

Chromate Inhibition of Filiform Corrosion on Organic Coated AA2024 T3 Aluminium Alloy Investigated using a Scanning Kelvin Probe

H. N. McMurray, G. Williams and S. O'Driscoll
Department of Materials Engineering

University of Wales Swansea, Singleton Park, Swansea
SA2 8PP, UK.

The scanning Kelvin probe technique (SKPT) is used to study the influence of in-coating strontium chromate (SrCrO_4) dispersions on the kinetics and mechanism of filiform corrosion affecting polyvinyl butyral (PVB) coated AA2024 T3 aerospace aluminium alloy. Recent studies have shown that the SKPT is capable of spatially resolving free corrosion potential (E_{corr}) distributions associated with individual filaments and of following the evolution of E_{corr} distributions over time as filaments initiate, propagate and terminate.^{1,2}

AA2024 T3 samples are bar coated with an ethanolic solution of PVB, in which is dispersed any required amount of SrCrO_4 (primary particle size $<1 \mu\text{m}$). Air drying then gives a dry PVB film thickness of $30 \mu\text{m}$. A 1 cm long penetrative defect is scribed in the coating normal to the rolling direction and filiform corrosion initiated by introducing $1 \mu\text{l}$ of 0.5 mol dm^{-3} aqueous HCl into the defect region. Post-initiation, samples are maintained at 20°C and 93% R.H. SKPT scans encompassing the scribed defect are carried out immediately following initiation and at regular intervals thereafter. Repeated SKPT scanning is used to generate time-lapse animations showing the dynamic evolution of localised free corrosion potential (E_{corr}) patterns associated with filiform corrosion.

In the case of uninhibited coatings E_{corr} values beneath the intact PVB coating are ca. -200mV vs. SHE which is consistent with the coated aluminium surface existing in a substantially passive state. In the head region of propagating filaments E_{corr} values fall to ca. -500 mV vs. SHE indicating local depassivation, as shown in figure 1. However, figure 1 also shows that E_{corr} values in the filament tail region are ca. 100mV vs. SCE, indicating local superpassivation. The position of filiform heads in any SKPT scan may therefore be determined by locating the associated E_{corr} minima. Following the position of individual filament heads in successive SKPT scans shows that filaments propagate at a constant speed of $1.3 \pm 0.2 \mu\text{m min}^{-1}$ along the rolling direction and do not intersect. A schematic representation of the filiform corrosion mechanism and its correspondence to the E_{corr} profile observed along the long axis of the filament is shown in figure 2.

As the SrCrO_4 content of the PVB coating is increased from zero to 1 vol% so E_{corr} values measured beneath the intact coating decrease from -200mV to -400mV vs. SHE. This shift in potential is consistent with SrCrO_4 acting primarily as a cathodic inhibitor, possibly due to the cathodic deposition of Cr(III) (hydr)oxide at the metal-coating interface. As SrCrO_4 levels from 1 to 10 vol% no further decrease in E_{corr} values beneath the intact coating are observed. Filiform corrosion may readily be initiated on samples containing in-coating dispersions of SrCrO_4 . However, the rate of filament propagation is markedly inhibited, being reduced by nearly 2 orders of magnitude at 5 vol% SrCrO_4 .

E_{corr} values measured in the head region of propagating filaments are substantially independent of coating SrCrO_4 content and remain similar to the uninhibited case, *ie. ca.* -500mV vs. SHE. However, E_{corr} values in the filament tail region are strongly influenced by SrCrO_4 levels and are shifted downwards from the uninhibited case (100mV vs SHE) to -50 mV for 5 vol% SrCrO_4 and -150 mV for 10 vol% SrCrO_4 . The absence of any anodic shift in E_{corr} values suggests that SrCrO_4 does not significantly increase the polarisation of anodic processes occurring in the filament head region. This is possibly due to the high solubility of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) salts and Cr^{3+} cations (the reduction product of dichromate) at the low pH values prevailing at the filiform corrosion cell anode site. Conversely, the cathodic shift in E_{corr} values in the filament tail region suggests that SrCrO_4 does increase the polarisation of cathodic processes occurring at sites in the filiform corrosion cell where the local pH is high enough for insoluble Cr(III) (hydr)oxide to be the predominant reduction product of CrO_4^{2-} .

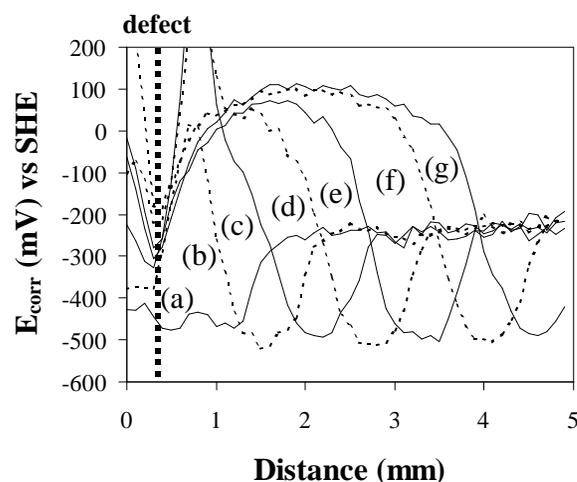


Fig 1. Time-dependent E_{corr} distributions along the axis of filament propagation: (a) 9.24h, (b) 16.12h, (c) 23.30h, (d) 30.41h, (e) 37.41h, (f) 46.17h and (g) 54.22h.

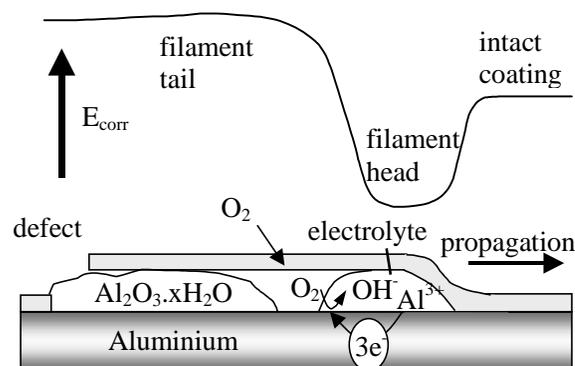


Fig 2. Schematic correlation between E_{corr} distribution and filiform corrosion cell.

REFERENCES

- W. Schmidt and M Stratmann, *Corrosion Sci.*, **40**, 1441. (1998).
- G. Williams, H. N. McMurray, D. Hayman and P. C. Morgan, *PhysChemComm*, **6**, (2001).

Keywords: SKPT, Kelvin probe, filiform corrosion, AA2024, aluminium alloy