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Cathodic disbonding of an unpigmented epoxy coating on mild steel under semi- and full-immersion conditions

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ABSTRACT

Cathodic disbonding of an unpigmented epoxy coating around a defect was studied with samples fully- and semi-immersed in 3.5 wt.% NaCl solution. Disbonding and the growth of blisters were monitored by scanning acoustic microscopy, which showed growth of blisters within the disbond for both type of samples. Scanning Kelvin probe potential maps suggest that blisters first form at local anodes. For semi-immersed samples, disbonding of the immersed part and the non-immersed part propagate with parabolic kinetics at identical rates, similar to fully-immersed samples. This implies that ion transport is along the coating–metal interface in both cases.

1. Introduction

Cathodic disbonding is an important degradation mechanism for organic coatings on steel structures subjected to coating damage that exposes bare metal to the environment. The start of attack on the exposed metal initiates cathodic reduction of oxygen beneath the surrounding paint that leads to loss of adhesion. Early papers showed that disbonding only occurs in solutions that contain alkali metal cations [1–7] which led to the conclusion that alkali generated by cathodic reduction of oxygen to hydroxyl ions is the cause of adhesion loss. However, more recently it has been argued that free radicals produced from oxygen reduction, not alkali, cause the damage [8], and Sorensen [9] demonstrated that adding radical scavengers to the paint suppresses disbonding – good evidence for this mechanism. However, tests with a variety of coatings showed that such additions were not always effective [9].

Several investigations have shown that the distance over which disbonding has taken place increases as the square root of time, or equivalently that area increases linearly with time, from which it has been argued that transport of cations along the interface is rate-controlling [3,4,8,10–17].

A correlation of disbonding rate with cation mobility or diffusivity was first noted by Leidheiser [4], though Sharman [10] found that although this was observed for unpigmented chlorinated rubber paint, addition of iron oxide pigment greatly reduced this dependence and suggested that in this case oxygen diffusion was rate limiting.

Many of these conclusions been confirmed and much further understanding has been gained using the scanning Kelvin probe (SKP) to follow the disbond front and to investigate electrochemical behaviour beneath the coating [8,18–23]. SKP is a non-contact, non-destructive device for measuring the work function (WF) difference between a sample and a vibrating probe; if there is a potential difference across the gap an alternating current (AC) is generated as the capacitance varies, so that by applying a bias to minimise the AC current the WF difference between sample and probe tip can be deduced. Stratmann [24,25] first showed that it can also be used as a quasi-reference electrode to measure the corrosion potential, so that potential maps can be plotted, even beneath an insulating coating. In disbonding experiments a steep change in potential is seen between the disbonded and intact areas, so that the progress of disbonding can be monitored. Potential within the disbond is also recorded. SKP measurements are generally made in humid air with only the defect exposed to salt solution, on the premise that if the critical species for disbonding are transported along the metal–coating interface, there is no need for solution to be present above the coating, or for an electric field to be present through the coating. Not all the evidence supports this. For instance in a classic series of double-cell tests, with one medium on the defect and another above the surrounding area of coating [4], it was shown that disbonding was influenced when either medium was changed. From similar double-cell tests Skar [9] deduced that ions pass through the coating above the defect. Deflorian and Rossi used a similar divided cell to show that applying cathodic polarisation to the defect alone had little effect on delamination rate, whereas with the whole panel polarised rate increased [26]. Various studies have shown that disbonding rate falls

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if the thickness of the coating is increased [4,10,13,16], typically a linear trend with negative slope, indicating a possible role for transport through the coating though the rate is not inversely proportional to thickness as would be expected for control by transport through the coating.

No single model seems able to account for all the observations, indeed it may be that mechanisms vary from case to case. To better understand the process of cathodic disbonding, two types of tests: full-immersion tests and semi-immersion tests have been compared in this work, using mild steel samples with unpigmented epoxy coating scribed to expose a controlled area of bare metal. The full-immersion tests characterise cathodic disbonding under normal immersion conditions. In the semi-immersion tests the scribed sample is immersed vertically in a covered beaker of solution with the horizontal scribe along the water line so that the coating below the defect is completely immersed in 3.5 wt.% NaCl solution, and that above the defect is exposed to water-saturated air. This design provides a critical comparison between two testing conditions (full-immersion *vs.* exposure to water-saturated air) on the same sample and helps to distinguish the route for ion transport or current flow. If there is a big difference between disbonding rates above and below the defect, then transport through the coating must be playing a significant part; if there is no significant difference, then the most likely explanation is that transport is mainly along the coating–metal interface in both cases. It can check whether SKP tests that only immerse the defect, while exposing the remainder of the panel to high humidity successfully replicate normal cathodic disbonding with the sample completely immersed in the solution.

Scanning acoustic microscopy (SAM) has been used to examine the coating–metal interface during disbonding and monitor processes beneath the coating. SAM is an *in situ* technique where focussed pulses of ultrasound are transmitted into the sample and reflected by interfaces in the sample [27]; contrast arises from differences in acoustic impedance, z, at the coating–metal, coating–water and water–metal interfaces ($z = \rho \cdot v$, where ρ = density of the material; v = acoustic wave velocity in the material), with contrast generated by point-to-point variations in elastic properties or separation. The signal is transmitted to the sample through a bath of water. Kendig, Addison and Jeanjaquet [28,29] conducted the first SAM studies of cathodic disbonding of hydroxyl-terminated polybutadiene on steel. It was found that circular features appeared within the disbond and propagated away from the scribe with increasing exposure time. Crossen has used SAM to examine adhesion loss during water exposure [30,31] and for the *in situ* examination of changes at the interface during cathodic disbonding of an epoxy-polyamide coating from mild steel exposed to a dilute NaCl solution [32]. He observed that within the first hour a region of disbonding developed adjacent to the scribe, followed by the arrest of disbonding and the growth of blisters ahead of the disbonded front. Alig [33,34] has recently used SAM to investigate cathodic disbonding of a series of coatings, and showed that addition of a clear coat to a primer radically changed its behaviour, suggesting that here transport through the coating is relevant. Disbonding takes place by a different mechanism involving the merging of blisters. The primer plus clear system exhibited linear disbonding kinetics, not parabolic.

2. Experimental

2.1. Sample preparation

Substrate: Cold-rolled mild steel Q-panels, from Q-Lab Corporation were used as substrate. They were 0.8 mm thick, 102 mm wide and 152 mm long, complying with ASTM A-366 and QQS-698, and ground on one side, specified by the manufacturer as having a roughness of 0.51–1.27 μm on the ground surface.

Organic coating: All coatings were provided by Akzo Nobel Ltd. (International Paint). Epoxy resin DER660-X80 (Dow chemicals) was supplied as 80% solution in xylene. The amine curing agent was a proprietary in-house phenalkamine epoxy adduct with an equivalent weight of 291 supplied as a 60% solution in xylene/butanol 3:1 by weight. The epoxy resin and amine curing agent were mixed at 71% stoichiometry, i.e. epoxy:amine 1:0.71 based on equivalent weights. The stoichiometry is the same as used in the commercial coating product from which the experimental formulations were derived. It is normal practice to formulate epoxy–amine coatings off stoichiometry and rich in epoxy resin.

Sample preparation: Mild steel panels were degreased with acetone and dried. The coating was applied with a steel rod (7 mm diameter) to the ground face of the panels using the draw-down method with one or more thicknesses of adhesive tape acting as a gauge that controlled wet-film thickness. The coating was cured at ambient temperature in a dust-free environment for at least 2 weeks before testing. After drying, the dry film thickness (DFT) of the coating was measured with a SHEEN SS120 film thickness gauge. Samples with DFT of 40 ± 5 μm were selected and cut to the size of 7 cm × 5 cm. A wire was soldered to the sample to allow tests with SKP. The back and the edges were sealed with a hot mixture of beeswax/colophony resin (4:1 by weight) covered by an additional layer of adhesive tape on top (to further protect the beeswax/colophony). A linear defect, 10 mm × 1.5 mm, was created at the centre of each sample in a direction parallel to its shorter side using a sharp 1.5 mm wide chisel-edged cutter. All defects were visually inspected for cleanliness and uniformity and for absence of damage to the surrounding coating. The samples were tested both fully- and semi-immersed in naturally-aerated 3.5 wt.% NaCl solution at room temperature. Fig. 1 gives a schematic diagram of the semi-immersion arrangement. Panels were hung vertically in a covered 1 L beaker with the waterline at the middle of the defect so that the part below the defect was completely immersed with the defect wet, while the part above the defect was exposed to water-saturated air.

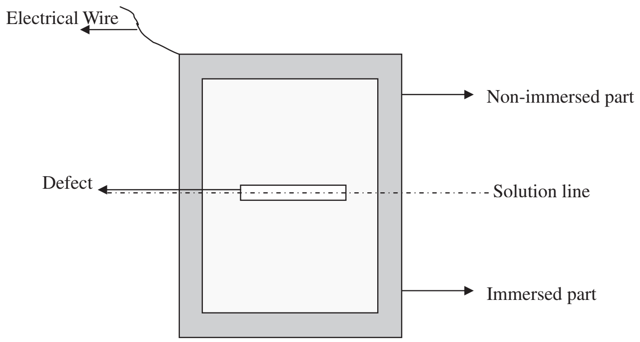

Fig. 1. Schematic diagram of the semi-immersion test (not to scale).

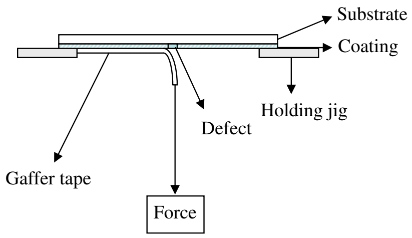

Fig. 2. Schematic diagram of peel test.