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

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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.
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 by 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 FeCl$_3$ and 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 $P_{corr}$ 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 $P_{pass}$. 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 $P_{corr}$. 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 $t \sim n^2$, 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 mechanochanical effect [46]:

$$ i_p = i_0 \left( \frac{\Delta \varepsilon}{\varepsilon_0} + 1 \right) \exp \frac{\Delta PV_m}{RT} $$

where $i_0$ 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 mechanochanical effects.
3. Results and discussion

3.1. Transient current characteristics of pit interactions

Fig. 1 shows transient currents and transient current density curves for the growth of metastable double pits and single pit on stainless steel under loading conditions. In the model, the simulation parameters $P_{\text{corr}}$, $P_{\text{pass}}$, and $P_{\text{diss}}$ were all set to 0.1; the size of each cell and the time scale of each iteration were $2.5 \times 10^{-8}$ m and $2.5 \times 10^{-2}$ s, respectively. The detailed method for calculating the current can refer to Ref. [47]. The two breakdown locations of the double pits were made in the surface passive film of the stainless steel at 3/8 and 5/8 of the width of the sample, and the breakdown location of the single pit was in the middle of the sample. The transient currents of the corrosion pits shown Fig. 1a both increase rapidly with time. The transient current of the metastable double pits shows a significant step increase around $t = 1.6$ s. This indicates that the double pits have begun to coalesce and subsequently the transient current of the double pits increases more quickly than that of the single pit. The metastable double pits and single pit have similar transient current densities, as shown in Fig. 1b. The transient current density is approximately constant, 5.8 A/cm², for both types of pits when the time is under 1.25 s. Such a current density characteristic is consistent with the experimental data for stainless steel under no stress [43,44]. After this time, however, the transient current density increases rapidly, and it can be seen that the double pits have a slightly higher transient current density than the single pit.

3.2. Mechanochemical behavior

In order to understand the mechanochemical behaviour of the corrosion pits, the plastic strain distributions from the finite element model under a tensile stress of 200 MPa is shown in Fig. 2. Both plastic and elastic deformation can increase the anodic current shown in Eq. (1), where the mechanochemical effect of plastic deformation is dependent on the magnitude of the plastic strain, and that of elastic deformation is associated with the hydrostatic pressure. Compared with the plastic strain, the effect of elastic strain is not significant, as shown by many experiment studies [48,49].

It can be seen from Fig. 2 that the plastic strain is only located at the bottom of corrosion pits, and the side walls of the pits are within the elastic limit. This means that the corrosion rate at the bottom of pits is higher than that at the walls, so the corrosion pits tend to get deeper rather than wider. At the early stage of pit growth, the maximum plastic strain at the bottom of pits is not significantly different for metastable single pit and double pits, about 1.75% and 1.68%, respectively at $t = 1.25$ s. Fig. 1a also shows that the transient currents of single pit and double pits are approximately the same, about 2.5 μA at $t = 1.25$ s. The transient current density at $t < 1.25$ s is consistent with that under no stress as shown in Fig. 1b. This means that the mechanochemical effect is not significant at the early stage of pit growth. However, the magnitude of the plastic strain becomes larger with increasing pit depth due to stress concentration. The double pits have higher plastic strain than the single pit, about 29.98% and 6.37%, respectively at $t = 1.75$ s as shown in Fig. 2. During the simulation of double pits, we only consider the transient current of one pit before coalescence (the corrosion pits will become one after pit coalescence). Hence, the transient current of the double pits shown in Fig. 1a has a step increase. Even though the corrosion zone of double pits is twice than that of single pit, the transient current of double pits is more than twice that of the single pit. It can be seen in Fig. 1a that the transient current at $t = 1.75$ s is 8.3 μA and 19 μA for single pit and double pits, respectively. This can be ascribed to the higher plastic strain for double pits. The transient current density at $t > 1.25$ s deviates from the equilibrium value, and continues to increase with time as shown in Fig. 1b. This indicates that the mechanochemical effect becomes more significant. The corrosion pit without applied stress has a typical hemispherical shape and the transient current density is constant [43]. However, the narrow growth of a pit and the higher transient current under stress should lead to a deviation in the behavior of the transient current density. For double pits, because the tensile stress is applied on the right-hand edge of the sample, the corrosion pit on the right-hand-side should be subject to higher stress than that on the left-hand-side, as shown in Fig. 2d. Hence, the corrosion pit on the right grows more rapidly, and the growth direction of the pit tends to the right-hand edge. However, the transient current density of double pits is only a little higher than that of a single pit, as shown in Fig. 1b. This indicates that the increase of current per unit area is not significant because of average effect. In the simulation processes, the breakdown locations of double pits are fixed at 3/8 and 5/8 of the width of the sample. This distance can affect the mechanochemical behavior. When the distance between the double pits becomes shorter, the pits coalesce earlier. Because the pits are smaller at the time of coalescence, the mechanochemical effect caused by pit coalescence is not significant. When the distance between the double pits decreases to the limit, the double pits become one single pit.
caused direct repassivation of the pit, except for the case of very large pits, which could survive [50]. The transient current of the double pits increases sharply about 1.6 s because of the pit coalescence. Subsequently, the transient current of the double pits drops followed by a rapid rise after the breakdown of the pit cover at $t_b = 1.75$ s. This indicates that the metastable double pits transform into stable pits. Wu et al. used a stochastic approach to model the pitting process in stainless steel, in which stable pitting occurs due to cooperative interaction between neighbouring pits [51]. Fig. 3b shows the pit stability products for the growth of metastable double pits and single pit. Pistorius and Burstein [43] have proven that stable growth can be maintained for an open corrosion pit when the pit stability product is between 0.3 A/m and 0.6 A/m. For a single pit, the pit stability product just reaches the threshold value of $ia = 0.3$ A/m when the pit cover is broken at $t_b = 1.75$ s, and therefore the metastable single pit repassivates. The pit stability product of the double pits at $t_b = 1.75$ s is far larger than the threshold value of $ia = 0.3$ A/m, therefore the metastable double pits become stable. Fig. 4 shows the transient currents and pit stability products for the growth of metastable double pits and single pit when the pit cover is broken at $t_b = 1.9$ s. As shown in Fig. 4a, the transient current of the single pit decreases rapidly followed by a slow increase after the breakdown of the pit cover, whereas that of double pits drops, followed by a rapid increase. Both double pits and single pit enter the stable growth phase. The pit stability products of metastable double pits and single pit as shown in Fig. 4b, both far exceed the threshold value of $ia = 0.3$ A/m, with that of the double pits reaching a maximum critical value of $ia = 0.6$ A/m.

When the corrosion pit forms, the metal cations dissolve continuously into the solution, where they can undergo hydrolysis and increase the acidity inside the pit. If the concentration of the metal cations in the solution reaches saturation, they can combine with chloride ions to form a salt film. When the pit cover is broken, there is a significant concentration difference between the pit solution and the bulk solution, which creates a driving force for the diffusion of hydrogen ions from the pit solution to the bulk solution. The increase of pH inside the pit will lead to a decrease in the anodic dissolution rate of the metal. This effect can be seen in Figs. 3 and 4 where the transient currents begin to drop when the pit cover is opened at $t_b = 1.75$ s and 1.9 s. Once the pit solution is diluted, the salt film dissolves again into the solution and hydrolyzes, decreasing the pH of the pit solution. The subsequent current characteristics are dependent on the competitive relationship between diffusion and hydrolysis. It is an effect that causes the repassivation of the metastable single pit, while the metastable double pits continue into the stable growth regime, as observed in Fig. 3a. When the pit cover is broken at $t_b = 1.75$ s, the double pits have already coalesced and hence have a higher peak current than that of the single pit. This suggests that there are more dissolved metal cations and salt film in the pit solution for double pits. Large salt films can hydrolyze to compensate the electrolyte dilution when the hydrogen ions in the pit solution diffuse outwards into the bulk solution. When the pit cover is broken at $t_b = 1.9$ s, as shown in Fig. 4a, the peak currents of the double pits and single pit are both higher than those at $t_b = 1.75$ s shown in Fig. 3a, indicating more salt film inside the pit which has also become deeper over time. The pit depth is a natural barrier to the diffusion of hydrogen ions. Therefore, the growth rate of double pits at $t_b = 1.9$ s is faster than that at $t_b = 1.75$ s after the breakdown of the pit cover. The single pit at $t_b = 1.9$ s can also continue to grow slowly and become stable, unlike repassivation observed at $t_b = 1.75$ s.

In order to compare the breakdown effect of the pit cover on the growth of metastable double pits, the transient currents under different breakdown times are shown together in Fig. 5. When $t_b = 1.25$ s, the pit cover has been opened before the pits coalesce. The peak current is very small and the pit depth is also very shal-

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**Fig. 2.** Plastic strain distributions from the finite element model under a tensile stress of 200 MPa, when (a) $t=1.25$ s and (b) $t=1.75$ s for metastable single pit; (c) $t=1.25$ s and (d) $t=1.75$ s for metastable double pits.

### 3.3. Pit cover

The pit cover is a very important factor in the growth of metastable corrosion pits. Fig. 3a shows the transient currents for the growth of metastable double pits and single pit on stainless steel under loading conditions when the pit cover is completely open. The conditions used in the model were $t_b = 1.75$ s, $e_b = 1$, and $D_D = 5.0 \times 10^{-5}$ cm$^2$/s, where $t_b$ is the breakdown time of pit cover, $e_b$ is the degree of breakdown, and $D_D$ is the diffusion coefficient of hydrogen ions. The transient current of the single pit decreases quickly followed by a steady state when the pit cover is broken. This indicates that the metastable single pit repassivates. Isaacs and Kissel found that destroying the pit cover during pit growth
low, and therefore the metastable double pits repassivate. But the repassivation does not mean that the pit stops growing absolutely. It can be seen in Fig. 5 that there exists a maintaining passivation current, and the corrosion pit continues to grow very slowly, which causes the delay of pit coalescence. When the pit cover is broken at $t_b = 1.5$ s, the breakdown time is close to the pit coalescence time. The delay time of pit coalescence is very short and the metastable double pits still repassivate. As mentioned previously, the peak current and pit depth increase with time, therefore the metastable pits enter the stable growth regime gradually when the breakdown time of the pit cover increases to 1.75 s and 1.9 s.

The results discussed so far were under the conditions of a completely open pit, i.e., $e_p = 1$. The influence of the degree of breakdown of the pit cover on the growth of metastable double pits under loading conditions at $b_0 = 1.25$ s and $D_H = 5.0 \times 10^{-5}$ cm$^2$/s is shown in Fig. 6. The degree of breakdown $e_p$ is defined as the ratio of the amount of removed pit cover to the width of the pit mouth. The metastable double pits at $e_p = 1/2$ and $e_p = 1$ have similar transient current characteristics, both of them repassivate. The delay time of pit coalescence at $e_p = 1/2$ is shorter than that at $e_p = 1$, and the maintaining passivation current at $e_p = 1/2$ is also higher than that at $e_p = 1$. However, when $e_p$ decreases to 1/5 and 1/10, the metastable double pits enter the stable growth regime. Even though the pit cover is broken at $t_b = 1.25$ s, the transient current at $e_p = 1/5$ increases continuously and begins to decrease at $t = 1.45$ s, and the delay time of pit coalescence becomes shorter. Furthermore, the transient current at $e_p = 1/10$ does not decrease even after

**Fig. 3.** (a) Transient currents and (b) pit stability products for the growth of metastable double pits and single pit on stainless steel under loading conditions when $t_0 = 1.75$ s, $e_0 = 1$, and $D_H = 5.0 \times 10^{-5}$ cm$^2$/s.

**Fig. 4.** (a) Transient currents and (b) pit stability products for the growth of metastable double pits and single pit under loading conditions when $b_0 = 1.9$ s, $e_0 = 1$, and $D_H = 5.0 \times 10^{-5}$ cm$^2$/s.

**Fig. 5.** Influence of breakdown time of pit cover on the growth of metastable double pits under loading conditions when $e_0 = 1$ and $D_H = 5.0 \times 10^{-5}$ cm$^2$/s.
the breakdown of the pit cover and pit coalescence is not delayed. The growth rate of the corrosion pit at \( e_0 = 1/10 \) is much faster than that at \( e_0 = 1/5 \) after the pit cover is broken. When \( e_0 \) becomes smaller, the remaining pit cover can more easily act as a barrier to prevent the pit solution from diffusing into the bulk solution. The corrosion pit is difficult to repassivate in an aggressive pit solution. If \( e_0 \) is low enough, the diffusion barrier can greatly increase the diffusion path to the bulk solution for hydrogen ions in the pit solution. This will delay the time for observing a decrease in the transient current after the breakdown of the pit cover.

3.4. Diffusion

Fig. 7 shows the influence of diffusion rate on the growth of metastable double pits under loading conditions for a completely open pit at \( t_b = 1.25 \) s. When the diffusion coefficient of hydrogen ions \( D_H \) is equal to \( 1.2 \times 10^{-5} \) cm²/s, the metastable double pits can return to the passive state with a maintaining passivation current only a little higher than that at \( D_H = 5.0 \times 10^{-5} \) cm²/s. The delay time of pit coalescence at \( D_H = 1.2 \times 10^{-5} \) cm²/s is shorter than that at \( D_H = 5.0 \times 10^{-5} \) cm²/s. When \( D_H \) decreases to \( 3.1 \times 10^{-6} \) cm²/s, the metastable double pits move into the stable growth regime. The metastable double pits at \( D_H = 7.8 \times 10^{-7} \) cm²/s also survive after the breakdown of the pit cover, and the growth rate is faster than that at \( D_H = 3.1 \times 10^{-6} \) cm²/s. Similar to the degree of breakdown of pit cover, when \( D_H = 3.1 \times 10^{-6} \) cm² or \( 7.8 \times 10^{-7} \) cm²/s, the transient currents do not decrease after the breakdown of the pit cover and increase continuously until pit coalescence occurs. The diffusion coefficient can be used to comment on the diffusion rate to some extent. When this value decreases, it means that more hydrogen ions remain in the pit solution, which will decrease the pH inside the pit. The low pH can prevent the metal from passivating and allow active dissolution.

4. Conclusions

We have used a cellular automaton/finite element model to predict corrosion pit interactions under mechnochemical effects at a mesoscopic scale. The transient current of metastable double pits has a significant step increase around \( t = 1.6 \) s, and the double pits begin to coalesce. Subsequently, the transient current of the double pits increases more quickly than that of single pit because of a higher plastic strain. We analyzed the growth kinetics of metastable double pits using the transient current characteristics and pit stability products when the pit cover was broken under different conditions. The corrosion pit interactions can increase the amount of dissolved metal cations and hence salt film in the pit, and compensate the electrolyte dilution caused by the outward diffusion of the hydrogen ions from the pit solution to the bulk solution after the breakdown of the pit cover. This process assists the metastable pits to reach the stable growth regime more easily.

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References

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