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Cooperative Spreading of Pit Sites as a New Explanation for Critical Thresholds

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INTRODUCTION

Threshold potentials, temperatures and corrodant concentrations are important factors in many if not all localized corrosion phenomena[1-4]. At these thresholds, significant increases in pit density are seen, as shown in Figure 1[5], as well as growth of stable pits[1]. Although corrosion engineers make significant use of such thresholds, the fundamental origins are not completely understood. Traditional studies have often focused on the stabilization of single pits[6-8] and generally do not consider explosive increases in pit sites are often observed at critical thresholds. In this study we consider the role of cooperative interactions between such sites as a cause of explosive spreading of pit sites across metal surfaces at a critical threshold.

OBJECTIVE

The objective of this paper is to investigate the sudden onset of pitting corrosion manifested at a threshold condition as an exponential increase in the number of pitting sites in conjunction with transition from random to clustered spatial distribution of pit sites.

APPROACH

Interactions between metastable pitting events were investigated using a mathematical model of metastable pitting that simulated the hypothesized processes and conditions associated with local environmental changes that can cause pitting interactions[9, 10]. In this study, the competing processes of ohmic potential shielding vs. surface damage via aggressive species enhancement were contained in a two-dimensional model where initial pitting sites were chosen at random. The conditions were varied between low, intermediate, and high pit generation rate simulating either high or low corrodant concentration or applied potential. The model results were expressed in time-lapse video sequences of spatial surface memory (surface susceptibility) and as x-y locations of metastable pit sites. The pit sites were further investigated using point pattern analysis[11-13] to determine whether the spatial distribution of pit site locations were random or clustered. This enabled determination whether interactions were occurring between individual metastable pitting events.

Metastable pitting experiments were conducted to augment model predictions. Potentiostatic experiments on AISI 316 stainless steel in 0.05 M NaCl at 47^{o}C were conducted at potentials that simulated either low, medium, or high metastable pitting activity. Interactions were detected after one hour by taking optical micrographs of electrode surfaces and analyzing the patterns of metastable pitting events using point pattern analysis techniques[11-13]. Point pattern analysis techniques were able to detect patterns of pitting sites that were random or clustered indicating whether interactions were occurring. The degree of cooperative growth of interaction patterns were also detected by point pattern analysis.

RESULTS

Model predictions showed a transition from random to highly clustered pitting behavior with changes from low to high pit generation rate. Similarly, point pattern analysis of simulated metastable pitting sites shows transition from random behavior (low activity) to clustering at short distances (intermediate activity) to higher clustered behavior (high activity). The size of a zone of intense interactions was seen to grow with applied potential. Identical results were observed in experimental studies. At low applied potentials few pitting events were observed in current-time series and spatial distributions were random. At medium potentials larger numbers of metastable pitting events were observed with possible coupled bursts of events on a current-time series. Transition from metastable to stable pitting behavior was observed at high potentials. Point pattern analysis of experimental metastable pitting sites showed transition from random behavior to highly clustered behavior as applied potential increased. In fact, the change occurred abruptly coinciding with threshold potential associated with pit stabilization. At high potentials clusters grew across the electrode surface. The close resemblance of experimental and modeling results confirms the notion of cooperative spread.

DISCUSSION

Not only do these results suggest a critical transition due to explosive cooperative spread of local corrosion sites across planar surfaces but results suggest a second explanation for strong thresholds in the pitting processes. The critical potential, temperature, or corrodant concentration may be associated with pit stabilization of single sites as classically shown but thresholds may also be associated with explosive lateral growth of pits sites across the surfaces. In both the model and experimental studies not only was the density of pits found to increase but the pits sites occurred as clusters instead of being randomly located as activity increased. If the factors that control cooperative spreading can be better understood then they can be used to devise better ways of designing materials to be intrinsically resistant to explosive growth of pits sites. For example if the controlling factor is a critical type, spacing, or size of initiation site, then material design can be manipulated to mitigate the process of cooperative spreading.

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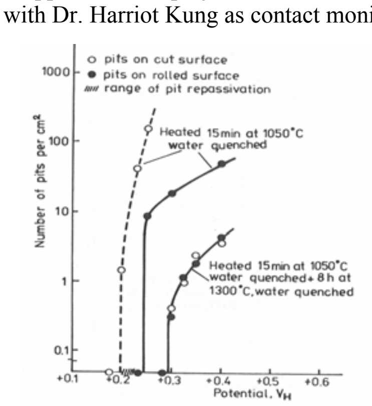

Figure 1. Pit density after polarization of steel in 1 M NaCl showing pits density at a threshold potential [5].