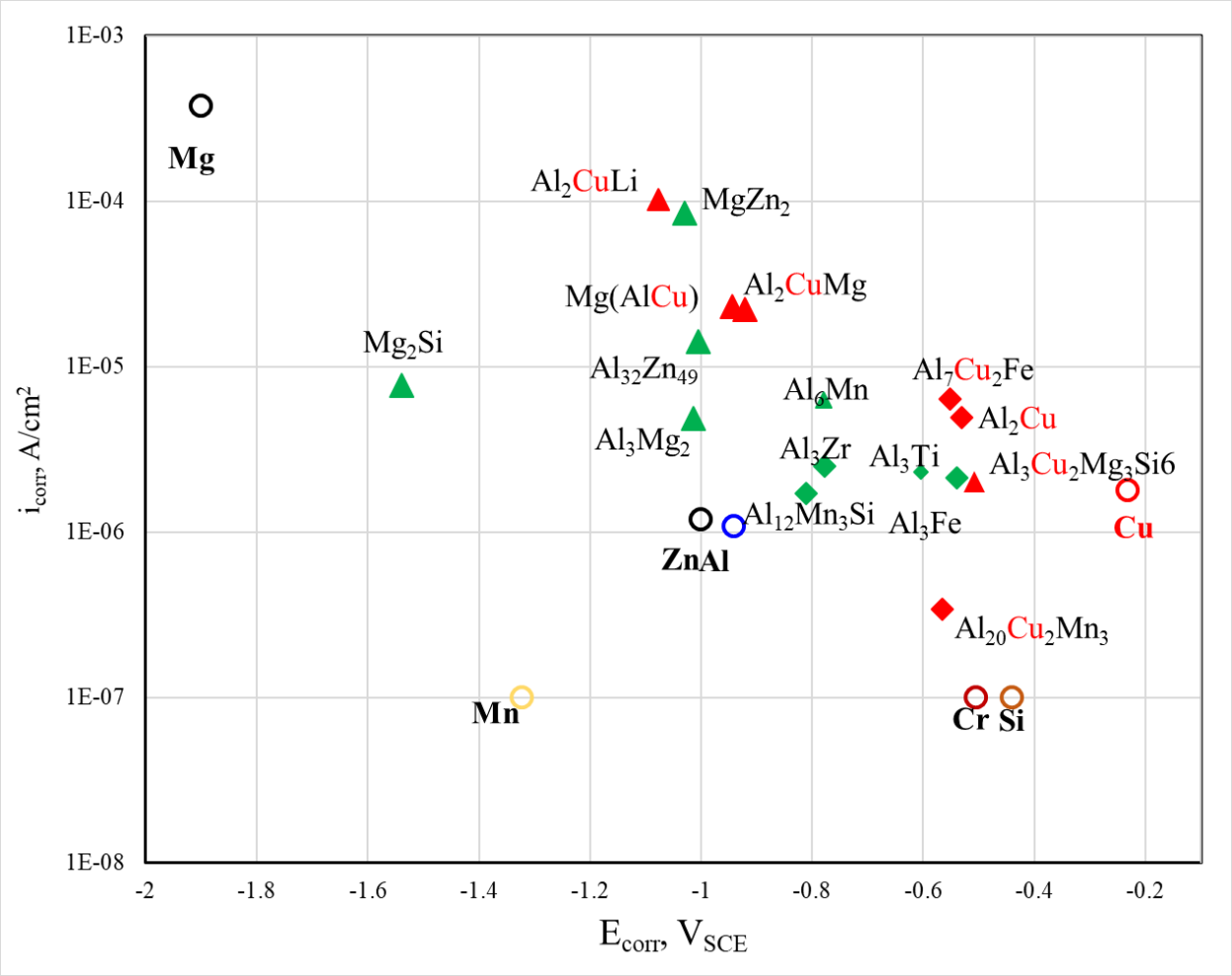
Cu behaviors in CALP process, heat treatment and pretreatment and its impact on the filiform corrosion of Al alloys

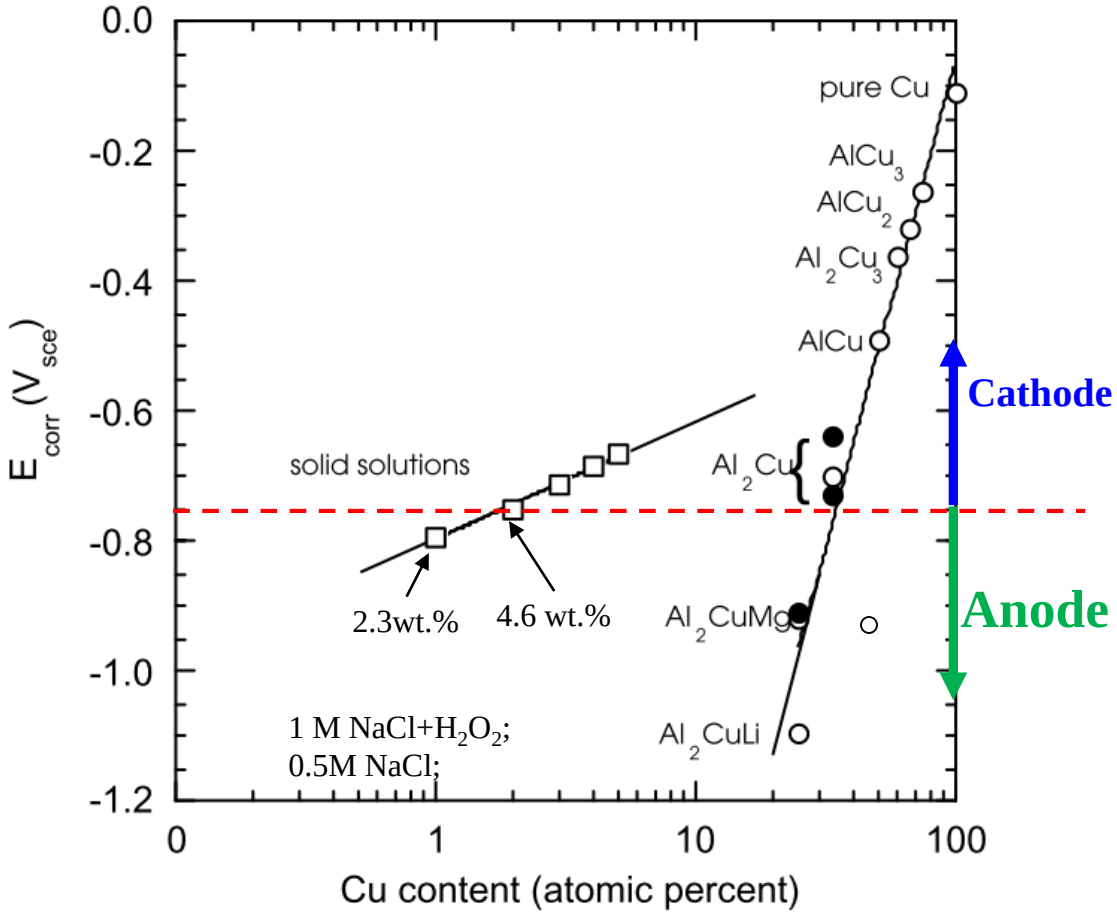
Jichao Li

Team
Constellium: Jichao Li; Phil Dodge
Ford: Niamh Hosking; Javier Esquivel Guerrero; Sabrina Peczonczyk; Daniel Freiberg
PPG: Mark McMillen; Mary Lyn Lim

3/31/2022
Automotive Corrosion Symposium in Detroit MI

Secondary phases in Al alloys show different electrochemical properties from the surrounding matrix

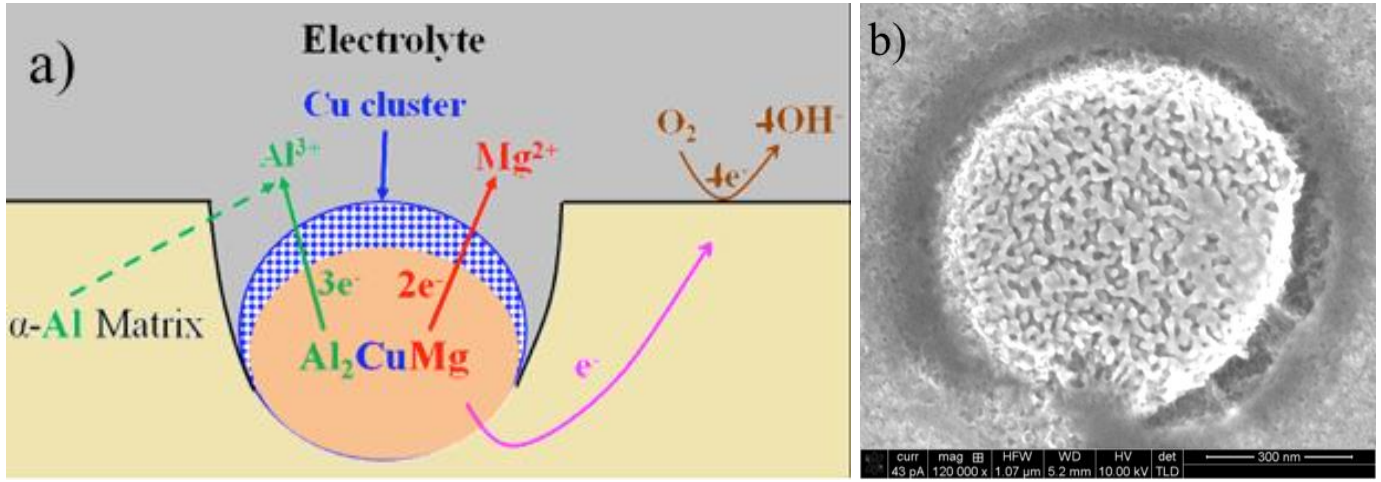




Cu-containing particles can be anode or cathode depending on the composition;
Cu variation in the solid solution can also lead to localized galvanic corrosion.

Localized corrosion is associated with IMCs/precipitates

- Dissolution/dealloying around strongly/weakly anodic phases

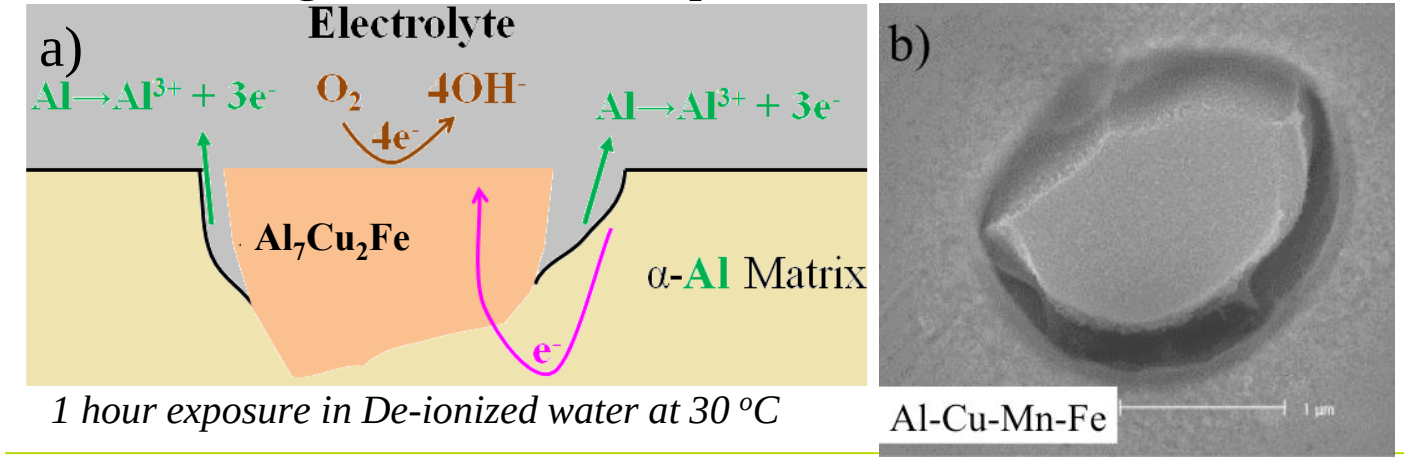


1 hour exposure in aerated De-ionized water at 30 °C

Anode:
Al_3Mg_2, Mg_2Si, $Al_{32}Zn_{49}$…

Dealloying
Al_2CuMg; Al_2CuLi; $AlCuMg$; $AlCuMgSi$…

- Trenching around cathodic phases



1 hour exposure in De-ionized water at 30 °C

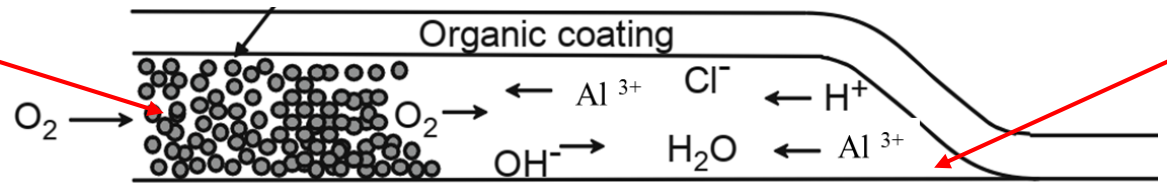
Cathode:
Al_7Cu_2Fe, Al_2Cu, Al_3Zr, Al_3Fe,…

Jichao Li, Jie Dang, Metals, 2017

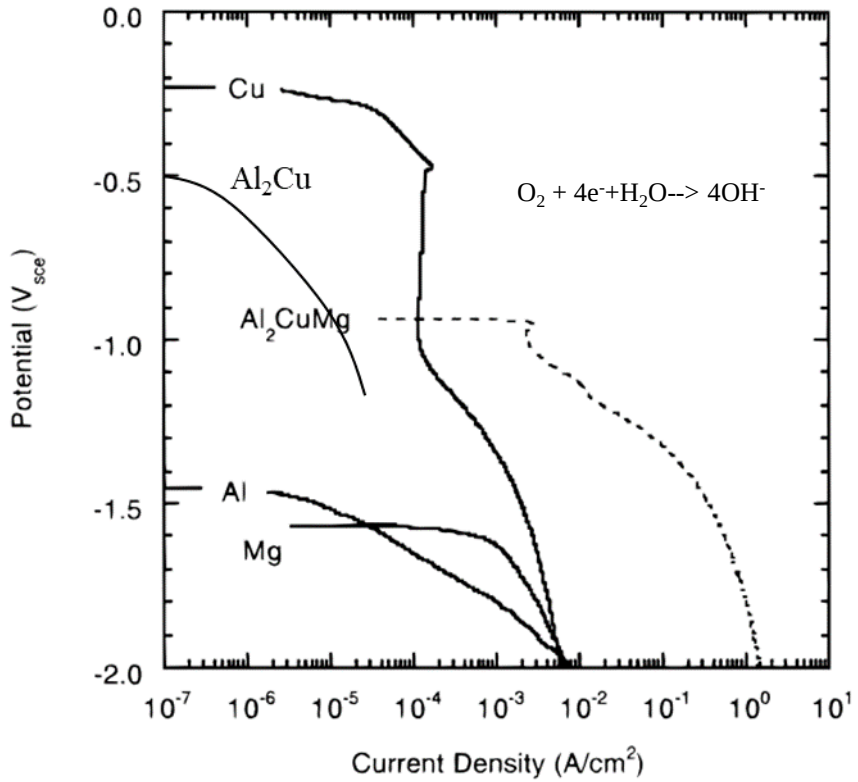
The strong cathodic ability of Cu can also increase filiform corrosion susceptibility

Cathode at the tail:
$O_2 + 4e^- + H_2O \rightarrow 4OH^-$

Filiform corrosion



Anode at the head:
$Al \rightarrow Al^{3+} + 3e^-$

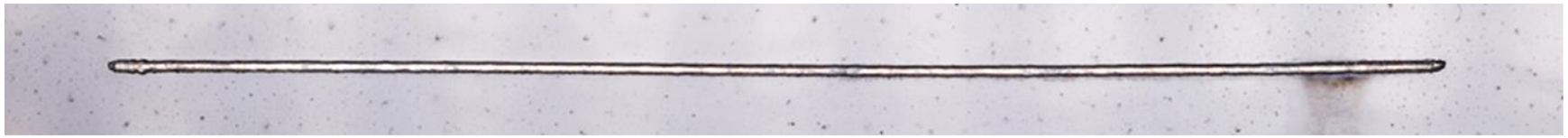


- The different oxygen concentration at the head and tail of filament leads to a potential difference;
- The cathodic reaction is oxygen reduction reaction;
- Cu is a strong cathodic catalyst for oxygen reduction reaction;

Introduction to Corrosion Science, 2010; JES, 162 (10) C563-C571 (2015); JES, 146 (12) 4424-4428 (1999)

Adding Cu to aluminum alloys strongly impacts filiform/blister corrosion

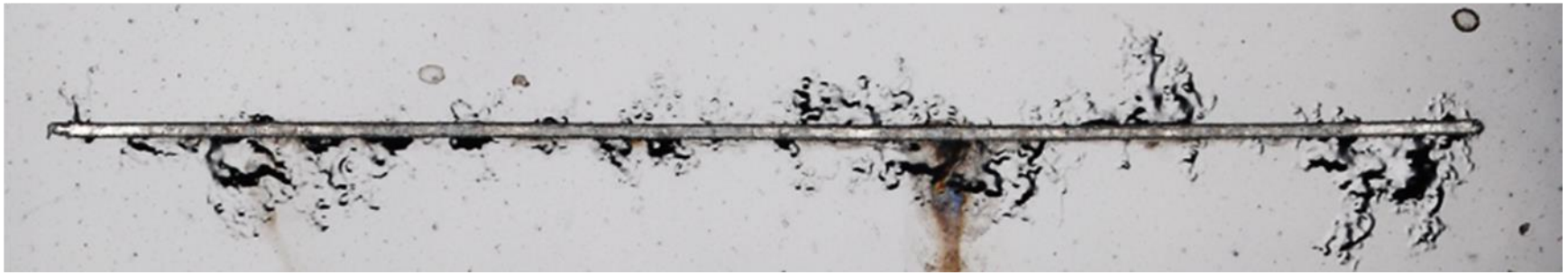
5xxx (<0.1 wt%)



Low-Cu 6xxx (<0.2wt%)

High-Cu 6xxx (>0.7wt%)

High-Cu 7xxx (>1.5wt%)



Thin film pretreatment, Painted panels, Ford L-3190

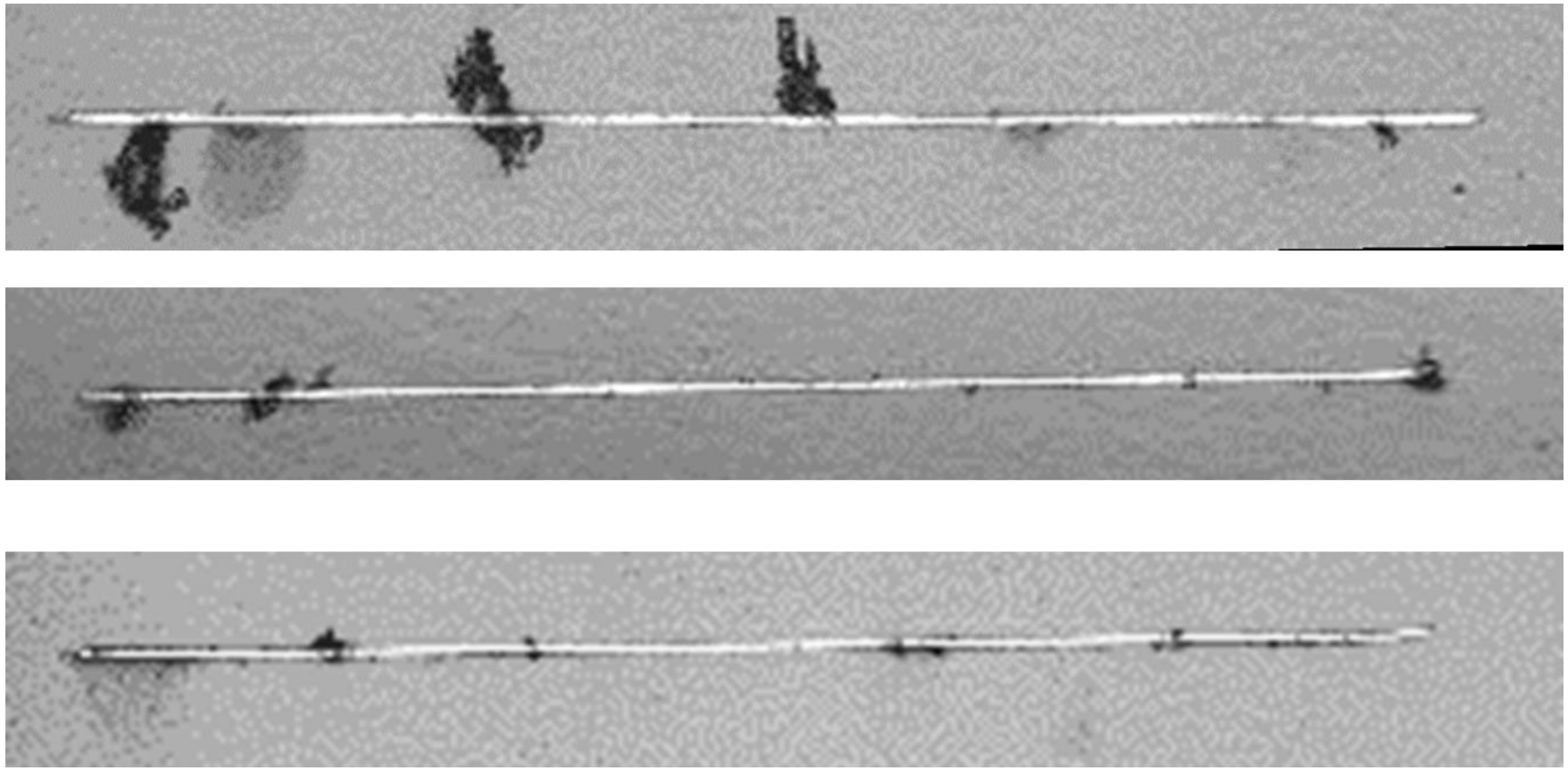
Substrate temper and pretreatment affect corrosion performance

AA6111, Fast quench, 25ppm Cu^{2+}

T4
0.5 min cleaning

Pretreatment
(5min cleaning)

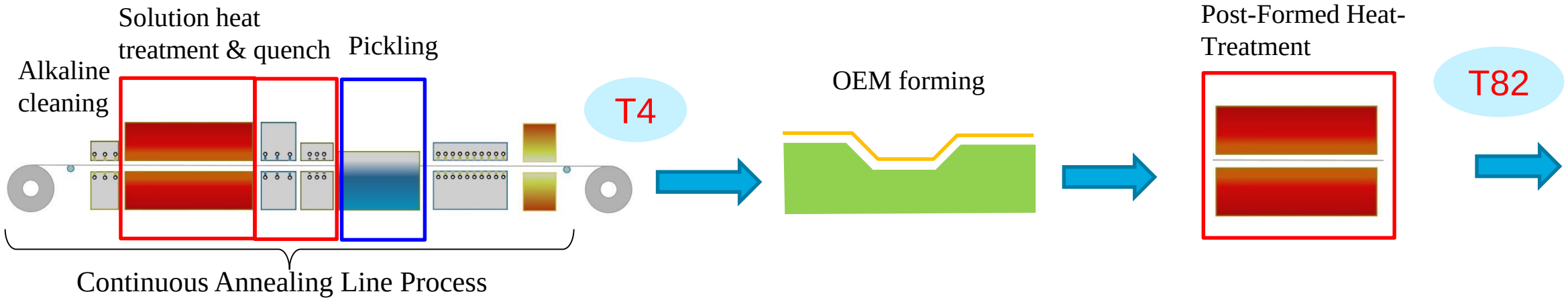
T82 Heat
Treatment
(225C 30min)

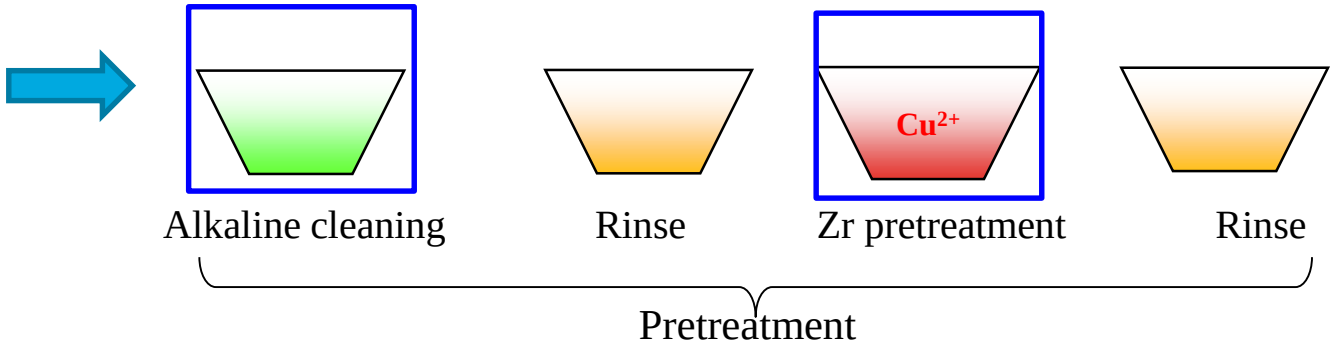


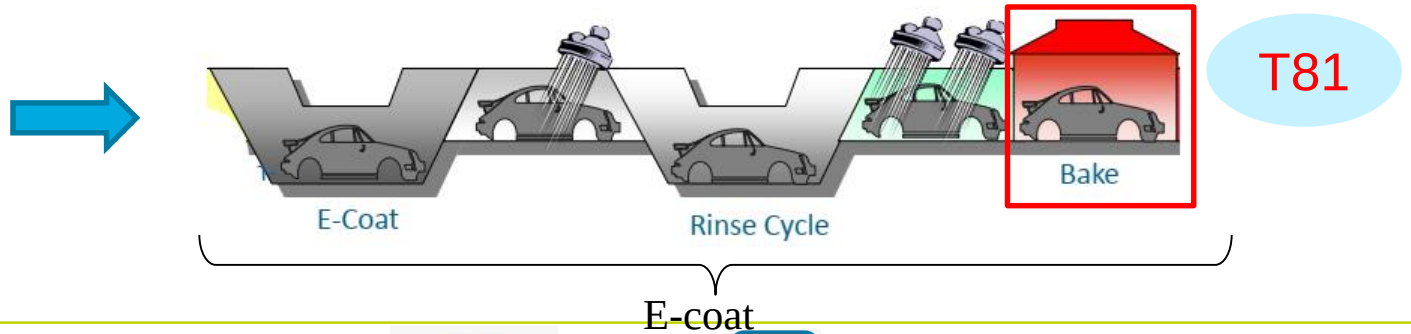
Both heat treatment and surface treatment should be considered to have a comprehensive understanding about the corrosion performance

T81: 175C 30min
T82: 225C 30min

A general flow chart of aluminum body sheet







Key process affecting Cu

in the substrate: Aluminum Alloy 6111

on the top surface:

Detailed work will be presented at
- FOCUS in May;
- EurrCorr in August;

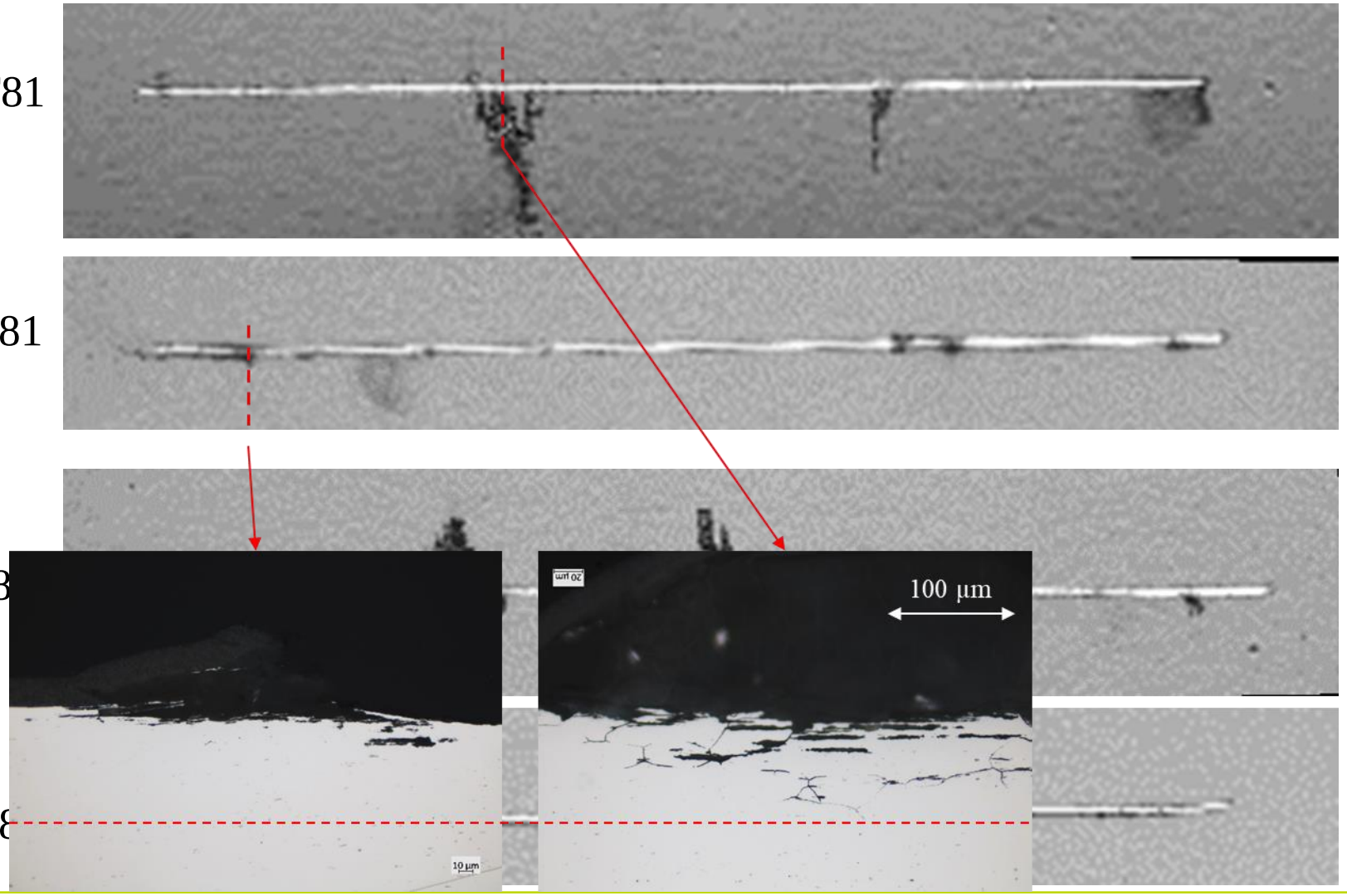
T82 post form heat treatment significantly improve the filiform corrosion performance

AA6111, 0.5min cleaning, 25ppm Cu^{2+}, e-coated panels, 12 weeks, Ford L-3190

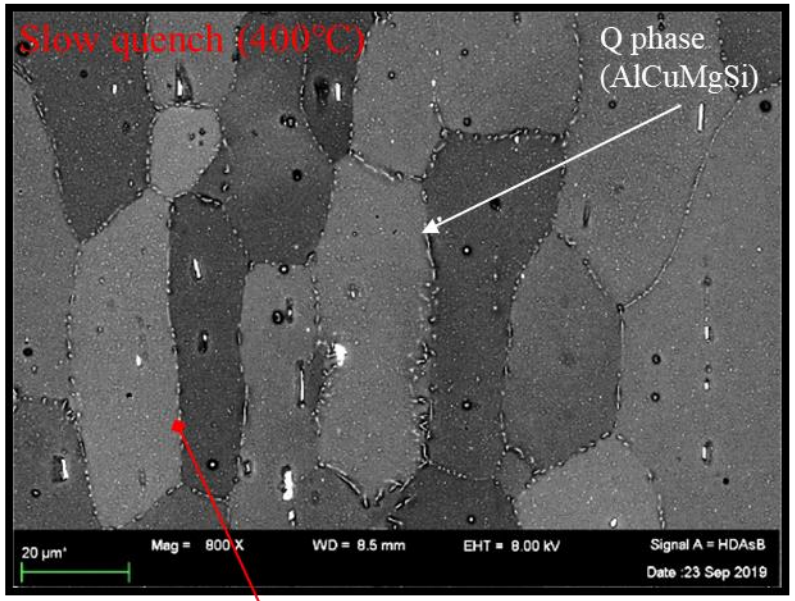
T81: 175C 30min
T82: 225C 30min

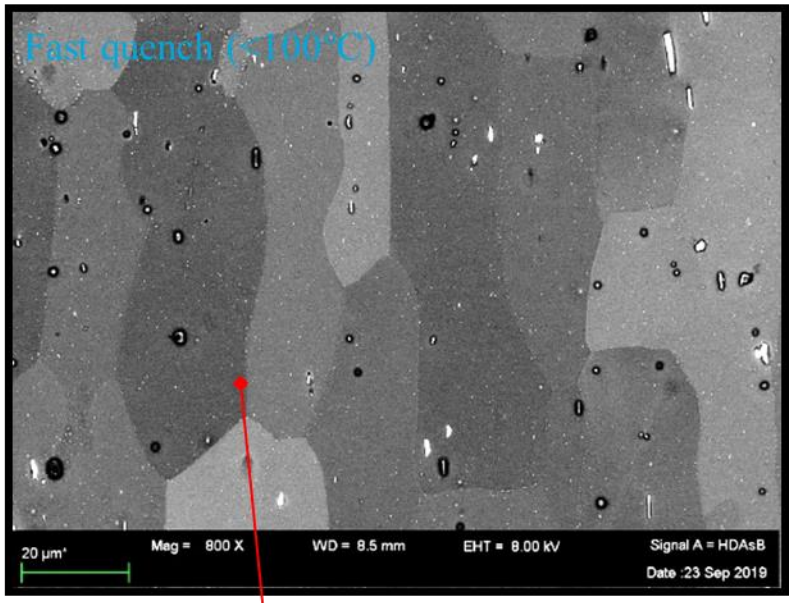
Slow quench (400C)
- T4 +T81
- T82
- T4+T82+T81

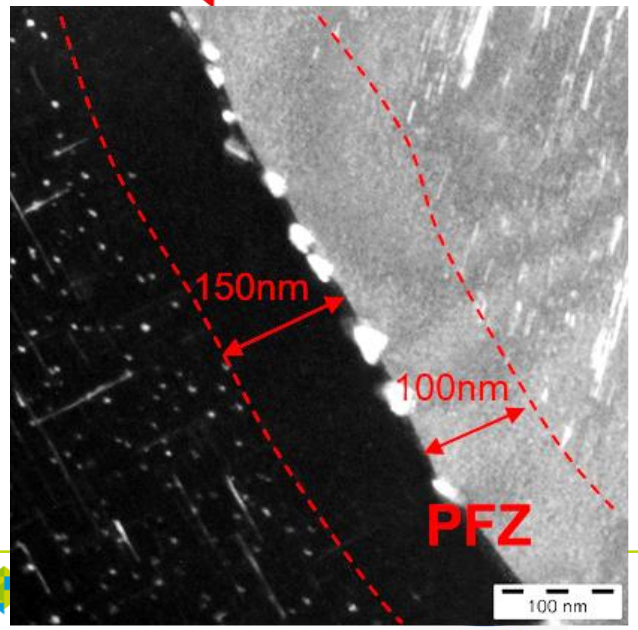
Fast quench (<100C)
- T4 +T8
- T82
- T4+T82+T8

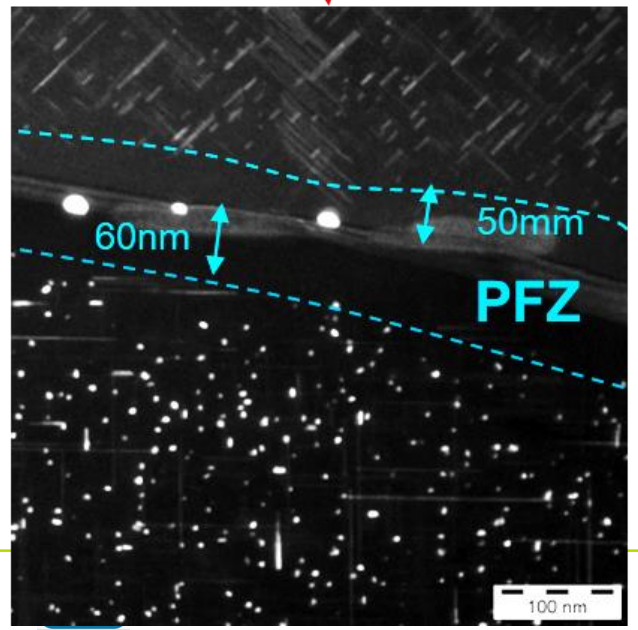


AlCuMgSi and precipitate free zone (PFZ) at the grain boundary









- Slow-quenched sample exhibits larger fraction and size of GB precipitates and wider precipitate free zone (PFZ);
- Coarse (Al,Mg,Si,Cu) precipitates (>85nm length) and smaller β''/β' and/or Q' precipitates at the grain boundary
- Localized galvanic corrosion:
  - AlMgSiCu precipitates/PFZ;
  - Surrounding matrix/PFZ;

Corrosion transforms from intergranular to pitting with paint bake/post-form heat treatment

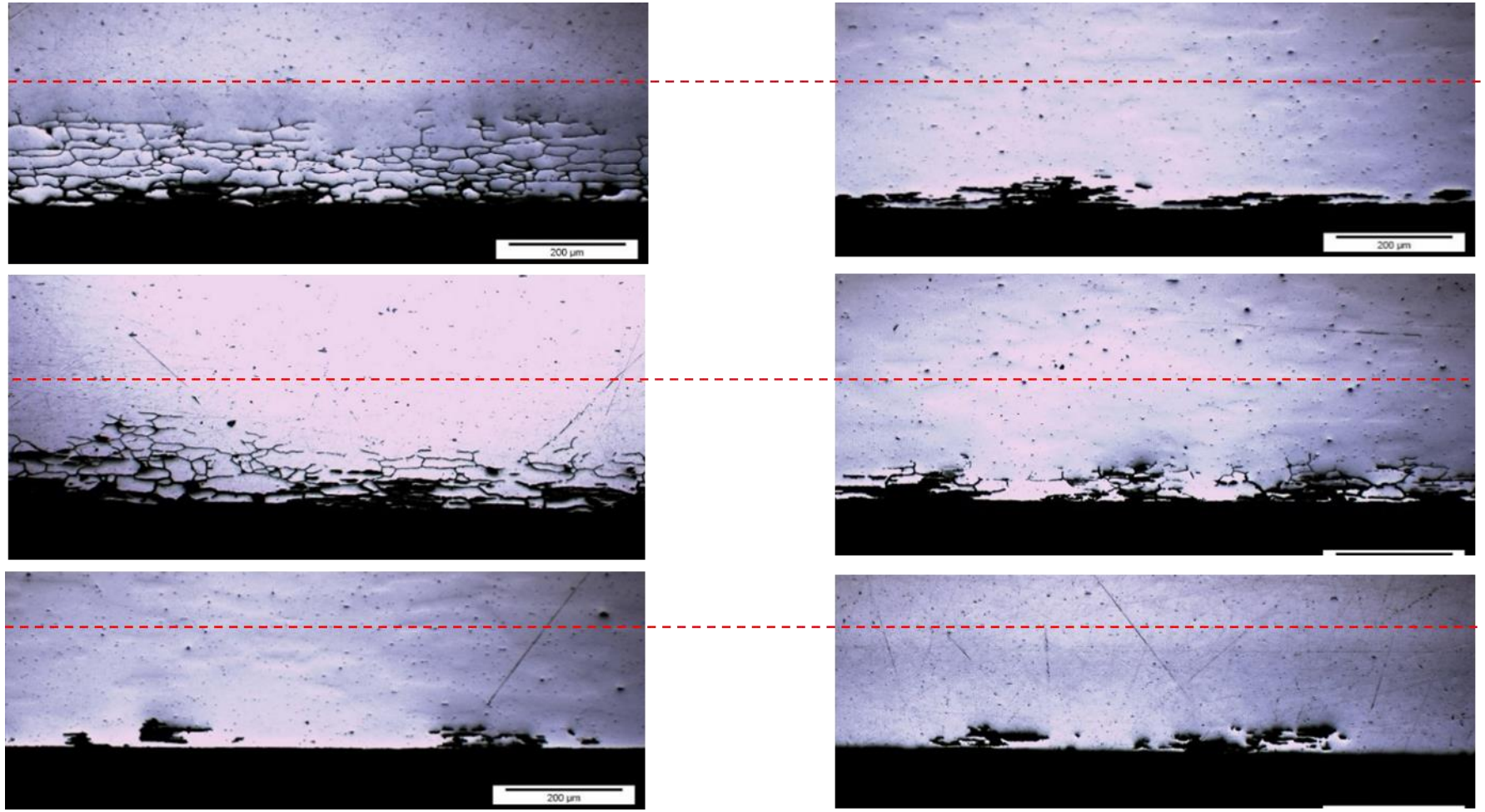
AA6111
T81: 175C 30min
T82: 225C 30min

Slow quench (400C) ← Fast quench (<100C)

T4

T4+
T81

T4+
T82+
T81



200 µm

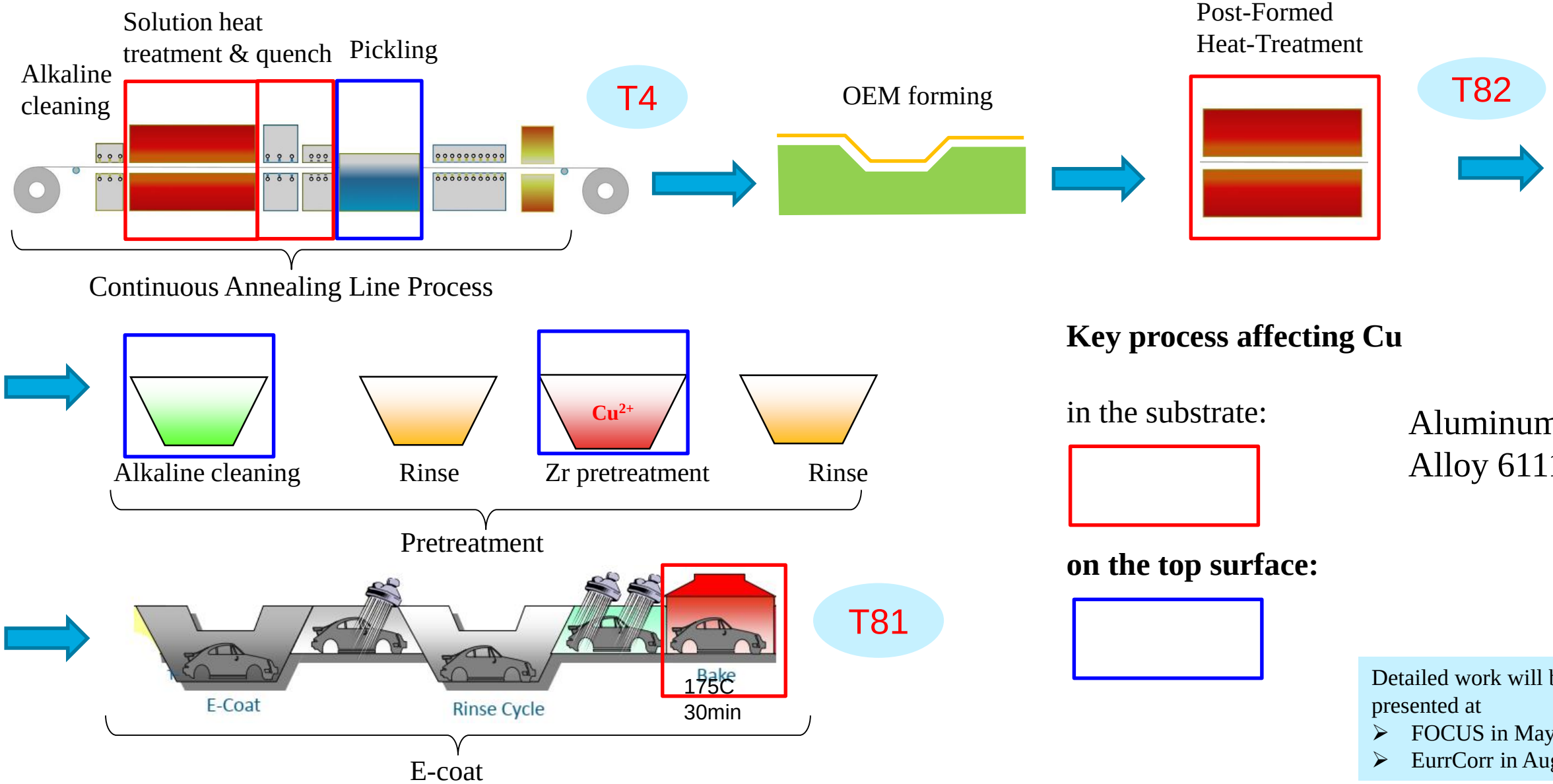
200 µm

200 µm

ISO 11846

T81: 175C 30min
T82: 225C 30min

A general flow chart of aluminum body sheet



Key process affecting Cu

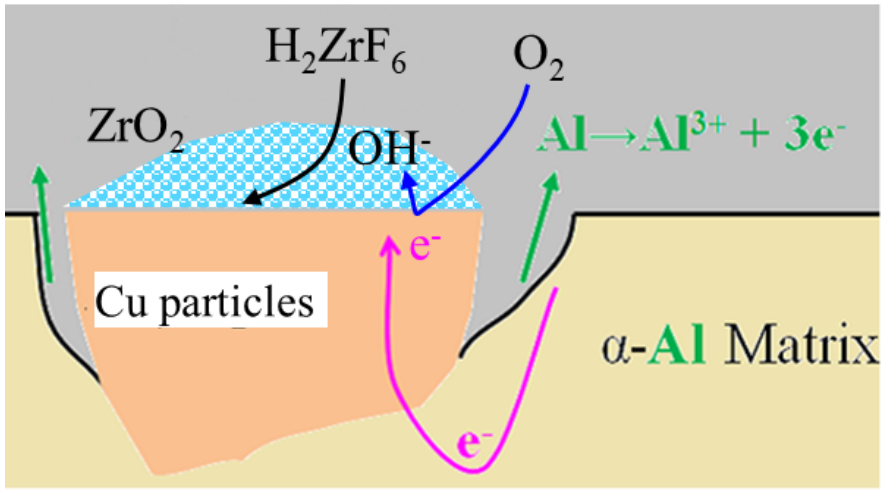
in the substrate:

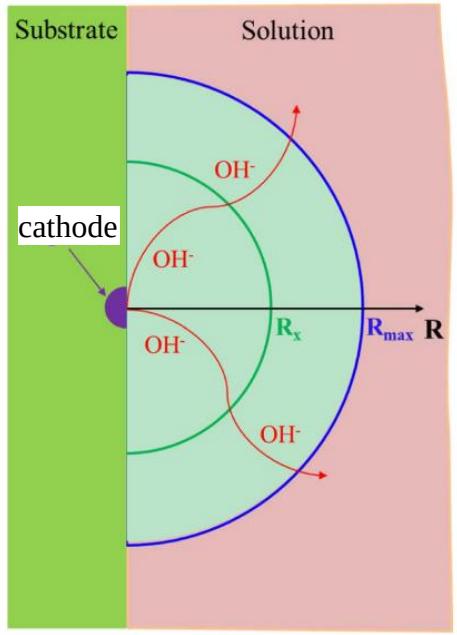
on the top surface:

Aluminum Alloy 6111

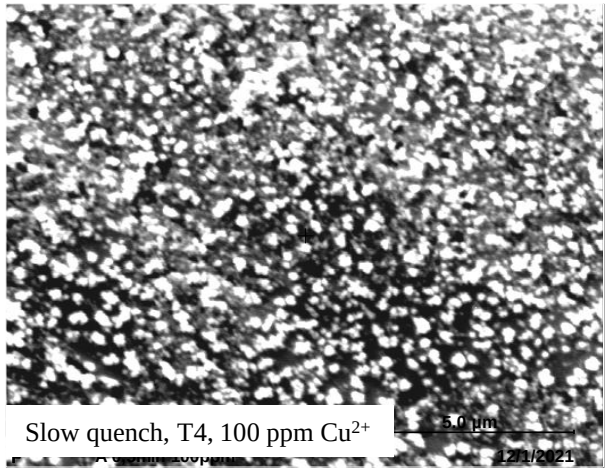
Detailed work will be presented at
- FOCUS in May;
- EurrCorr in August;

pH increase near the substrate surface cause Zr oxide precipitates.





Zr precipitates on 6111

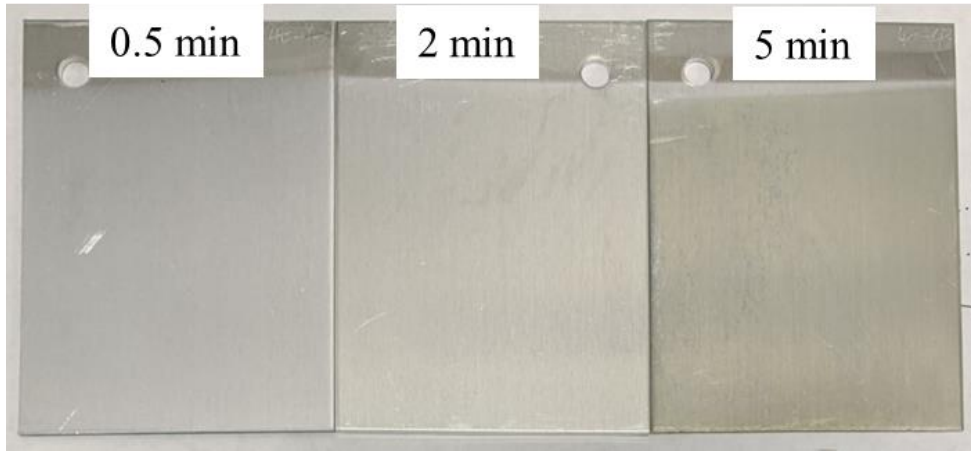


- Oxygen reduction on the surface increases the pH near the substrate surface; H_2ZrF_6 becomes unstable as pH increases and forms precipitates on the cathodic area;
- Cu-containing particles in the substrate or Cu deposition from the pretreatment solution are strong cathodic sites where Zr precipitates prefers to form;
- These precipitates have a round shape, and their distribution is affected by Cu enrichment/ deposition;

Alkaline cleaning may lead to enrichment of Cu on the surface, which has a strong cathodic ability

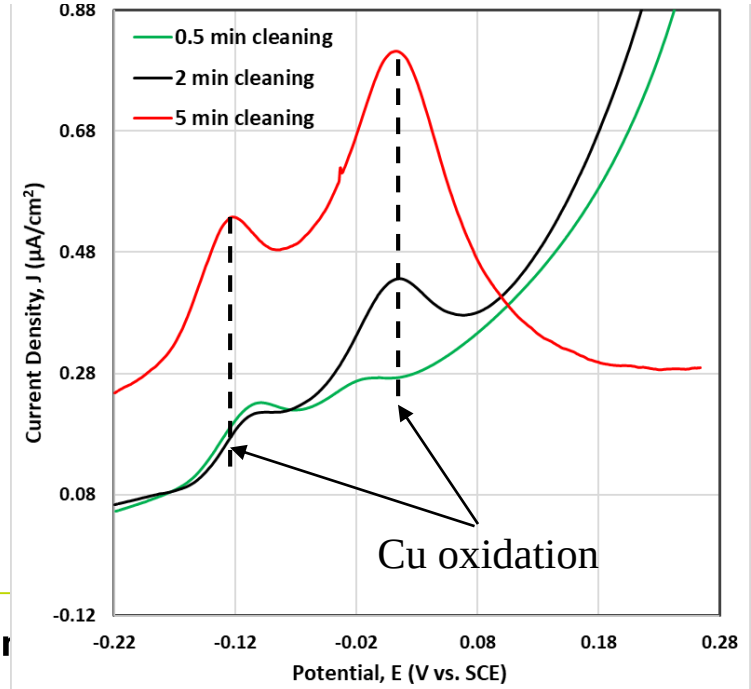
AA6111;slow quench;T4;

Al surface after etching in alkaline solution

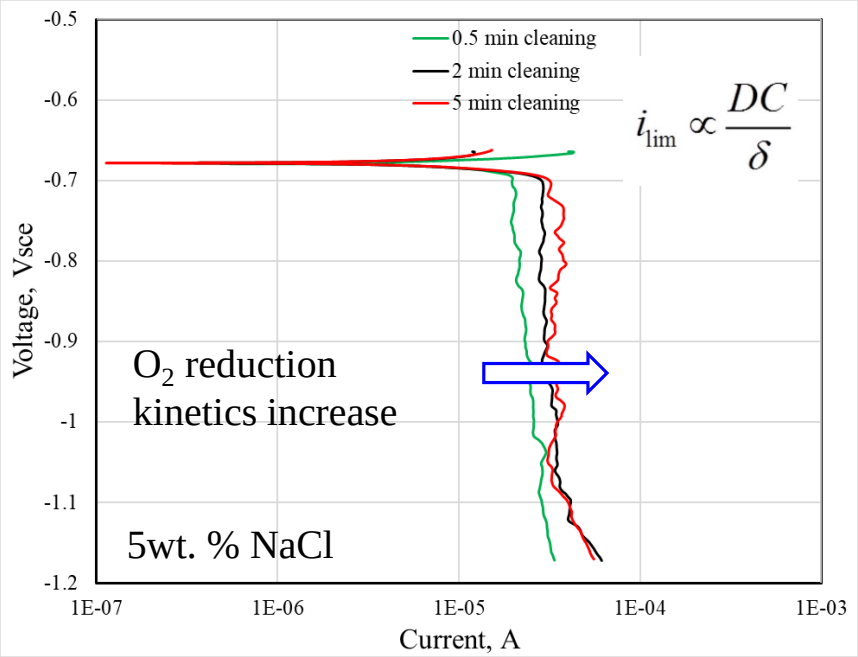


$$\begin{cases} 2Al + 2OH^- + 2H_2O \text{ --> } 2AlO_2^- + 3H_2 \\ Cu + 2H_2O \text{ --> } Cu(OH)_2 + H_2 \end{cases}$$

Cu enrichment on the surface leads to a higher oxygen reduction reaction kinetics, and can affect the subsequent Zr pretreatment.



pH 8; deaerated;
4.31 g/L $Na_2B_4O_7$
7.07 g/L H_3BO_3



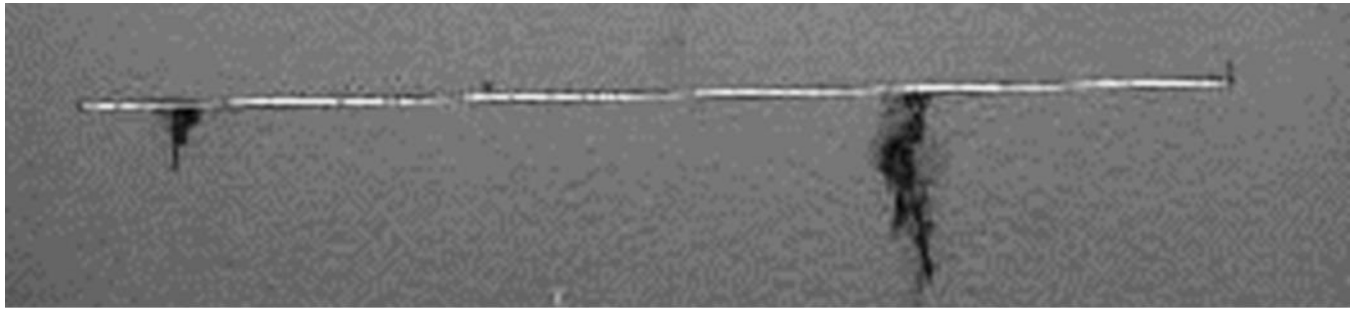
Effect of Cu enrichment during the alkaline cleaning on filiform/blister corrosion (normal Cu^{2+} in Zr pretreatment)

6111, slow quench, T4, e-coated;
12 weeks Ford L319

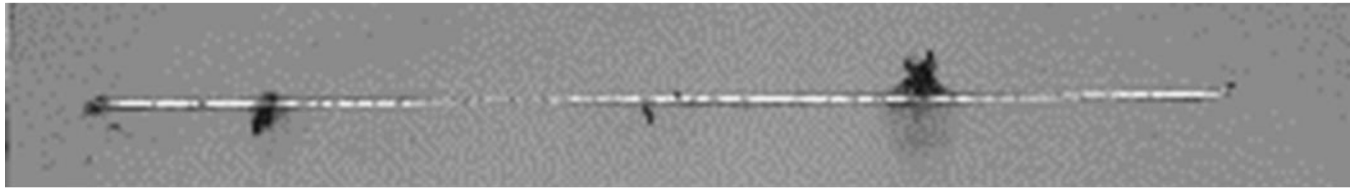
Cleaning time in alkaline solution

Cu^{2+} in Zr pretreatment: 25 ppm;

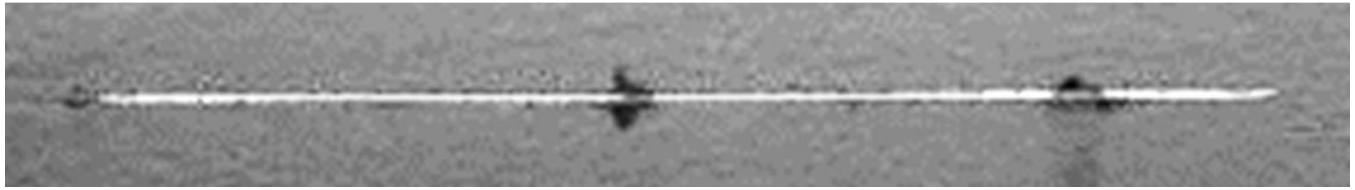
0.5 min

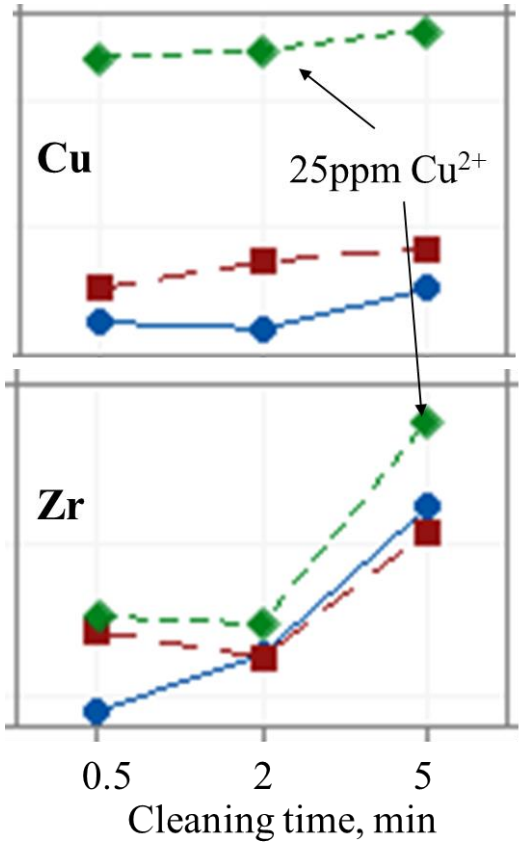


2 min



5 min





Cu enrichment during the alkaline cleaning does not lead to bad filiform corrosion performance, as its strong ability for O_2 reduction promote thin film formation.

Effect of Cu deposition from pretreatment solution on filiform/blister corrosion (high Cu^{2+} in pretreatment solution)

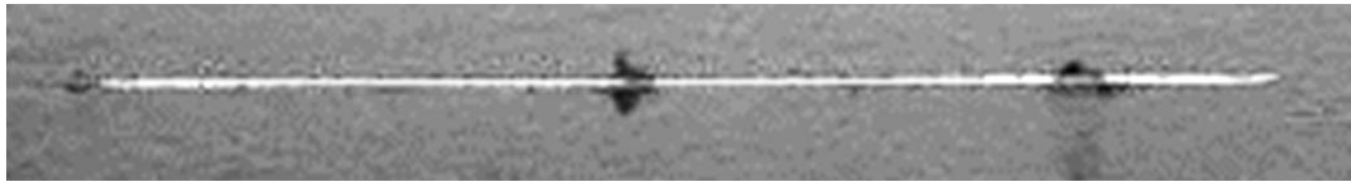
6111, slow quench, T4, E-coated
12 weeks Ford L319

Cu^{2+} in Zr pretreatment

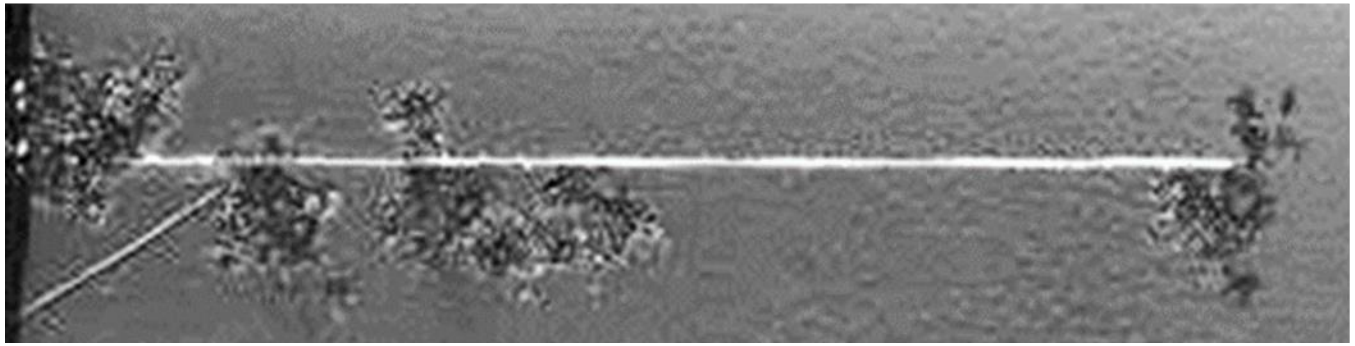
Alkaline cleaning time: 5 min;

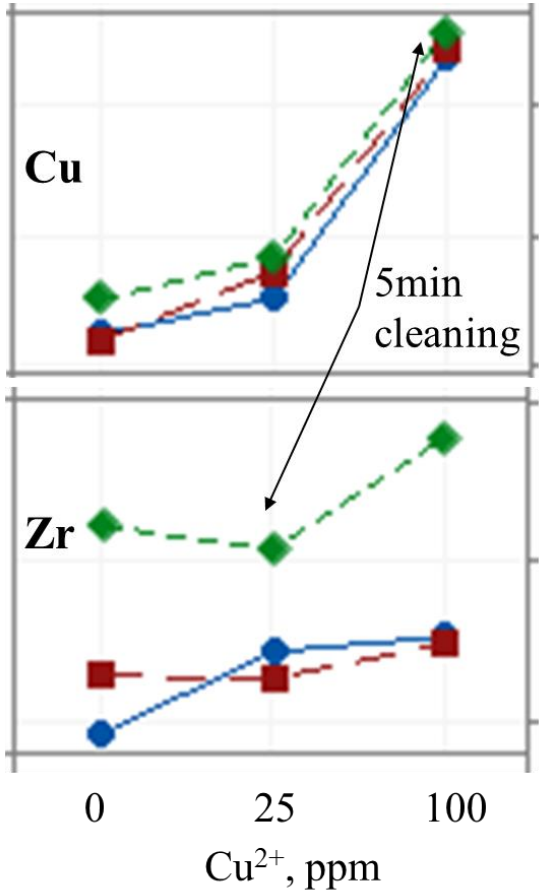
0 ppm

25 ppm



100 ppm





High Cu^{2+} addition is not beneficial for corrosion improvement, as Cu deposition may not be fully covered by thin film pretreatment.

Summary

- Copper in the alloy can cause increased filiform corrosion when it sensitizes the grain boundaries to IGC. When Cu-rich precipitates form at the GB, which is associated with a strongly Cu-depleted PFZ, the different electrochemical properties between PFZ/precipitates and PFZ/the adjacent matrix in the grain body drive filiform propagation quite quickly due to fast IGC. When the metal is heat treated to reduce the IGC sensitivity and the dominant form of corrosion attack transforms to pitting, filiform corrosion propagates much less.

- Copper added as an accelerant in the pre-treatment solution can precipitate out on the surface and drive filiform irrespective of the alloy state. Too much Cu^{2+} addition in the pretreatment can deteriorate FFC.

- Alkaline cleaning can lead to Cu enrichment on the surface, and its impact on FFC can be counteracted by thin film precipitates.

Questions

Contact
Jichao Li
Jichao.Li@Constellium.com