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The effect of oxygen partial pressure on the filiform corrosion of organic coated iron

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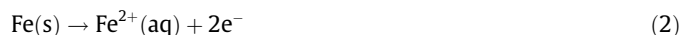
ABSTRACT

An *in-situ* time-lapse optical microscopy study, using a novel dual-compartment cell is used to gain mechanistic understanding of filiform corrosion (FFC) affecting an organic-coated iron surface. The apparatus allows independent control of environments surrounding the filament head and tail regions. When oxygen-containing environments surround the filament head, an anterior cathodic arc is formed, constraining the filament head electrolyte. When oxygen is removed from the vicinity of the head, FFC propagation rates remain unchanged, although the constraining arc is not present. Maximum propagation is observed when oxygen is available for transport through the filament tail to the rear of the head.

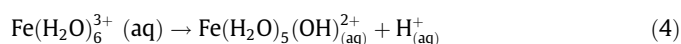
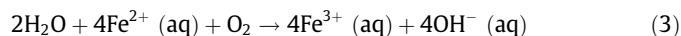
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1. Introduction

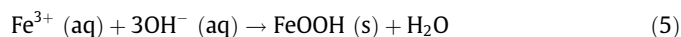
First accurately described by Sharman in 1944 [1], the term filiform corrosion (FFC) refers to a type of atmospheric corrosion affecting organically coated metal at high relative humidity, characterised by the appearance of filamentary (“worm-like”) trails of underfilm corrosion products. FFC has been shown to occur on iron, aluminium and magnesium surfaces and the subject has been extensively reviewed elsewhere [2–8]. The mechanism of filiform corrosion (FFC) propagation on organic coated iron (steel) remains contentious, with various processes including anodic undermining [2,9,10] cathodic disbondment [11–14] and mechanical disbondment through electro(osmotic) forces [2,15] proposed as the primary cause. Briefly, FFC occurring on organically coated iron (steel) consists of electrolyte filled filament heads, containing Fe^{2+} and Fe^{3+} cations and aggressive anions (typically Cl^-). Generally it is agreed that a differential aeration cell is created and maintained in the head electrolyte due to facile gaseous oxygen transport through the dry, porous filament tail [2–6]. The common consensus is that the principal site of cathodic oxygen reduction, reaction (1), lies at the back of the filament head and that anodic metal dissolution according to the reaction (2) occurs close to the filament leading edge.



Reaction (2) is thought to result in the undercutting of the organic coating at the filament head leading edge, and has been proposed as the principal cause of coating disbondment. Other reactions also occur within various regions of the electrolyte filled head, including the oxidation of Fe^{2+} cations by atmospheric O_2 and the ensuing hydrolysis of the aqueous hexa-aquo Fe^{3+} cations thus formed, represented by Eqs. (3) and (4) respectively.



A low pH is maintained in the filament head electrolyte by an partial Fe^{3+} cation hydrolysis, for which the first hydrolysis step is represented by (4) above. pH values of *ca.* 1 have been measured by others [3] in the vicinity of the leading edge of the filament head electrolyte. Sufficient alkalinity exists at the filament head/tail junction as a consequence of reaction (2) to cause complete hydrolysis of aqueous Fe^{3+} cations, producing insoluble solid corrosion product according to reaction (5).



As filament advance proceeds, a tail of corrosion product remains which progressively dries out with time, with the boundary between the filament head electrolyte and the tail marked by a discreet boundary, frequently observed as V-shaped feature.

The most contentious point in the mechanism of filiform on iron remains the role of cathodic oxygen reduction (reaction (1)) in the coating disbondment process. Since organic-coated iron is well

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known to undergo delamination via a corrosion driven cathodic disbondment mechanism when a group (I) chloride electrolyte is used to initiate underfilm corrosion [9], several authors have proposed that this process is also the primary cause of coating disbondment in FFC. Funke suggested that cathodic oxygen reduction occurs at a remote site which precedes the filament-head by a measurable distance [11,12], whereas others propose that cathodic disbondment occurs over a narrow region at the periphery of the filament-head leading edge. Using scanning Kelvin probe force microscopy (SKPFM), Leblanc and Frankel showed evidence of an anterior arc of cathodic activity extending outward beyond an advancing corrosion filament head [13]. The cathodic arc is formed via differential aeration, in an analogous manner to the localisation of corrosion within a water droplet placed on a steel surface, where O_2 diffusing vertically down through the organic coating to the underlying metal surface does so most rapidly where the electrolyte layer is thinnest, i.e. at the leading edge (or limb) of the electrolyte-filled FFC head. The subsequent generation of a zone of high pH at the iron/coating interface within the anterior cathodic ring was subsequently thought to play an important role in FFC propagation.

In this paper we employ micrographic *in-situ* time-lapse photography of organic coated iron samples undergoing FFC to elucidate the processes occurring within, and in the vicinity of propagating corrosion filament heads [16]. Experiments are carried out using an apparatus consisting of two separate chambers, allowing different oxygen partial pressure environments to be supplied independently to both the head and tail regions of individual FFC filaments. The main aim of the work was to quantify the effect of head and tail region O_2 partial pressure on both filament head morphology and propagation rate. Such studies in turn will reveal the relative importance of the possible oxygen transport routes to the FFC head, either through-coating or via the porous corrosion-product filled tail. A further aim of the work was to investigate the influence of the cathodic ring which precedes the electrolyte-filled head on FFC kinetics, to clarify its role in the overall mechanism of FFC propagation and determine whether cathodic disbondment is a rate controlling factor in iron FFC.

2. Experimental details

2.1. Initiation of filiform corrosion

Polyvinylbutyral-co-vinylalcohol-co-vinylacetate (PVB), molecular weight 70,000–100,000 was obtained from the Aldrich Chemical Company. All other chemicals were obtained from Aldrich Chemical Co. in analytical grade purity. A 15.5% w/w ethanolic solution of PVB, was applied to a 5×5 cm iron coupon of 1.5 mm thickness (99.9% Fe-supplied by Goodfellow Metals Ltd.) using a bar casting technique, leaving an air dried film thickness of ca. 30 μm , as measured using a micrometre screw gauge. FFC was initiated by creating an artificial defect 4 mm away from a central hole of radius 2 mm which had previously been drilled through the iron sample. A 2 μl solution of 0.0025 mol dm^{-3} FeCl_2 (aq) was carefully dispensed using a glass microcapillary along a linear 2 mm scribe cut through the coating using a clean scalpel blade. When the solution had dried along the penetrative defect, the sample placed in a constant humidity chamber and held at 93% relative humidity (rh) and a temperature of 20 $^\circ\text{C}$ for 14 days to allow FFC growth. Aqueous FeCl_2 was used as an initiating electrolyte as previous studies [9] have shown that when a Group (I) chloride is applied to a coating defect, a corrosion driven cathodic disbondment process occurs prior to the initiation of FFC. Since the present study seeks to quantify FFC propagation rates on an iron surface where the organic coating remains adherent, a chloride salt

comprising a cation which is incapable of carrying ionic current through the alkaline under-film electrolyte layer produced by cathodic disbondment was selected for the current investigation [9].

2.2. Dual compartment gas cell design

When a suitable individual filament had propagated a minimum distance of 2 mm from the defect, a glass dome of 6 mm diameter was sealed onto the surface of the coated iron sample using epoxy-adhesive. The dome was positioned in such a way that the filament head was outside the dome, with the scribed coating defect inside the dome, as illustrated in Fig. 1. The sample was then placed within a dual compartment cell, shown schematically and photographically in Fig. 2a and b respectively, consisting of two 200 mm diameter circular nylon vessels of 20 mm depth, clamped one on top of the other. The bottom vessel comprised a central well of depth 10 mm and diameter 100 mm, accommodating a layer of aqueous saturated salt solution required to maintain constant relative humidity. The top chamber also included a well of the same dimensions, within which a layer of aqueous saturated salt solution was placed, but also comprised a drilled hole of 2 mm diameter in a central circular raised platform of 50 mm diameter. The coated iron sample was sealed on top of this raised platform, again using epoxy adhesive, ensuring complete overlap of the holes in both sample and the base of the vessel. Both vessels were also fitted with gas inlet and outlet pipes, allowing different gas mixtures to be introduced to both chambers. A sheet of optically flat, clear Perspex placed over the top chamber allowed the sample to be viewed and photographed *in-situ*. An arrangement of rubber O-rings between the respective chambers and the Perspex viewing window ensured that all joints were gas tight. The whole assembly was clamped together using eight bolts inserted into threads machined into the bottom chamber.

This experimental setup was specifically designed to allow separation of the head and tail of a corrosion filament so that each could simultaneously be exposed to different gaseous atmospheres. The head of the filament, outside of the sealed dome, remains in contact with the gas in the upper coating compartment, while the coating defect and tail of the filament held within the dome is exposed to the environment in the bottom chamber. For all experiments reported in this paper, a relative humidity of 93% rh was maintained in both compartments throughout all experiments via the use of saturated sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) aqueous solution. However, the gas supplied to

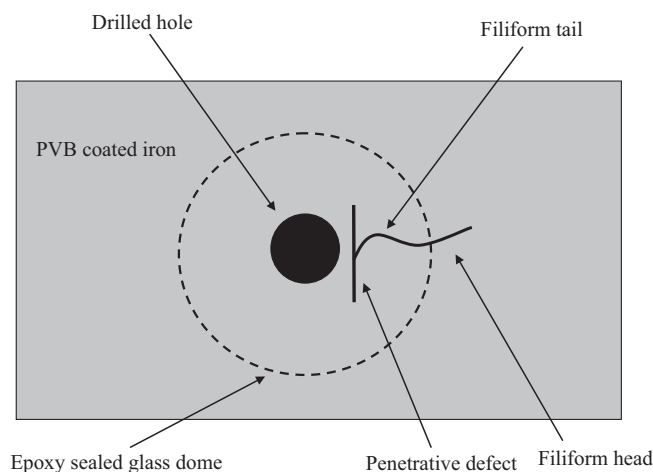


Fig. 1. Schematic diagram of sample preparation for dual-compartment cell.

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