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INFLUENCE OF PRIOR ELECTROCHEMICAL HISTORY ON THE PROPAGATION OF LOCALIZED CORROSION

by

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The protection potential is defined by Pourbaix (1) as the potential above which active pits will grow, and below which (in the absence of other reducible species) active pits "have been found to become inactive and harmless." As work by Pourbaix (1), Wilde and Williams (2), and Wilde (3) has shown, pitting, once initiated above the critical pitting potential (E_R), will continue to propagate at electrochemical potentials more noble than the protection potential (E_P). In order to determine the effect of the protection potential on the propagation of pits initiated below the critical pitting potential, a technique of controlled pit initiation was developed (4).

A modification was made of an electrochemical corrosion cell (5) to allow insertion of a glass probe with a diamond point. This was positioned to allow scratching of the sample surface while controlling sample potential through the Luggin-Haber probe. Brown and Mears have shown (7,8) that scratches on waxed samples exhibit electrochemical behavior similar to that of naturally occurring pits.

The samples used were Fe-16.9 Cr and their preparation was the same as for the Fe-Cr samples in the work by Verink and Pourbaix (5). The samples were potentiostated at the potentials indicated by the letters, A, B, and C on the experimental Pourbaix

Diagram for Fe-16.9 Cr shown in Fig. 1 (4). During the test, current output of the potentiostat was monitored using a strip chart recorder.

The electrolyte was 0.10 molar NaCl buffered to pH 8.8 with 0.10 molar $NaHCO_3$. This solution was vacuum deaerated and saturated with hydrogen gas for the duration of the experiment. The temperature of the electrolyte was maintained at 23° ±1°C.

A sample was first polarized at -0.500 V_{sce} (Point A), below both E_R and E_P. The current density was allowed to attain a steady state value (several minutes), at which time the surface was scratched with the diamond point. Each time the surface was scratched, the current density increased and immediately returned to the steady state value. These spikes are schematically shown in Section A of Fig. 2, where each spike represents one scratch.

The sample was then potentiostated at -0.100 V_{sce} (Point B), a value between E_R and E_P [E_R = +0.090 V_{sce} and E_P = -0.280 V_{sce} (4,6)] and allowed to attain a steady state current density. Once again, each time the sample surface was scratched a current spike occurred, and the current returned to the steady state value. This is represented in Section B of Fig. 2.

When the sample potential was raised to +0.400 V_{sce} (Point C), above the rupture potential, the current density immediately began to increase with no evidence of decreasing. This is represented in Section C of Fig. 2.

In a second experiment, the sample was scratched once with the diamond stylus after being placed in deaerated electrolyte

(.1M NaCl, pH = 8.8). The sample was momentarily polarized to +1.00 V_{sce} in order to "activate" the scratch. The potential was then lowered to -0.100 V_{sce} and the current density was monitored. The current density increased with time indicating that the scratch was still active at potentials between E_P and E_R. The potential was next lowered to -0.500 V_{sce} (below E_P). It was found that the current density now decreased sharply with time indicating deactivation of the scratch. This is shown schematically in Fig. 3.

Conclusions

It has been shown that in chloride solutions, a binary Fe-Cr alloy containing 16.9% Cr and 0.15% C, may be activated for pitting corrosion by subjecting it to potentials at and above the pitting potential (or rupture potential, E_R).

Once activated, pits will continue to propagate at potentials between E_R and the protection potential E_P.

For this alloy, active pits cease to be active when the potential is lowered below the protection potential E_P.

It also has been shown for this alloy that unless the potential has been raised above the pitting (or rupture) potential, even intentional scratches do not propagate as active pits.

Acknowledgements

This work was performed as a part of the research program supported by ARPA Contract N00014-68-A-0173-0003 and the Office of Naval Research Contract N-00014-68-A-0173-0015.

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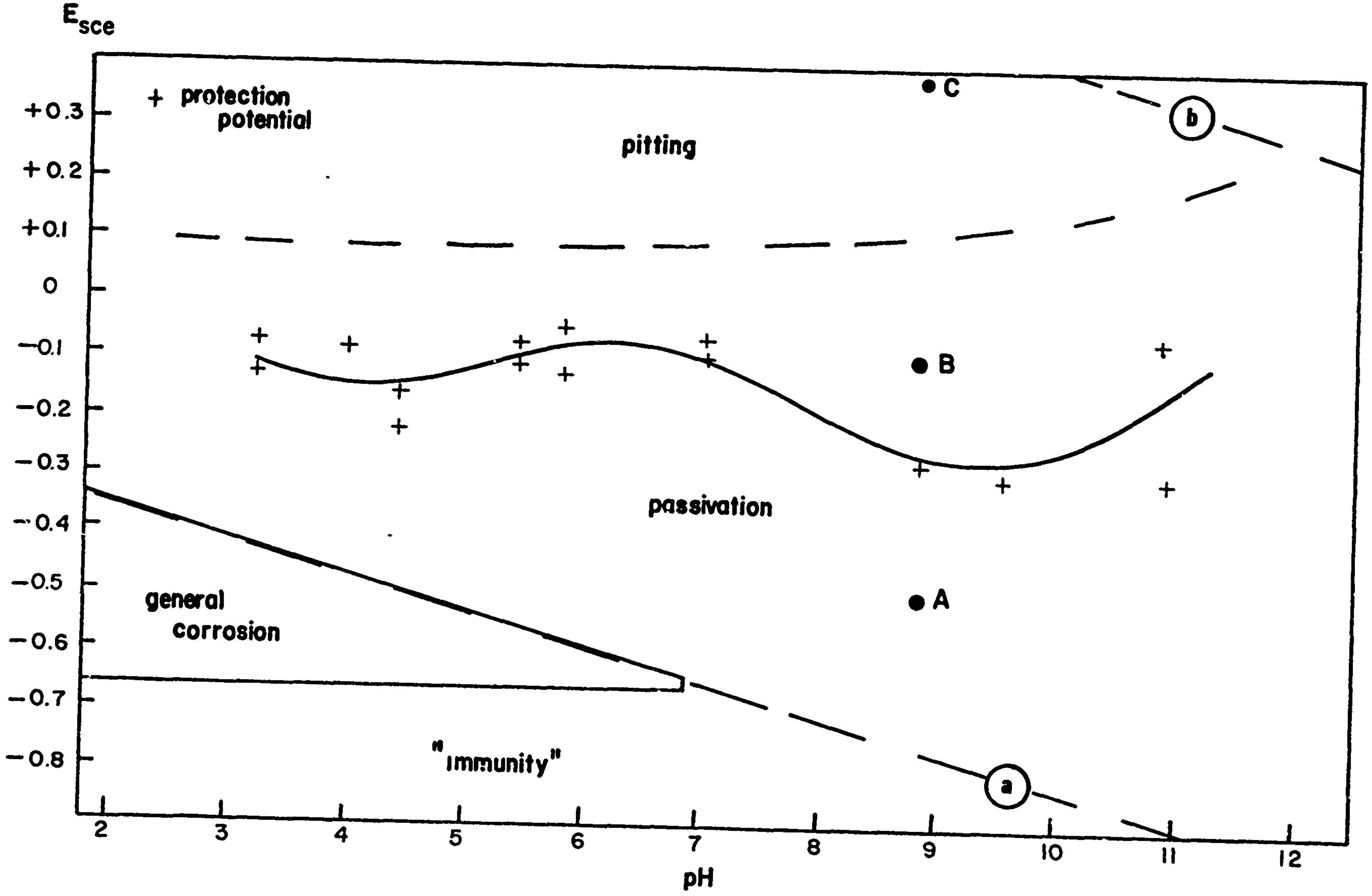

Figure 1 Experimental potential versus pH diagram for binary Fe-Cr alloy containing 16.9% Cr and 0.15% C. Electrolyte was 0.1M NaCl at 23°C ±1°C and atmospheric pressure.

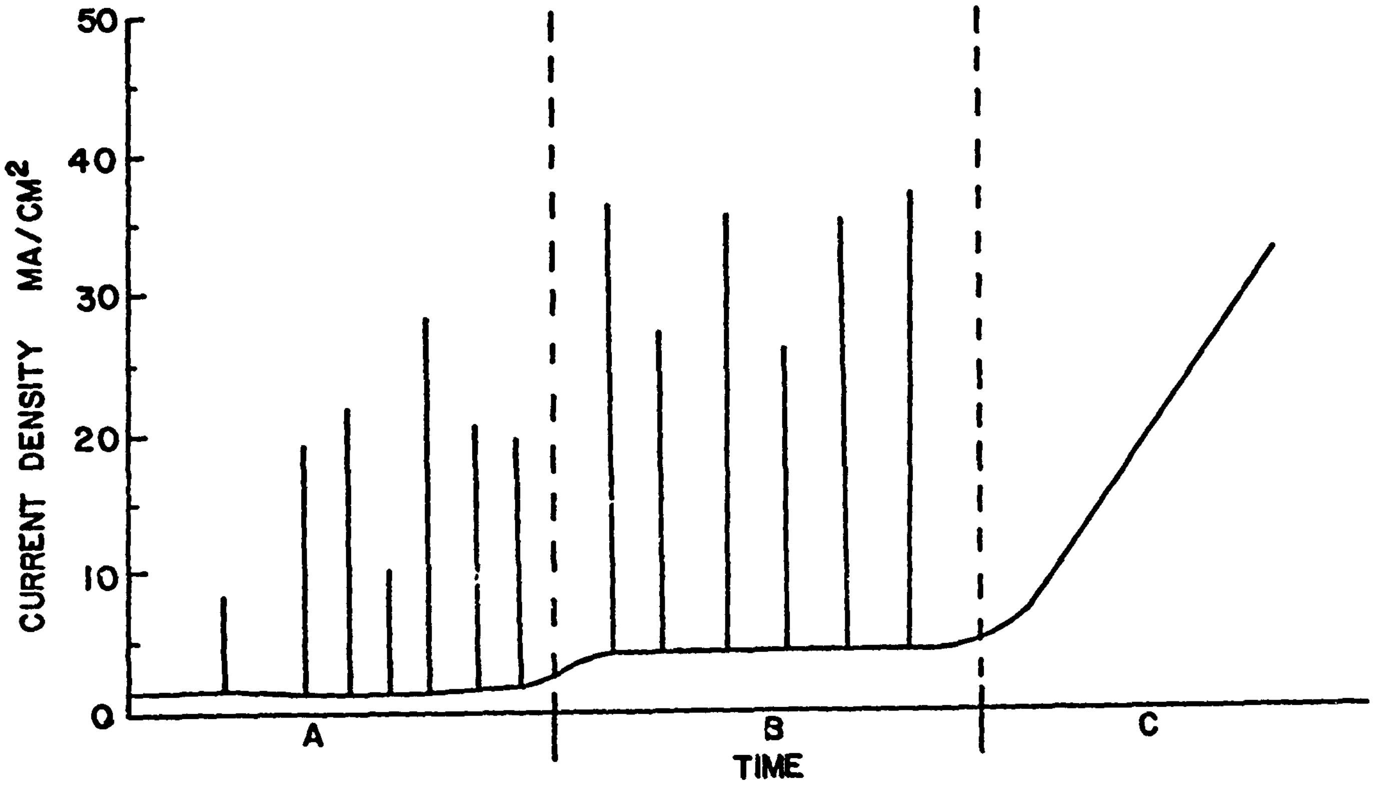

Figure 2 Influence of potential on the tendency of intentional scratches to result in active propagation of pits for a binary Fe-Cr alloy containing 16.9% Cr. Electrolyte was 0.1M NaCl buffered to pH = 8.8 using 0.1M $NaHCO_3$. Sample first polarized to (A) -.500 V_{sce} (below protection potential), (B) -.100 V_{sce} and (C) +.400 V_{sce} (above pitting potential).

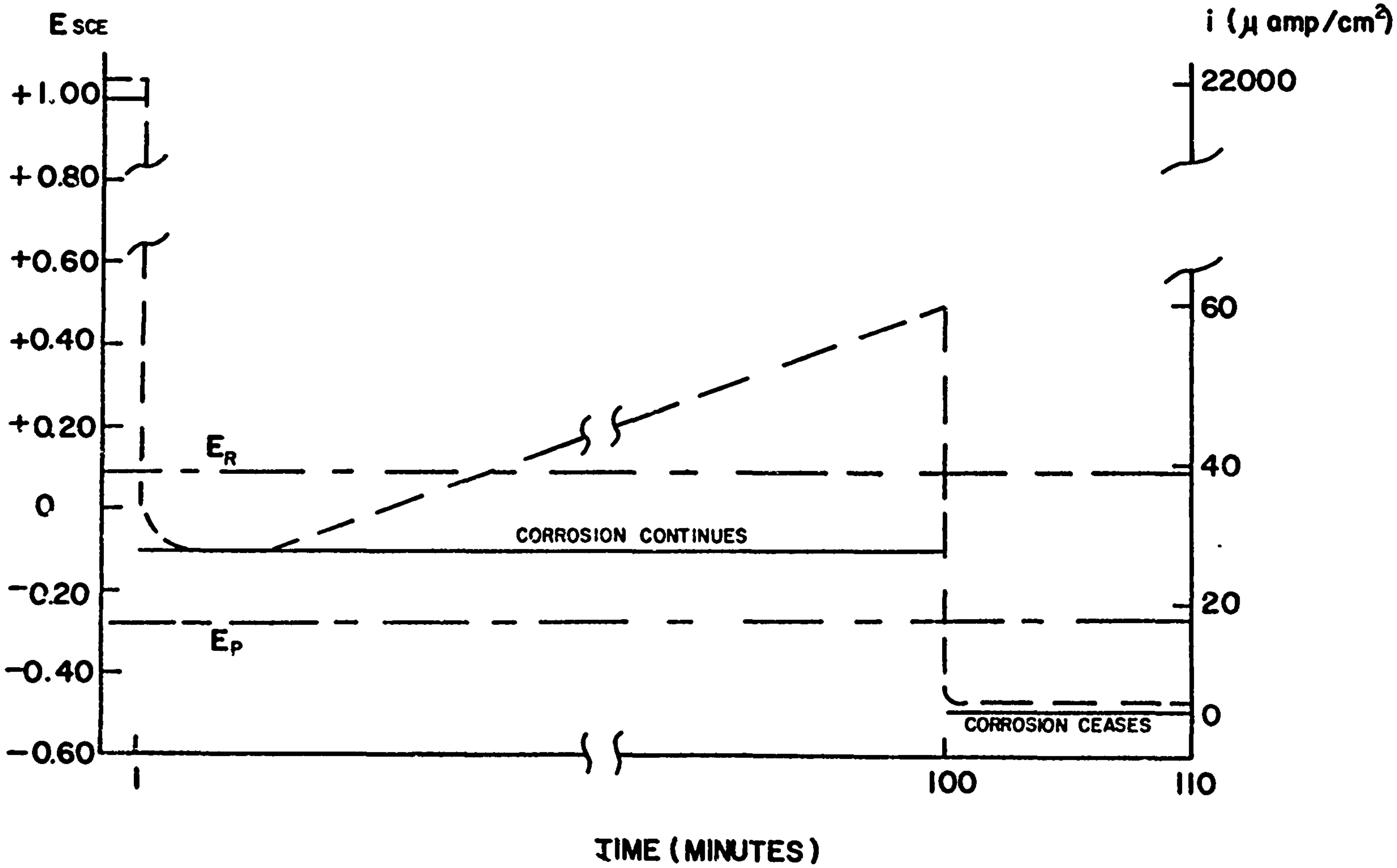

Figure 3 An "activated" scratch on a binary Fe-Cr alloy containing 16.9% Cr continues to corrode at potentials between E_p and E_R. (The dashed line shows the corrosion current density.) When the potential is lowered below E_p corrosion decreases abruptly to a vanishingly small rate.