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# Computational simulation of corrosion pit interactions under mechanochemical effects using a cellular automaton/finite element model

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## ABSTRACT

Metastable corrosion pit interactions on stainless steel under mechanochemical effects are investigated using a cellular automaton/finite element model. The transient current of metastable double pits increases faster after pit coalescence than that of metastable single pit. The mechanochemical effect becomes more significant with increasing pit depth. For metastable double pits, the corrosion pit near the load side grows more rapidly than that further away, with the growth direction tending towards the load side. After the pit cover is broken, the corrosion pit interactions can cause the metastable pits to enter the stable growth regime more easily.

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## 1. Introduction

It is well known that stainless steels are sensitive to pitting corrosion when exposed to aqueous solutions containing corrosive anions such as chloride ions. The destructive nature of pitting corrosion is due to high local dissolution rates at potentials above the pitting potential. However, the transient anodic currents less than the pitting potential can occur and have been attributed to metastable pitting events [1–16]. Metastable pitting, observed as short-lived current transients with the time ranges of seconds, are indications of localized activation events, such as pit nucleation, growth and repassivation [17–32]. Regardless of the specific mechanism that causes the breakdown of the passive film, a small occluded cavity will be created in which a local chemistry can develop and metastable growth can occur. Metastable pitting behavior is closely related to that of stable pitting of metals. The stable pits go through a metastable growth stage before stabilizing. Specific conditions must be present to sustain the continuous growth of metastable pits.

The cellular automaton (CA) model is based on a discretized description of time, space, and state [33–36]. It has been used in many different fields to model the behavior of various systems, including pitting corrosion problems. Vautrin [37] used a

cellular automaton model to investigate pitting corrosion with specific anodic and cathodic reactions in the corrosion pit, and observed a transition between the stationary regime and the diffusion-limited regime. Van der Weeën [38] developed a three-dimensional CA-based model describing pitting corrosion, and estimated the model parameters by means of an experimental time series for a metal electrode in different chloride concentrations. Di Caprio [39] considered passivation and depassivation events using a CA model with a probability that depended on the depth of the pit, and reproduced a range of morphologies including narrow pits, larger cavities, and rough surfaces.

We have previously studied metastable corrosion pit development in stainless steel subject to mechanical stress using a model combining cellular automaton and finite element analysis. The results showed that the growth rate of metastable pitting is far higher when the material is under stress [40]. In the previous work, we only considered single metastable pitting events. The interactions between metastable pitting events can lead to clustering of pit locations on the surface, and increase the degree of corrosion damage [41,42]. The aim of the present work is to investigate the metastable corrosion pit interactions on stainless steel under mechanochemical effects using an updated cellular automaton/finite element model, and elucidate the mechanisms for pit interactions.

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## 2. Methodology

### 2.1. Cellular automaton model

In this work, we consider an electrochemical system where a stainless steel is exposed to an aggressive chloride solution. The stainless steel samples had passive surface oxide layers, which can be damaged in the presence of chloride anions. We included two breakdown locations in the passive film in order to study only pit propagation not pit nucleation. In the case of stainless steel, almost all of the cathodic reactions take place outside the pits [18], therefore, we only needed to consider the anodic reactions inside the pits in this model. The autocatalytic processes occur during pit propagation. The metal corrodes in an acidic solution and repassivates in a neutral solution. The passivity is always in a continuous process of breakdown and repair depending on the properties of the local solution. Because the metastable pits are very small, we do not consider the IR drop inside the pits. With the development of concentrated pit solution chemistry a salt film precipitates on the pit walls from a supersaturated solution. A pit cover forms from remnants of the passive film and corrosion products, which provides a stabilizing cover for the pit growth, acting as either a diffusion barrier [43] or a resistive barrier [44], preventing the pit from repassivating.

The cellular automaton model describing these corrosion mechanisms was defined on a two dimensional square lattice with Von Neumann 4-connectivity, which consists of a mesh of  $1024 \times 1024$  with periodic boundary conditions in the horizontal direction. We define four main species in this lattice: solution sites, metal sites, passivation sites and salt film sites. Solution sites provide the neutral and acidic environment for the electrochemical reactions, occupied by water or hydronium ions, respectively. Metal sites are occupied by metal. Passive sites are occupied by passivated metal. Salt film sites are occupied by salt films of  $\text{FeCl}_2$  and  $\text{CrCl}_3$ . One site is only occupied by one species based on the exclusion rules. However, salt film site which represents salt deposit can occupy one site with solution site as an exceptional case.

A layer of surface passive film was included horizontally in the middle of the lattice. The upper part of the surface passive film was fully occupied by neutral solution sites, and the lower part was fully occupied by metal sites. Two breakdown locations were made on the surface passive film, with the acidic solution sites placed within these positions. Once a metal site is in contact with at least one acidic solution site, corrosion will occur. This metal site will be transformed into an acidic solution site with a probability  $P_{\text{corr}}$ , and a salt film site is placed on this acidic solution site. When a metal site is in contact with neutral solution sites, it will be passivated. This metal site is changed to a passivation site with a probability  $P_{\text{pass}}$ . Passivation sites do not permanently exist in the lattice. If a passivation site is in contact with at least one acidic solution site, it will be dissolved and replaced by a neutral solution site with a probability  $P_{\text{diss}}$ . When a salt film site has neighboring neutral solution sites, the latter will be replaced by acidic solution sites. A salt film site can release four acidic solution sites, and it can continuously move downwards under gravity until its lower part is not a solution site. In this model, we wanted to simulate the individual growth and coalescence of two corrosion pits. Hence, the sites were labeled with respect to the pit they belong to. When the metal or passivation sites shared by two corrosion pits are corroded or dissolved, it can be determined that the corrosion pits are beginning to coalesce.

During the pitting corrosion processes, the local solution chemistry is constantly changing. Firstly, the electrochemical reactions on the pit surface change the local electrolyte balance. The CA transformation rules discussed previously can describe this process. Secondly, the solution migration can also change the local

environment. To simplify the CA model we only consider the diffusion of the hydrogen ions. After the breakdown of a pit cover, the hydrogen ions diffuse from the pit electrolyte into the bulk solution driven by a concentration difference. We used a block algorithm [45] to simulate the diffusion process in the CA model. An advantage of this algorithm is that the physical time scale of each iteration can be quite large, and simulations over long time regimes can be obtained much faster than using traditional random walk methods (because the time a Brownian particle needs to explore a block of linear size  $l$  is proportional to  $l^2$ ). The implementation of the reaction and the diffusion steps in the block algorithm assume that each particle has visited the entire block in one iteration. Thus, the physical time  $t$  of this process scales as  $t \sim nl^2$ , where  $n$  is the number of iterations. Therefore, the efficiency of this algorithm is very high, provided that  $l$  is large enough. In order to realize the block algorithm, the CA lattice was divided into equal square blocks of size  $l$ . The solution sites in each block were labeled corresponding to the pit to which they belong. All the solution sites in each block were randomly distributed in their own group. After that, each block was shifted half a block down and half a block left to redistribute the solution sites.

### 2.2. Finite element model

A constant tensile stress of 200 MPa was applied to the stainless steel sample where pitting corrosion occurred. Even with a constant applied stress, the growth of corrosion pits changes the stress distribution on the pit surface because of stress concentration. Gutman reported a kinetic equation for the anodic current  $i_p$  of stressed metal far from equilibrium, which was considered as a mechanochemical effect [46]:

$$i_p = i_a \left( \frac{\Delta \varepsilon}{\varepsilon_0} + 1 \right) \exp \frac{\Delta P V_m}{RT} \quad (1)$$

where  $i_a$  denotes the anodic current of unstressed metal,  $\Delta \varepsilon$  denotes the plastic deformation magnitude,  $\varepsilon_0$  corresponds to the onset of strain hardening,  $\Delta P$  is the spherical part of macroscopic stress tensor (i.e., hydrostatic pressure) depending on the applied load, and  $V_m$ ,  $R$  and  $T$  denote the molar volume, gas constant, and temperature, respectively.

In order to determine the anodic current of stressed metal, we used the finite element model to calculate the stress state on the surface of corrosion pits. The real-time morphologies of the double pits produced by the CA electrochemical model were exported to the Abaqus finite element model. A 2-D planar section of the double pits was built in the FEM, where a Young's modulus of 210 GPa, a Poisson ratio of 0.28, and a yield strength of 290 MPa were assigned for stainless steel. The tensile stress was applied on the right-hand-side of the section with the left and bottom edges restricted. The edges of the double pits were defined with a higher density of mesh seeds than other edges to ensure computational accuracy. The quadrilateral bilinear plane stress elements and triangle linear plane stress elements were mixed to assign the meshes. After the job was completed, the FEM calculated the hydrostatic pressure and plastic strain of all nodes on the edges of the double pits using a path map. The local anodic current increment under stress on the surface of corrosion pits (determined by the Gutman model based on the FEM results) was continuously fed back into the CA electrochemical model. This cellular automaton/finite element model can simulate the growth and interactions of double pits considering mechanochemical effects.

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