ON THE USE OF ELECTROCHEMICAL ADDITIVE MANUFACTURING (ECAM) TO GENERATE VARYING BINARY METAL COMPOSITIONS FOR ELECTROCHEMICAL TESTING

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ABSTRACT

When metal is exposed to a corrosive solution the electrochemical response is the sum of all the activities happening on the surface at any point in time, which is dependent on the nature and composition of the metallic substrate. In alloys, an increasing amount of one metal, copper for example, will vary both the Ecorr and Icorr values. The composition of alloys, however, are not able to be varied linearly.

Recently, electrochemical additive manufacturing (ecAM) has shown to be a useful method for depositing metals from solution in a controlled manner. Essentially a 3D electroplating pen with all the electroplateable metal solutions available, it becomes another unique tool in the additive manufacturing (AM) toolbox.

Through using samples generated by ecAM, we will discuss how the Ecorr and Icorr vary along a linearly increasing binary metallic system and how this affects corrosion inhibitor performance.

Keywords: aluminium alloys, electroplating, additive manufacturing, electrochemistry

INTRODUCTION

The electroplating of metal from solution using an overpotential is well known and has been a commercial process for over 150 years. Masking techniques are typically used to electroplate in selective areas and the use of an electroplating brush preceded the appearance of an electroplating 'pen' nib by Staemmler *et al* around 20 years ago [1] in which they used a pulled glass capillary as the writing tip to produce Cu dots around 400 nm in diameter. More recently the technique has been improved upon by others [2-7] by adding a 3D stage to generate 3D microstructures with overhang [2-3], voxel-based printing [4], low-cost desktop printing [5] which was used to print a bimetallic Cu-Ni thermo-mechanical actuator [6] and electroless printing of long micro- and nano-fibres [8].

These ecAM writing methods are rapidly developing as efficient AM tools for depositing metals and materials in a spatially controlled manner. Metals capable of being electroplated inside the redox window of water from aqueous solution are a large chunk of the periodic table, whereas the replacement of water with ionic liquids that have a wider electrochemical window allows for the deposition of other metals such as Al [9], AlMg alloys [10] and others [11, 12].

The electrochemical response of a metal surface to an electrolyte is the average of all the electrochemical processes happening at that point in time. Where the metal is an aluminium alloy with multitudes of embedded intermetallic particles, the electrochemical response (Ecorr, Icorr etc.) is still an average of all the anodic and cathodic processes of the exposed surface, even though microscopically many complex processes (dealloying, trenching etc.) are occurring locally [13, 14].

The ecAM writing method allows modification of both the metal composition on the substrate surface and its spatial location and allows for electrochemical examination as the metal : metal ratio is increased linearly but can also be used as a model for dealloying by instigating metal deposition adjacent to selected intermetallic particles. Our initial investigation shown in this paper, begins with the ecAM deposition of copper metal onto aluminium 7475 alloy.

METHODS AND MATERIALS

Aluminium 7475-T76 alloy was obtained from Kaiser Aluminum and AA7075-T6 obtained from Airport Metals. Copper C110 electronic grade was obtained from A&E Metals. Analytical grade copper sulfate was from Sigma-Aldrich and was made to a 1 M $CuSO_4$ solution with high purity milliQ water.

ECAM SETUP

The ecAM writing setup, shown in figure 1 used a plastic pipette tip which contained the copper sulfate solution with an immersed copper wire as the anode. The cathode was an aluminium alloy substrate in direct contact with a copper sheet with a wire connection. Both wires were connected to a GW Instek Laboratory DC power supply held potentiostatically at either 2 or 3 V during the metal deposition. The plastic pipette tip was sealed at the wider end and connected by tubing to a screw-adjustable volume pipette to balance air pressure and prevent liquid leakage from the pipette tip.

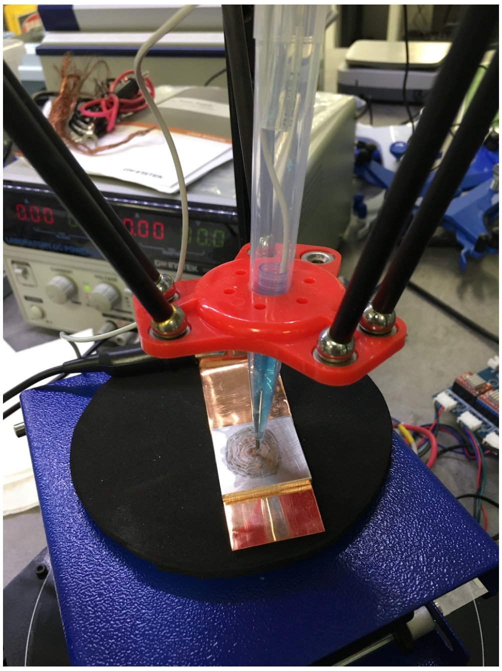


FIGURE 1: THE ECAM WRITING SETUP.

Electrochemical measurements, open-circuit potential (OCP) and potentiodynamic scanning (PDS) were performed on a Biologic VMP300 potentiostat with EC-lab software. Metal samples were prepared initially by abrading with 3M scotchbrite VFN (purple) alumina abrasive under running water, rinsed with milliQ deionised water and air-dried and later by abrasion and polishing with SiC paper to 4000 grit followed by being rinsed with milliQ deionised water and air-dried. Samples were clamped to a cell with a 2 cm diameter O-ring with a 3-electrode setup (WE – metal sample, RE – calomel electrode with a double junction tube, CE – mixed metal oxide on titanium mesh). Solution volume was 180 ml of 0.1 M NaCl solution. Samples were allowed to sit at OCP until stable before PDS of ± 250 mV was applied at 10 mV/min in a single scan starting cathodically.

RESULTS

Aluminium alloys (2xxx – 2024, 2024CLAD, 3xxx – 3003, 3004, 5xxx – 5052, 5083, 6xxx – 6016, 6060, 6061, 7xxx – 7075, 7075CLAD, 7475) as replicates were tested for stability of the OCP signal and reproducibility of the PDS result. Of these both AA7075 and AA7475 gave a stable and reproducible OCP after around 6 minutes (Figure 2) which was similar also to AA2024.

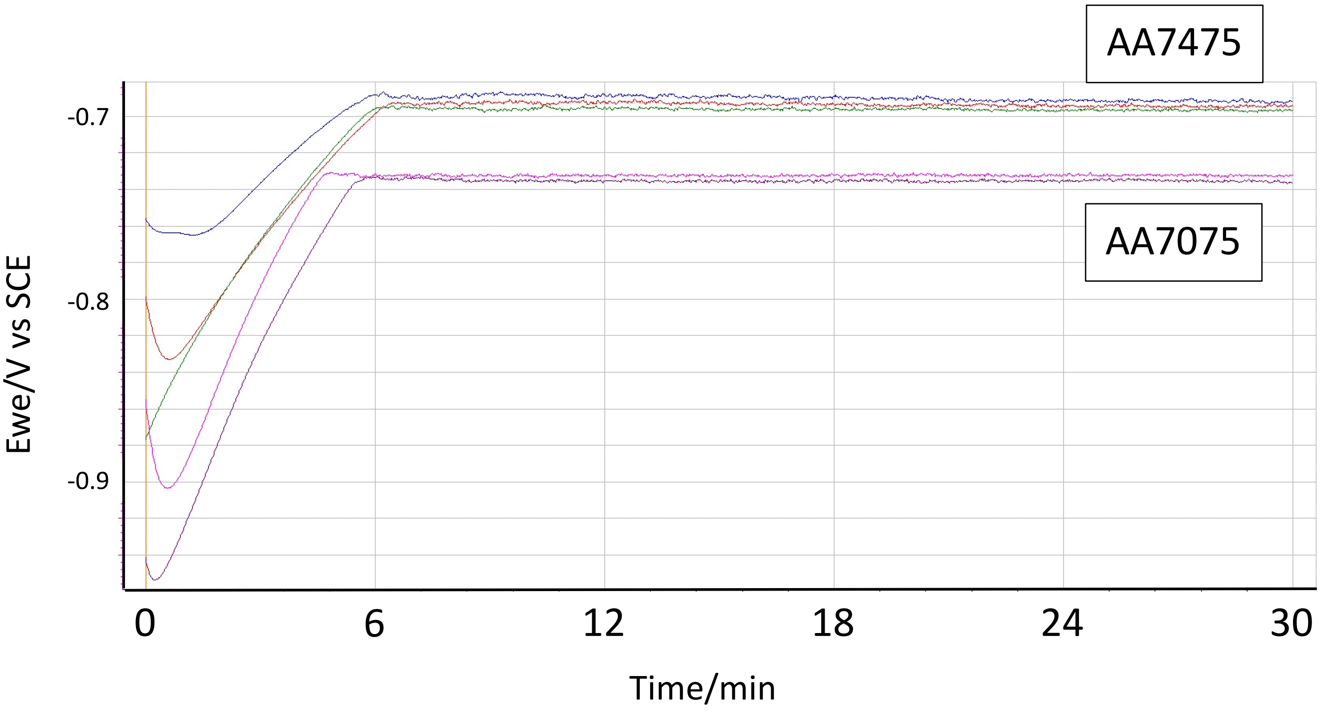


FIGURE 2: OCP STABILITY REPLICATES OF AA7075 AND AA7475 OVER 30 MINS .

Electrochemical deposition of Cu metal from copper sulfate solution using the ecAM pen setup and a manual XYZ stage can be seen in Figure 3 which is an image from a movie that shows drawing a line of copper metal on a polished metallic surface. The size and stability of the liquid meniscus at the bottom of the tip determines the width of the deposited Cu line and this meniscus must be in direct contact with the metal substrate to complete the electrical circuit.

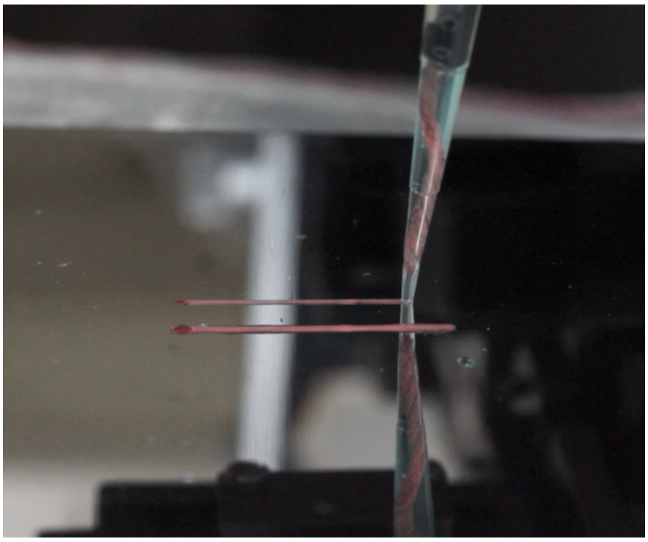
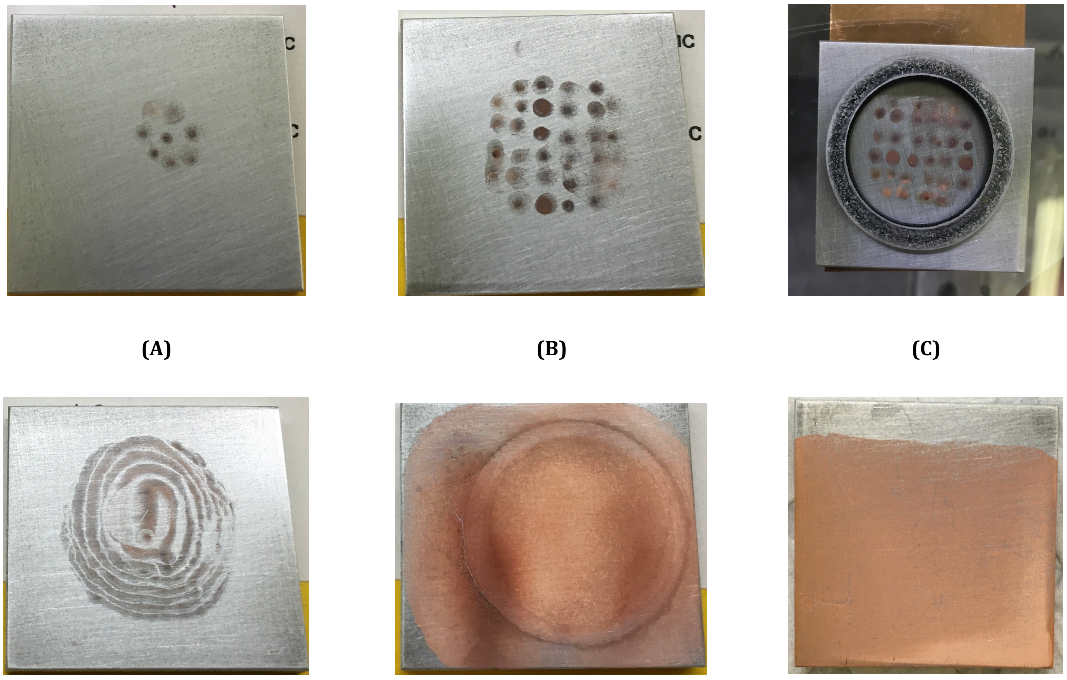


FIGURE 3: DEPOSITION OF A LINE OF COPPER USING THE ECAM WRITING TIP. THE LINE IS APPROX 1 MM WIDE AND 20 MM LONG

In the setup used for the electrochemical experiments the pipette tip was held stationary and the substrate was brought in liquid meniscus contact with the metal substrate with the vertical use of a lab jack. The power supply was switched on for 20 sec to deposit Cu metal as circular dots. The position of the substrate was changed and the process repeated to increase the number of dots. In this way AA7475 samples with an increasing amount of Cu dots were generated (Figures 4A and 4B). The stability of the liquid meniscus on the metal surface, however was compromised by the surface preparation by abrasion which gave leakages of the copper sulfate solution and which unfortunately resulted in inconsistent sizes of copper dots. To increase the amount of copper deposited to cover the exposed metal surface inside the O-ring (figure 4C), the sample was manually moved continuously in contact with the tip meniscus (figure 4D). By way of comparison to larger deposits of copper the ecAM tip was replaced with a large droplet (figure 4E) or dipped in solution (figure 4F) and electroplated directly. Improvements to the copper dot deposition technique are shown in figure 6B on a polished AA7475 surface.



(A) (B) (C)

(D) (E) (F)

FIGURE 4: AA7475 SAMPLES WITH AN INCREASING AMOUNT OF COPPER DEPOSITED BY ECAM (A, B, D) AND BY ELECTROPLATING (E,F), FIGURE C SHOWS FIGURE B IN THE ELECTROCHEMICAL CELL O-RING.

AA7475 samples 4A, 4B, 4D and 4E (from figure 4) of increasing amounts of deposited Cu were electrochemically tested potentiodynamically (PDS) over the range -250 mV to +250 mV and compared with the starting AA7475 and pure copper metal (Figure 5). The expected progression of the Ecorr value from AA7475 (-0.689 V) to copper (-0.148 V), a difference of 540 mV, did not eventuate with the samples with deposited copper only moving up to 30 mV anodically.

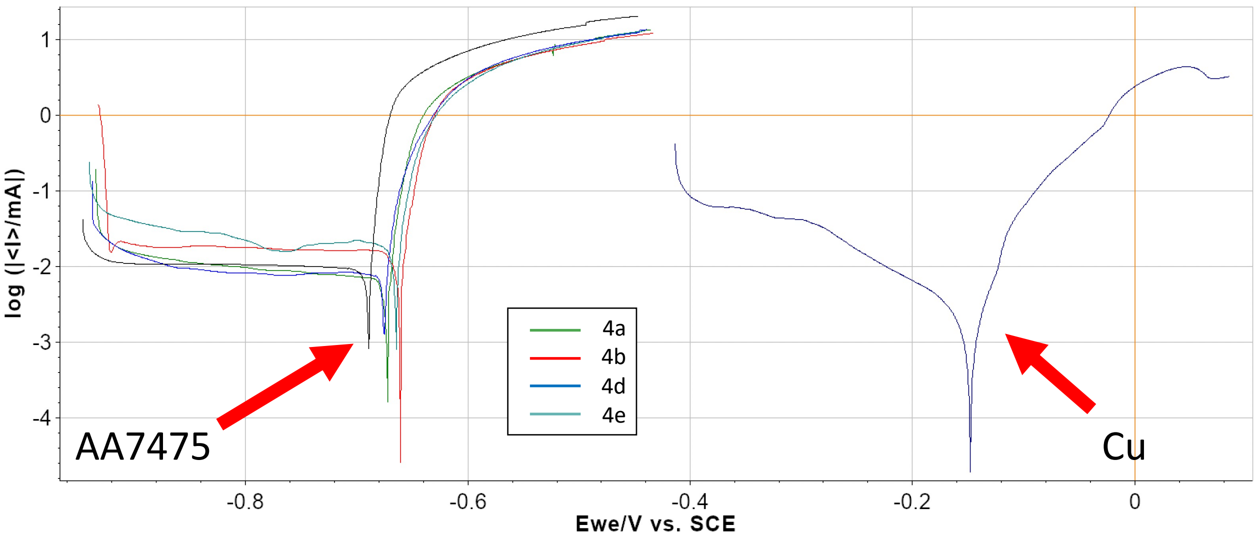


FIGURE 5: POTENTIODYNAMIC SCANS OF AA7475, SAMPLES OF CU DOTS ON AA7475 AND CU.

DISCUSSION

Twelve different aluminium alloys from five different grades of alloy (2xxx, 3xxx, 5xxx, 6xxx, 7xxx) were electrochemically tested by OCP and PDS for stability and reproducibility. AA7475 was chosen for experimental use in this paper although AA7075 and AA2024 gave similar reproducibility. The OCP of all three alloys was stable after only 6 minutes, whereas some of the other alloys tested had not stabilised sufficiently after 2 hrs. The stability and reproducibility of the substrate is important as the changes to Ecorr and Icorr values by Cu metal deposition could only be reliably determined from a reproducible starting point.

The use of ecAM as a method to electrochemically deposit different metals seems relatively easy once certain details have been overcome. The generation of a stable meniscus at the pipette tip in contact with the metal substrate is imperative, however. The difference between the experimental conditions used for the copper line shown in figure 3 and the copper dots shown in figure 4 may be due to the quality of the substrate surface preparation. For the Cu line the substrate was polished to a mirrored surface, whereas for the Cu dots the surface was only abraded. It is most likely that the additional surface roughness is sufficient to disrupt the surface tension of the meniscus droplet, causing leakages.

The potentiodynamic scans of the aluminium samples with increasing amounts of copper deposited did not show the expected linear progression from that of AA7475 to copper metal. This was surprising as the coverage by eye, of the aluminium surface by copper appeared complete, certainly in the case of sample 4F from figure 4. Re-examining the copper surfaces, however, showed that by tilting the surface with respect to light, the underlying aluminium surface was visible (Figure 6). It is likely the same roughly abraded surface which caused meniscus problems and leakages mentioned above also likely causes the electrochemical deposition and electroplating of copper selectively onto the aluminium surface, mostly likely on the top of the ridges of the abraded surface and leaving the ridge valleys remaining as uncoated aluminium. Initial experiments on a polished AA7475 surface showed better control of the droplets and subsequent copper deposition (figure 6B). Once these teething problems are solved, ecAM would be a powerful tool for depositing many different metals spatially on a surface for both electrochemical and corrosion inhibitor investigation. For example, an array of different metal dots deposited on a surface could conceivably be used as a high-throughput screening tool for corrosion inhibitors.

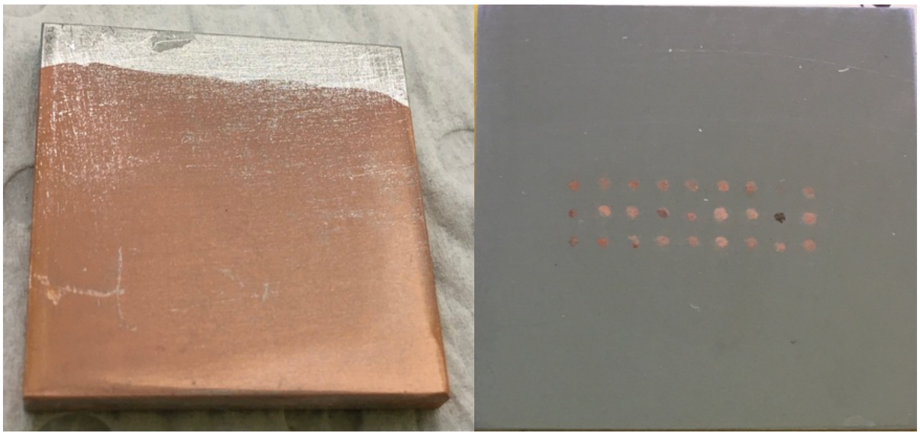


FIGURE 6: (A) SAMPLE 4F TILTED TO SHOW THE REFLECTION OF ALUMINIUM THROUGH THE ELECTROPLATED COPPER AND (B) IMPROVEMENTS IN THE DEPOSITION OF COPPER DOTS ON A POLISHED AA7475 SURFACE

CONCLUSIONS

Twelve different aluminium alloys were electrochemically tested and AA7475 was chosen as the preferred substrate for metal deposition by ecAM writing, due to its rapid and stable OCP. Copper metal dots were deposited on the metal surface in increasing amounts but insufficient surface preparation meant that the writing meniscus was unstable and leakages occurred. The same poor sample preparation was thought responsible for the incomplete deposition of copper, even when the sample appeared to have complete coverage. Possibly due to this, results from the potentiodynamic scans of the as-deposited copper on aluminium surfaces did not show the linear progression of Ecorr from aluminium to copper as expected.

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AUTHOR DETAILS

	Dr Paul White is a Principal Research Fellow at RMIT University. He has developed new high-throughput techniques for corrosion inhibition together with the data capture and data analysis of the resulting cavalcade of ensuing experimental data, resulting in various patents relating to corrosion inhibitor protection of aerospace aluminium alloys and steel.
	Felix Nugraha Lomo completed his Bachelors & Masters by Research in Engineering at RMIT University (Melbourne, Australia). During his Masters, he developed a design & fabrication framework for 3D titanium components fabricated via cold spray additive manufacturing. This included composite selection, FEA simulation, and implementation of manufacturing constraints into design topology optimisation. He started his PhD at RMIT in July 2023, which focuses on new, high-performance titanium alloys development via AM.
	Ivan Cole is a Professor of Engineering at RMIT. Research interests are corrosion modelling and sensing and development of new inhibitors. His modelling work focuses on linking scales from the molecular to the continental to understand both the fine scale process and the factors controlling corrosion. His sensor work concentrates on AI to enhance sensor data interpretation while he is developing rapid discovery methods (for inhibitors) combining molecular modelling , AI and robotic electrochemistry