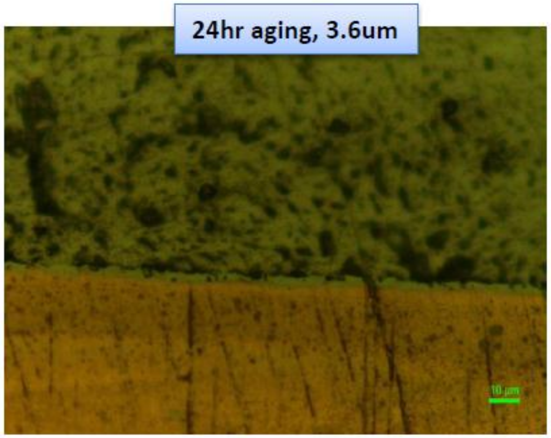


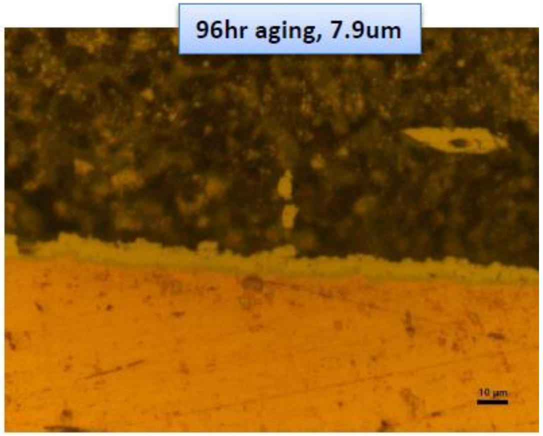
63Sn-37Pb

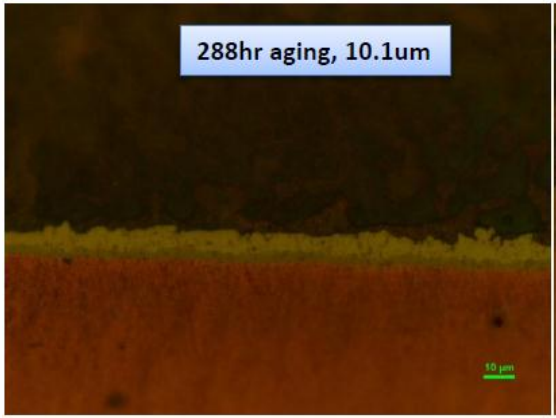
Kinetics of IMC growth at 150°C

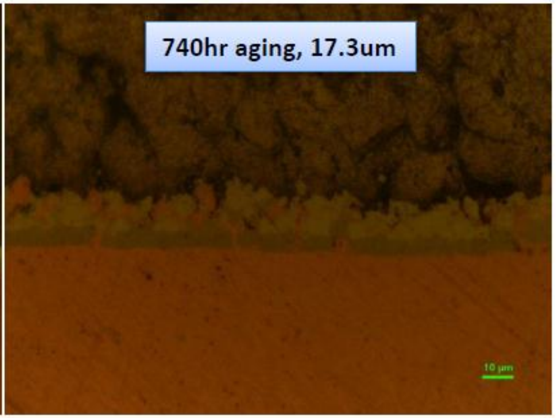
Spread test was done at 260°C for 40s using NC258

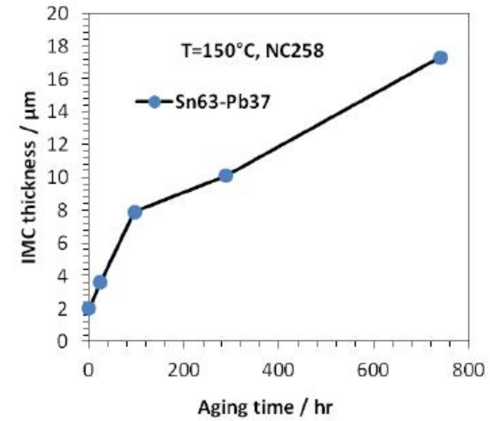








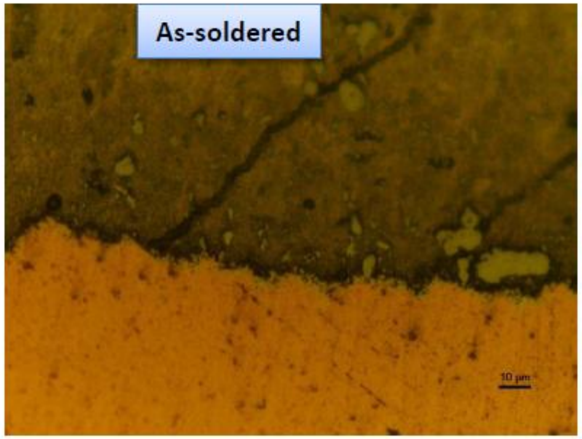


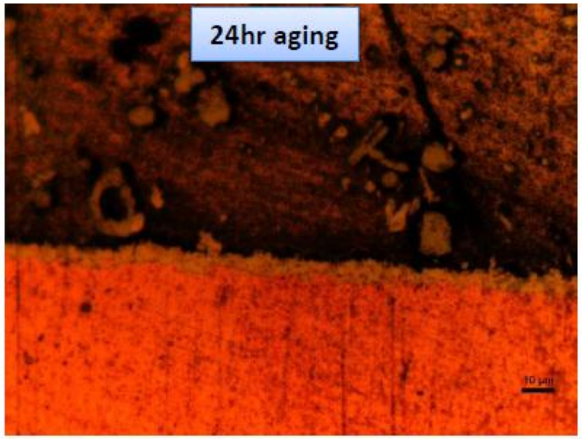


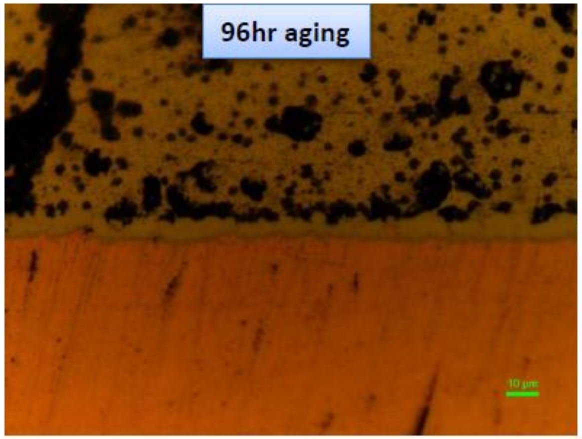
Alloy #89

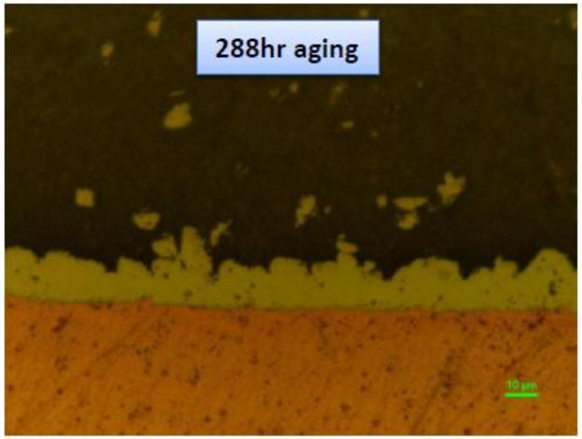
Kinetics of IMC growth at 150°C

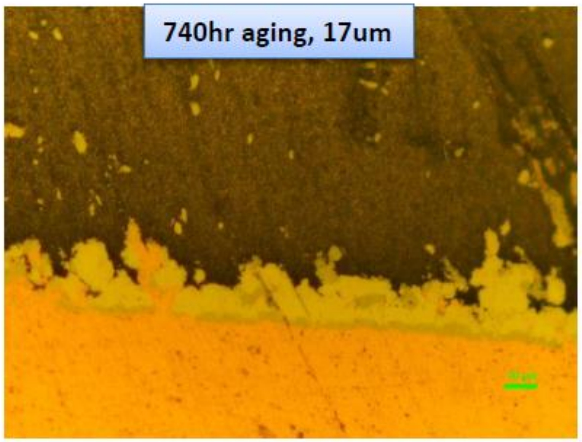
Spread test was done at 260°C for 40s using NC258

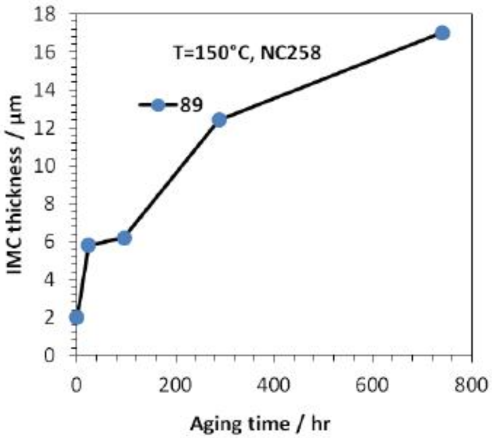








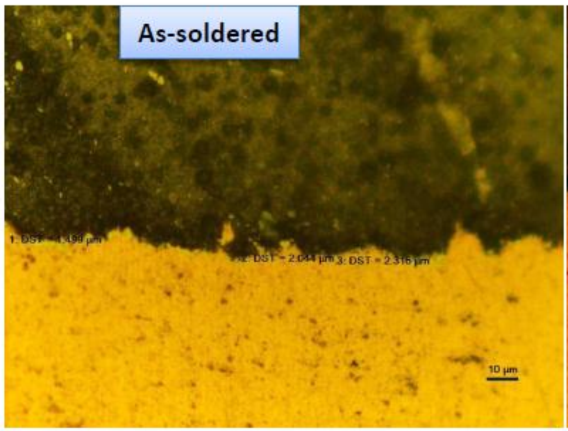


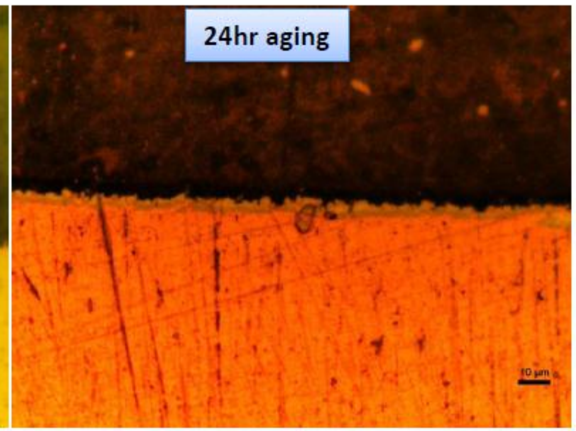


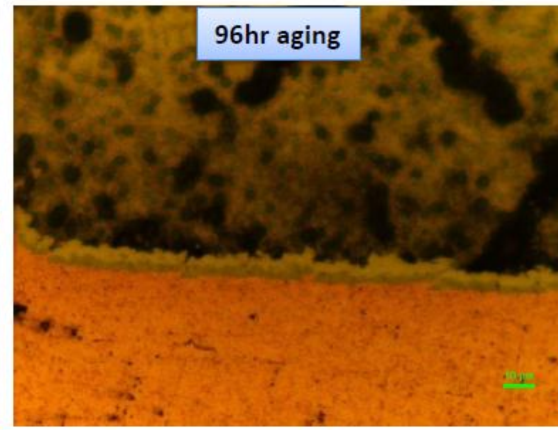
Alloy #87

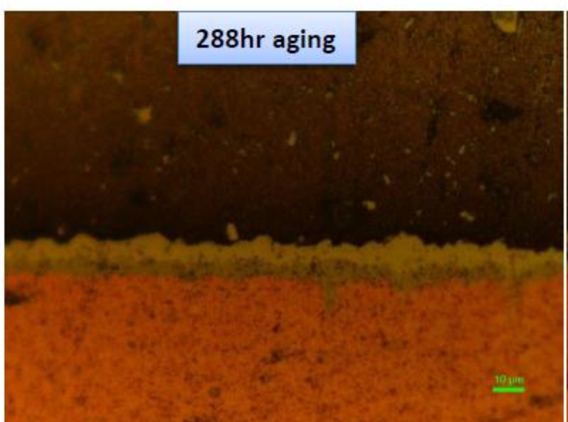
Kinetics of IMC growth at 150°C

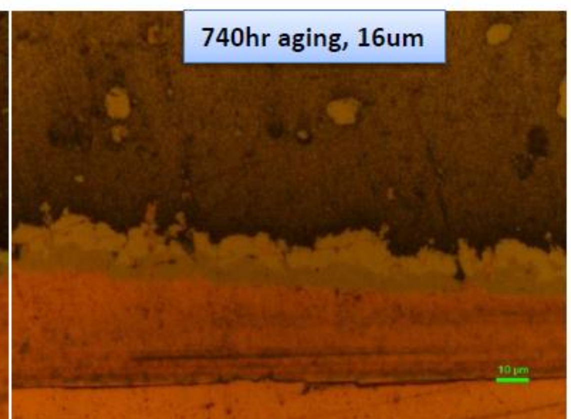
Spread test was done at 260°C for 40s using NC258

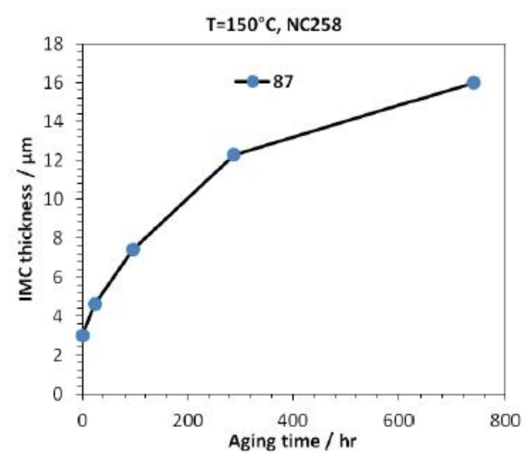








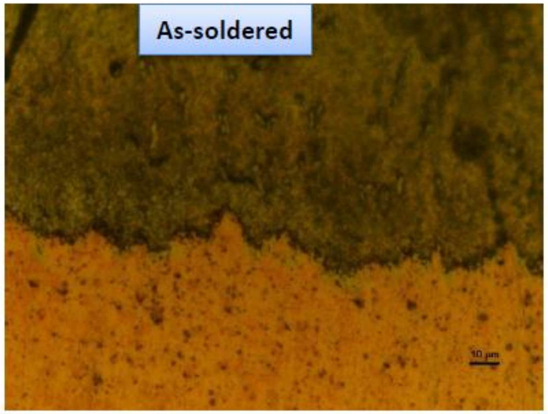


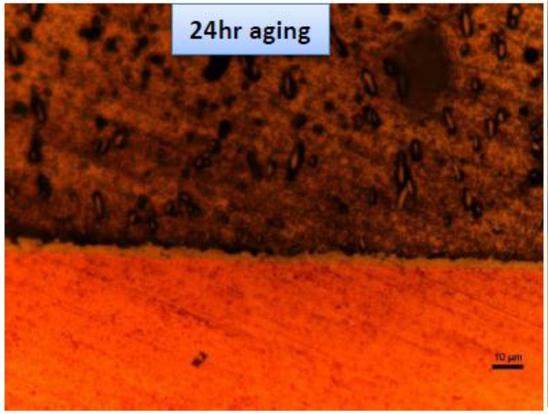


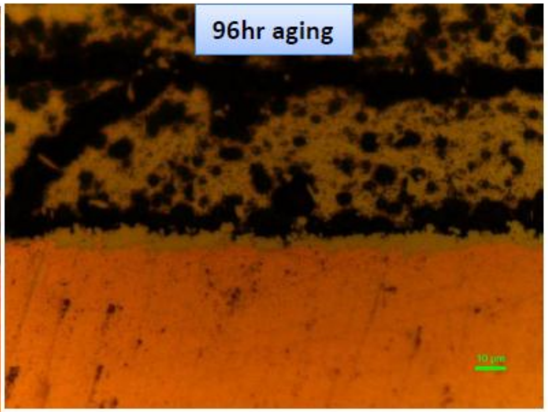
Alloy #90

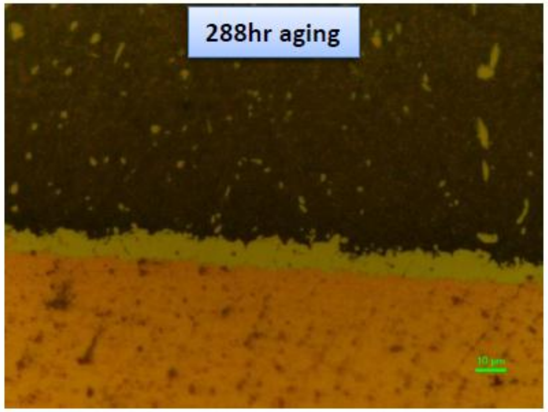
Kinetics of IMC growth at 150°C

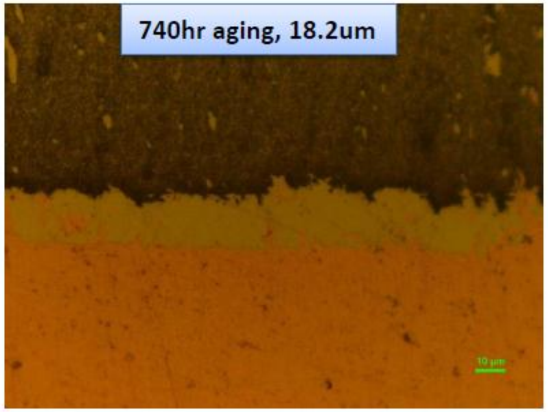
Spread test was done at 260°C for 40s using NC258

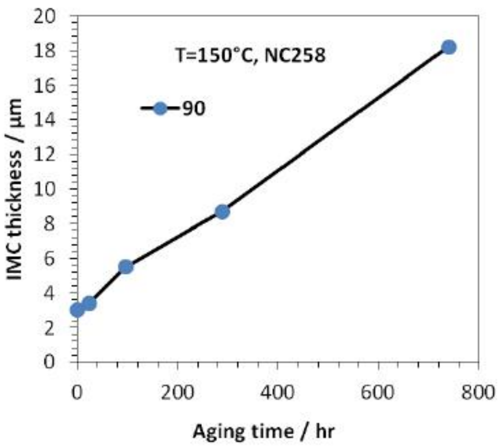




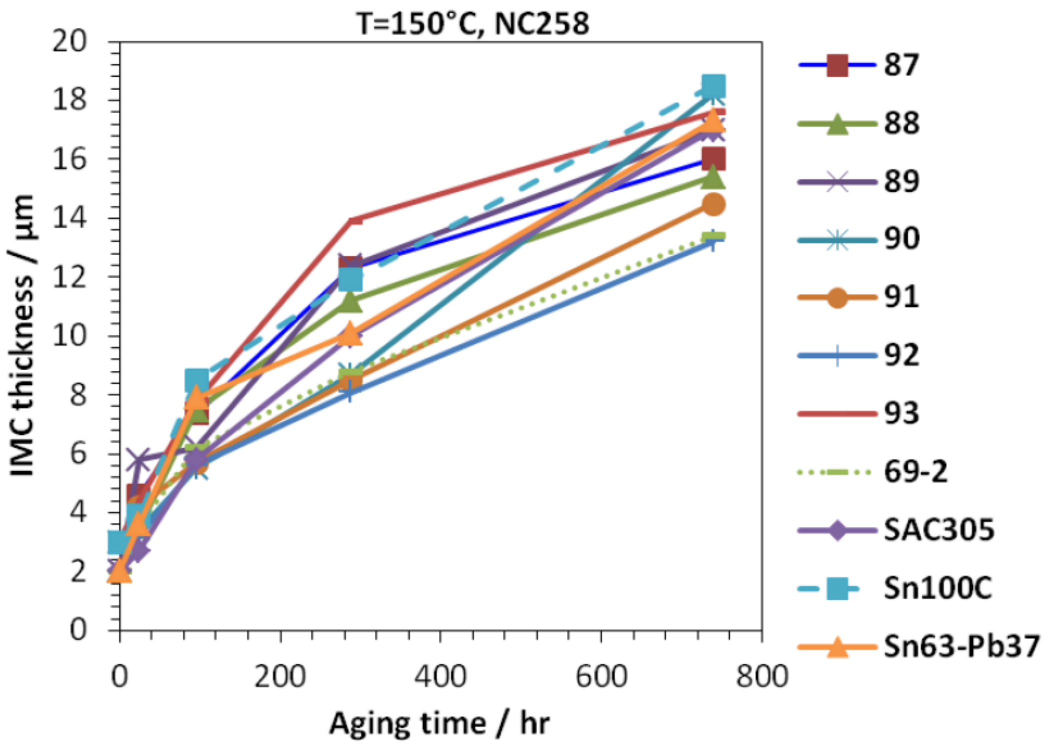






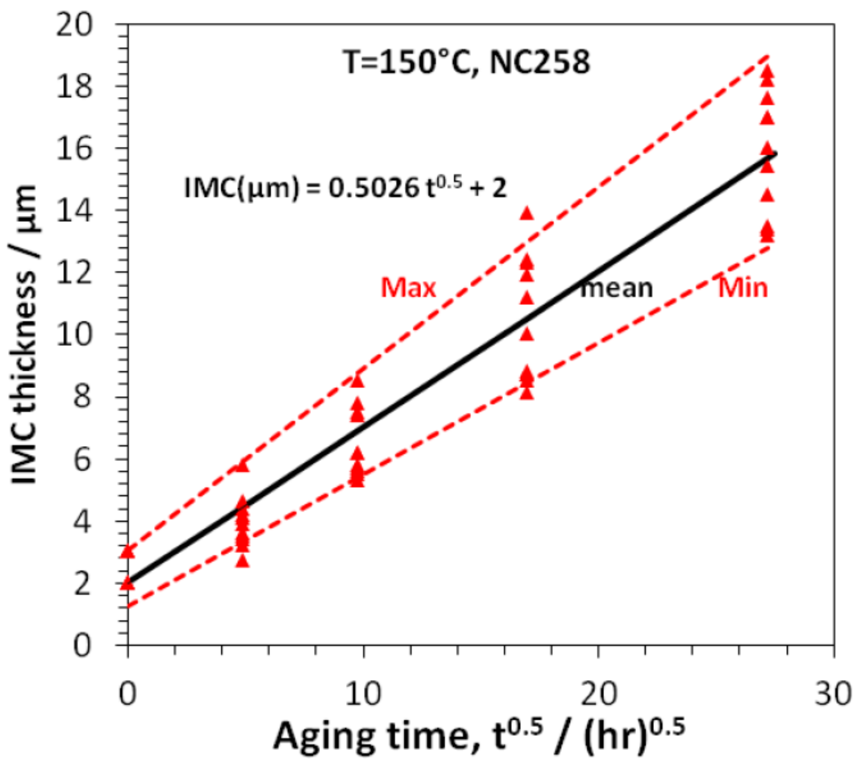


Kinetics of IMC growth at 150°C

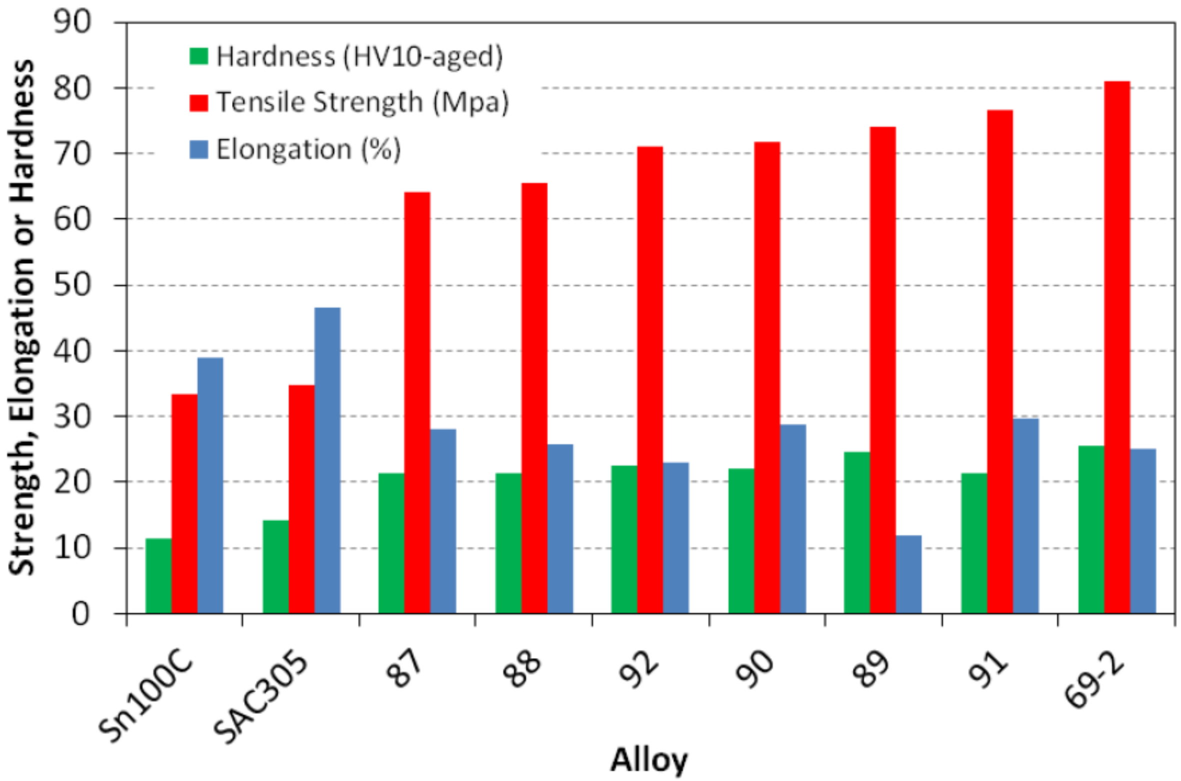


Kinetics of IMC growth at 150°C

Variation of IMC thickness with square root of time ($t^{0.5}$) follows linear trend. For all the alloys studied IMC thickness falls within two linear curves (max and min). With a simple equation we can estimate the mean growth kinetics of IMC as a function of time as shown in the diagram.



Mechanical properties

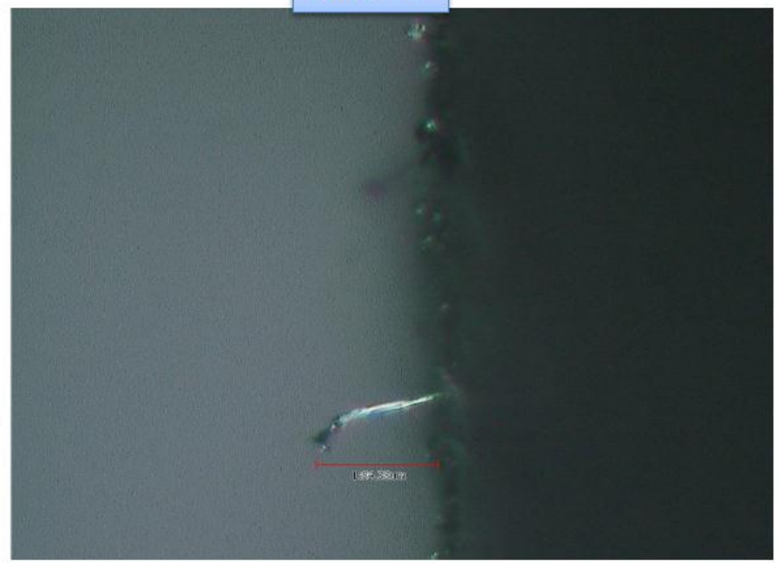


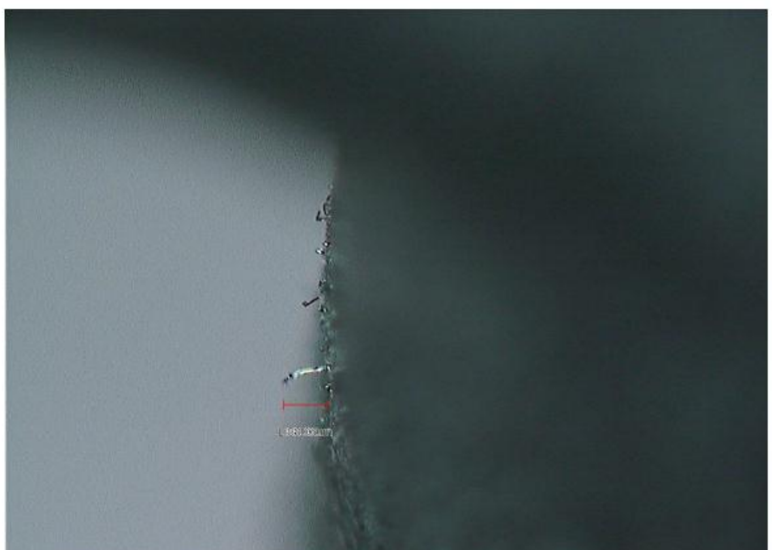
- **Bi content plays a dominant role in increasing strength and hardness of the solder alloys.**

Tin whiskers

- After about 2600 hr in humidity chamber (85%RH and 60°C), as a preliminary result we could observe tin whisker growth in **SAC305** using optical microscope , as shown in the pictures.
- However, we did not detect tin whiskers in the alloy **69-2** (Sn-0.6Cu-0.6Ag-3B).
- For clarification further analysis using SEM will be done.

SAC305





Summary results

Alloy	T_{onset}(°C) (Heating)	Pasty range (°C)	Wetting Time, ta (s) (NC265, 265C)	Wetting Force, F1 (mN) (265C)	Hardness (HV10) (aged 96hr 125C)	Tensile strength (Mpa) (aged 96hr 125C)	Elong. (%)
87(Sn-0.7Cu-2Bi-0.026Al)	216	12	1.44	2.28	21.5	64.1	28.2
88(Sn-0.6Cu-2Bi-0.052Ni)	217	12	1.54	1.6	21.5	65.6	25.8
89 (Sn-0.6Cu-2.8Bi-0.049Ni-0.049Fe)	214	15	1.28	2.71	26.6	74	12
90 (Sn-0.66Cu-2.1Bi-0.074Zn)	215	12	1.17	0.51	22	71.8	28.9
91 (Sn-0.66Cu-0.53Ag-2Bi-0.038Al)	207	18	1.09	3.73	21.3	76.7	29.6
92 (Sn-0.5Cu-0.5Ag-2Bi-0.7Sb)	205	22	1.13	3.74	22.5	71.2	22.9
#69-2 (Sn-0.6Ag-0.7Cu-3Bi**)**	204	20	0.95	4.35	25.6	81	25
SAC305	217	12	0.95	4.38	14.2	34.9	46.6
Sn100C	226	10	2.1	0.1	11.5	33.3	38.9

- The kinetics of intermetallic growth are not dependent on the composition of the alloys studied. With a single equation, the approximate IMC thickness can be estimated as a function of aging time.
- 0.6wt% Ag has a big impact on the wetting behavior of the alloys.
- “Bi” plays a dominant role in strengthening of the solder alloys.
- Preliminary results on tin whisker growth shows the presence of tin whisker in SAC305 after about 2600 hr. in the chamber. However, whiskers were not detected for the alloy 69-2 (Sn-0.6Cu-0.6Ag-3Bi)
- Other alloys (with microalloying elements) are still in the chamber for tin whisker analysis (has not reached 2000hr yet).
- Wetting contact angle is under investigation.

Final Overview Of All Stages (to date)

- High silver alloys tend to grow more whiskers and longer whiskers
- Bismuth helps reduce whiskers
- High bismuth has negative impact on mechanical properties needed for soldering
- Lower bismuth doped with other additives eliminates and/or reduces whiskers growth

Some alloys in this presentation are currently patent pending

THANK YOU