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# SHORT COMMUNICATION

## AGGRESSIVE EFFECTS OF PITTING "INHIBITORS" ON HIGHLY ALLOYED STAINLESS STEELS

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Anions such as sulphate inhibit pitting of stainless steels by raising the pitting potential. One might, therefore, expect sulphate to raise the critical pitting temperature (CPT), below which no stable pitting occurs at any potential. Surprisingly, this expectation turns out to be false. Addition of 0.5M $Na_2SO_4$ to 1M NaCl lowers the CPT of type 904L steel from 49 to 38°C. Since metastable pitting of this alloy occurs even at room temperature, the effect of sulphate concerns the ability of metastable pits to become stable. Microscopic examination reveals that the stabilization is associated with the lacy metal cover that develops over the pit. When the inhibitor is present, the enhanced passivation reduces the porosity of the pit cover and helps the pit to retain its local environment.

Introduction

The effects of the main environmental variables on pitting of 300-series stainless steels were established by Uhlig and others in the 1960s [1,2]. The pitting potential increased with decreasing chloride concentration, decreasing temperature and increasing pH or concentration of non-chloride anions such as sulphate or nitrate. Even at that time some alloys were known that did not pit at all at room temperature, but it was much later that the existence of a sharply defined *critical pitting temperature* (CPT) for higher-alloyed stainless steels was discovered by Brigham [3-5] (in fact, modern low-sulphur 304 or 316 steels have measureable CPTs, but these are below room temperature). The CPT is now known to be defined to within 1°C for a particular steel and surface finish [6]. The CPT is a transition related to the *early growth* of *stable* pits - metastable pitting, or propagation of large pits, can occur at much lower temperatures [7].

The effects of inhibitors on pitting of stainless steel follow a pattern that is consistent with Galvele's pit model [8]. In simple terms, complete inhibition is achieved at or near a critical *ratio* of chloride to non-chloride anion concentration. According to Galvele, this is because the anions compete to migrate into a pit nucleus, and provided the two anions involved have similar mobilities, they are enriched in the same ratio. For several anions, including sulphate, the concentration required to inhibit pitting at all potentials is similar to the chloride concentration. Apparently chloride must be the predominant anion inside a pit in order for the pit environment to promote a sufficiently anodic high dissolution rate.

There are many similarities between the effects of decreasing temperature and increasing inhibitor concentration on pitting of stainless steel, and one might guess that the effects would in some way be additive. However the issue of pit stability has recently become complicated

by the claim that a lacy metal cover plays a key stabilizing role by retaining the local pit environment [9]. It was suggested that since formation of the lacy cover involves passivation near the rim of the pit, the presence of a passivating influence (inhibitor or decreased temperature) could have a double-edged effect on pit stability. In this paper we show that pitting inhibitors can indeed promote pitting when this is assessed by CPT measurement, rather than by comparing pitting potentials recorded above the CPT.

## Experimental Procedure

The steel used was type 904L (20Cr, 25Ni, 4.3Mo, 1.5Cu, 1.4Mn, < .003S). Rod specimens 4.5 mm in diameter and 50 mm long were machined from plate material supplied by Avesta Sheffield. One end was abraded to a hemispherical shape, and immersed in the test solution along with 40 mm of the cylindrical section, leaving a waterline that never acted as a preferred site for pitting [10]. The test cell was a conventional 3-electrode arrangement and the solution was 1M NaCl or 1M NaCl + 0.5M $Na_2SO_4$. Tests were also carried out in higher concentrations of NaCl, to ensure that the observed effects of sulphate were not due to the increase in conductivity.

The CPT measurement was carried out by repetitive potentiodynamic experiments on freshly prepared surfaces at successively higher temperatures. For each test, the specimen surface was abraded to a 320 grit finish and immediately immersed in the solution. An anodic scan from the corrosion potential at 1 mV/s was carried out until stable pitting occurred. Some care was necessary in detecting the onset of pitting, as the pits grew much more slowly with sulphate present. Four tests were carried out at each temperature. Pitting was confirmed microscopically, and the pit morphology was examined, both on the test surfaces and also on highly polished planar surfaces to improve resolution.

## Results and Discussion

A remarkable *reduction* in the CPT occurred on addition of the "inhibiting" sulphate ion - Figure 1. For this form of material and surface finish, the CPT was reduced from 49 to 38°C. Above the CPT, the normal inhibiting effect of sulphate was evident as an increase in the pitting potential.

In the solution containing sulphate, the increase in current above the breakdown potential was much more gradual than in the plain chloride solution. One possible reason is a decrease in the *number* of pits when sulphate was present, and this was certainly the case, but the main effect of sulphate was to decrease the growth rate of individual pits. This difference (at least a factor of 3) was much more than could be explained by a reduction in solubility of the metal salt in the pit. This ability of the pits to grow slowly and stably without repassivating was clearly responsible for the lower CPT, and the reason was apparent on SEM examination: the lacy cover formed in the solution containing sulphate was much less porous, and correspondingly more effective in retaining the pit contents - Figure 2. In particular, the hole in the centre of the cover was always smaller with sulphate present. In other words, the lacy cover acts like a crevice and increases the *effective* pit depth. Since the pits in the sulphate-containing solution can dissolve at a slow rate and still retain their environment, they can do so at a lower temperature, as explained by Newman and Liew [11].

The effect of sulphate might be due to an increase in the solution conductivity, but this was

shown to be irrelevant by carrying out CPT measurements in pure chloride solutions up to 2M in concentration. No CPT less than 47°C was found in these cases, as expected from earlier literature [6].

The thicker and denser lacy cover formed in the sulphate solution is fully in accord with the ideas presented by Ernst et al. [9,12]: the addition of sulphate increases the ratio of the critical pit chemistry (dissolved cation concentration, $C^*$) to the saturation chemistry (concentration $C_{sat}$). This promotes lacy cover formation by enhancing passivation at the rim of the pit. A similar densification of the pit cover, this time caused by a decrease in temperature to sub-ambient values, can be seen in 304 or 316 steels [12], and may help to interpret previously unexplained reversals in the performance of these alloys at low temperatures [13]. It would be interesting to explore further the suggestion that pitting may be most prevalent *just above* the CPT. Finally, in dilute media such as potable waters, pitting of stainless steel is associated with deposition, often of biogenic material [14] and leads to large sub-surface cavities. We can now suggest that, since these media are often quite inhibiting in terms of their non-chloride anion content, the formation of covered pits is promoted on that account and not by some biological effect.

## Further comments and conclusions

In real life, pits that cause component failure are always covered. Usually this cover is assumed to consist of corrosion product, and this might be the case in many systems. However stainless steels are able to produce a lacy metal cover that provides protection in its own right as well as a support for corrosion product deposition. The present results suggest that the most dangerous lacy covers (those that promote the greatest pit stability) are formed in rather inhibited solutions. Pure chloride solutions produce rather open pits that are vulnerable to repassivation by loss of the pit environment.

Pitting is subject to a form of natural selection in real systems. Pits compete for the available cathodic current, and those that survive are those that retain their protective covers most efficiently. Suleiman [15] showed that such competition could be conveniently studied in laboratory tests with mild anodic galvanostatic polarization. The exclusive use of potentiostatic or potentiodynamic techniques has caused investigators to miss a wealth of interesting and practically important phenomena.

## References

1       H.P. Leckie and H.H. Uhlig, J. Electrochem. Soc., **113**, 1262 (1966).
2       Z. Szklarska-Smialowska, *The Pitting Corrosion of Metals*, Ch. 12, 1st Edition, NACE, Houston (1986). [note Eq. 12.1 and Table 12.2 in this reference use different definitions of *a* and *b*]
3       R.J. Brigham and E.W. Tozer, Corrosion, **29**, 33 (1973).
4       R.J. Brigham and E.W. Tozer, Corrosion, **30**, 161 (1974).
5       R.J. Brigham and E.W. Tozer, J. Electrochem. Soc., **121**, 1192 (1974).
6       R. Qvarfort, Corros. Sci., **29**, 987 (1989).
7       N.J. Laycock, M.H. Moayed and R.C. Newman, "Metastable Pitting and the Critical Pitting Temperature", J. Electrochem. Soc., in press (1997).
8       J.R. Galvele, J. Electrochem. Soc., **123**, 464 (1976).

9       P. Ernst, M.H. Moayed, N.J. Laycock and R.C. Newman, Corros. Sci., **39**, 1133
        (1997).
10      G.S. Frankel, L. Stockert. F. Hunkeler and H. Boehni, Corrosion, **43**, 429 (1987).
11      R.C. Newman and K.H. Liew, Corrosion, **43**, 58 (1987).
12      P. Ernst, M.H. Moayed, N.J. Laycock and R.C. Newman, "Shapes of Corrosion Pits
        in Metals", in *Pits and Pores*, eds D.J. Lockwood and P. Schmuki, The
        Electrochemical Society, in press (1997).
13      J. Horvath and H.H. Uhlig, J. Electrochem. Soc., **115**, 791 (1968).
14      S.W. Borenstein, Mater. Perf., **30**, 52 (1991).
15      M.I. Suleiman and R.C. Newman, Corros. Sci., **36**, 1657 (1994).
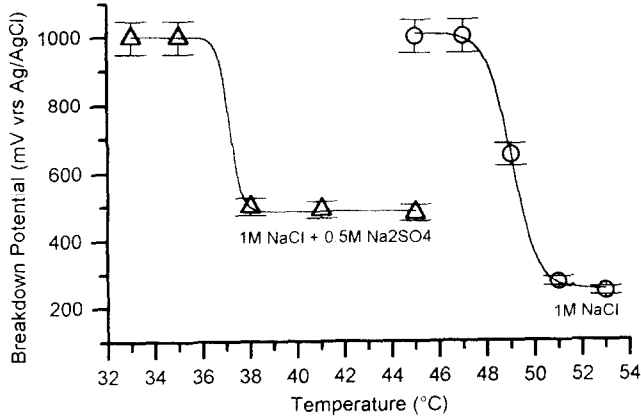
Figure 1      Breakdown potentials for 904L steel in Cl and Cl/$SO_4^{2-}$ solutions.



Figure 2      Covered pits formed on 904L steel in (a) Cl and (b) Cl/$SO_4^{2-}$ solutions at 66°C
and 750 mV.