CHARACTERIZATION OF CONDUCTIVE DIE ATTACH DELAMINATION TO C19210 COPPER AND ITS OXIDES

Obed, Rommel Jr. S.[1]
Tabucanon, Mark Andrew T.[2]
Castillo, Jocy P.[3]

Materials Engineering – Quality Department[1,2,3]
Ampleon Manufacturing Philippines Inc.
rommel.obed@ampleon.com[1]; markandrew.tabucanon@ampleon.com[2]; jocy.castillo@ampleon.com[3]

ABSTRACT

Adhesive-to-copper substrate delamination was seen during a material evaluation trial. Initial results showed that the adhesive is not completely adhering to the copper substrate.

Scanning Acoustic Tomography (SCAT) showed indication of delamination which was confirmed on SEM-EDX (Scanning Electron Microscope – Energy Dispersive Xray). SEM images show a delamination between the die attach material and the copper substrate. The presence of copper oxide was also seen in the failure area indicating possible oxidation.

To solidify the effect of copper oxidation on adhesion, oxidation trials were done to characterize the stages of copper oxidation where adhesion will be compromised. This was done through progressive contact angle measurements.

Results show a direct relationship between the progression of copper oxidation through copper weathering and an increase in contact angle. Copper and the progression of its oxides have a detrimental effect on the adhesion of epoxy-based adhesives.

1. 0 INTRODUCTION

Ampleon molded packages are made with cost effectiveness, performance, and reliability as top priorities. Copper is a common component in the electronics industry. This is due to its abundance which makes it cheap while still maintaining high electrical properties.

A copper alloy suited and chosen for Ampleon products is the C19210 alloy, which balances strength, machinability and good electrical performance[1].

Oxidation is a common cause of manufacturing rejections throughout the semiconductor industry. Humidity and heat are primary contributors, and both are also prevalent challenges for manufacturing electronics in the Philippines. C19210 is manufactured to optimize corrosion resistance through the addition of phosphorus but copper oxidation is more often only controlled and not completely prevented.

For die attach, conductive die-attach adhesives are a common solution for die attach processes. This adhesive consists of two main components, namely metallic particulates for electrical and thermal performance; and the organic component for adhesion and mobility. The adhesion relies on the organic component of the conductive adhesive.

The optimal interaction between the copper C19210 substrate and the die attach adhesive ensures the quality of the connection of the sub-components of molded packages.

This study focuses on how degree of copper oxidation affects the adhesion of the conductive die attach material through contact angle characterization. Ionic contamination like corrosion is a continuous problem in semiconductor manufacturing. There is no standard in the detection of ionic contamination due to the various proprietary methodologies done by different organizations[2].

2. 0 REVIEW OF RELATED WORK

Copper is relatively near the anodic side of the Galvanic series table. This means copper is less noble or generally less stable compared to those less anodic to it. The C19210 alloy has a phosphorus additive that improves the corrosion resistance of copper.

Copper naturally corrodes at normal atmosphere. This is due to naturally occurring atmospheric elements (moisture, carbon dioxide, sulfur, acidic stimuli, etc.)

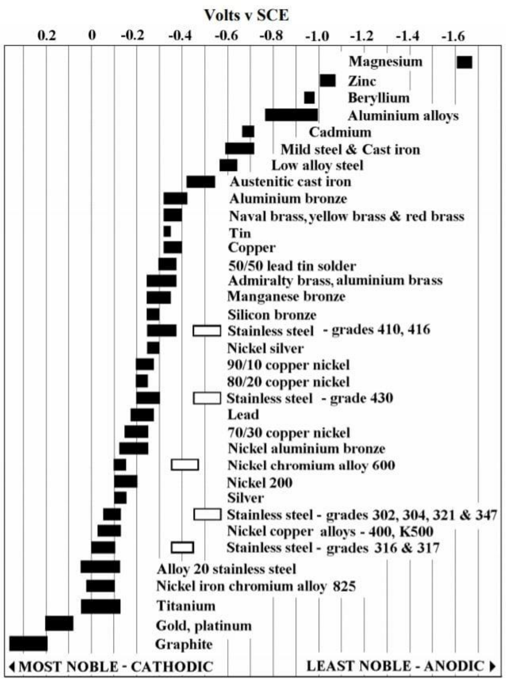


Fig 2.1 Galvanic series table showing that copper is not as noble as precious metals[3]

Fig 2.2 Copper Alloys Finishes – Natural Weathering[4]

Figure 2.2 shows a visual guide for normal copper weathering. Copper starts oxidizing from an orange color going towards darkening then transitions to greenish color. In the case for this study, C19210 alloy could cause some deviations from the weathering chart but is expected to relatively adhere to the trend show on the chart.

Copper is known to oxidize depending on the stimuli and temperature. Oxidation at lower temperatures promotes more cuprous oxide (Cu_2O) while oxidation at higher temperatures promotes mostly cupric oxide (CuO)[5].

For copper weathering, initial oxidation will be cuprous oxide (Cu_2O) since the stimuli will not be extremely high temperatures. Cu_2O will stabilize into CuO and will then continue to react with water and carbon dioxide to form the greenish patina $Cu_2CO_3(OH)_2$.

(1) $4Cu + O2 \rightarrow 2Cu_2O$
(2) $2Cu_2O + O2 \rightarrow 4CuO$
(3) $2CuO + CO_2 + H_2O \rightarrow Cu_2CO_3(OH)_2$

For measuring the effectivity of adhesion to the copper surface. Contact angle measurement through water drop test was done. The angle recorded from contact angle measurement is a widely known method to measure adhesive performance. The interaction of the water to the substrate can effectively characterize the cohesive forces between common fluids and a substrate. This is true for the epoxy in the conductive epoxy used in this study[6].

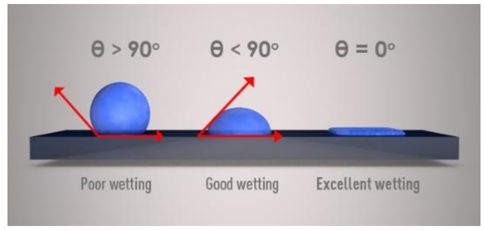


Fig 2.3 Surface Contact Angle reference for Wettability[7]

3.0 METHODOLOGY

Defective units were captured using SCAT (Scanning Acoustic Tomography). After identifying the failure area. The reject unit was analyzed through cross section then SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-ray) for elemental analysis. This was done to investigate the failure area to look for the material that is mainly contributing to the delamination fail mode.

To begin simulating the hypothesized failure mode on the copper substrate, using a hot plate set on a 60% relative humidity (RH) room, several strips of copper lead frame were heated. This was to create multiple oxidized copper samples to produce the different color variations from the copper weathering chart in Figure 2.2

Contact angles were measured using a water drop test station. Three units were measured for each color produced during the heating of the copper samples. Deionized water was on the backside of each heatsink. It was made sure that only copper was covered by the droplet. Contact angle was then calculated using a high-resolution camera.

4.0 RESULTS AND DISCUSSION

4.1 SCAT and SEM/EDX Failure Mode Analysis

A SCAT image was obtained of the fail/NG (no good) unit. The image taken on Fig 4.1 shows a bright spot on the molded package which indicates a possible delamination.

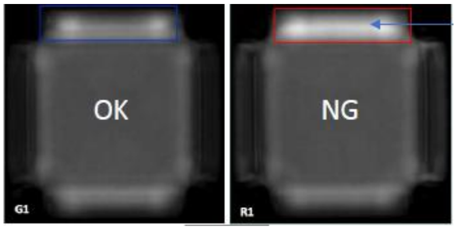
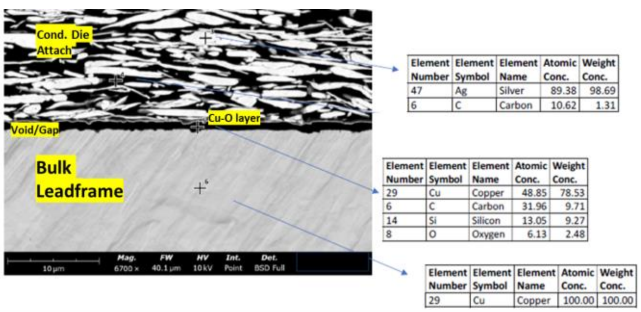


Fig 4.1 SCAT image of the molded package showing a delamination on the NG unit.

SEM/EDX on the NG fail area shows the void between the conductive die attach and the lead frame. As seen on Fig 4.2, the shape of the die attach interface shows the die attach material initially conforming to the shape of the lead frame before detaching. This indicated that the lead frame failed to permanently attach/join to the lead frame.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
47	Ag	Silver	89.38	98.69
6	C	Carbon	10.62	1.31

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
29	Cu	Copper	48.85	78.53
6	C	Carbon	31.96	9.71
14	Si	Silicon	13.05	9.27
8	O	Oxygen	6.13	2.48

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
29	Cu	Copper	100.00	100.00

Fig 4.2 SEM-EDX of Conductive Die Attach to Copper Substrate (Lead frame) fail/ delamination area.

The investigation singled out either the conductive die attach material or the copper substrate as the possible cause of the issue. Zooming out on the SEM image on Fig 4.3 reveals that the same phenomenon was seen also on the mold compound adhesion to the substrate. There are no abnormalities seen on the mold compound as it is used in a wide variety of products using the same material. The common failure mode shared by both the conductive die attach and the mold compound led the investigation to focus more on the copper substrate.

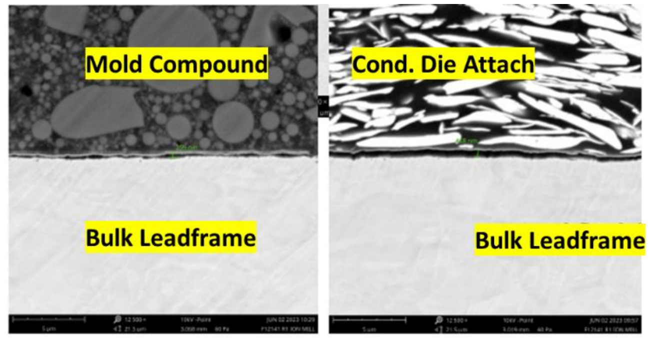


Fig 4.3 SEM image of difference/ similarity of the failure signature between the mold compound and the die attach material against the same copper lead frame.

The EDX results (shown on Fig 4.2) show oxygen presence on the delamination gap which indicates oxide formation from the copper. This focused the investigation more on copper and its oxides.

4.2 Copper Oxidation Simulation

Seen on Fig 4.4 are the results of the hotplate visual inspection. Pictures were taken as the hot plate ramped up in temperature and changed in color.

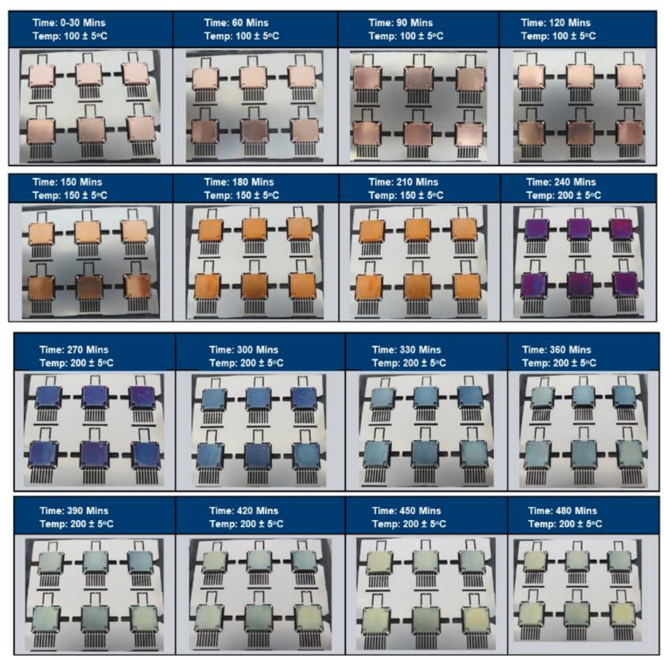


Fig 4.4 Progression of the colorations of copper as it goes through higher temperatures and time.

The visual appearance aligns the theoretical reaction for copper weathering.

(1) $4Cu + O2 \rightarrow 2Cu_2O$
(2) $2Cu_2O + O2 \rightarrow 4CuO$
(3) $2CuO + CO_2 + H_2O \rightarrow Cu_2CO_3(OH)_2$

These three reactions coincide with what was observed during the copper oxidation trial. For Reaction 1, it promotes the formation of Cu_2O which is a red compound. This coincided with the initially pale copper color to become redder in color. Reaction 2 converts CuO to Cu_2O, a naturally occurring black oxide. This is signified by the darkening of the orange color to a bluish color. Reaction 3 converts Cu_2O to the $Cu_2CO_3(OH)_2$ patina which causes the color to turn green.

4.3 Wettability Characterization (Contact Angle)

To characterize the effect and change on the cohesion/ adhesive force for each form of copper oxidation, contact angles were measured for each significant coloration.

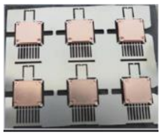
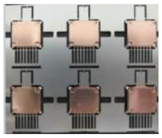
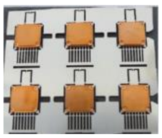
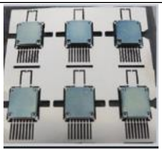
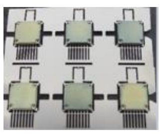
Leadframe	Time (mins)	Temp (oC)	Contact Angle (Deg)
	0	Room Temp	69.00
	120	100	75.33
	240	150	87.00
	360	200	91.33
	480	200	97.33

Fig 4.5 Contact angle measurements for every color observed.

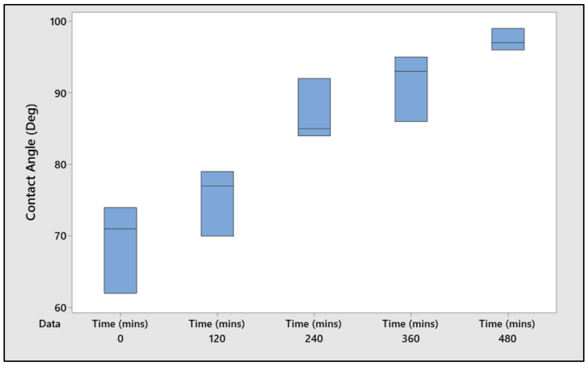


Fig 4.6 Contact angle plot showing increased contact angle as the copper oxidized.

The trend seen on the plot shows the contact angle increasing as the Copper oxidizes. Thus, showing the high risk of using oxidized copper on die bonding and adhesion in general. This confirms that the formation of latter oxides of copper, namely the Cu_2O and the $Cu_2CO_3(OH)_2$ present high to delamination.

Contact angle significantly increased during the transition from the base pale orange color to a darker more reddish orange color. This color change signifies the formation of the cuprous oxide, Cu_2O. This indicates that oxide formation no matter what compound is detrimental to wettability due to a noticeable increase in contact angle.

5.0 CONCLUSION

The study showed that change in copper color is an immediate sign of oxidation. This oxidation has been proven to have a negative effect on adhesion of epoxy adhesives to the copper.

Based on Fig 2.2, the 4-month indication where copper turns from pale to a darker orange color is already detrimental. The contact angle results show an average of 87 degrees which is near the hydrophobic limit of 90 degrees. This creates a risk of delamination already at the first indication of color change of the base color of the copper.

It is recommended that to prevent and de-risk delamination for copper, change in color from the base pale copper color should be rejectable already.

The study showed how copper oxidation in ambient conditions negatively impacts the adhesion of epoxy-based die attach materials. This can be applied to conductive epoxy die attach and other epoxy-based adhesives. This study could apply to air cavity sealing commonly using pure epoxy-based glues.

Copper weathering can be traced to equipment mishandling, namely ovens, furnaces, and heater blocks. Prevention of oxidation means limiting the time of copper materials to long and high amounts of heat.

6.0 RECOMMENDATIONS

The study dealt with materials dealing with epoxy as the agent for adhesion. This does not represent solder-based bonding which bonds metal-to-metal. An extension of this study can focus on that as well.

An extension of this study can also focus on silver sinter bonding as there is an organic component to that kind of die attach bonding.

With the findings of this activity, it is advisable to take note of the conditions where lead frames are stored in bulk for a long time.

7.0 ACKNOWLEDGMENT

The authors would like to thank the following for their support of this study:

- Romeo Peralta – Sr. Director, Quality & Reliability, Ampleon Phils., Inc.
- Olga Rivera – Director, Materials & Design Engineering/ Sustainability/ NPI-BET Quality, Ampleon Phils., Inc.
- Manolito Maalat – Sr. Manager, Failure Analysis/ Reliability and Calibration, Ampleon Phils., Inc.
- Marilou Bigcas – Director, Assembly Process, Ampleon Phils., Inc.

8.0 REFERENCES

1. "C19210" Copper Development Association Inc. 2023. https://alloys.copper.org/alloy/C19210

2. Ignatius J. Rasiah and Ho Pei Sze. " Ionic contamination in the component materials of IC packages" Ionic contamination in the component materials of IC packages. doi: 10.1109/EMAP.2000.904184.

3. "An Introduction to the Galvanic Series: Galvanic Compatibility and Corrosion" Corrosionpedia. November 12, 2020. https://www.corrosionpedia.com/an-introduction-to-the-galvanic-series-galvanic-compatibility-and-corrosion/2/1403

4. "Copper Alloys Finishes – Natural Weathering" Austral Wright Metals. 2000-2001. https://www.australwright.com.au/technical-data/advice/copper-brass/copper-alloys-finishes-natural-weathering/

5. Víctor-Hugo Castrejón-Sánchez, Antonio Coyopol Solís, Roberto López, Cecilia Encarnación-Gomez, Francisco Morales Morales, Orlando Soriano Vargas, Jorge Edmundo Mastache-Mastache, and Gerardo Villa Sánchez. "Thermal oxidation of copper over a broad temperature range: towards the formation of cupric oxide (CuO)" Mater. Res. Express 6 075909. doi: 10.1088/2053-1591/ab1662.

6. Brighton Science " Why Knowing Water Contact Angle is Important for Successful Adhesive Performance" Brighton Science. April 2021. https://www.brighton-science.com/blog/why-knowing-water-contact-angle-is-important-for-successful-adhesive-performance

7. "Surface Wetting" Masterbond. https://www.masterbond.com/techtips/surface-wetting

9.0 ABOUT THE AUTHORS

Rommel S. Obed Jr. is a graduate of BS Materials Engineering from the University of the Philippines - Diliman. He is a Sr. Materials Engineer currently at Ampleon Philippines, Inc where he handles BOM material qualifications and material cost saving initiatives.. He is a product of the Ampleon Cadet Engineering (ACE) program. He specializes on die attach technologies like 80Au20Sn, Silver sinter, Pb soft solder. He also specializes in substrate surface level material analysis.

Mark Andrew T. Tabucanon is a University of the Philippines – Diliman alumnus who graduated with a degree of B.S. in Materials Engineering. He has an experience in the research field and worked as a Science Research Specialist in academe settings. Currently, he is employed as a Jr. Materials Engineer at Ampleon Philippines, Inc.

Jocy P. Castillo is a Materials Engineering Technician in Ampleon. She started her career in Ampleon Philippines as a FA/ Reliability inspector and then as a Specialist inspector for Incoming Quality Inspector. Her expertise are on Material specifications compliance, product reliability, material-level risk assessment and material characterization.