The Mechanism of Chloride-Induced Filiform Corrosion on Iron Investigated by Time-Lapse Photomicrography.

T.M.Watson, H.N.McMurray, G.Williams, A.Coleman
Materials Research Centre, School of Engineering,
University of Wales Swansea,
Singleton Park, Swansea, SA2 8PP, UK.

The term filiform corrosion (FFC) was first used by Sharman in 1944, to describe filamentary trails of corrosion product forming on organic-coated iron (steel) surfaces at high relative humidity in air.[1] Filament heads are electrolyte-filled, containing Fe^{2+} and Fe^{3+} cations and aggressive anions such as Cl^-. Electrolyte pH towards the leading edge of the filament head is typically low (as low as pH 1) as a result of cation (Fe^{3+}) hydrolysis.[2,3] Conversely, filament tails are filled with dry, porous, corrosion product. Filament advance is driven by differential aeration arising from facile mass transport of gaseous O_2 through the filament-tail.[2,3] This implies that the principal site of cathodic oxygen reduction must lie towards the trailing-edge and that of anodic metal dissolution towards the leading-edge of the filament-head. Nevertheless, the mechanism of coating disbondment remains unclear. Mechanical prising by osmotic forces, anodic undermining and cathodic delamination have all been suggested as principal causes.[2,3] Knowledge of the chloride-induced FFC disbondment mechanism is obviously essential to the rational design of corrosion inhibitor and pretreatment systems for organic-coated iron and carbon steel exposed to severe marine environments. It has therefore been our aim to determine that mechanism and here we describe new insights obtained using a completely non-perturbing optical approach.

FFC is initiated by applying aqueous NaCl to an artificial penetrative defect on polyvinylbutyral (PVB) coated iron and allowed to propagate at 93% relative humidity. Animated, time-lapse image sequences are obtained using a metallographic microscope in conjunction with a specially designed optical gas cell, as shown in Fig 1. The gas cell allows O_2 partial pressure (pO_2) in contact with the head and tail portions of an individual filament to be varied independently. When both the filament-tail opening (at the penetrative coating defect) and the PVB coating over the filament-head are in contact with an N_2/O_2 atmosphere containing $pO_2 = 0.2$ Atms the filament is observed to advance in a saltatory fashion. Furthermore, filament saltation is linked to the formation of successive rings of dark precipitate at the perimeter of the filiform head, as seen in Fig 2. That is to say, the filament-head remains stationary whilst which each ring forms and forward movement occurs through ring rupture. When the filament-tail opening is maintained at $pO_2 = 0.2$ and the atmosphere over the filament-head is maintained at pO_2 = zero both ring formation and saltation cease and the filament-head advances smoothly. The diameter (width) of the filament-head is also observed to increase when filament-head pO_2 = zero. However, the time-averaged rate of filament advance is independent of head pO_2.

We proposed that the dark rings seen in Fig 2. form as a result of through-coating cathodic O_2 reduction acting to increase local pH at the perimeter of the filament-head.[4] This increase in pH leads in turn to the precipitation of $Fe(OH)_3$ through hydrolysis of Fe^{3+} cations present in the filament-head electrolyte droplet. On this basis, the finding that pO_2 over the filament-head does not affect filament propagation rate suggests that cathodic disbondment of the organic coating is not a rate determining process in FFC as it occurs on PVB coated iron.[5] Conversely, the finding that filament width is inversely dependent on pO_2 over the filament-head does seem to suggest that through-coating cathodic O_2 reduction is important in limiting the lateral spread of the filament-head electrolyte droplet

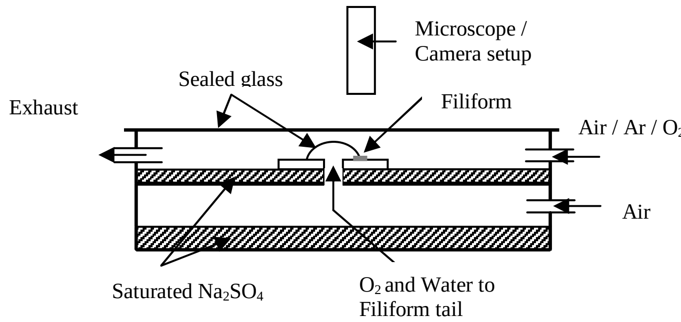

Fig 1. Optical gas-cell apparatus

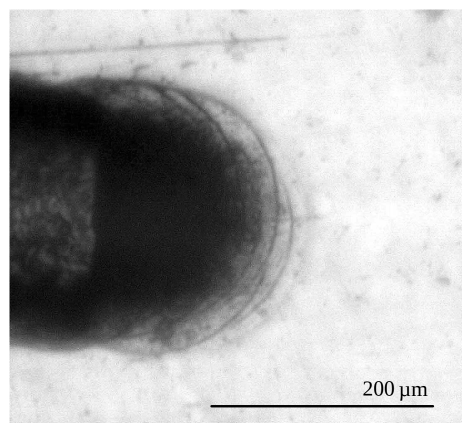

Fig 2. Filament-head micrograph (in air)

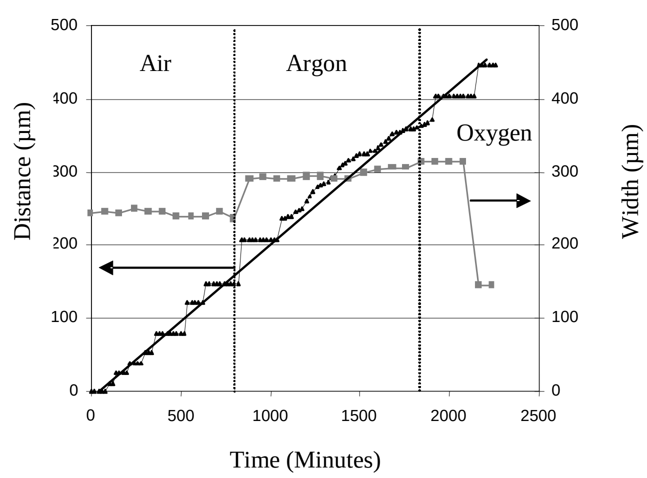

Fig 3. Filament distance traveled and filament width vs. time. Atmosphere labels refer to head compartment. Tail compartment atmosphere is air.

References

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