Direct Copper Metalization of Aluminum: Elimination of Zincate

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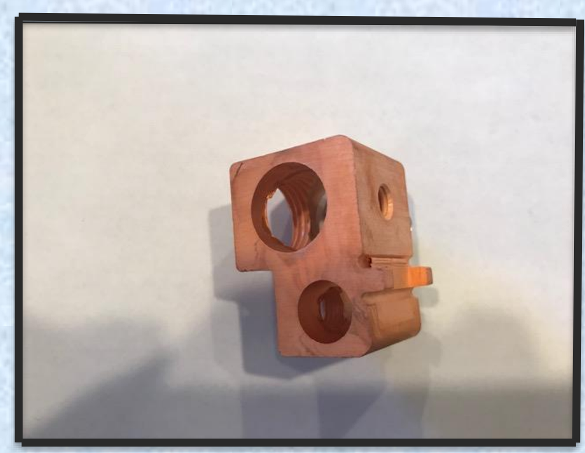
Today's Discussion

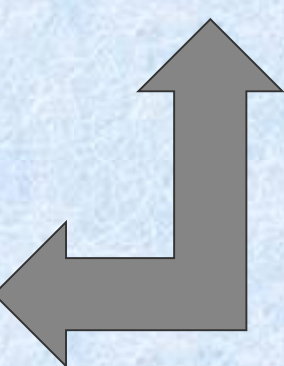
- Direct Copper Metalization skematic
- Reasons for Interest
- Direct Copper Metallization: claims and considerations
- Existing Process (POR) versus Alternate Process
- Electrolyte Process Sequence and Characteristics
- Deposit Layer Characteristics
    - Adhesion under stress
    - Silicon Content
- Obstacles to overcome
- Expanded Applications
- Summary and Conclusions
- Next Step / Way Forward

Direct Copper Metallization of Aluminum

Aluminum

Copper plated Aluminum





Heat stressed copper plated Aluminum 260 C for 60 mins

SAC 305 Solder Test Temp 255 C Time 10 secs

Direct Copper Metallization of Aluminum - high value ?

- There are **numerous potential applications** for lightweight Aluminum to be used as a replacement for **heavier and more costly metal structures.**
- **Applications** for expanded use of Aluminum in electronics include **bus bars, switch gears and terminal boards**. In these applications Aluminum would **replace copper**.
- Additionally, in the **Automotive industry**, although Aluminum is commonly used, its **use has been somewhat restricted** due to the **costly and complicated soldering techniques** required to attach Aluminum to other metal surfaces.
- If **Aluminum** could be provided with **a thin layer of well adhered copper**, the utility of Aluminum's inherent light weight and strong properties could be dramatically expanded.
- The **current Process of Record (POR)** to achieve adhesion utilizes a **zincate conversion layer** that is costly, unreliable and wears-away at the Aluminum surface - **causing undesirable dimensional variation**.

Direct Copper Metallization of Aluminum: **Major Claims**

- **Simplify and reduce the number of steps** required to plate copper on Aluminum substrates by eliminating the required Zincate conversion steps

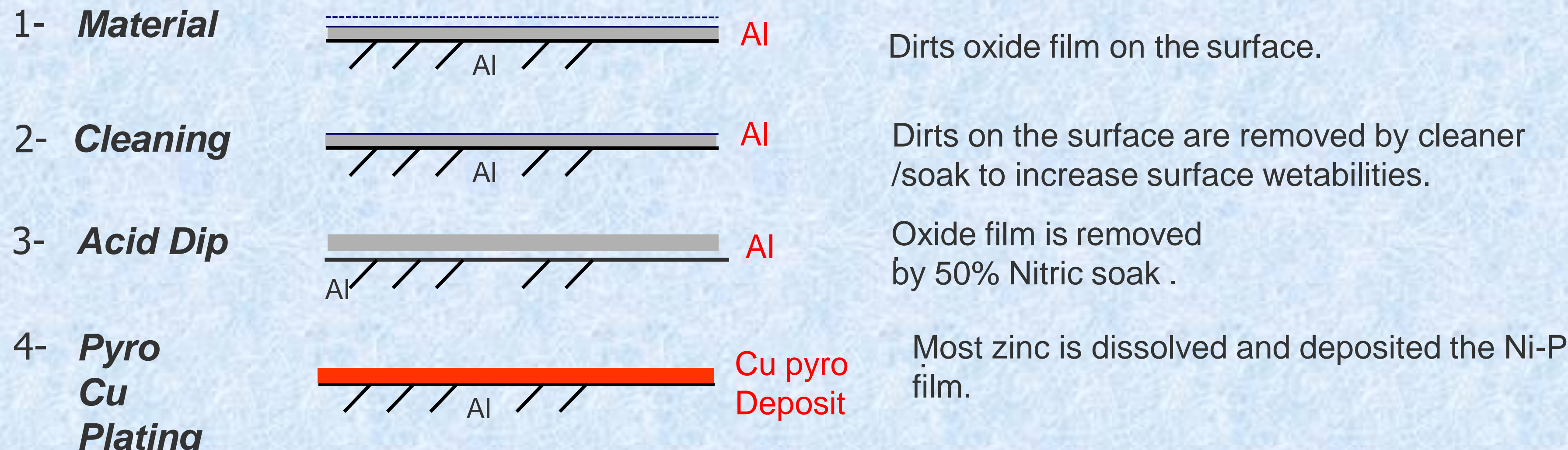
- **Address the adhesion of the copper to low potential** substrates such as Aluminum, Steel and Stainess steel
  - Demonstrate that the copper adhesion to the aluminum substrate can be **successfully soldered with lead free solder without peeling or blistering.**
  - Demonstrate that an Alkaline CN Free copper can provide adhesion performance to **pass ASTM-B-571 spec for thermal baking 240 C for 60 minutes**

- The Improved process should **result is minimal or no removal Aluminum metal** in the pretreatment steps

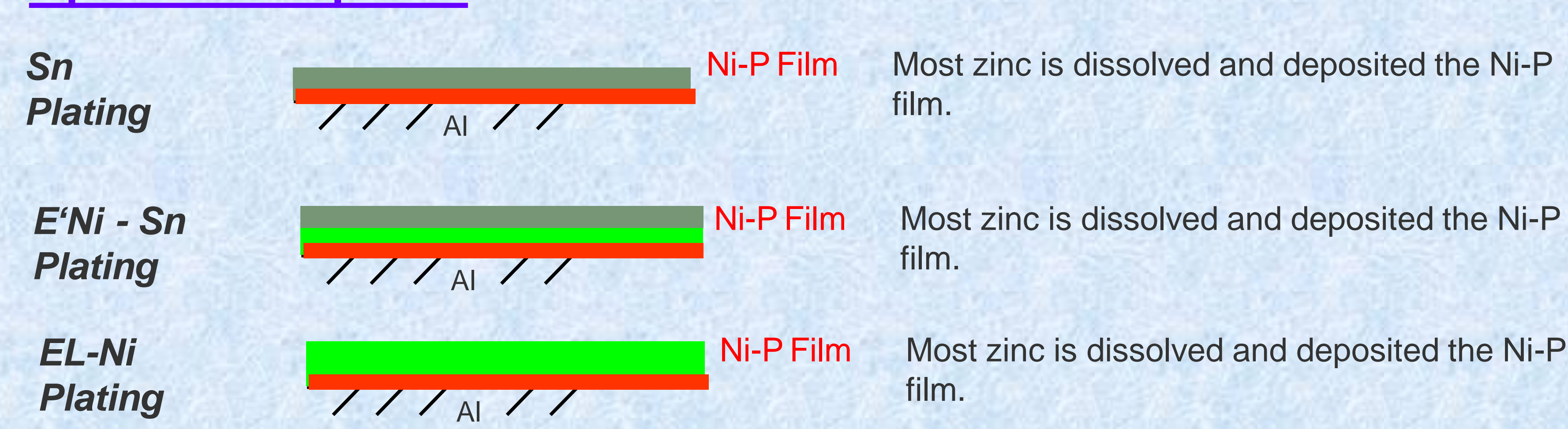
Typical Electroless Zincate process Sequence

Step	Layer	Description
1- ***Material***	Al	Dirts oxide film on the surface.
2- ***Cleaning***	Al	Dirts on the surface are removed and increase surface wetabilities.
3- ***Etching***	Al	Oxide film is removed.
4- ***Acid Dip***	Al	A thin oxide film is formed by acid dipping.
5- ***1st Zincate***	Zincate Film	Aluminum is dissolved and zinc ions are deposited. A rough zinc film is formed.
6- ***Zinc strip***	Al	Zinc films are dissolved and a thin oxide film is re-formed.
7- ***2nd Zincate***	Zincate Film	A uniform zinc film with enhanced adhesion is formed.
8- ***EL-Ni Plating***	Ni-P Film	Most zinc is dissolved and the Ni-P film is deposited.

Alkaline Copper Direct Metallization process Sequence



Optional overplates



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Alkaline Cyanide Free Copper Plating Process

NC Copper Plating Bath Make up Components

Operating Parameters	Optimum	Range
1- Metal Salt	80 g/l	40 - 100 g/l
Copper as metal	28/g/l	20 - 34 g/l
2- Conductivity Salt	270 g/l	240- 300 g/l
3- Complexing Agent	50 ml/l	40 - 60 ml/l
4- Brightener	10 ml/l	8 – 15 ml/l
Temperature	149°F	140-158 °F
pH	7.5	7.0 – 8.5

- Simple 4 component system
- Complexor allows near “Neutral pH operating range
- “EDTA Free” Biodegradable Complexor System
- Additives replenishement by Amp hours

Alkaline Cyanide Free Copper Plating

NC Electrolytic CN Copper Deposition Reaction

$$Cu^{2+}\ {}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O^{-}}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O^{-}}{|}}{P}}-O^{-}\quad Cu^{2+}$$

Copper pyrophosphate is the main raw material for the preparation of this copper plating bath. It reacts in the bath with potassium pyrophosphate, the complexing agent, to form pyrophosphate copper ligand ion:

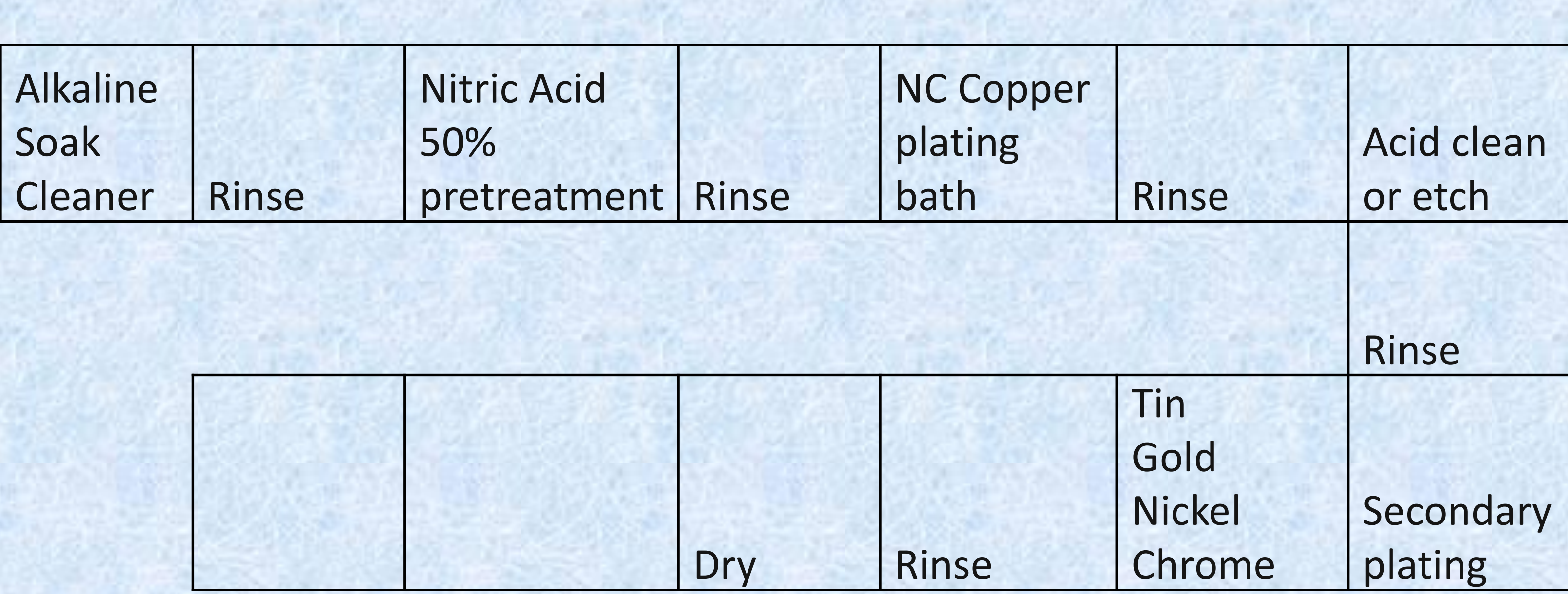
Cu2P2O7+3K4P2O7 = 2K6[Cu (P2O7) 2]

converts→6K++[Cu (P2O7) 2]6 ⟶ Cu ++

Cu++ (+) 2e- ⟶ Cu

Alkaline Cyanide Free Copper Plating

NC Copper Plating Bath Process Flow



NC Alkaline Cyanide Free Copper Plating

Alkaline Soak Cleaner - Asahi C-4000

Operating Parameters:	Optimum	Range
Temperature:	50°C	38 - 60°C
	122°F	110 - 140°F
Concentration:	10% b.v.	8 -12% b.v.
Immersion Time:	5 min.	3-8 mins.
Typical Bath life:	125 -300 sq.ft./gal.	

Generic Alkaline Aluminum micro-etchant

NC Alkaline Cyanide Free Copper Plating

Nitric Acid oxide removal step

Operating Parameters:	Optimum	Range
Temperature:	27 ^{o}C	24 - 35°C
	80°F	75 - 95°F
Concentration:	50% b.v.	40-60 b.v.
Immersion Time:	5 min.	4 - 6 mins.
Typical Bath life:	2 weeks	or when Al @ 500ppm

Technical grade Nitric 50% oxide removal

Alkaline Cyanide Free Copper Plating

NC Copper Plating Bath

Operating Parameters	Optimum	Range
➢ Copper as metal	**28/g/l**	**20 - 34 g/l**
Temperature:	65 °C	60 -70 °C
	149°F	140-158 °F
➢ pH	**7.5**	**7.0 – 8.5**
Current Density Rack Plating	20 ASF	10-40 ASF
Current Density Barrel Plating	5 ASF	10 ASF
Anode to Cathode ratio Rack	2:1	2:1
Anode to Cathode ratio Barrel	1:1	1:1
Filtration continuous	4.0 STO	~ 4.0 STO
➢ Electrolyte movement	**air or eductor**	**air or eductor**
Heater	STD SS	STD SS

Note: Current must be on before entering the plating bath

Alkaline Copper Pyrophosphate Copper Plating

Electrolyte Operating Considerations

- **Copper content** in plating bath has a significant effect on the **cathodic polarization** and the current density operating range. The result will be low brightness and smoothness
- The **copper content** in plating bath must be **controlled at 20~34 g/L**
- **High copper content** will decrease the cathode polarization and result in a **rough plating coat.**
- **High copper and high build up of orthophosphate** reduces the conductive ability, **increases the competing immersion copper reaction and of the plating bath and** a potential for adhesion loss will increase.
- **Bath agitation** is very important for **ion replenishment** we have worked on specialty eductor design for this bath but air agitation has been successfully used

Requires tighter bath control than acid or cyanide copper electrolytes

NC Alkaline Cyanide Free Copper Plating

NC Plating rate versus Copper Concentration

Plating Rate mil/ min

0.01
0.008
0.006
0.004
0.002
0

Working range

High copper content
-Brighter deposit,
-Rough plating
-Decreased Cathodic polarization
-Higher Specific G
-Less efficiency
-Possible Loss of adhesion

Low copper content
-Slower plating rate
-Increased Cathodic polarization
-Narrow current density range
-Less bright, less smooth

8 12 16 20 24 28 32 36 40 44 48

plating rate

Cu Concentration mg/L

NC Alkaline Cyanide Free Copper Plating

Current Density versus Deposit Quality Index

Operating current density as has a wide range, but Thickness control and uniformity is important

Alkaline Cyanide Free Copper Plating

NC Working Range Plating rate versus pH

Low pH precipitates the Complexor
High pH precipitates CuOH

Alkaline Copper Pyrophosphate Copper Plating

Properties compared to Cyanide and Acid copper

- Copper pyrophosphate baths are characterized by **high stability**
- **Meticulous crystalline coating**, and a **better coverage-ability** than that of acidic copper plating
- **Higher cathodic current efficiency** than cyanide copper plating. Excellent bath for plating thick copper.
- A thick coating can be obtained with **low embrittlement** due to no gas generated from the electroplating process.
- **Electrolyte is neutral pH,** non-toxic and not corrosive to equipment, making it especially suitable for circuit printing and zinc alloy die castings

NC Alkaline Cyanide Free Copper Plating

Electrolyte Tolerance to Impurities

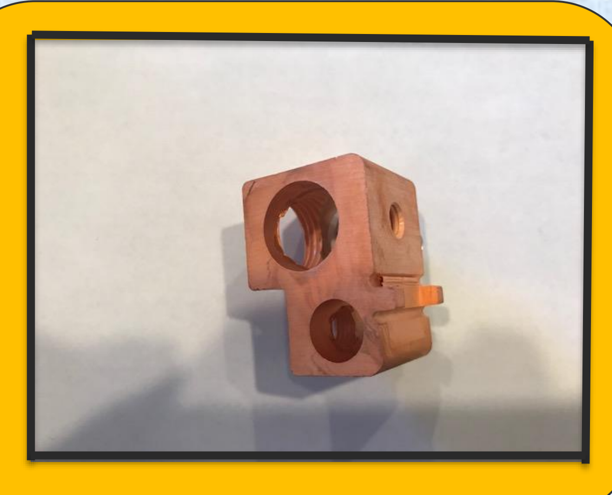
2X - 4X Improvement

Electrolyte Type	Tolerance to Impurities
NC Cyanide Free Copper	Zn, Al, Fe to 500 mg/l
Bright Nickel	Zn und Cu up to 50 -100 mg/l
Electroless Nickel	Zn und Cu up to 25 - 50 mg/l

Direct Copper Metallization of Aluminum

Aluminum

Copper plated Aluminum



STRESS TEST Conditions #1

SAC 305 Solder Test
Temp 255 C Time 10 secs

Alkaline Cyanide Free Copper Plating

Stress Testing :

SAC 305 Solder Shock @ 255 C, 10 sec immersion

Sample #	Copper Plating Thickness	Result **SAC 305 Solder Shock @ 255 C, 10 sec immersion**
1	0.5 mils	No delamination
2	0.75 mils	No delamination
3	1.0 mils	No delamination
4	1.5 mils	No delamination
5	2.0 mils	No delamination
6	2.5 mils	~ 20 % Failure (AlCu interface separation)
7	3.0 mils	> 25 % Failure (AlCu interface separation)

NC Alkaline Cyanide Free Copper Plating

NC Plating Thickness versus Adhesion Pass Rate

Adhesion Pass percentage

120
100
80
60
40
20
0
-20

Working range

SAC 305 Solder Test Temp 255 C Time 10 secs

Sample: Al 3003 – Cu plate

0 0.25 0.5 0.75 1 1.25 1.5 1.75 2 2.25 2.5 2.75 3

Plated Copper thickness (mils)

Adhesion Pass Rate

NC Alkaline Cyanide Free Copper Plating

Stress Testing :

SAC 305 Solder Shock @ 255 C, 10 sec immersion

1- 0.5 mils Cu, No separation

2- 0.5 mils Cu, No separation

3- 1.0 mils Cu, No separation

4- 1.0 mils Cu +Ni, No separation

NC Alkaline Cyanide Free Copper Plating

Stress Testing :

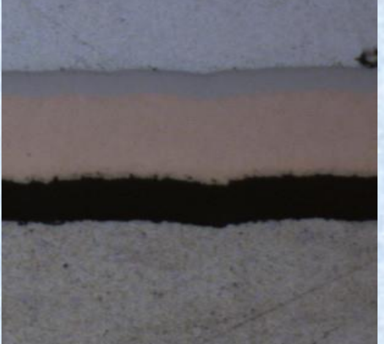
SAC 305 Solder Shock @ 255 C, 10 sec immersion

1-2.5 mils Cu, No separation

2- 2.5 mils Cu No, separation

3- 2.5 mils Cu +Ni, No separation

4- 2.5 mils Cu+ Ni delamination

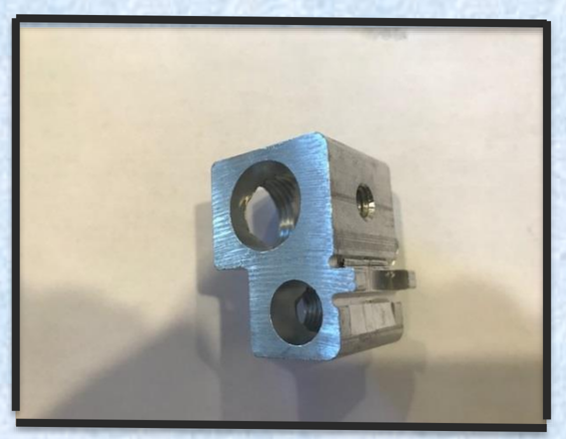


5- 2.5 mils Cu+Ni, Failure, separation

Conclusion: Solder Shock puts stress in the AlCu interface and higher Cu plating thicknesses increases failure rate

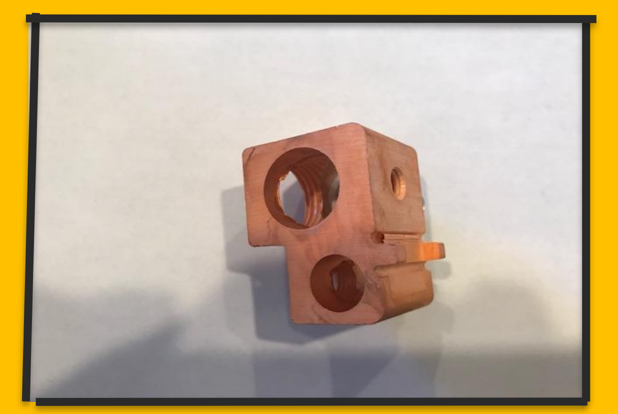
Direct Copper Metallization of Aluminum

Aluminum



Heat stressed copper plated Aluminum 260 C for 60 mins ASTM-B-571

Baked Copper plated Aluminum



Copper plated Aluminum

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NC Alkaline Cyanide Free Copper Plating

Stress Testing :

Thermal Bake 240C for 60 minutes + immediate water quench as per ASTM-B-571

Sample #	Copper Plating Thickness	Result **Thermal Bake 240C for 60 minutes + immediate water quench as per ASTM-B-571**
1	0.5 mils	No delamination
2	0.75 mils	No delamination
3	1.0 mils	No delamination
4	1.5 mils	No delamination
5	1.75 mils	~ 5 % Failure (AlCu interface separation)
6	2.0 mils	~ 10 % Failure (AlCu interface separation)
7	2.5 mils	~ 20 % Failure (AlCu interface separation)
8	3.0 mils	~ 25 % Failure (AlCu interface separation)

NC Alkaline Cyanide Free Copper Plating

NC Plating Thickness versus Adhesion Pass Rate

Adhesion Pass percentage

120
100
80
60
40
20
0
-20

Working range

Sample: Al 3003 – Cu plate

Test Conditions:
Thermal bake 240 C 60 min
+ water quench ASTM-B-571

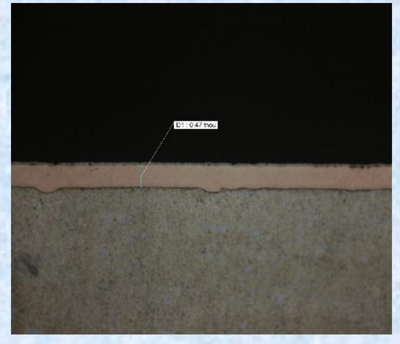
0 0.25 0.5 0.75 1 1.25 1.5 1.75 2 2.25 2.5 2.75 3

Adhesion Pass Rate

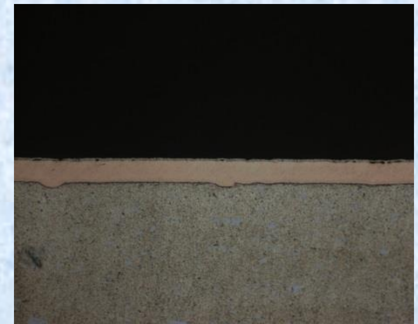
NC Alkaline Cyanide Free Copper Plating

Stress Testing :

Thermal Bake and Quench 240C for 60 min ASTM

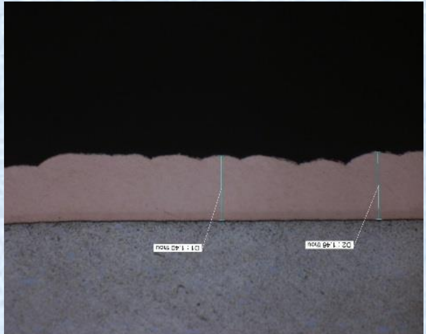


1- 0.5 mils Cu, No separation

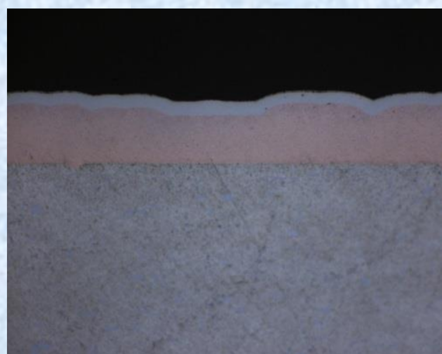


2- 0.5 mils Cu, No separation

3- 0.5 mils Cu +Ni, No separation



4- 1.0.5 mils Cu, Pass no delamination

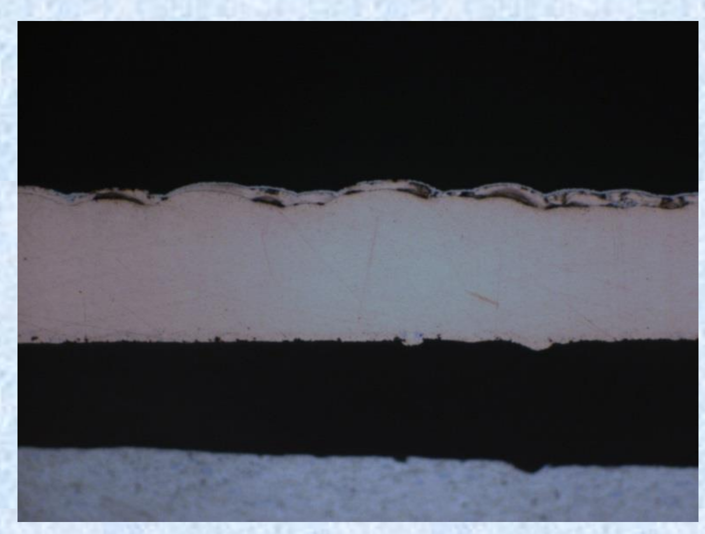


5- 1.3 mils Cu+Ni, Pass, no delamination

NC Alkaline Cyanide Free Copper Plating

Stress Testing :

Thermal Bake and Quench 240C for 60 min ASTM



4- 2.0 mils Cu, Failure, interface delamination

5- 2.0 mils Cu, Failure, no delamination

Conclusion: Thermal bake and quench stress is more severe than Solder shock and higher Cu plating thicknesses show increased failure rate

NC Alkaline Cyanide Free Copper Plating

NC Plating Thickness versus Adhesion Pass Rate

Adhesion Pass percentage

120
100
80
60
40
20
0
-20

Working range

Sample: Al 3003 – Cu plate

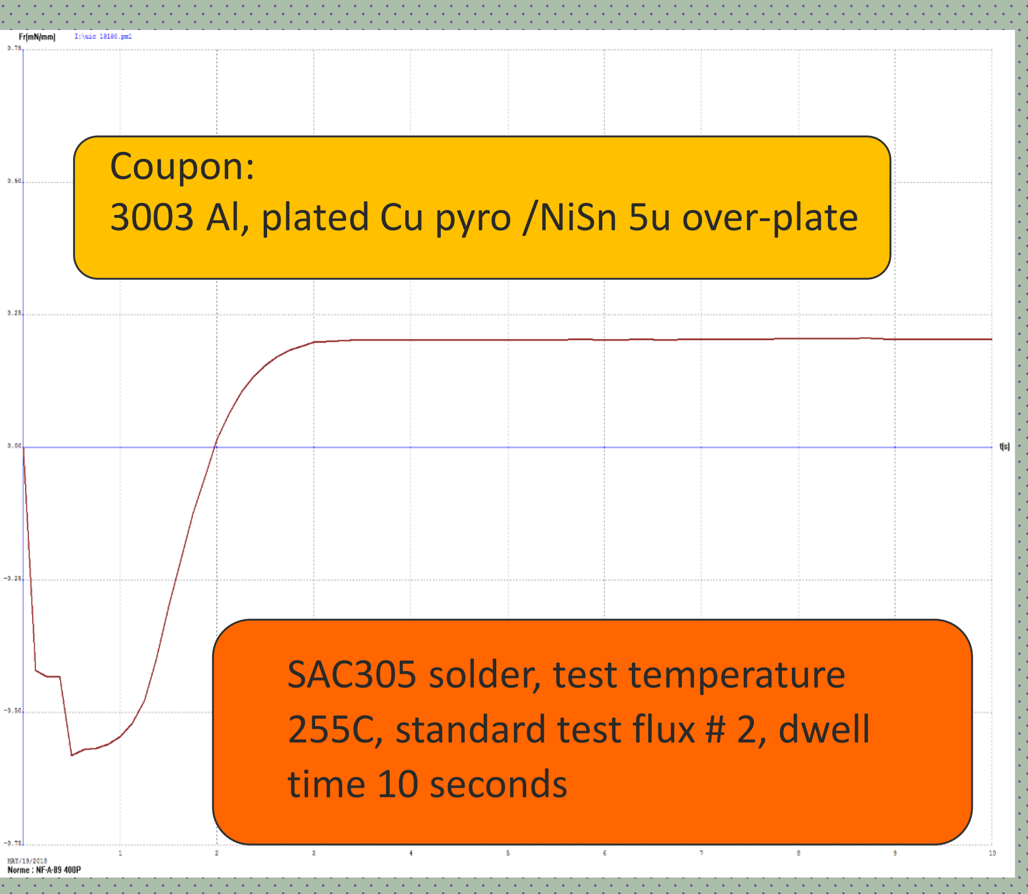
0 0.25 0.5 0.75 1 1.25 1.5 1.75 2 2.25 2.5 2.75 3

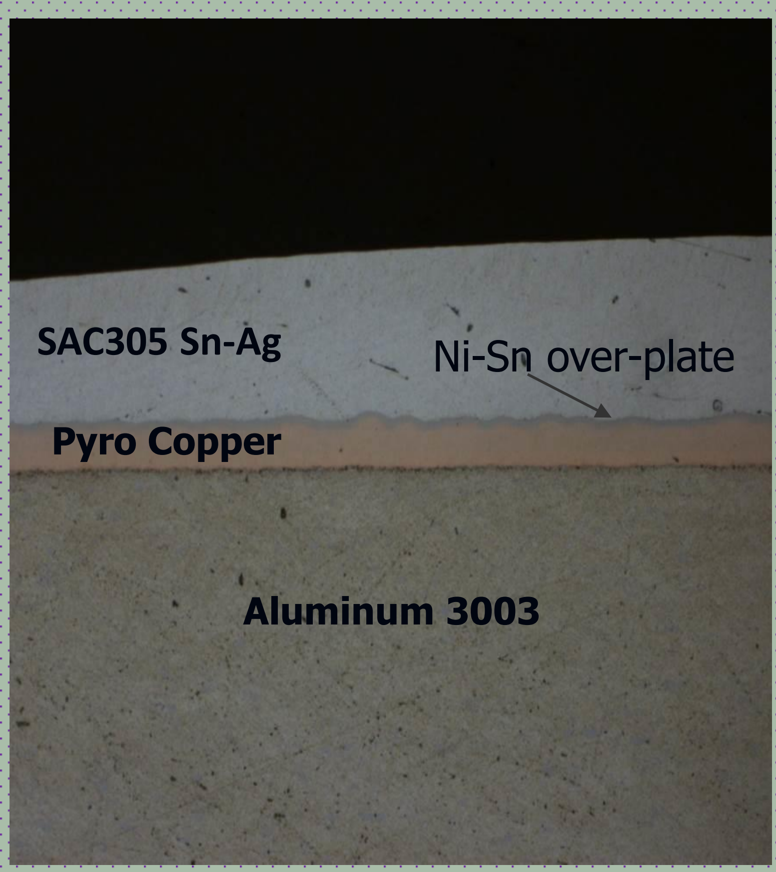
SAC 305 Immersion 10 secs

Thermal bake 240 C, 60 min

NC Alkaline Cyanide Free Copper Plating

Wetting balance Testing - Solderability





NC Alkaline Cyanide Free Copper Plating

Compatible Alloys tested passed with less than 1% silicon content

Aluminum Alloy	Silicon content	Results after plating test	Results after bake 240C 60 minutes
1008	0.40 %	Pass	Pass
2024	0.25 %	Pass	Pass
3003	0.6 %	Pass	Pass
4130	0.25 %	Pass	Pass
5052	0.25 %	Pass	Pass
6061	0.6 %	Pass	Pass
7050	0.12 %	Pass	Pass
4006	1.0 %	Pass	Fail 5 - 10% adhesion loss

NC Alkaline Cyanide Free Copper

Pretreatment Step for Aluminum Alloys

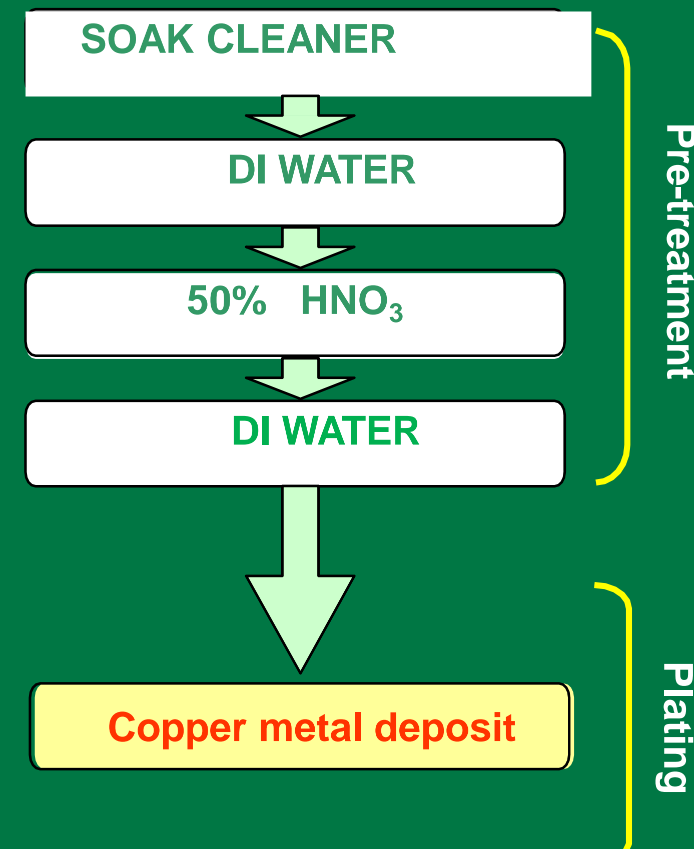
Cleaner

Rinse

Acid Soak Nitric

Rinse

Electrolytic Copper Pyro



NC Alkaline Cyanide Free Copper

Pretreatment Step for Zinc Die Casting

Step	Process	Stage
Electroclean	SOAK CLEANER	Pre-treatment
Rinse	DI WATER	Pre-treatment
Acid Soak Sulfuric Acid	1% Sulfuric Acid	Pre-treatment
Rinse	DI WATER	Pre-treatment
Electrolytic Copper Pyro	Copper metal deposit	Plating

NC Alkaline Cyanide Free Copper

Pretreatment Step for Stainless Steel

Step	Process
Cleaner 4000	SOAK CLEANER
Rinse	DI WATER
Electroclean 4000	Acid cleaner
Rinse	DI WATER
Electrolytic Copper Pyro	Copper metal deposit

Pre-treatment: SOAK CLEANER → DI WATER → Acid cleaner → DI WATER

Plating: Copper metal deposit

Alkaline Cyanide Free Copper Features / Conclusions

1- Successful Direct Metalization of Aluminum with a thin neutral cyanide free **copper overplate can be achieved**.

2- Zincate adhesion layers can be eliminated for a variety of common Aluminum Alloys

3- There is a **direct and causal relationship between plated copper thickness and resulting adhesion**. Copper deposits of 1.0 mils or less can be successfully soldered and survive thermal baking at 240 C for one hour without adhesion loss

4-Opportunities exist to expand the use of Aluminum to replace steel and copper in the **Aerospace and Automotive** Industry

5- The **use of Neutral pH Cyanide Free Copper as a "super strike bath" seem apparent** and should enhance common over-plates such as silver, palladium, bright Nickel.

Alkaline Cyanide Free Copper Way Forward

1- We plan to evaluate **combining a thin Copper-pyro strike deposit** with a **high elongation bright Acid copper** to enhance adhesion and manage expansion mismatch

2- We have begun to look at **specialty Aluminum micro-etches to increase mechanical anchor** and increase adhesion of Copper to Aluminum.

3- Continue work **with Copper pyro strike** on other **"low EMF potential"substrates** such as **stainless steel and titanium.**

4- Continue on-going work with **Ion Exchange manufacturers** to find the **most effective resin** options to remove weakly complexed copper from rinse water.

Thank You

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