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SHORT COMMUNICATION

THE MECHANISM OF LACY COVER FORMATION IN PITTING

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An open hemispherical pit in stainless steel is unstable because the concentration of dissolved cations must fall well below saturation near the rim of the pit, leading to passivation. Various pit morphologies including flask shapes and lacy metal covers are possible depending on the initial shape evolution and the critical chemistry required to stabilize dissolution in the pit.

Since the 1960s it has frequently been mentioned that pits in stainless steel tend to grow under the metal surface, leaving a porous metallic cover [1-7]. More recently, "bottle-shaped" or "flask-shaped" pitting has often been cited, usually in weld metal and in the context of microbially influenced corrosion (MIC) [8-10]. Covered pits are dangerous in practice because they are stable against the loss of their internal environment by diffusion or convection, especially if there is precipitated material over the mouth of the pit (as in many cases of MIC). If there was a random aspect to the development of pit shape, one could explain the prevalence of covered pits by natural selection: pits that developed with an open geometry would be susceptible to repassivation at an early stage of growth. A related argument was used previously to account for tunnelling of aluminium [11]. In this paper we argue somewhat differently: that a variety of pit shapes including lacy metal covers can be explained on deterministic grounds. The proposed mechanism is based on a critical cation concentration for pitting, not an IR drop argument as proposed for nickel by Wang et al. [12], since in stainless steel there is no critical current density in the saturated pit environment (or at least it is extremely high - tens of A/cm^2). The background to the model is as follows:

1 Early pit growth occurs in a hemispherical mode with the pit contents protected by perforated remnants of the passive film [13,14].

2 When the pit reaches a critical size, the pit cover is destroyed (or at least becomes ineffectual as a diffusion barrier), resulting in an open hemispherical cavity [13,14].

3 An open hemispherical pit cavity is an unstable shape, even if passivation is not an issue. As shown by Harb and Alkire [15], hemispherical pits growing under anodic diffusion control become saucer-shaped - that is, the parts of the pit surface that are nearer the bulk solution have a shorter diffusion length. For the same reason, if the current density over the pit surface is constant, the interfacial cation concentration is lower near the edges of the pit than at the bottom.

4 Stainless steel has a well-defined critical chemistry (dissolved [Fe,Cr] salt concentration), below which the extremely high current densities required for pit stability cannot occur. For an alloy such as 304SS at room temperature, this chemistry (c^*) is about 60-80% of saturation (c_{sat}) [16,17]. Addition of an inhibitor such as sulphate increases the ratio c^*/c_{sat} [18], while increasing the temperature decreases it [19].

The proposed mechanism for formation of the lacy cover is shown in two dimensions in Figure 1. The initially hemispherical cavity passivates near the mouth where $c < c^*$. Further dissolution undercuts the passivated material and emerges at the surface. Following this emergence, ions diffuse out of the hole thus created, and the material around the hole passivates (this takes a finite time, during which the hole continues to grow for a short while). The process then repeats itself. The spacing of the porosity in the lacy cover (w) is determined by the pit depth (h) and by the ratio c^*/c_{sat} (R). High values of R allow more of the pit wall to passivate and increase w, encouraging the formation of a strong and protective pit cover. Thus inhibitors of pit initiation may stabilize pit growth. A numerical finite-element model of this process is feasible, but we can already suggest that $w \sim Rh$. This implies that when $R = 1$, i.e. when dissolution can only occur with a salt film present, there will be no lacy cover but a flask shape will develop. This provides a possible explanation for the prevalence of flask shapes in freshwater MIC of stainless steels, since freshwater usually contains non-chloride ions that increase R. It is also possible that low conductivity *per se* helps the passivation process near the pit mouth by changing the relative contributions of diffusion and migration in the pit (it also renders the pit more susceptible to convection, which sweeps away conductive solution near the pit mouth).

The development of the lacy cover is conveniently studied by glueing a thin stainless steel foil between glass sheets and pitting it from one edge (Figure 2). The pit develops lengthwise

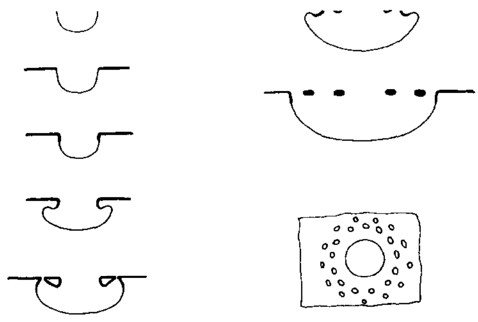

Figure 1 Proposed mechanism for lacy cover formation. Passive surfaces are indicated by thick lines.

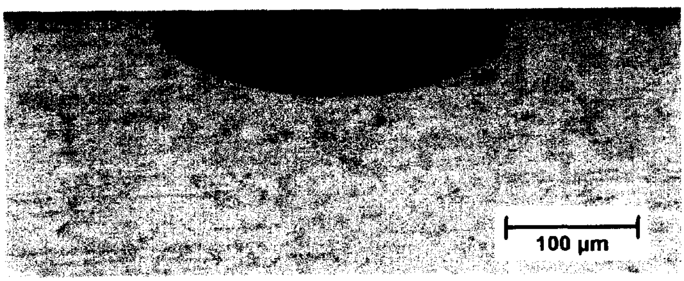

Figure 2 Optical side view of a growing "2-D" pit in a 302 stainless steel foil between glass sheets (1M NaCl, 500 mV SCE), showing the lacy cover in section.

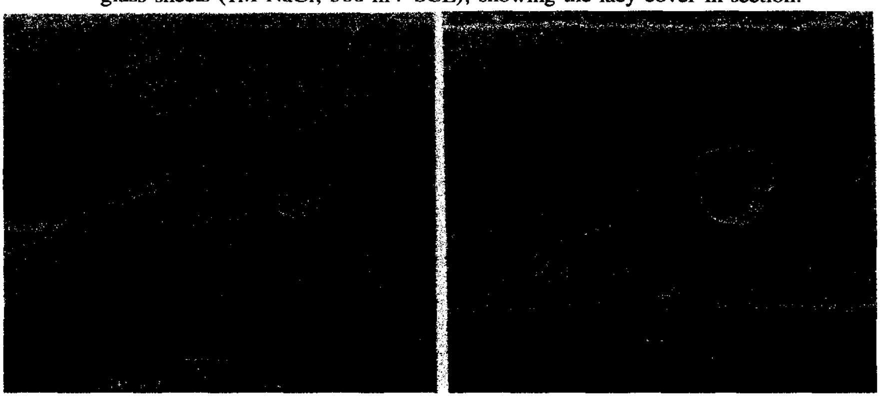

Figure 3 Top view of the lacy cover over the pit, taken in the SEM at two accelerating voltages: (a) 2.1 kV; (b) 20 kV.

much faster than in depth. The lengthwise growth is roughly linear in time, while the depth increases approximately parabolically. For this condition the pit base is shiny, salt-covered, and dissolving at a diffusion-controlled rate. The periodic events that occur at the edge of the pit are at least partly in the active state ($c^* < c < c_{sat}$), as evidenced by rougher (etched) surfaces. The lacy cover is a few microns thick and can be studied by varying the accelerating voltage in the SEM (Figure 3). Its modulated thickness is the result of repetitive wedge formation due to the hemispherical shape of the secondary pitting event when it re-emerges at the surface, as shown in Figure 1.

Deterministic pattern formation in corrosion deserves more attention, and has not been taken into account in long-term predictive schemes. The most dangerous pits are those that grow under the surface. Future work should use numerical modelling so that the relevant variables (h, R, etc) can be varied over a wide range.

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