

A localized investigation on the corrosion of AA2024-T3 galvanically coupled to graphite in NaCl solution: inhibitive effects of cerium chloride and triethanolamine

L.B. Coelho^a, M. Taryba^b, M. Alves^b, M.F. Montemor^b, M.-G. Olivier^{a,c}

^a Materials Science Department, Faculty of Engineering, University of Mons, 20 Place du Parc, 7000 Mons, Belgium

^b Centro de Quimica Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

^c Materia Nova asbl, Avenue Copernic 1, 7000 Mons, Belgium

Introduction

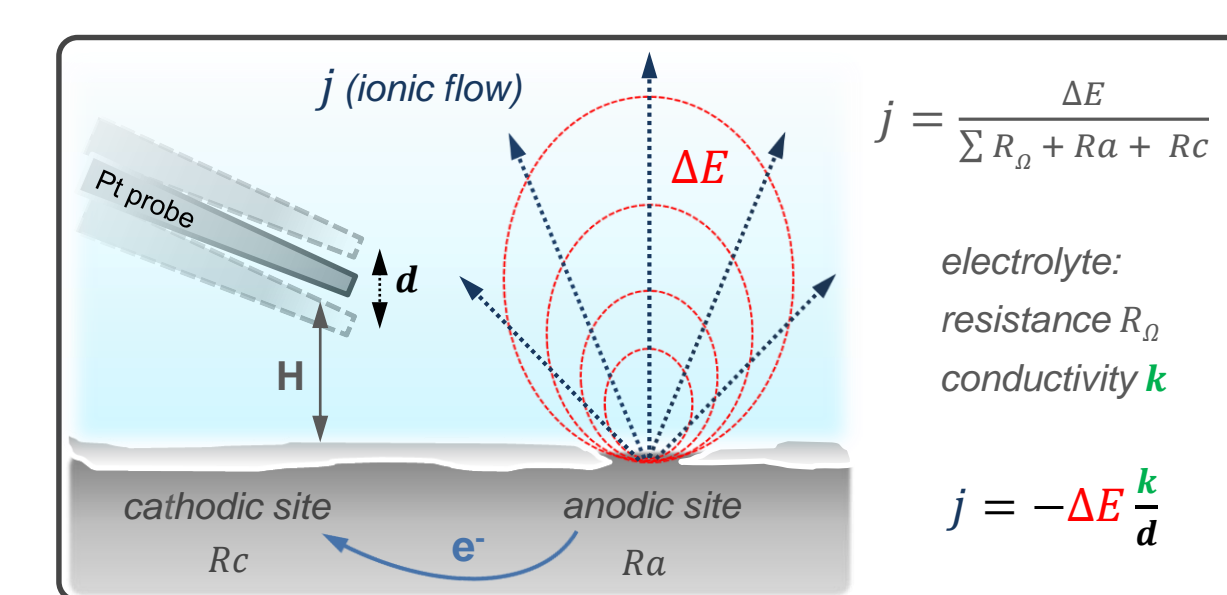
The inhibition mechanisms of cerium salt and triethanolamine on the galvanic corrosion of AA2024-T3/graphite exposed to NaCl solution was investigated by localised electrochemical techniques. Quasi-simultaneous localized measurements of ionic current densities and pH were achieved by employing the Scanning Vibrating Electrode Technique (SVET) and the Scanning Ion-Selective Electrode Technique (SIET). After the electrochemical tests, the surfaces were studied by Scanning Electron microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX). X-Ray Photoelectron Spectroscopy (XPS) analysis was applied to determine the valence state of Ce-based precipitates formed on both graphite and alloy surfaces. This work discusses the corrosion inhibition mechanism of cerium chloride or triethanolamine on two AA2024-T3/graphite galvanic couples, (electrodes area ratio 10 and 1.5).

Materials and Methods

M1 and M2: model galvanic couples made of AA2024 and graphite assembled to simulate the galvanic corrosion processes occurring at the AA2024/CFRP interface. The samples were mounted into an epoxy resin, a 0.13 mm thick graphite foil (99.8% pure, Alfa Aesar) in parallel either to the alloy coupon, AA2024-T3 (Q-Lab) (**M1**) or to the alloy rod (**M2**). The final ratios between the area of AA2024 and that of graphite were 10 and 1.5, respectively for M1 and M2.

SVET equipment (Applicable Electronics™) and software (Science Wares™). SVET/SIET measurements were performed quasi-simultaneously [2]. Insulated Pt-Ir probes (MicroProbes™) with a platinum black deposited on the probe tip were employed as microelectrodes for SVET measurements. The probe was vibrated in two perpendicular planes, vertical (Z) and horizontal (X), at frequencies of 124 Hz (Z) and 325 Hz (X), respectively. The probe diameter was 16 μm, the amplitude of vibration was 32 μm (peak to peak) and it was positioned 100±3 μm above the sample surface. Only the data obtained in the vertical plane of vibration (Z) were considered for further analysis. For the SIET pH measurements, glass capillary micro-electrodes with a tip orifice diameter of 1.8±0.2 μm were used. A pH selective ionophore-based membrane, specially developed for corrosion applications, was placed 50±5 μm above the surface [2]. A homemade Ag/AgCl/0.05M NaCl mini-electrode was used as external reference electrode. Both, current density and pH, were recorded on a 36×26 (sample M1) and 31×21 (sample M2) grid in 0.012 M NaCl solution. Corresponding distributions were recorded every hour. The scanned area was about 3.5 mm × 4.6 mm.

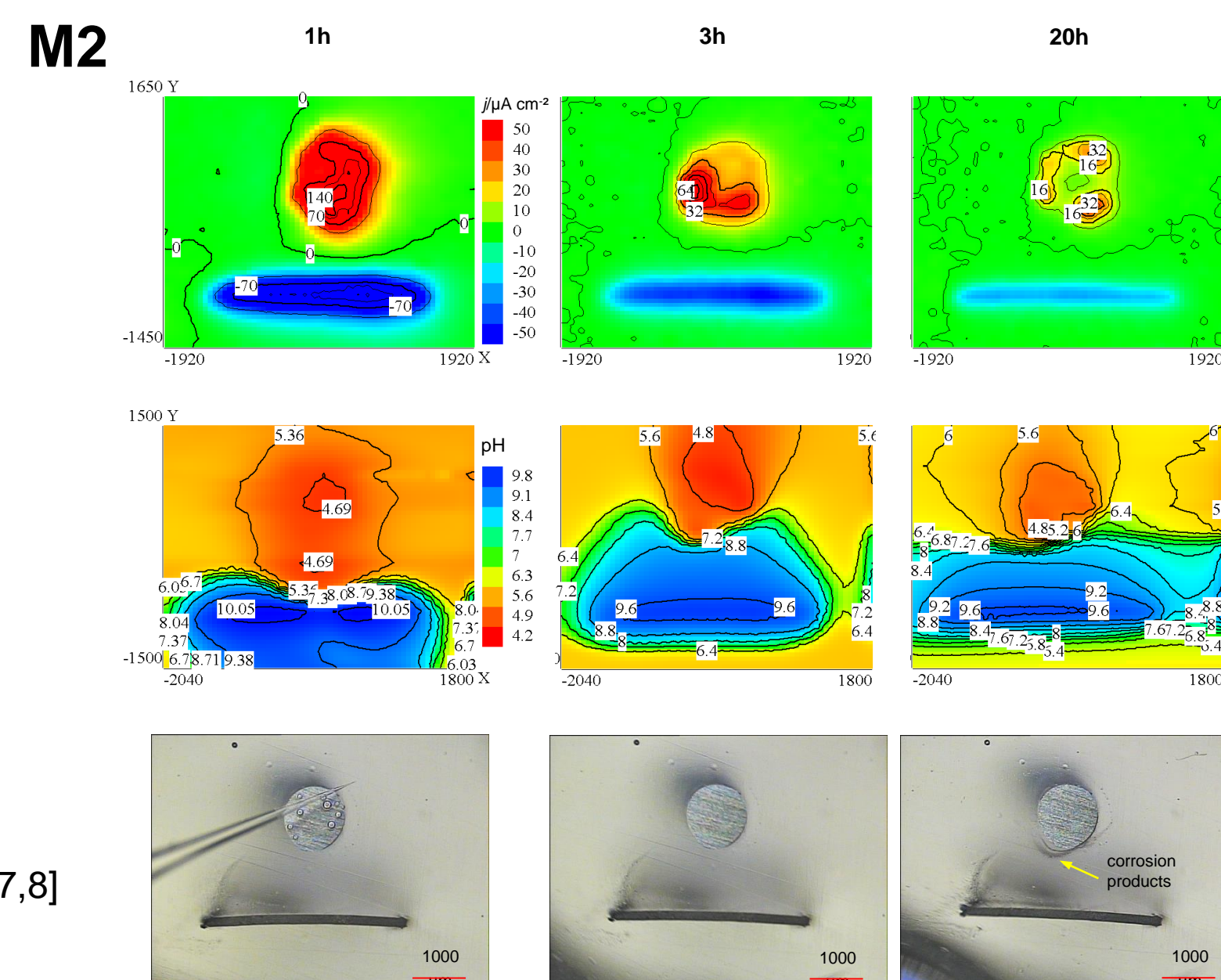
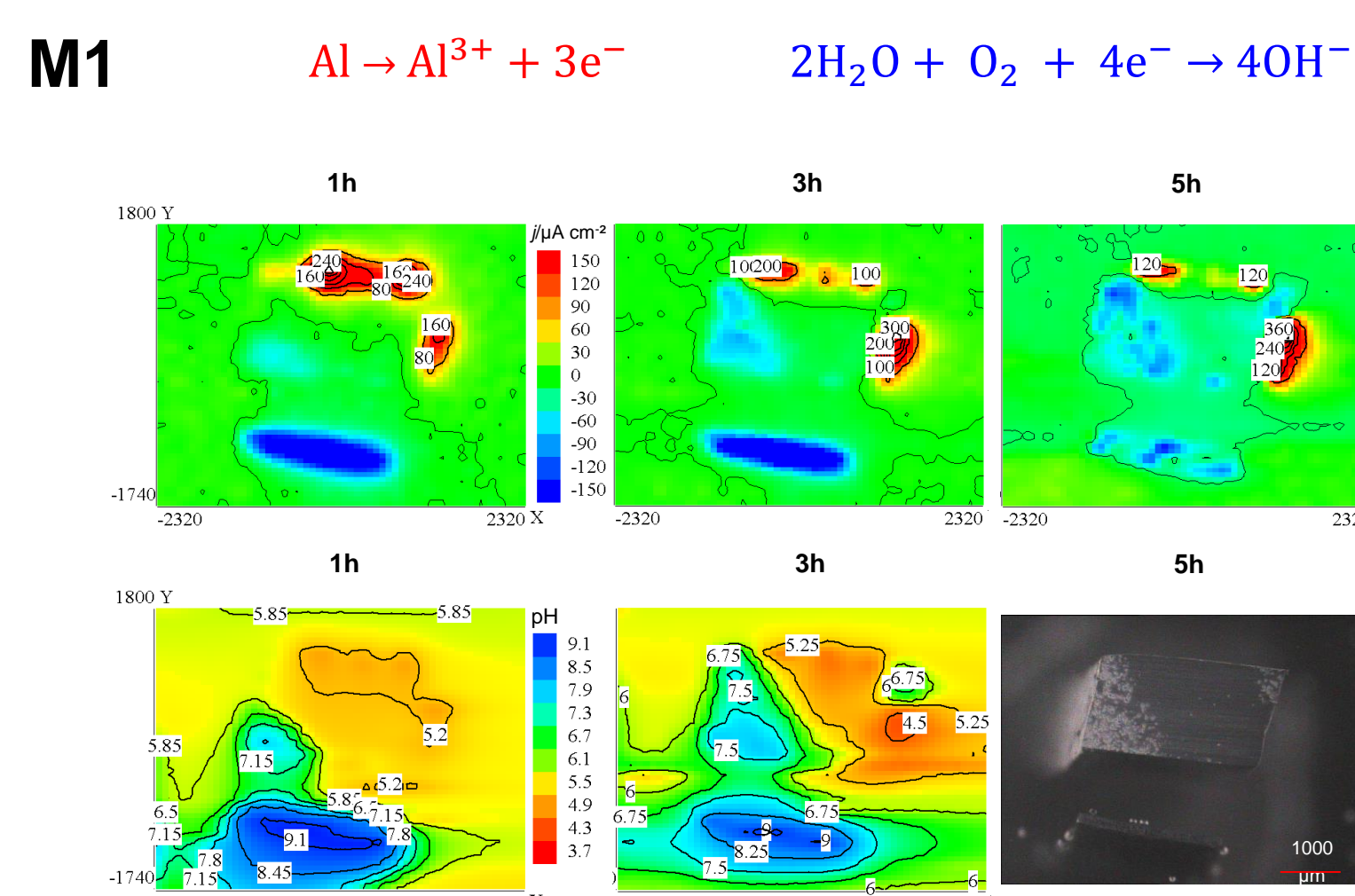
SVET: local characterisation of corrosion activity under freely corrosion conditions. Measurement of **electric potentials** generated due to **ionic flows** related to the **electrochemical reactions**. ΔE detected using a **vibrating probe** coated with Pt [3,4].



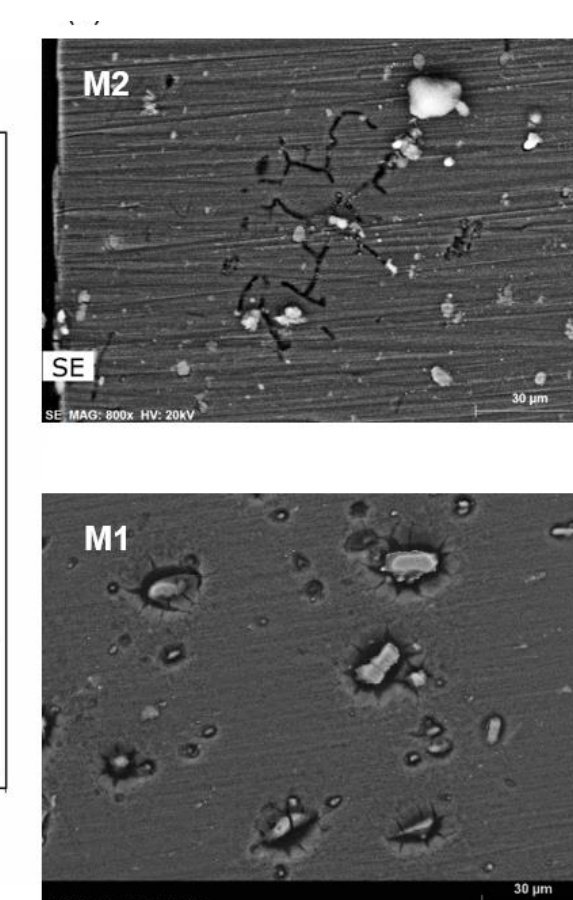
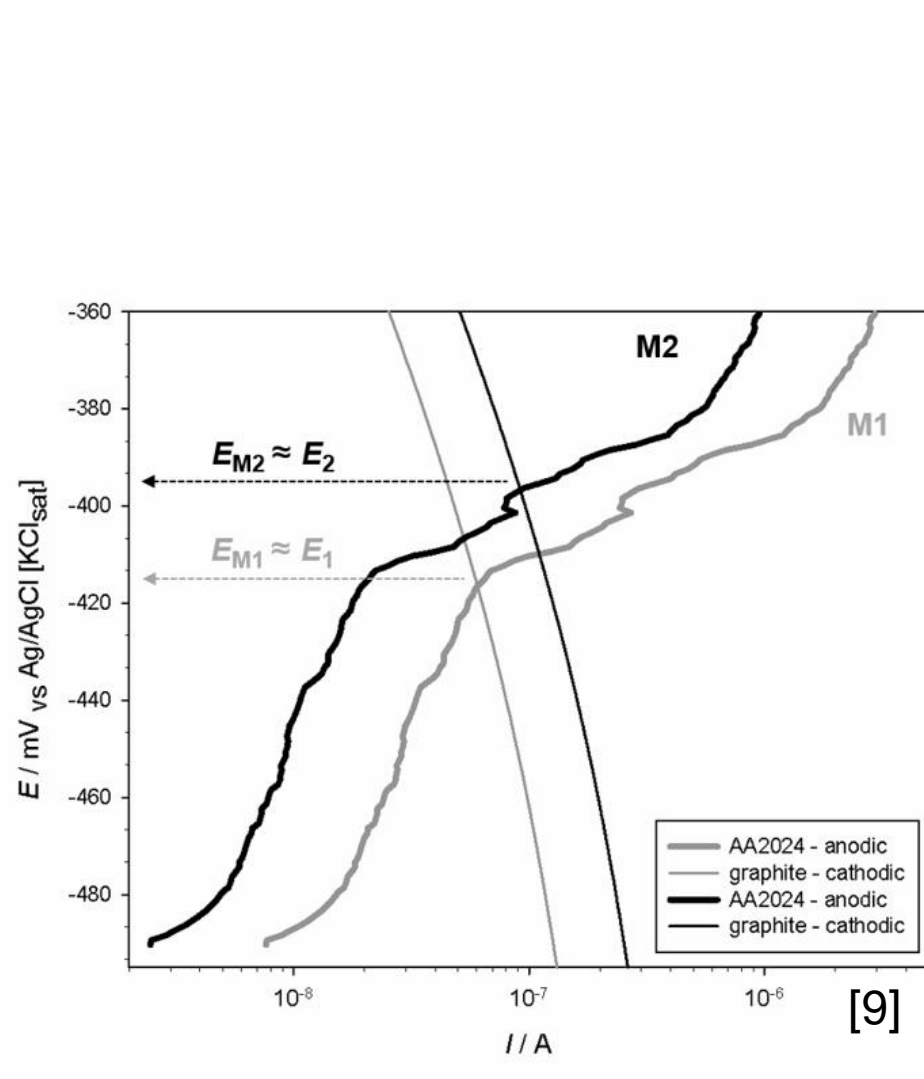
SIET: local distribution of ionic species (pH) using anion-selective microelectrodes [5,6]. Ionic concentration ↔ potential changes

Results

SVET/SIET analysis: corrosion behaviour in 12.00 mM NaCl solution



M1 vs. M2: corrosion behaviour in 12.00 mM NaCl

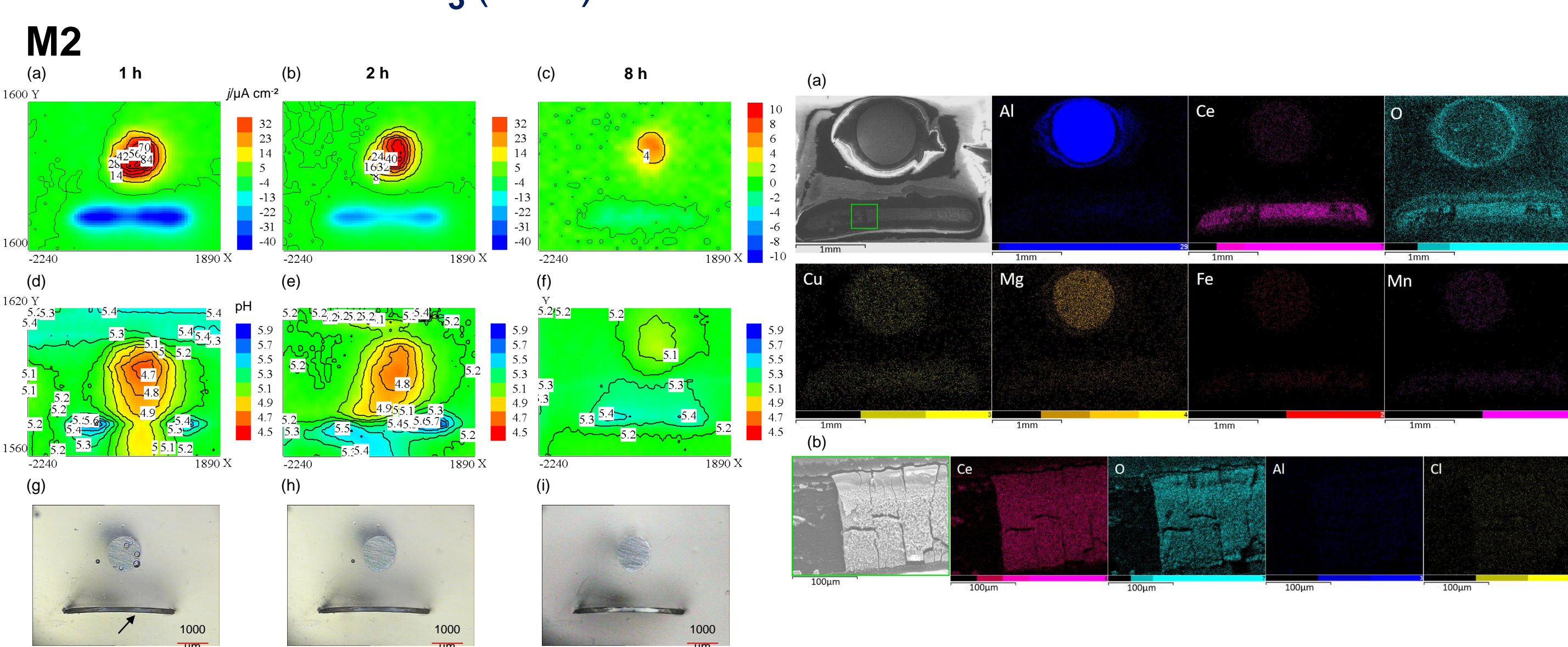
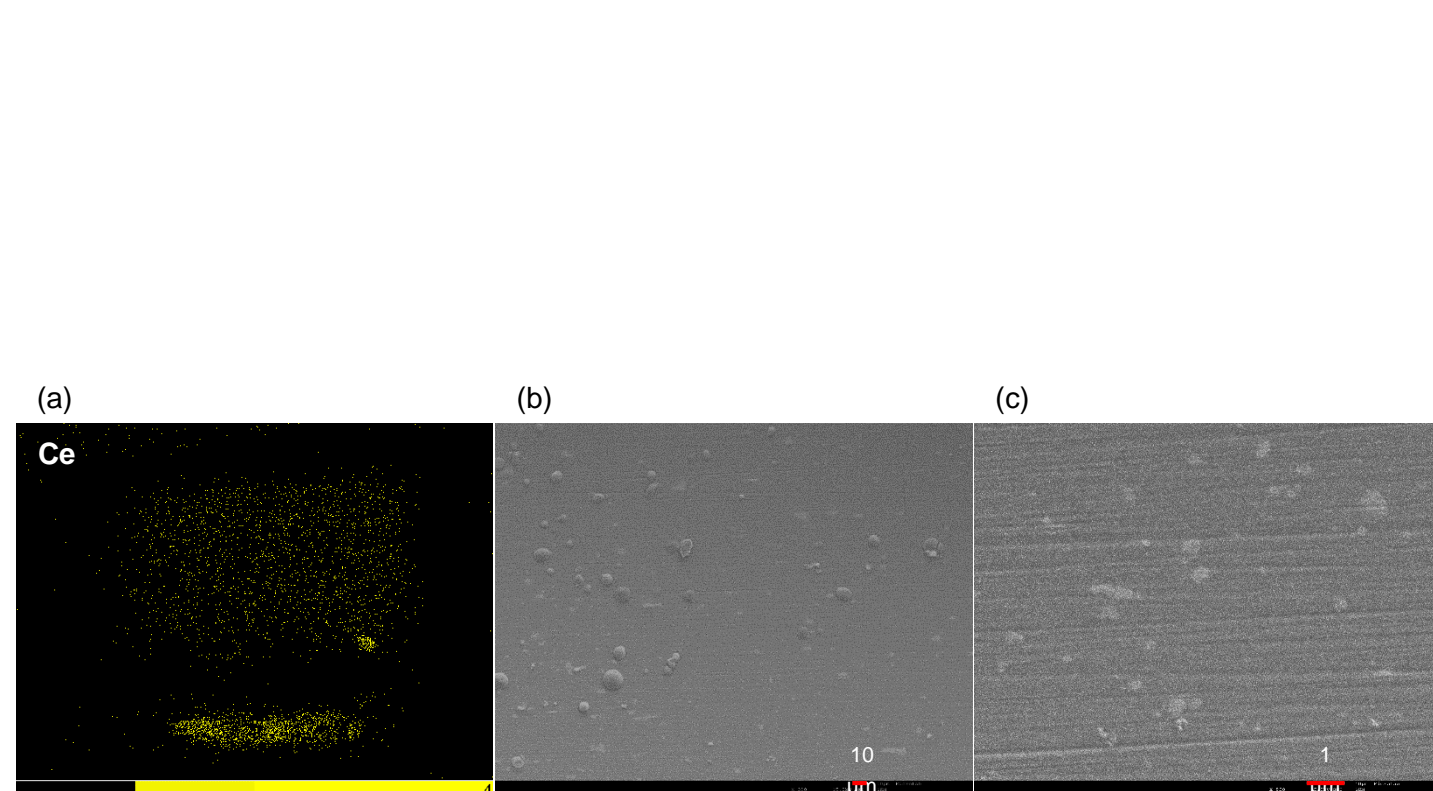
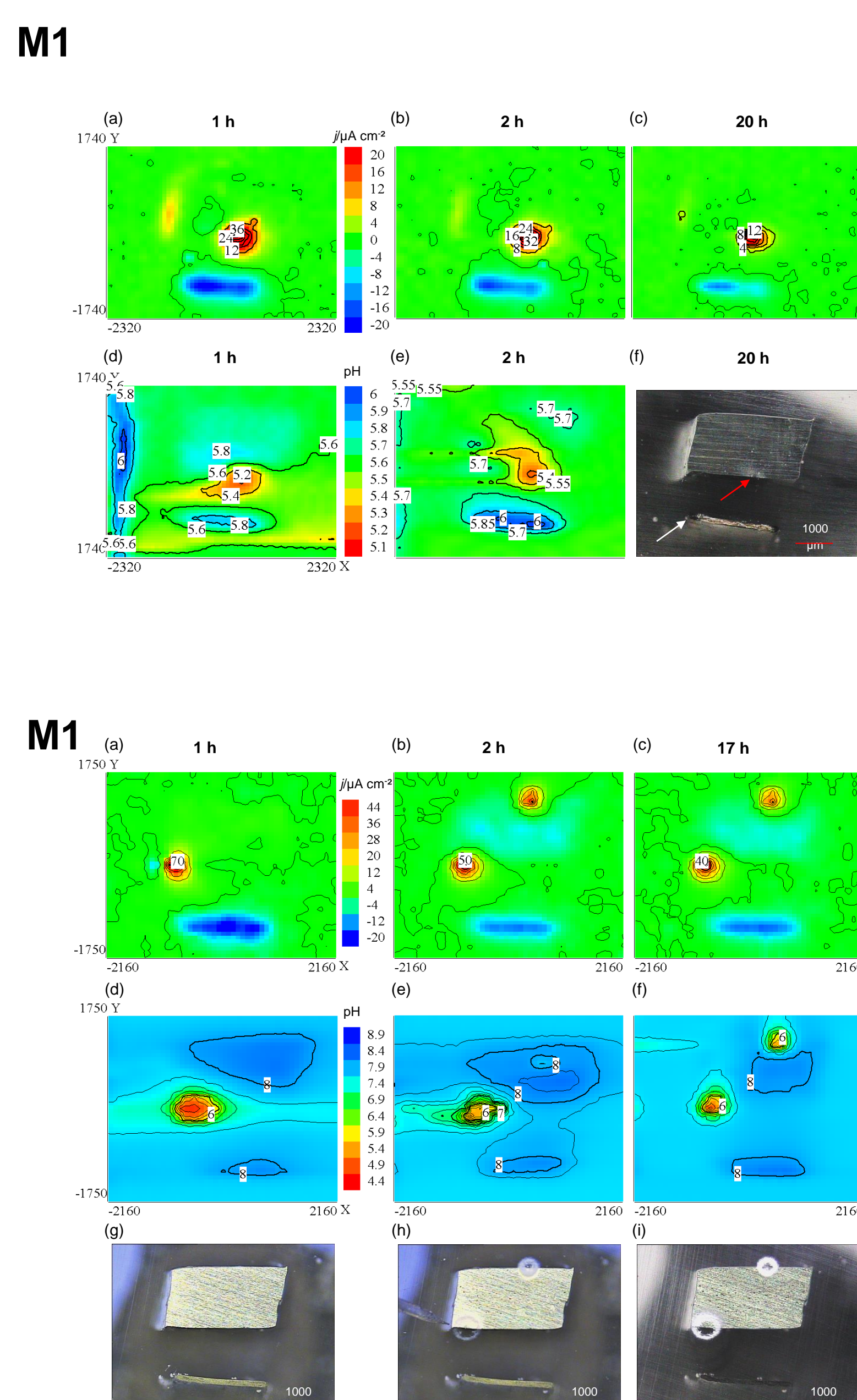


→ generalised dissolution of AA2024 matrix + intergranular corrosion

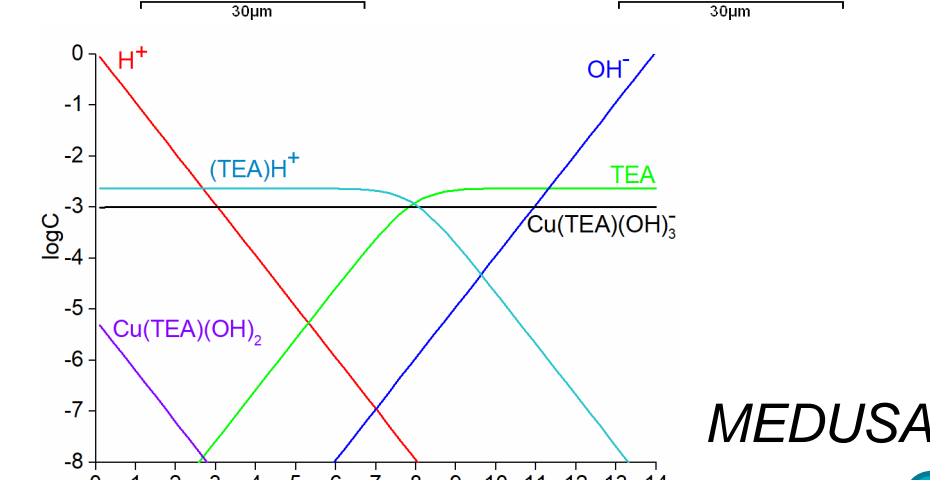
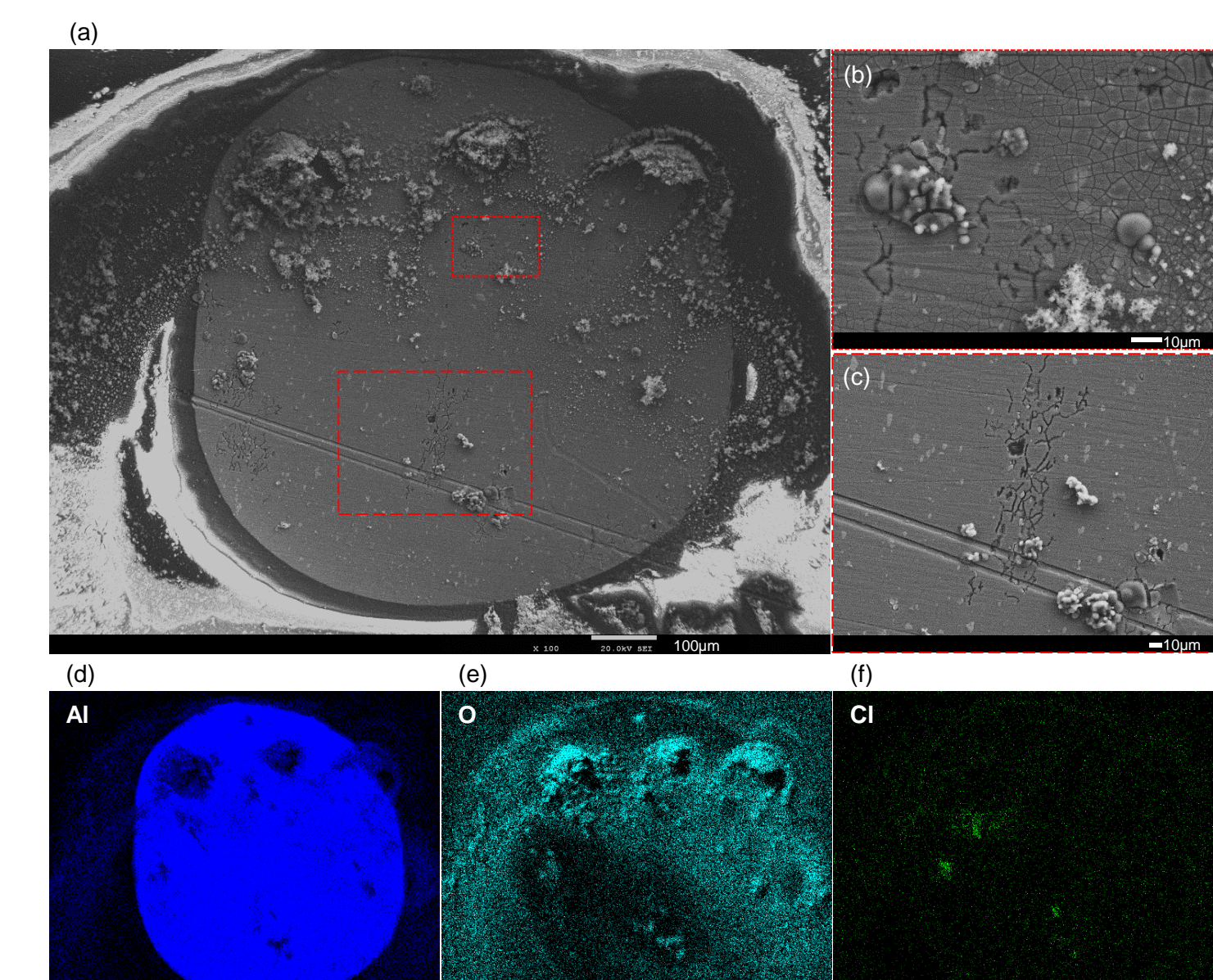
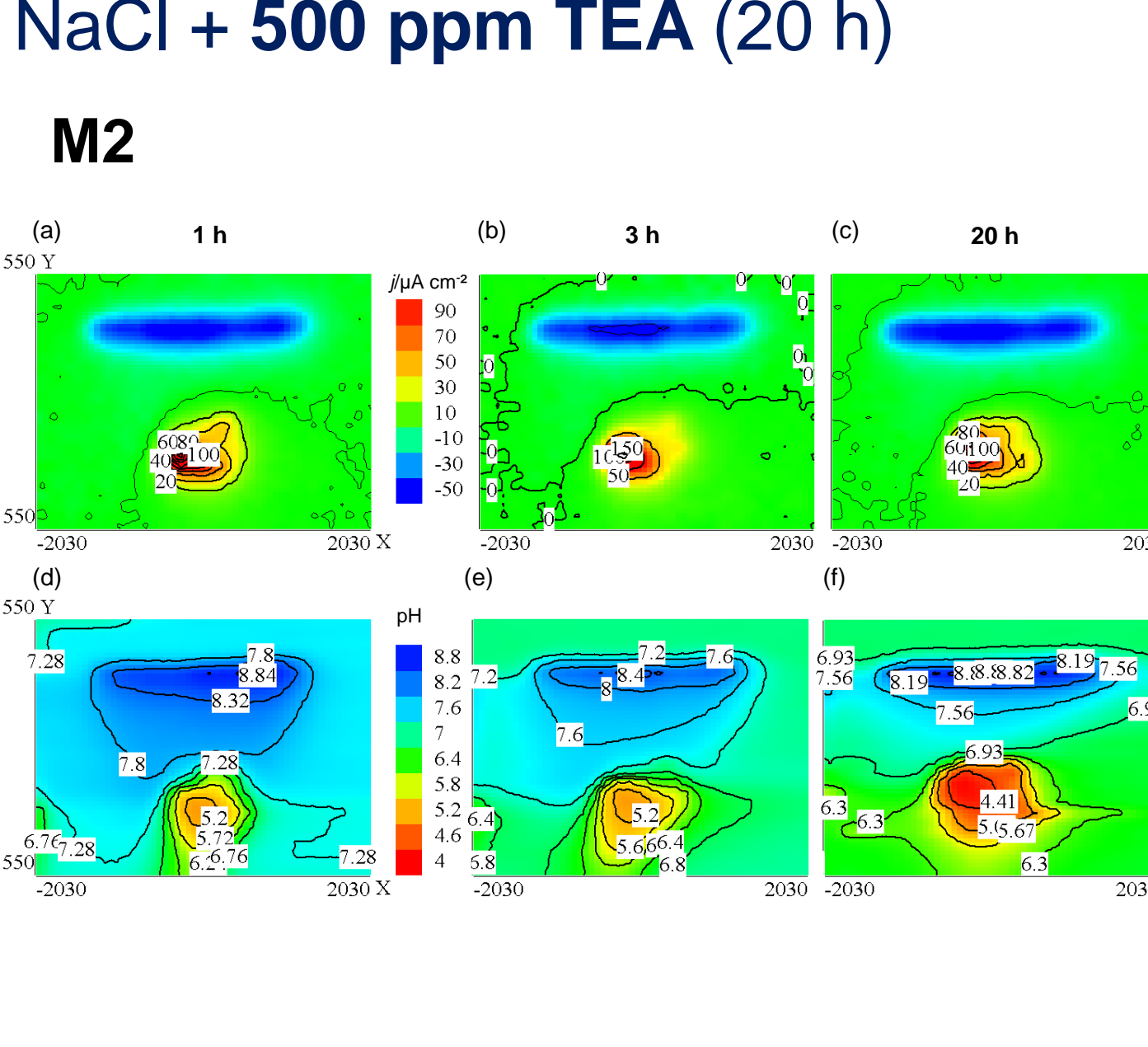
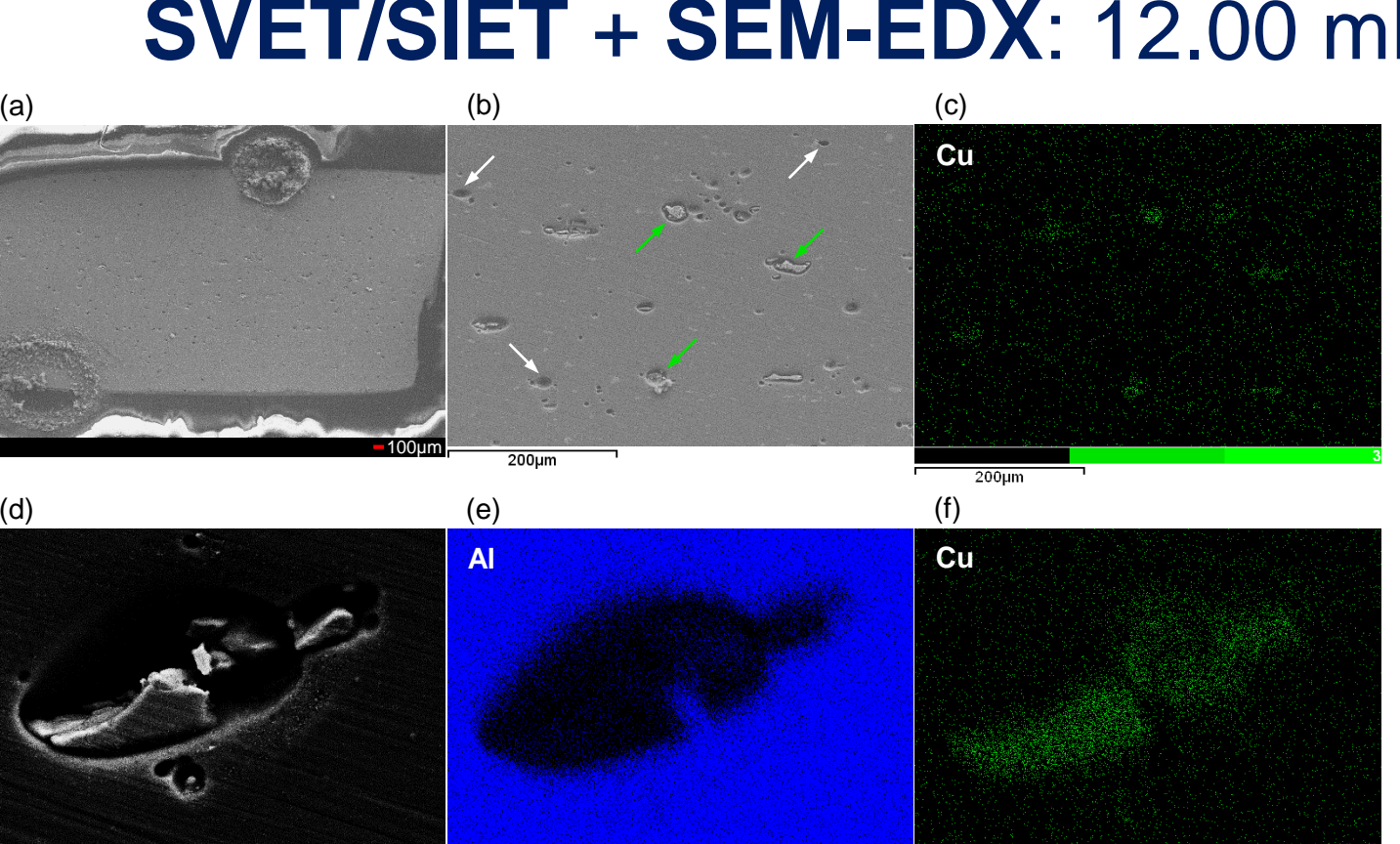
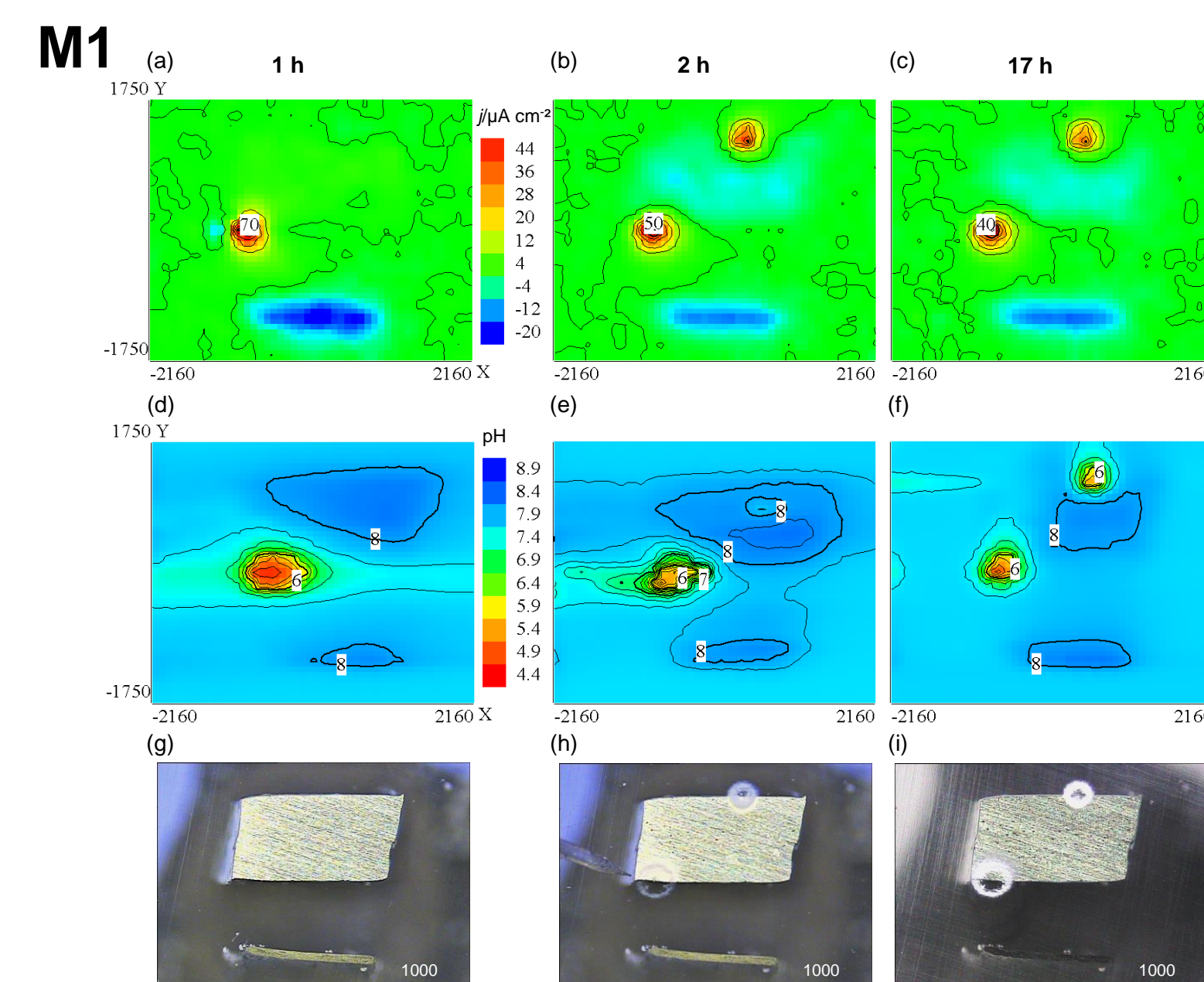
→ Cu redeposition [10-12]

→ trenching = chemical + electrochemical dissolution processes

SVET/SIET + SEM-EDX: 8.25 mM NaCl + 1.25 mM CeCl₃ (20 h)



SVET/SIET + SEM-EDX: 12.00 mM NaCl + 500 ppm TEA (20 h)



References

Conclusions

- ✓ quasi-simultaneous SVET/SIET: corrosion mechanisms of AA2024-T3/graphite models with different area ratios
- ✓ corrosion of AA2024: **M1** → trenching process; **M2** → generalised dissolution (matrix and grain boundaries)
- ✓ **CeCl₃**: inhibition of trenching and IGC (**M1**) but not of generalised dissolution (**M2**)
- ✓ **TEA**: inhibition of AA2024 self-corrosion (**M1**) due to complexation reactions with Cu ions

[1] L.B. Coelho, et al., Electrochim. Acta. 277 (2018) 9–19.
[2] S. V. Lamaka, et al., Electrochem. Commun. 13 (2011) 20–23.
[3] A.C. Bastos, et al., Port. Electrochim. Acta. 21 (2003) 371–387.
[4] H.S. Isaacs, Corros. Sci. 28 (1988) 547–558.
[5] B.R. Horrocks, et al. Anal. Chem. 65 (1993) 1213–1224.
[6] C. Wei, et al., Anal. Chem. 67 (1995) 1346.

[7] H. Shi, et al., Corros. Sci. 88 (2014) 178–186
[8] R.G. Buchheit, J. Electrochem. Soc. 144 (1997) 2621.
[9] Zhang, et al., Electrochim. Acta. 48 (2003) 1193–1210.
[10] G.S. Chen, et al. Corrosion. 52 (1996).
[11] P. Leblanc, et al., J. Electrochem. Soc. 149 (2002) B239.
[12] W. Qafsaoui, et al., Corros. Sci. 92 (2015) 245–255.