



Loughborough
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The Development of Post-Electroplating Surface Modification Treatments to Mitigate Tin Whisker Growth

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Electronic Materials and Processes for Space (EMPS) Workshops

The Seventh Workshop, EMPS-7

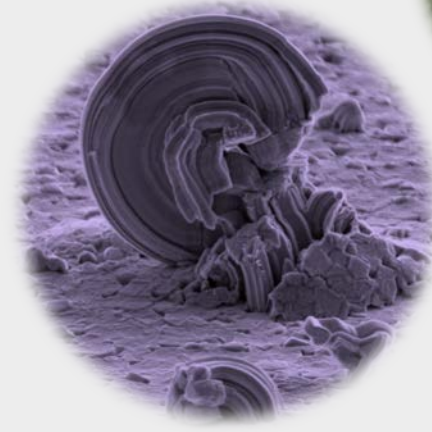
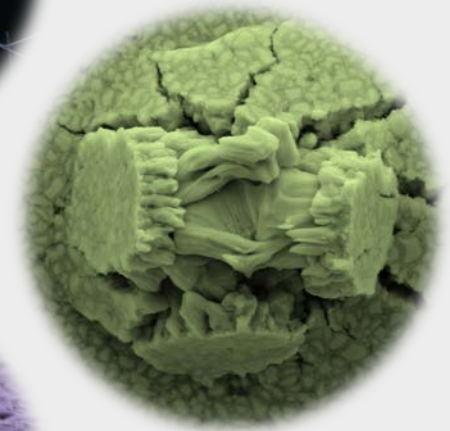
The University of Portsmouth, Portsmouth, UK

13th and 14th April 2016

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Outline of presentation

- Background
- Project objectives
- Experimental approach
- Results and discussion
- Summary



Factors that influence whisker growth

- Electroplating bath chemistry
 - Pure tin or tin alloy (Sn-Pb, Sn-Bi, Sn-Cu etc)
 - Use of brighteners
- Electroplating parameters
 - Current density, temperature, agitation
- Deposit characteristics
 - Grain size and morphology, orientation, deposit thickness, Sn oxide
- Substrate
 - Cu, brass, alloy 42
 - Intermetallic formation, elemental diffusion from substrate
- Environmental conditions
 - Temperature, humidity, thermal cycling, applied external stress

The role of the surface oxide in whisker growth

- In 1994, Tu proposed his “**cracked oxide theory**”¹
 - whisker growth occurs at certain weak spots on the surface where the oxide has been broken
 - In the absence of an oxide no whisker growth would occur
- Later adding² ...
 - “if the surface oxide is very thick, it will physically block the growth of any hillocks and whiskers”
- *Can we mitigate whisker growth by increasing the thickness of the surface oxide??*

¹ *Physical Review B* 49, 2030, 1994

² *Proceedings of the IEEE Electronic Components and Technology Conference*, 2002 p1194–1200

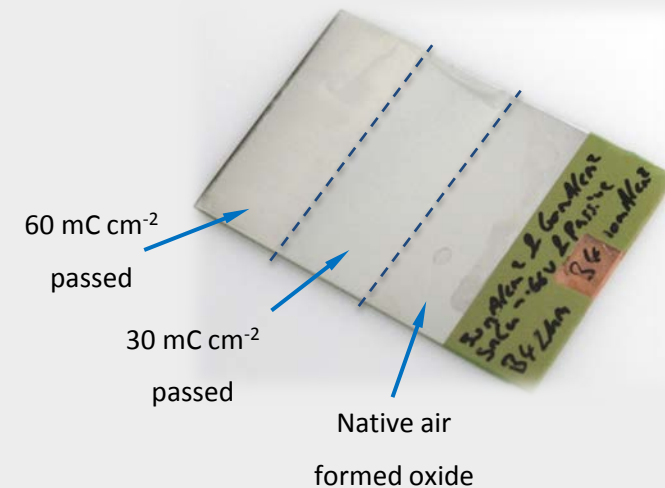
Aims and objectives

Investigate the effect of post-electroplating surface treatments on whisker growth from tin and tin alloy electrodeposits

- Use electrochemical oxidation and conversion coating techniques to develop surface oxides
- Evaluate the effect of process variables on oxide thickness
- Evaluate the ability of the applied surface treatments to mitigate whisker growth

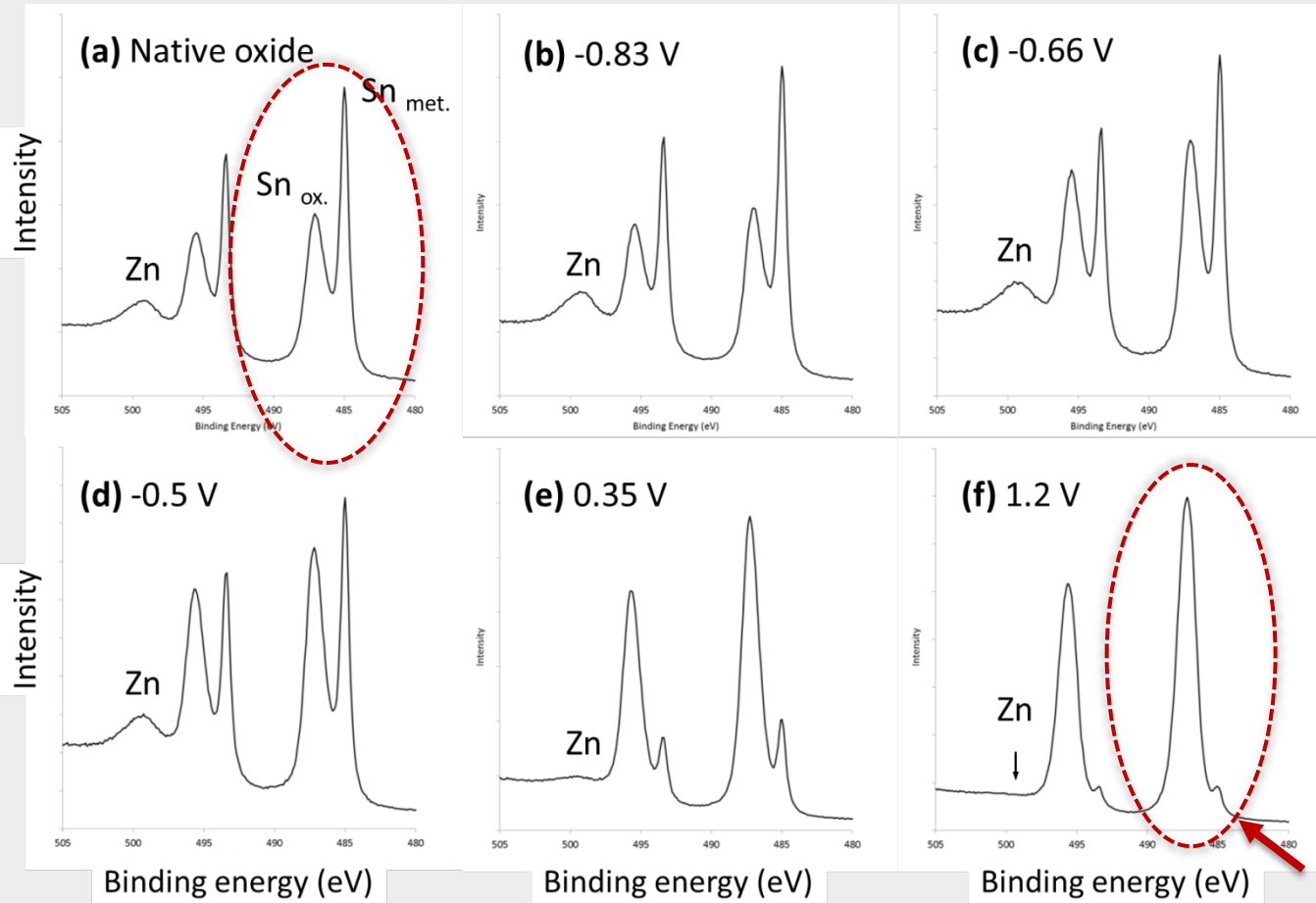
Experimental approach

- Surface modification treatments applied to electrodeposited Sn and Sn-Cu coatings
 - Electrochemical oxidation in pH 8.4 borate buffer and potassium carbonate/bicarbonate solutions
 - Application of a molybdate conversion coating
- XPS analysis to evaluate effect of process variables on the composition and thickness of the oxide layers formed
- Evaluate the effect of the surface modification treatment on whisker growth using SEM and optical microscopy



Whisker growth test sample

Effect of oxidation potential on oxide thickness

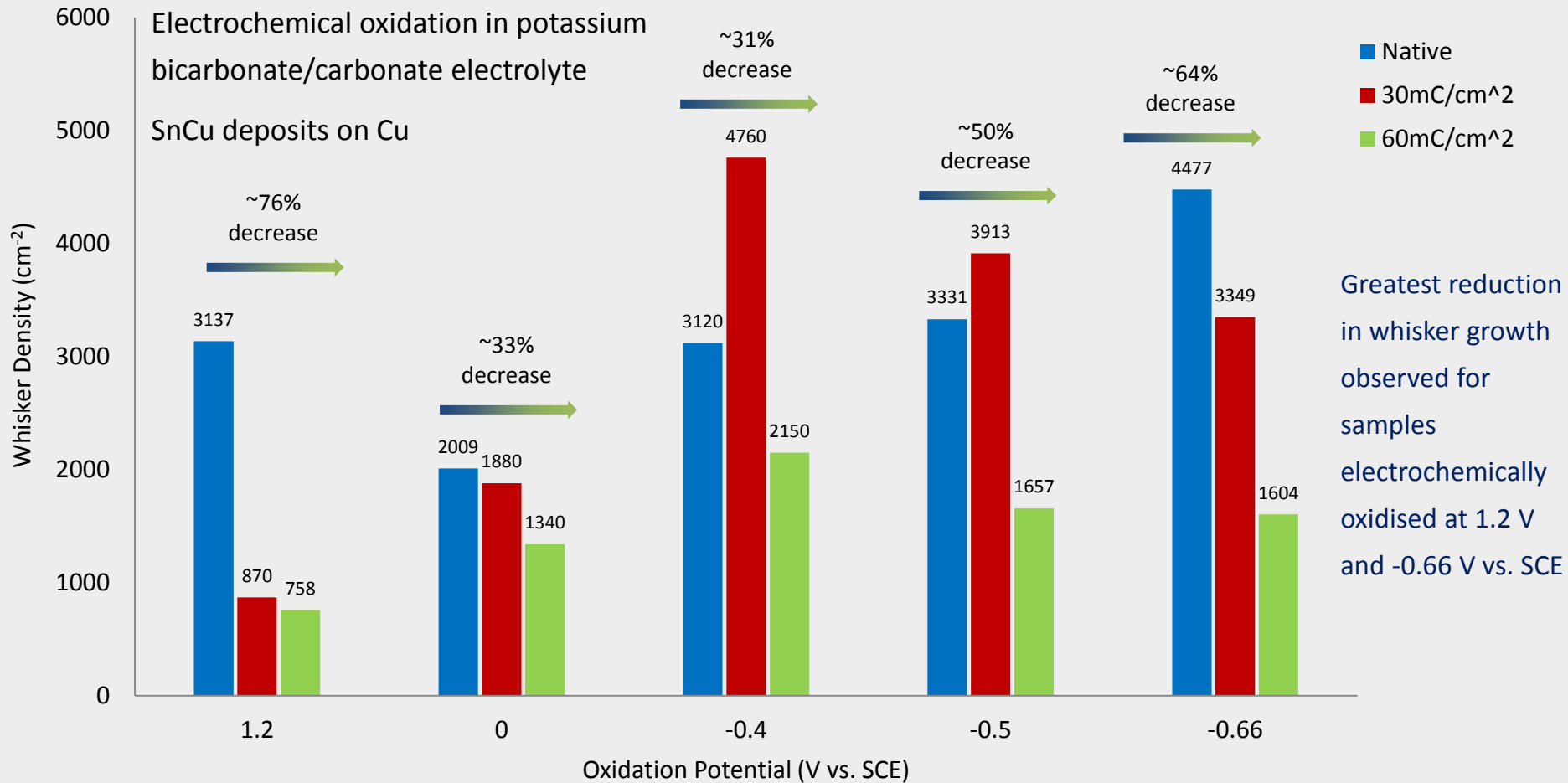


- High resolution XPS scans of the Sn 3d peak
- Equivalent charge passed
- 2 μm Sn deposits on brass
- 1 day after deposition
- Electrochemical oxidation in potassium bicarbonate-carbonate electrolyte

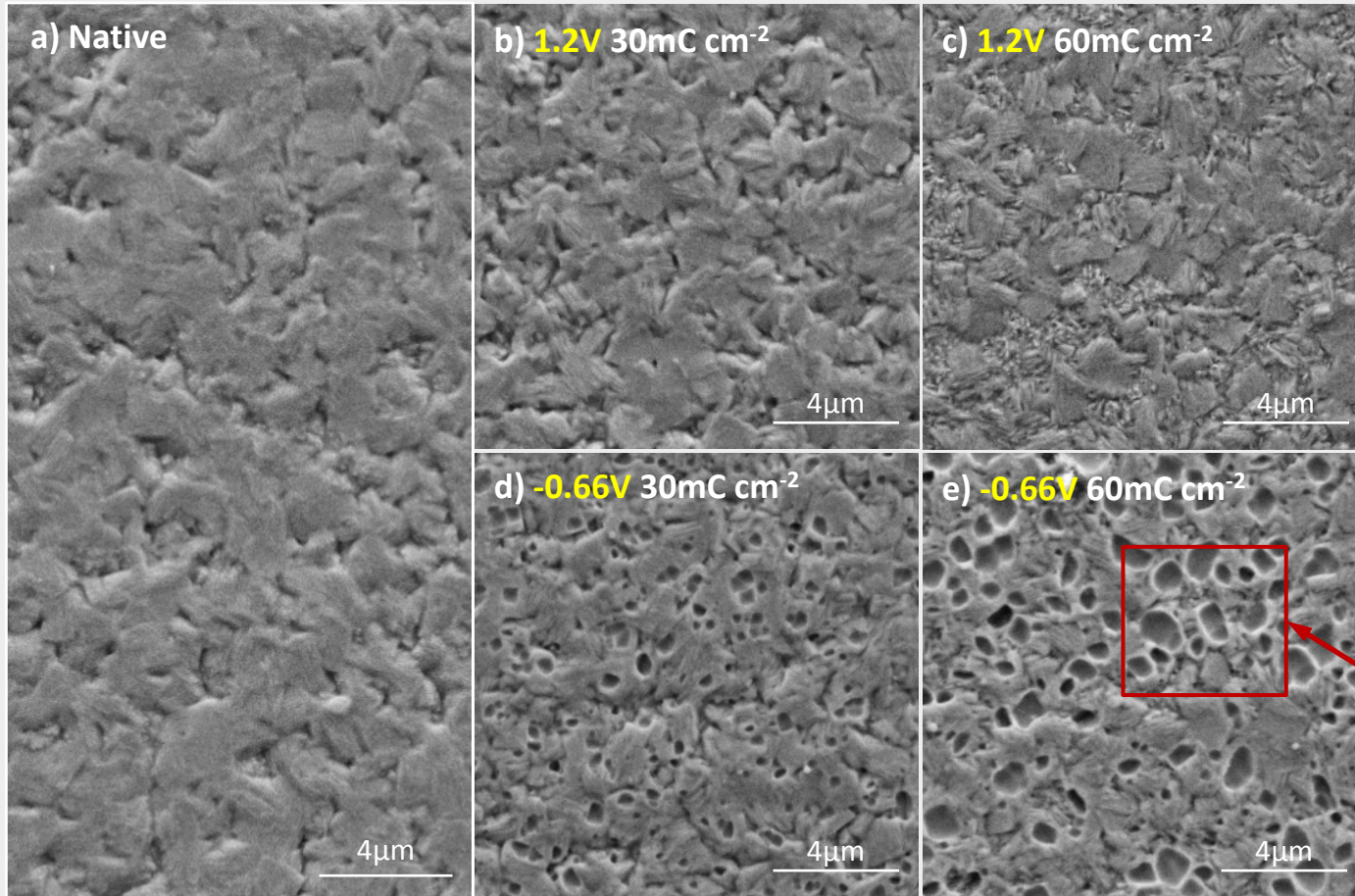
Thickest Sn oxide formed at 1.2 V

Effect of oxidation potential on whisker growth

Whisker growth evaluated after ~ 14 months



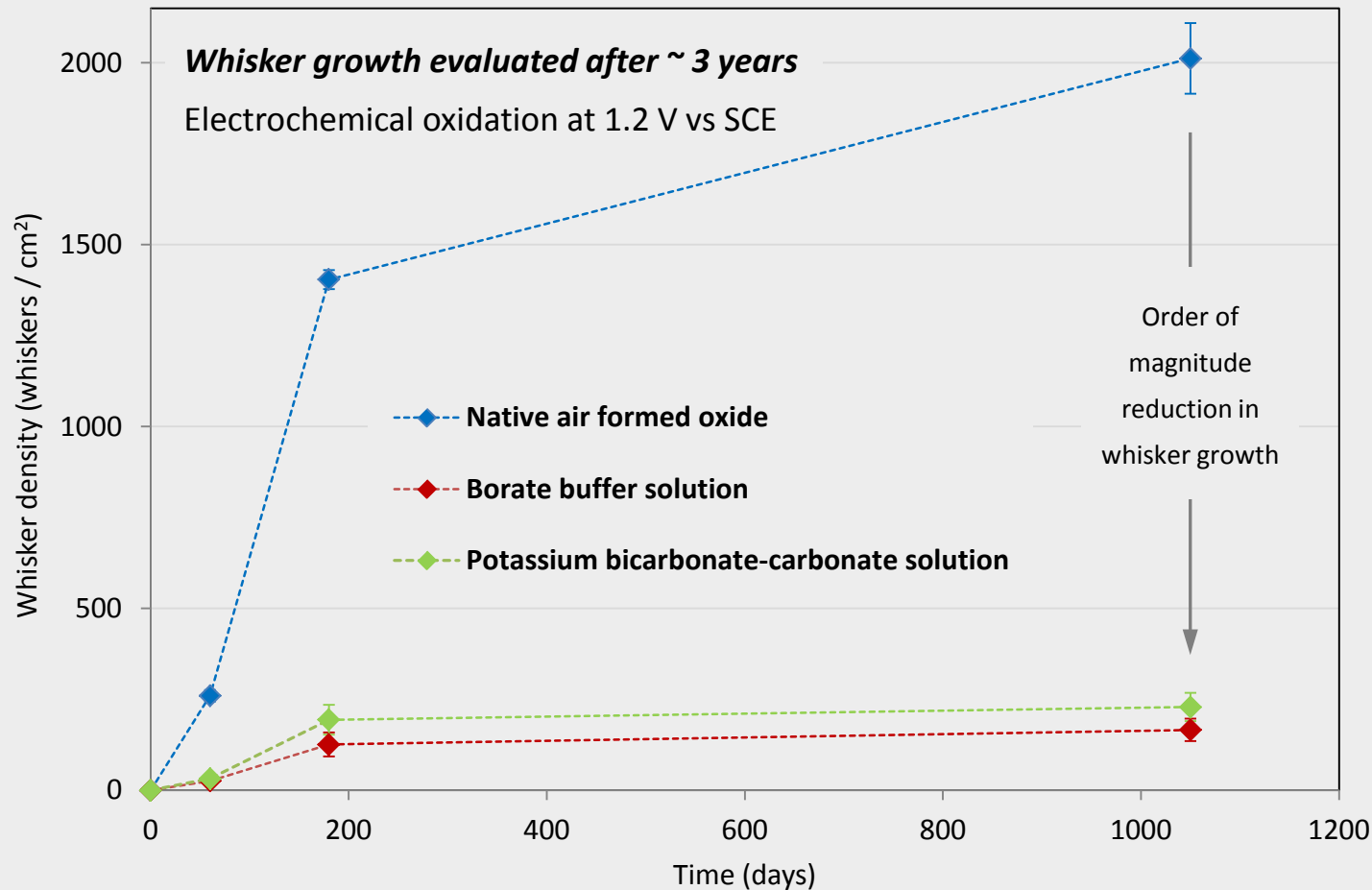
Optimisation of oxidation potential



Electrochemical oxidation at 1.2 V vs. SCE is preferred since it does not result in dissolution of the Sn electrodeposit

Sn dissolution occurs at -0.66 V vs SCE

Effect of electrochemical oxide on whisker growth



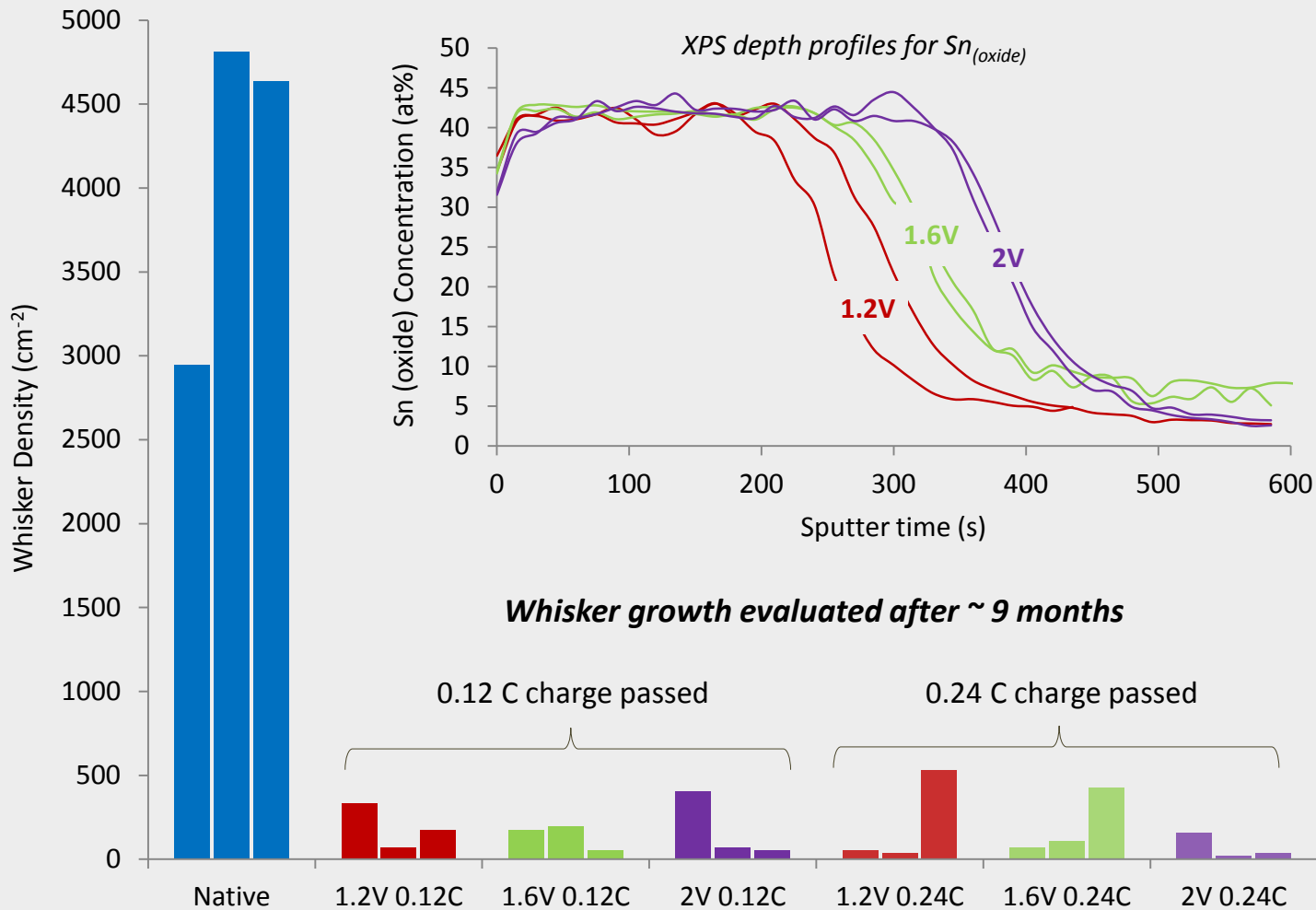
2 μm SnCu deposits on Cu electroplated at 10 mAcm^{-2}

Whisker growth is considerably reduced for samples given a post electroplating oxidation treatment at 1.2 V vs SCE

Comparable reduction in whisker growth achieved for borate buffer and potassium bicarbonate-carbonate solutions

Still effective at mitigating whisker growth after ~ 3 years

Electrochemical oxidation at higher potentials

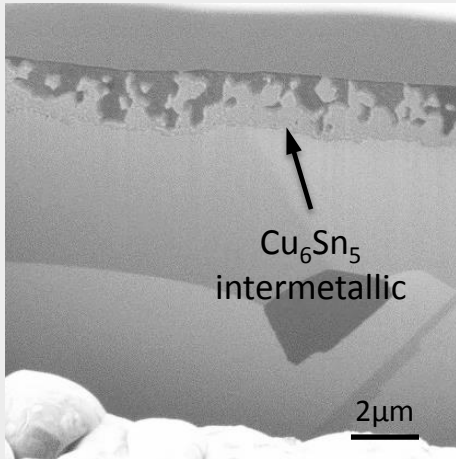


Electrochemical oxidation of SnCu deposits on Cu in potassium bicarbonate-carbonate electrolyte

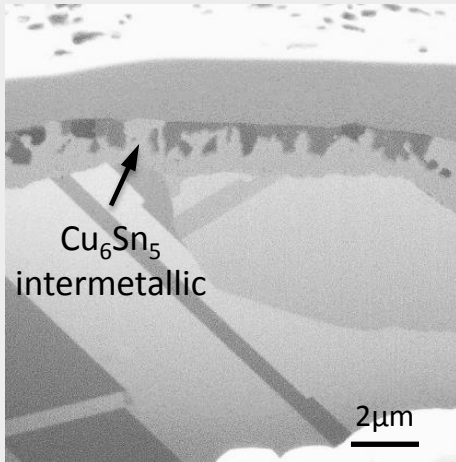
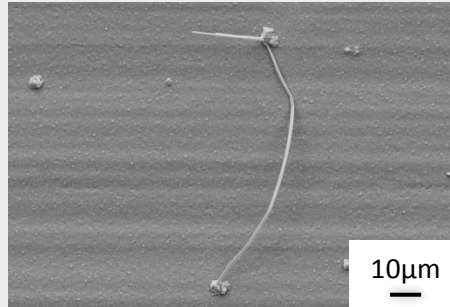
Oxide film thickness is increased at higher potentials

However, there is no clear improvement in whisker mitigation at higher oxidation potentials compared with 1.2 V

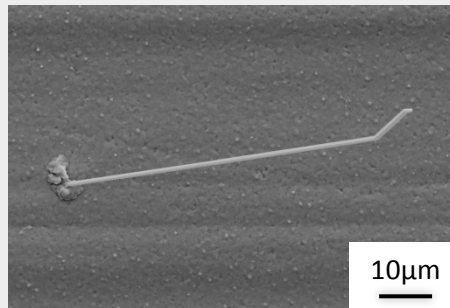
Whisker mitigation mechanism



Native air formed oxide

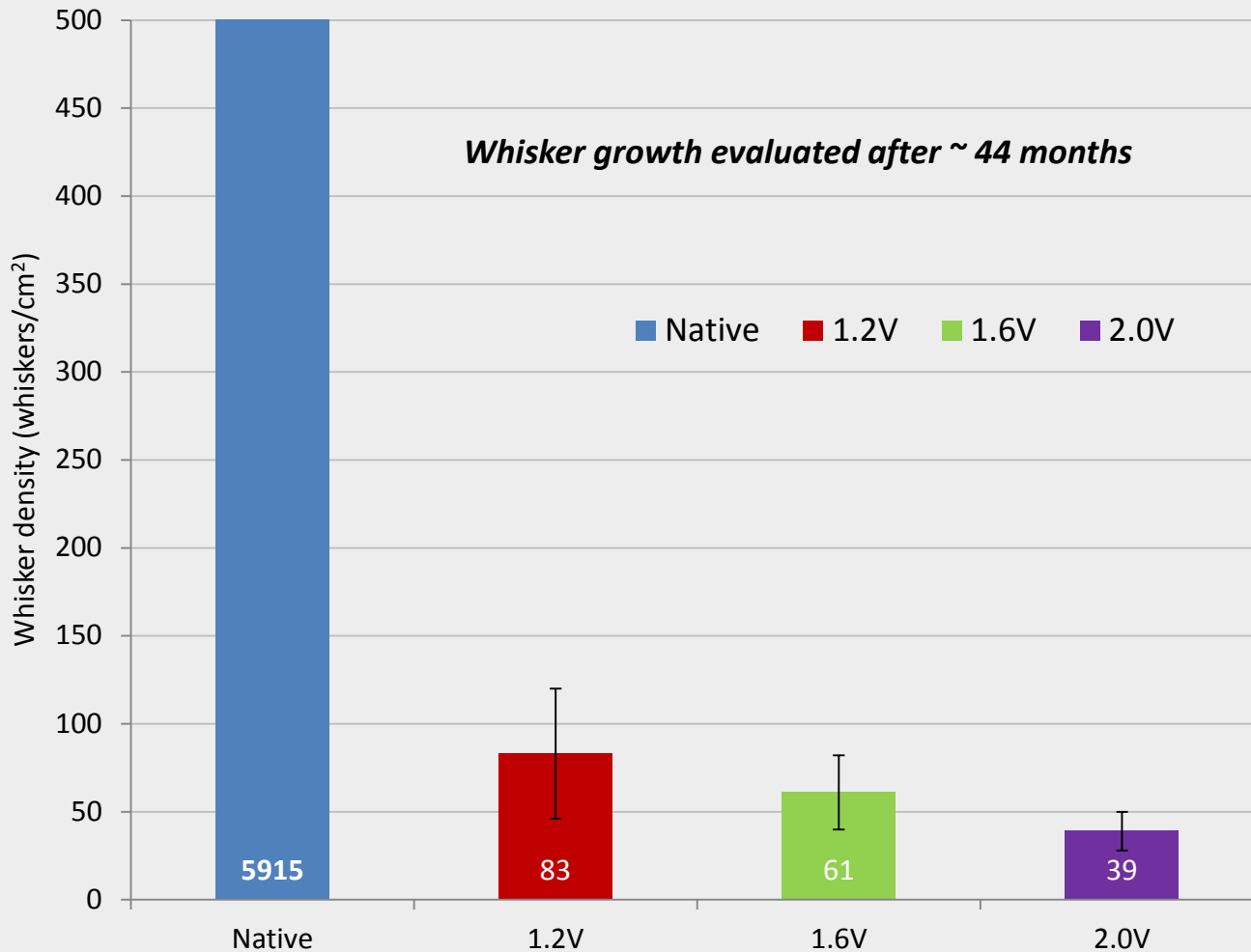


Electrochemical oxidation at 1.2V borate buffer



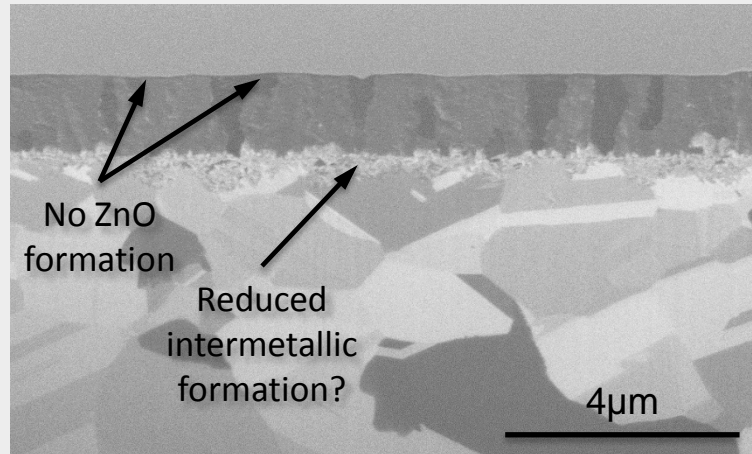
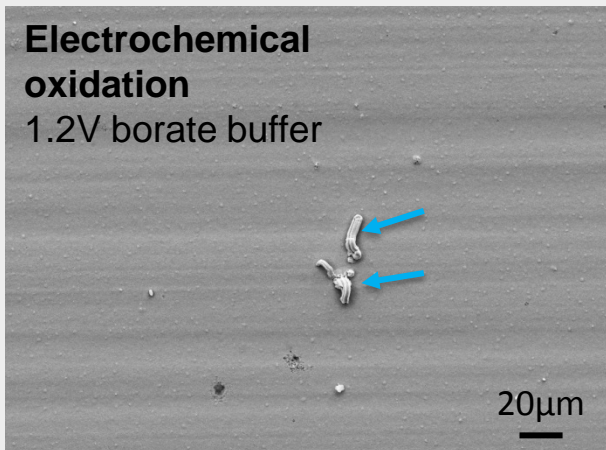
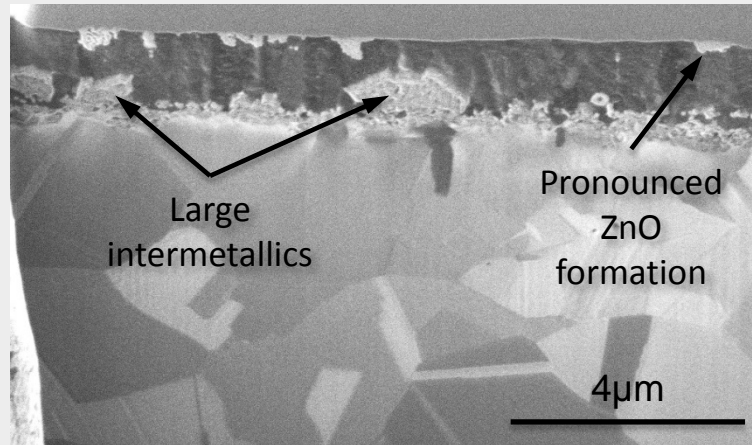
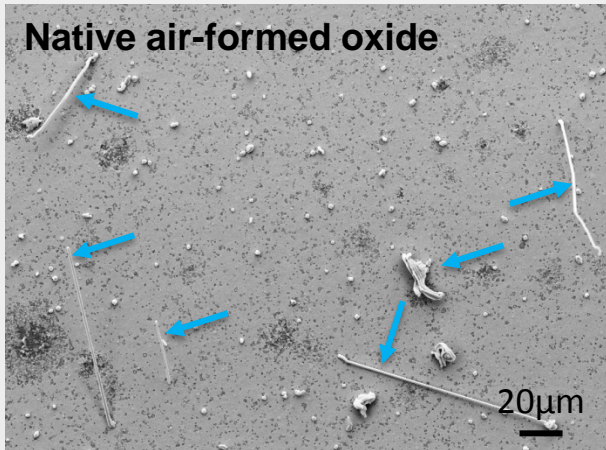
- IMC formation appears unaffected by electrochemical oxidation
- Whisker mitigation must simply be derived from the increased thickness of the oxide layer
- Although whisker density is greatly reduced for electrochemically oxidised SnCu deposits, long filament whiskers are still produced
- Electrochemical oxidation does not reduce the driving force for tin whisker growth (*intermetallic formation*)

Whisker mitigation: Sn deposits on brass



- Electrochemical oxidation of 2 μm Sn deposits on brass in borate buffer solution
- Whisker growth is greatly reduced for electrochemically oxidised Sn deposits on brass
- Whisker mitigation is more effective at the higher oxidation potential
- Still an effective barrier to whisker growth after almost 4 years

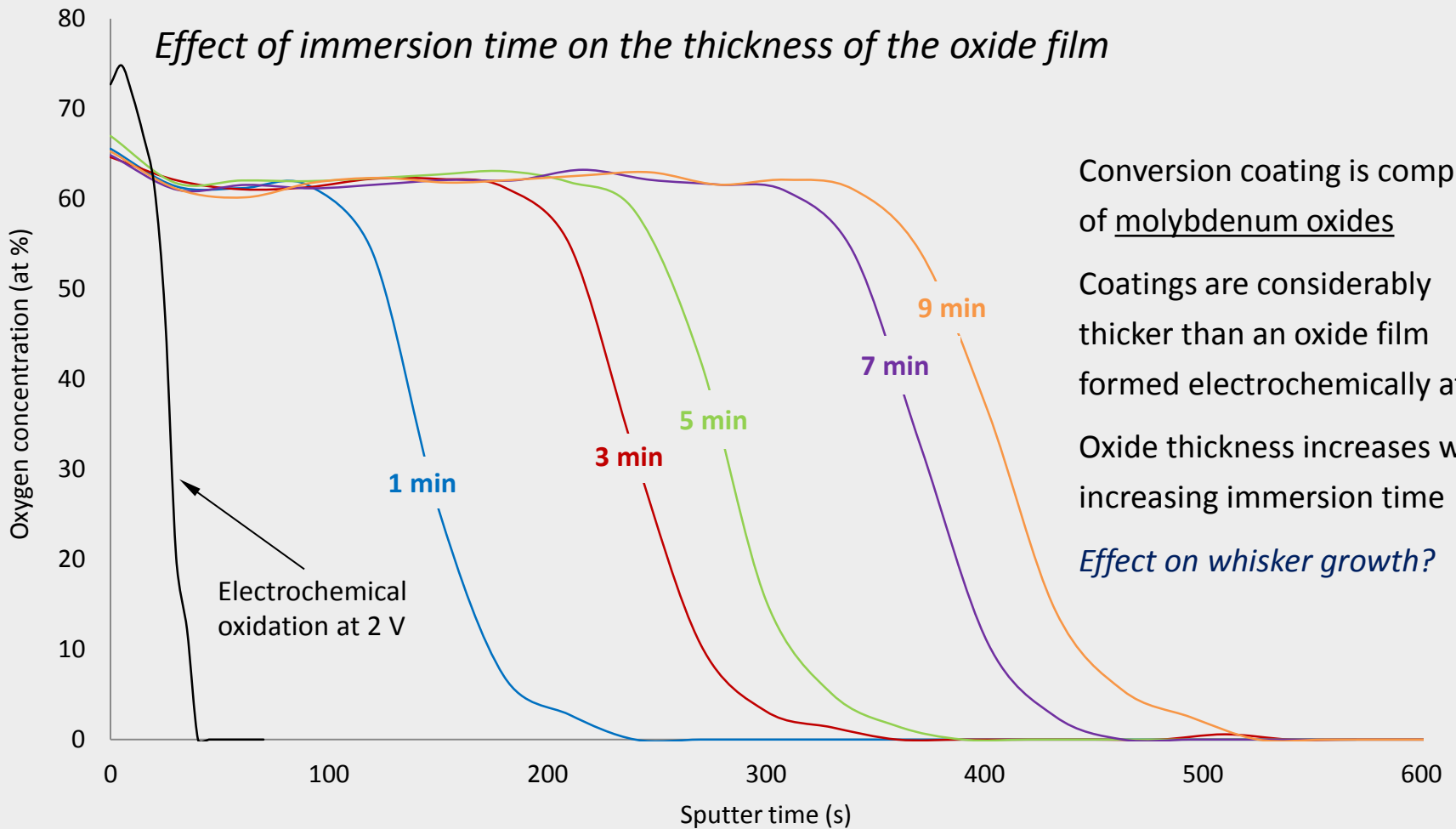
Sn deposits on brass



For Sn deposits on brass, electrochemical oxidation reduces whisker growth by preventing the formation of Zn oxide at the deposit surface

Reduced IMC formation in electrochemically oxidised samples may also influence whisker formation

Molybdate conversion coatings



Conversion coating is comprised of molybdenum oxides

Coatings are considerably thicker than an oxide film formed electrochemically at 2 V

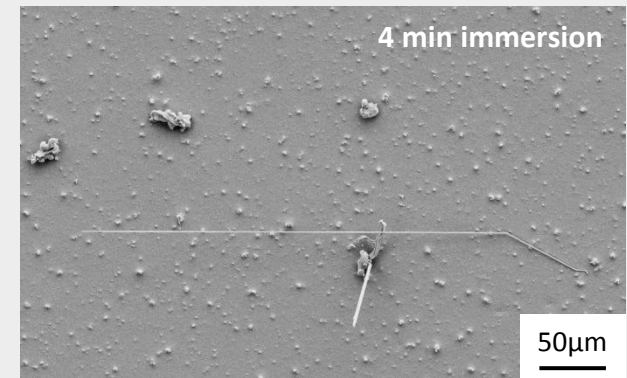
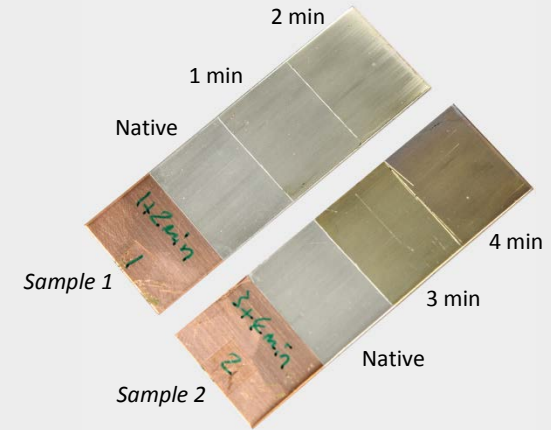
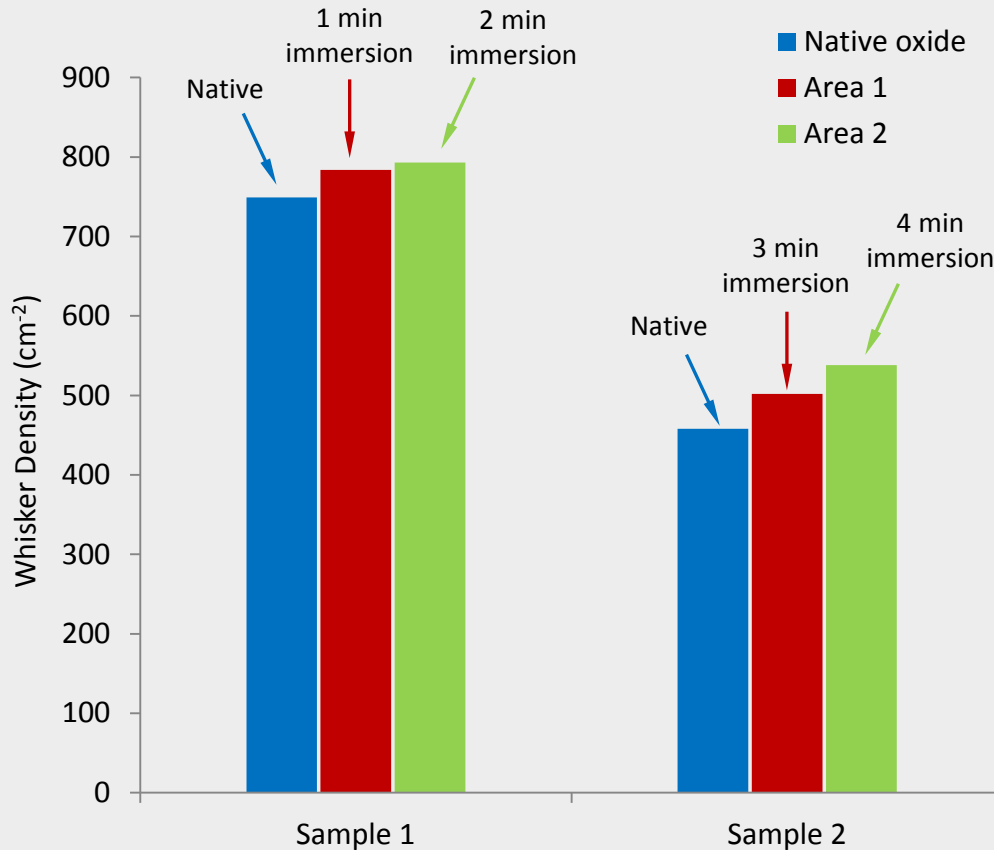
Oxide thickness increases with increasing immersion time

Effect on whisker growth?

Effect of molybdate conversion coatings

- preliminary whisker growth results

Whisker growth evaluated after ~ 2 months



- Preliminary results indicate that immersion molybdate conversion coatings (up to 4 min immersion) do not mitigate whisker growth

Summary

- Long term whisker mitigation (~ 3 years) has been demonstrated for electrochemically oxidised SnCu deposits on Cu
- Electrochemical oxidation also significantly reduces whisker growth for Sn deposits on brass
- The thickness of the oxide film developed by electrochemical oxidation is dependent upon the applied potential and charge passed.
- Comparable reductions in whisker growth were observed for deposits electrochemically oxidised in borate buffer and potassium bicarbonate-carbonate electrolyte solutions
- Initial results suggest that, although considerably thicker, molybdate conversion coatings formed by immersion are less able to mitigate whisker growth

Any
questions?



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