Determination of localised corrosion mechanisms using a scanning vibrating reference electrode technique

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A scanning electrochemical technique is used to show the influence of differential aeration on the kinetics and mechanism of corrosion reactions occurring at the exposed edge of galvanised sheet steels overcoated with organic layers of dissimilar thickness.

Mass produced organic coated galvanised sheet steel is of increasing importance in the construction industry. Metallic corrosion at exposed cut edges is a potential failure mechanism[1] which must be assessed when evaluating the performance of new coating technologies. Conventional methods for evaluating cut edge performance are empirical and rely on the measurement of coating delamination rates under accelerated corrosion conditions. This is often time consuming and gives little mechanistic information. Various conventional electrochemical techniques, most notably electrical impedance spectroscopy,[2–4] have been used to study the corrosion of organic coated metals. However, none of these techniques possess the spatial resolution necessary to investigate properly the highly localised electrochemical reactions occurring at the cut edge, where dissimilar metal surfaces are closely approximated. The scanning vibrating reference electrode technique (SVRET) enables the quantitative mapping of localised ionic current fluxes by the measurement of potential gradients in solution, and has been successfully used to investigate both galvanic[5–10] and pitting[11,12] corrosion. Here we describe the use of SVRET to elucidate the kinetics and mechanism of cut edge corrosion in a model series of laboratory prepared organic coated galvanised steel samples.

SVRET measurements are carried out in aqueous electrolyte and employ a vibrating microtip electrode which is mechanically scanned at a small fixed distance from the corroding surface. It has been shown[5] that the ac voltage signal detected by the vibrating electrode is proportional to the potential gradient (F) parallel to the direction of vibration which is in turn proportional to the current density component in that direction. Thus for a point current source (i) in a medium of conductivity κ, the value of F at any distance x, y and z from the source is given by:

$$F = \frac{iz}{2\pi\kappa(x^2 + y^2 + z^2)^{1.5}} \tag{1}$$

The apparatus used in this study comprised a 125 μm diameter platinum microdisc electrode vibrated normal to the scanned surface with a frequency of 140 Hz and amplitude of *ca.* 25 μm. The vibration frequency was set by a lock-in amplifier (EG & G model 5110) which also served to detect the SVRET signal. The vibrating electrode was positioned using a motorised, computer controlled, micromanipulator platform. All measurements were carried out in 0.86 M aqueous NaCl at 25 °C. The apparatus was calibrated using a known current density and was shown to exhibit an excellent linear response in the range 0.05–125 A m^{-2} at the scan height of 125 μm.

Laboratory prepared model samples were prepared from 1 mm thick sheet steel (composition: Fe 99%), which had been hot-dip coated in a molten zinc bath containing *ca.* 0.2 mass% Al to produce a 20 μm coating of practically pure zinc (composition Zn 99.85%, Al 0.15%) with minimal formation of iron–zinc intermetallic phases.[13] The galvanised samples were pre-treated with chromic acid to aid polymer adhesion before being overcoated on both sides with a 5 μm thickness of a heat cured epoxy based polymer (Beckers PVC primer supplied by Beckers Paints Ltd). This was performed on a continuous coil coating line with the organic coating applied using rollers. A 140 μm laminate coating, consisting of PVC, was then applied to one or both sides of the sheet to produce asymmetrically and symmetrically coated samples. The coated samples were cut into 2 × 1 cm coupons and all but one cut edge masked using epoxy adhesive. The exposed cut edge was carefully polished flat using fine emery paper (down to 1200 grade). The polished coupons were immersed in a shallow electrolyte bath which was in contact with room air. The concentration of dissolved oxygen (in bulk solution) was therefore assumed to be approximately constant at 2×10^{-5} mol dm^{-3}.[14] The exposed cut edge was positioned uppermost and horizontal, and scanned repeatedly with the vibrating probe moving in a plane 125 μm above the exposed metal surface. The results of this type of experiment are illustrated in Fig. 1(*a*)–(*c*) which show isocurrent contour maps of ionic current density in the plane of scan. Areas of positive current, associated with anodic activity at the metal surface, are shown as light and areas of negative current, associated with cathodic activity, are shown as dark. Free corrosion potentials of −0.65 and −1.05 V *vs.* SCE were measured in 0.86 M aqueous NaCl for mild steel and zinc respectively and it is therefore to be expected that zinc coating will cathodically protect steel at the cut edge. On this basis it is assumed that the predominant electrochemical reactions occurring under the experimental conditions are the anodic dissolution of zinc [eqn. (2)] and the cathodic reduction of oxygen at the steel surface [eqn. (3)].

$$\mathrm{Zn = Zn^{2+} + 2e} \tag{2}$$

$$\mathrm{O_2 + 2H_2O + 4e = 4OH^-} \tag{3}$$

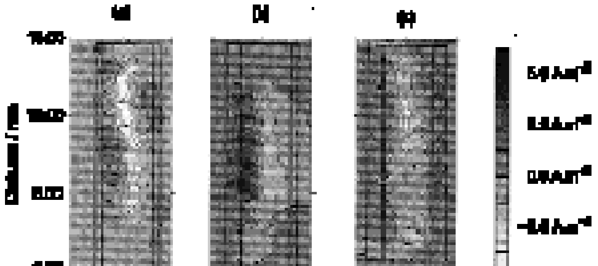

Fig. 1 Isocurrent contour plots showing the anodic (light) and cathodic (dark) current density distributions over (*a*) a corroding cut edge with 5 μm epoxy primer both sides, (*b*) an identical sample with a 140 μm PVC coating applied to one side and (*c*) an identical sample with a 140 μm PVC coating applied to both sides. The sample position is shown together with schematic representations of the relative coating thicknesses applied to each side of the sample.

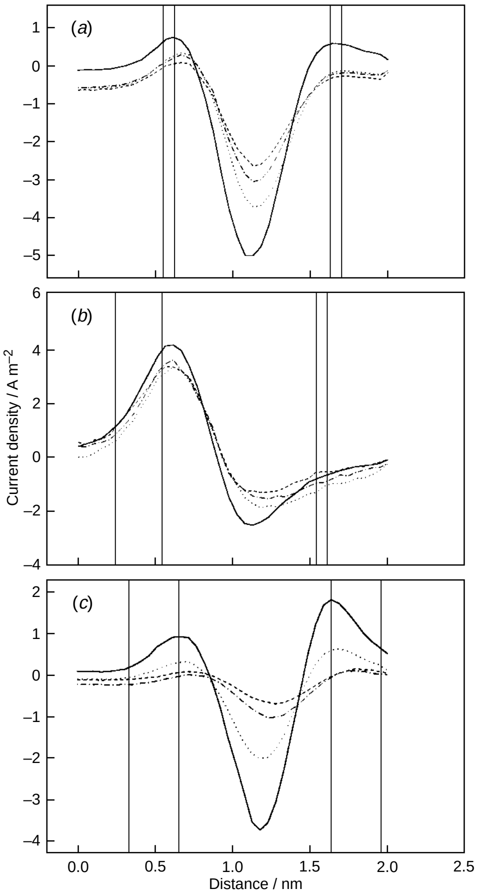

Fig. 2 Normal component of current density distribution in plane of the scan across the thickness of the cut edge for successive scans over a 6 h period for (*a*) 5 μm epoxy primer both sides, (*b*) an identical sample with a 140 μm PVC coating applied to one side and (*c*) an identical sample with a 140 μm PVC coating applied to both sides after 0 h (—), 2 h (···), 4 h (–·–·–) and 6 h (---) immersion in 5% NaCl. The sample position is shown together with schematic representations of the relative coating thicknesses applied to each side of the sample.

Fig. 1 shows the differences in localised corrosion behaviour exhibited by cut edge samples prepared with symmetric and asymmetric thickness of organic coating. Symmetrically coated samples [Fig. 1(*a*) and (*c*)] show the anticipated symmetrical pattern of electrochemical activity with the cathodic steel surface bounded on either side by strips of anodic zinc. However, asymmetrically coated samples show a marked displacement of cathodic activity to the side where the organic coating is thinner, with a corresponding concentration of anodic activity on the more thickly overcoated zinc layer. This finding is perhaps more clearly illustrated in Fig. 2 in which current density data from individual, hourly repeated, area scans have been summed along the length of the cut edge so as to derive a series of current profiles representing the average current distribution across the thickness of the edge as a function of time. It may be seen from Fig. 2 that, in addition to any instantaneous differences in current distribution, current values decay markedly with time for symmetrical organic coatings, whereas for the asymmetric coating currents are substantially undiminished after 6 h.

The sharp difference in current distribution observed between the asymmetrically and symmetrically coated cut edge samples is probably due to the establishment of a differential aeration cell in the asymmetric case [illustrated in Fig. 1(*b*) and Fig. 2(*b*)]. Differential aeration arises for two reasons. Firstly, the thinner organic coating presents a smaller geometrical obstacle to oxygen diffusing or convecting through the electrolyte to the exposed metal surface. Secondly, the oxygen permeability of a coating will be inversely proportional to the coating thickness.[15] Higher steady state oxygen concentrations at the solution contacting zinc surface lying on the side of the thinner coating favour local cathodic activity through reaction (3).

In recent work[16] it has been shown that the cathodic reduction of oxygen, and hydrolytic processes catalysed by the OH^- ions so produced, are key reactions in promoting the disbondment of organic polymer coatings. This implies that the extent of cathodic activity occurring immediately proximate to the polymer–metal interface will be the most significant factor determining rates of coating disbondment. The rapid decay of currents observed for the symmetrically coated samples may therefore be ascribed to blockage of the originally exposed metal surface by corrosion products with little or no fresh metal surface becoming available due to disbondment of the organic coating. Two basic chloride corrosion products [$6Zn(OH)_2 \cdot ZnCl_2$ and $4Zn(OH)_2 \cdot ZnCl_2$] have been identified for zinc corroding in NaCl solutions exceeding 0.1 M.[17] The much slower decay of currents observed for the asymmetrically coated samples may be ascribed to the continuous exposure of fresh metal surface through cathodic disbondment of the thinner organic coating as a result of intense cathodic activity immediately proximate to the zinc–polymer interface. Indeed, visible degradation of the thinner coating was observed in similar samples exposed to 5% NaCl for extended periods with *ca*. 500 μm delamination in 170 h.

The results obtained from the model system also indicate that differential aeration can be an important factor in the mechanism of cut edge corrosion in quiescent solutions of bulk electrolyte.

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Footnotes and References

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