Adsorption of organic acids onto the surface of AA2024T3 aluminium alloy: the role of intermetallic particles

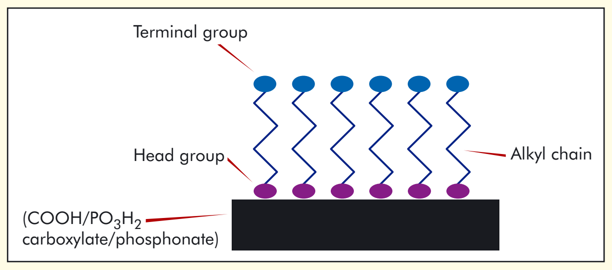
Adam Roberts[1], Dirk Engelberg[2], Yanwen Liu[2], George E Thompson[2] and Morgan R Alexander[2]

[1]Kratos Analytical, Manchester, UK [2]Corrosion and Protection Centre, UMIST, Manchester, UK

1 Introduction

Alkyl-phosphonic and carboxylic acid SAMs have been proposed as alternatives to conventional chrome-based pre-treatments in corrosion protection of aluminium.[1] It is intended that these form coupling layers between the air-formed aluminium surface and the resin component in paint and adhesive formulations where the terminal group is reactive. Such monolayers are also useful in rendering interfacial organic-metal interactions amenable to study using surface analysis techniques.

This is the first work to use imaging XPS to investigate the effect of intermetallics on the heterogeneity of SAM formation. After removal of the oxide at the surface of AA2024T3, copper rich areas have been identified from which spectra were acquired. The absence of Mg in these areas and the elemental composition suggests they are Al_7Cu_2Fe θ-like intermetallic particles.[2] The pre- and post-ion etch compositions and Cu 2p binding energy suggest that the oxide is primarily alumina with little if any incorporation of Cu in the oxide.



Alkyl-phosphonic acid was adsorbed to the surface of super pure Al and 2024T3 and its distribution mapped using the characteristic P 2s signal. The distribution of adsorbed SAM was found to be uniform and therefore not be influenced by the presence of the intermetallics. This is not surprising given the small influence of the particle on the oxide composition. This observation is in contrast to the work by Stratmann et al. who used Auger to identify preferential alkyl-phosphonic acid adsorption at iron-rich inclusions.[3]

2 Instrumentation and Materials

Super pure aluminium (99.999%) was used as a 100 nm thick layer magnetron sputtered onto a Piranha solution cleaned glass slide.

AA2024T3 was mechanically polished, finishing with diamond past and Kemel™ lubricating fluid.

Nominal composition of 2024T3:

Cu	Cr	Fe	Mg	Mn	Si	Ti	Zn	Other	Al
3.8-4.9	0.1	0.5	1.2-1.8	0.3-0.9	0.5	0.15	0.25	0.15	balance

Decyl phosphonic acid, $CH_3(CH_2)_9P(OH)_2(=O)$, SAMs were adsorbed from 5 mM ethanoic solutions for 5 days after immersion in a conditioning solution of 5 mM methyl phosphonic acid ethanoic solution for 15 minutes. Extensive contact angle, XPS and FTIR investigations have shown this to provide a fully ordered and complete monolayer.[4]

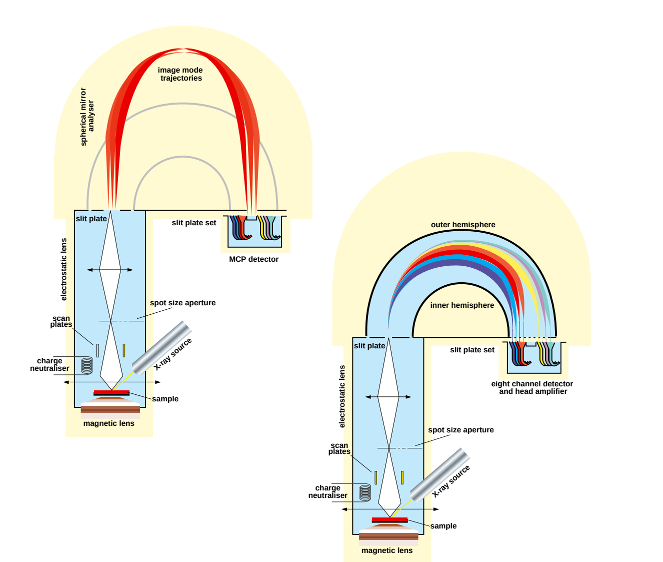


Figure 1 Spectroscopic and parallel imaging modes of the AXIS Ultra

3 Results

Decyl phosphonic acid (DPA) on super pure aluminium is determined to be relatively uniformly distributed over the surface using the P 2s core level (the P 2p is at the same position as an Al 2p plasmon) - Figure 2.

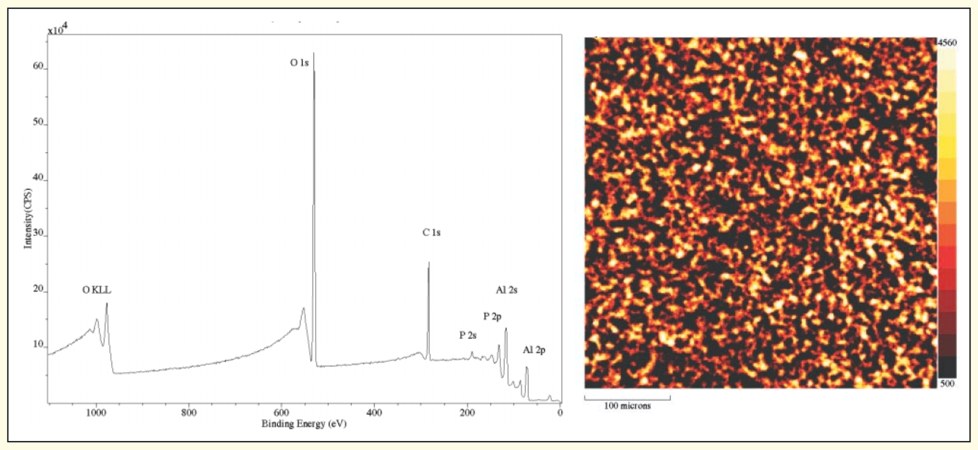


Figure 2 Wide scan and P 2s parallel image of DPA on super pure Al

AFM has proved useful in identifying features at the surface of the polished 2024T3 alloy that are consistent with intermetallic particles. The difference in hardness between particle and matrix causes the large angular intermetallic to stand proud of the surface. The shape, distribution and scale of these features are commensurate with the size of cavities caused by acid and alkali pre-treatment of 2024T3 as in Figure 3. [5]

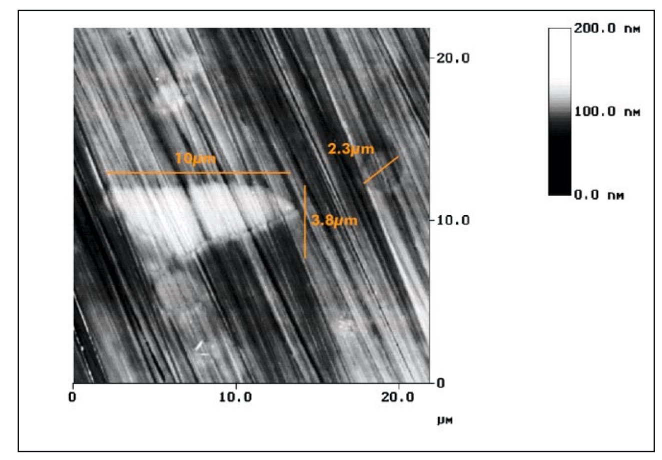


Figure 3 Tapping mode topographical image of polished 2024T3 surface including a large hard angular particle and some smaller spherical particles

The angular particle, standing proud of the surface in Figure 3, is consistent with those seen in the SEM image of the surface in Figure 4. The elemental composition suggests they are Al_7Cu_2Fe θ-like intermetallic particles.[2]

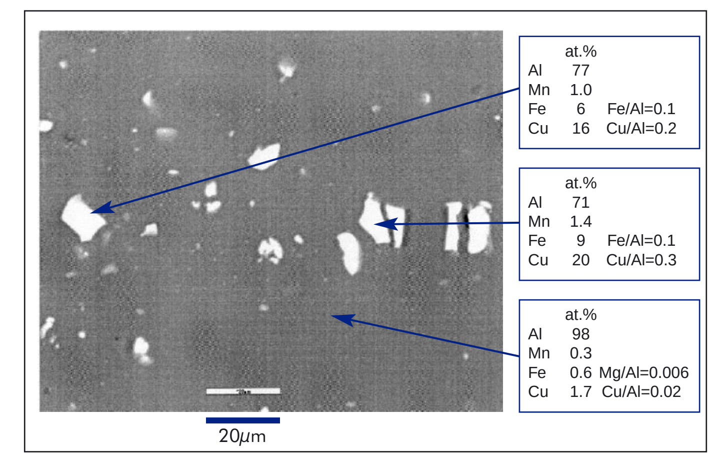
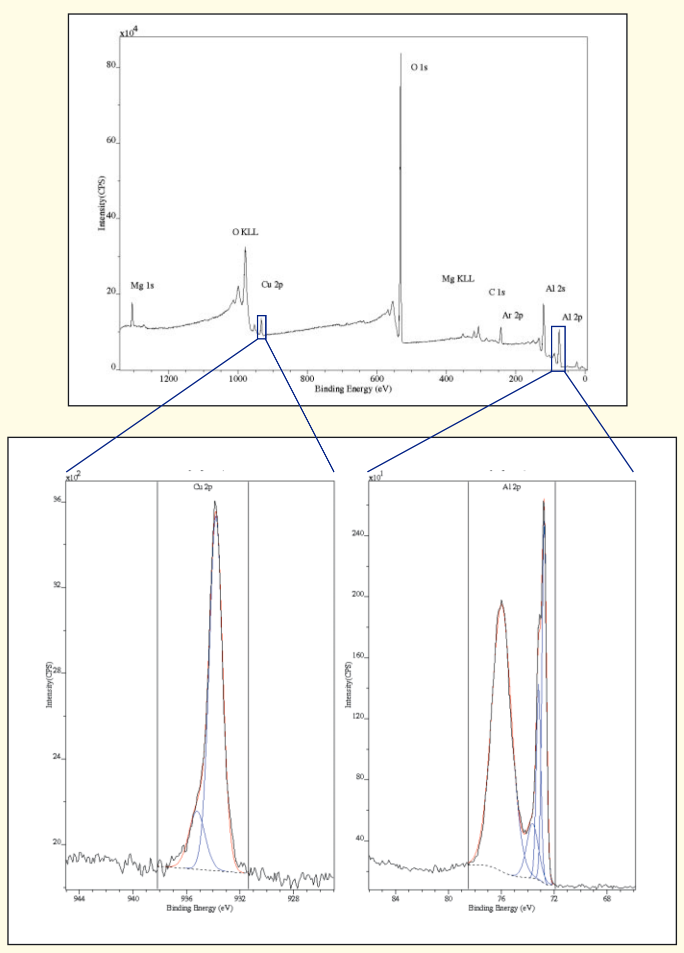


Figure 4 SEM from polished 2024T3 with EDX analysis

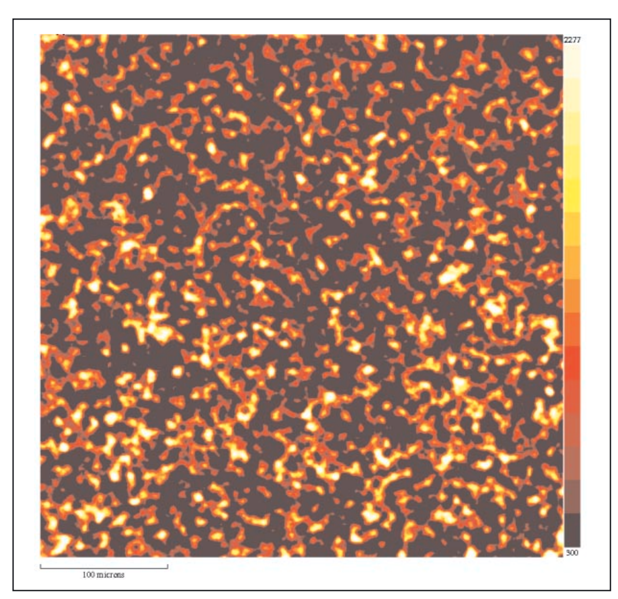
XPS of as introduced 2024T3 reveals significant concentrations of aluminium, oxygen, copper and magnesium at the polished surface as illustrated in Figure 5 where a light Ar-ion etch has been used to remove the adventitious hydrocarbon contamination. The binding energy of the Cu $2p_{3/2}$ (933.9eV) is consistent with literature values from intermetallics.[6]



Element	Core Level	Elemental composition at.%
Aluminium	2p	36
	(2p metallic)	(0.36)
	(2p oxide)	(0.64)
Carbon	1s	1
Copper	$2p_{3/2}$	0.8
Oxygen	1s	61
Magnesium	1s	1

Figure 5 XPS spectra and elemental quantification from large analysis area of 2024T3

Imaging the copper of the 'as introduced' polished 2024T3 surface reveals a homogeneous copper distribution, shown in Fgure 6. The homogeneous copper distribution is confirmed by elemental quantification from independent small areas.



Element	Core level	Apparent Cu-rich element composition (at.%)	Apparent Cu-depleted element composition (at.%)
Aluminium	2p	37	33
Carbon	1s	20	23
Copper	$2p_{3/2}$	0.20	0.3
Oxygen	1s	41	43
Magnesium	1s	1	1
Cu/Al		0.006	0.007

Figure 6 parallel image showing Cu distribution and quantification taken from 27 μm areas

Removal of the oxide overlayer, by Ar-ion etching, reveals strong heterogeneities in the copper concentration as seen in Figure 7. Small spot analysis has been used to quantify the elemental composition.

The XPS copper content of the matrix is in agreement with EDX SEM measurements which gives a copper concentration of 3.9 at.%. Assuming that the spot analysis contains a contribution from matrix as well as particle the increased Cu/Al ratio suggests that an Al_7Cu_2Fe stoichiometry for the particle is plausible.

Element	Core level	Matrix elemental composition at.%	Cu-rich elemental composition at.%
Aluminium	2p	89	94
Carbon	1s	1	1
Copper	$2p_{3/2}$	4	4
Oxygen	1s	6	1
Magnesium	1s	1	0.1
Cu/Al		0.04	0.11

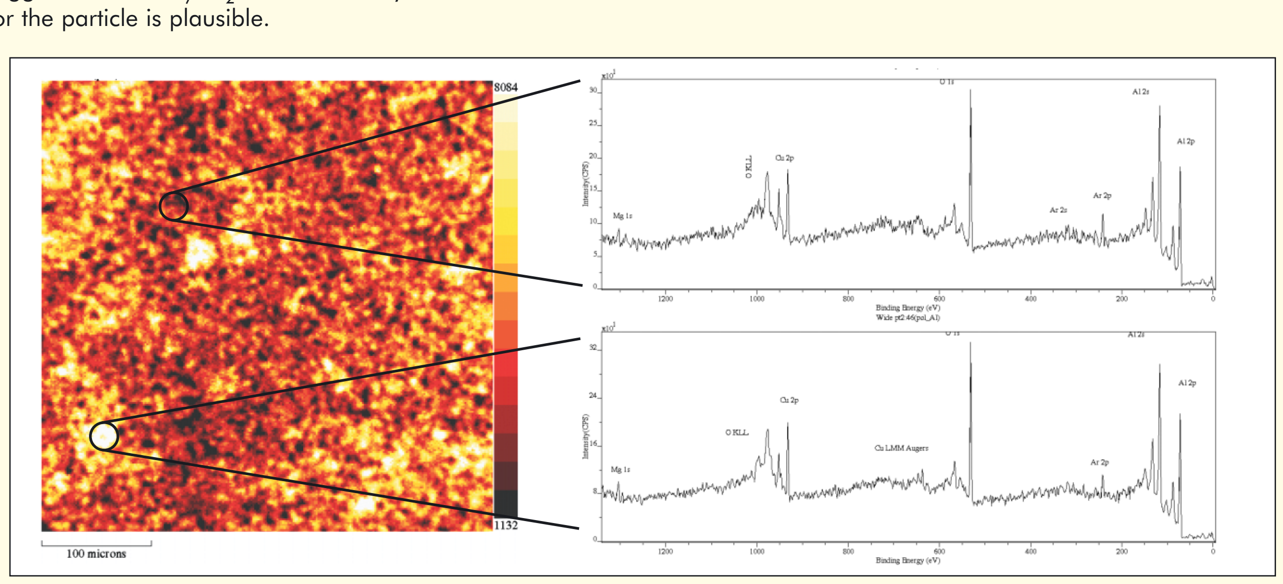
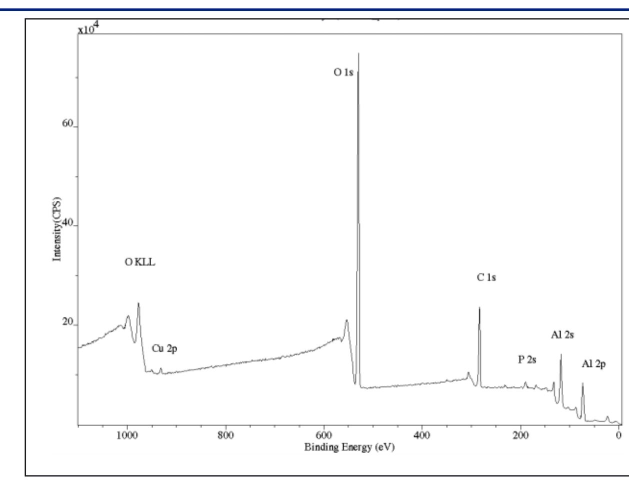


Figure 7 Copper image from etched 2024T3 and survey spectrum acquired from 27 μm selected areas

The distribution of DPA on 2024T3 has been mapped over a 0.4 x 0.4 mm area in Figure 7 before oxide overlayer removal. Comparison of the P 2s image with the uniform distribution seen on super pure aluminium (Figure 2) and the copper image suggests there is no correlation with the particle distribution of the type clearly resolved in Figure 6.



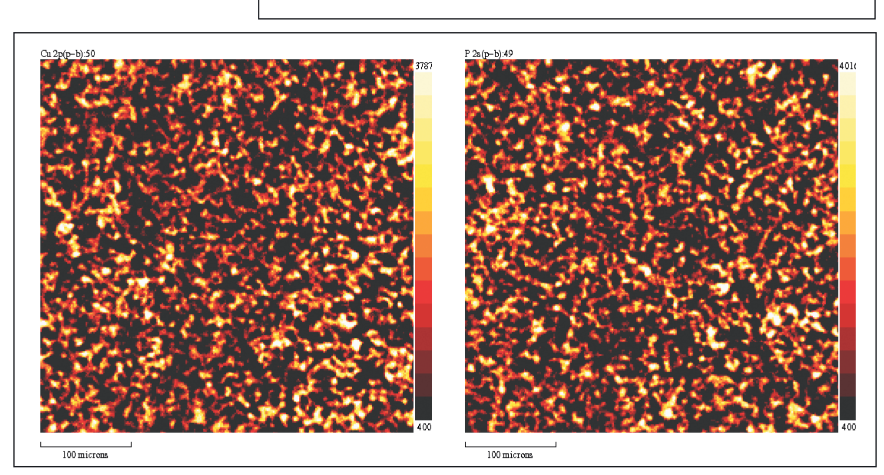


Figure 8 Image of P 2s intensity from SAM on 2024T3 showing no correlation of P with Cu

4 Conclusions

- AFM and SEM have revealed the presence of intermetallic phases at the surface of mechanically polished 2024T3. Angular particles with 10-20 μm dimensions are assigned as Al_7Cu_2Fe θ-like intermetallic phase.
- XPS before and after Ar-ion etching indicates that the copper rich particles are poorly resolved before oxide removal. It is implied that there is little if any incorporation of Cu in the oxide.
- After Ar-ion etching of the 2024T3 surface, the copper heterogeneities are revealed.
- The binding energy of the Cu $2p_{3/2}$ is consistent with copper existence in the intermetallic below the oxide.
- Decyl phosphonic acid SAMs were determined to be distributed uniformly across the surface of both super pure and 2024T3 aluminium surfaces. This is consistent with the homogeneous oxide composition despite the presence of intermetallics in this system.

References

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Acknowledgements

Dave Moore is thanked for his acquisition of the SEM/EDX data.