An alternate explanation for the abrupt current increase at the pitting potential

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Abstract

A critical transition potential is shown to be associated with the abrupt increase in the number of metastable pits and the onset of spatial clustering of pits amongst nearest neighbor defects in both commercial and model stainless steels. This critical transition potential is correlated with the parameter, $E_{\text{pit}}$, commonly observed in near-neutral NaCl solutions when stainless steels form pits. The explosive growth of pit sites, the onset of clustering of pits, and $E_{\text{pit}}$ all depend on the diffusion length associated with aggressive corrosion products formed at pits and thus on the stirring rate. $E_{\text{pit}}$ is observed to increase significantly and pit sites remain random to high potentials in both experiments and modeling when the diffusion length is decreased below the nearest neighbor distance (NND) associated with surface defects such as non-metallic inclusions that form a random array of susceptible sites across the otherwise passive surface. This phenomenon is confirmed by experiments and modeling using model stainless steel alloys with decreased inclusion densities and, thus, increased defect NNDs. If the NND is greater than the lateral diffusion length, then $E_{\text{pit}}$ will increase, clustering of pit sites will decrease and explosive growth in the number of pits will be suppressed at a given applied point.

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1. Introduction

The pitting potential at a given temperature and corrosive concentration is an important parameter in most localized corrosion phenomena because it describes the critical transition potential, above which passive materials become severely pitted [1–4]. At this threshold, significant increases in pit density are seen [5], as well as growth of stable pits [1,6]. Stable pitting is preceded by metastable pit formation which is indicated by anodic current spikes that form micrometer size pits, often at a sub-lattice or array of non-metallic inclusions that act as weak sites in the passive film [7,8]. Moreover, it is well known that there is a statistical correlation between metastable and stable pitting [9] and that the frequency of metastable pitting increases with increasing applied potential [8–12]. A trigger mechanism has also been proposed [13].

Although understanding of events near $E_{\text{pit}}$ have been studied extensively and corrosion engineers make significant use of such threshold potentials, an explanation of all the processes occurring is not completely available. Many previous studies focus on the stabilization of single pits and consider pit stabilization to be associated with a single weakest or most favorable site [14–16]. Stabilization occurs when the pit dissolution, cover, pit shape, surface roughness, and salt films all conspire to form a pit environment more aggressive than the critical chemistry needed to sustain pit growth [15,17–19]. Stabilization criteria for single pits are not questioned here. However, an explanation for the explosive growth of pit density [15,17,18] and associated spatial clustering of pits at a critical potential

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is lacking. Moreover, this alternate view of the phenomena causing an abrupt current rise at a critical potential should be considered when interpreting pit data. Indeed, Baroux has pointed out the possible existence of many critical potentials corresponding to different stages of pitting. All of these stages have their own critical potentials. Various existing models assume either that either pit initiation, or stabilization, or both can account for critical potentials [17]. Only one has speculated that interactions between pits cause the current rise [20].

Explosive increases in metastable pit generation rate and anodic current that occur upon slight changes in corroding conditions have recently been described as a cooperative critical phenomenon [21]. Cooperative interactions are triggered by physical processes that promote or suppress cooperative growth of pit sites [22,23]. These interactions are explained by the acid/halide pitting mechanism [15]. Aggressive species accumulation adjacent to active pits causes clustered formation of new pits due to a temporary presence of a more aggressive solution and subsequent persistent surface damage on nearby un-pitted surfaces [22]. Damage of sulfide inclusions in stainless steel have been considered by many [24–27]. Surface damage in commercial stainless steels (Fe–Cr–Ni–Mo–Mn alloys) is brought about by partial dissolution of Mn(Cr,Fe)S inclusions partially stainless steels (0.13% C, 2.25% Ni, 0.016% S, 0.35% Si, balance Fe in wt.%) supplied in the form of 250 μm wire, an MnS inclusion “free” model alloy (containing a few oxide inclusions) as well as three similar model stainless steel alloys (10.01–10.13% Ni, 16.29–17.78% Cr, 2.08–2.26% Mo, 0.06–1.11% Si, 0.0035–0.0058% C, 0.02–1.87% Mn, and balance Fe in wt.%) all supplied in the form of 6.35 mm diameter rods. These contained distinctly different sulfur contents (0.0068, 0.016, and 0.075 wt.% S) producing a range of inclusion densities and spacings. The commercial stainless steel wire was mill-annealed and the model alloys were annealed in an argon environment at 1050 °C for 1 h and air cooled.

The polyamide coated 316 wire and Fe–Cr–Ni–Mo stainless steels with different S contents were mounted in Armstrong® epoxy and were remarkably crevice free. Any results with crevice corrosion were discarded. All drawn or swaged samples were mounted perpendicular to the drawing direction. Each of these alloys contained a few similarly-sized large sulfide inclusions but the overall density of inclusions was reduced with lower S. Such stainless steel alloys have a mixture of (Mn, Fe, Cr)S, silicon rich and oxide inclusions that form an array of defect sites across a material surface [30]. MnS inclusions are the primary pit initiation sites in stainless steels and can make up anywhere from 20% to 100% of the inclusions [11]. The MnS inclusion density of the commercial 316 stainless steel alloy was 2800 inclusions/mm² with an average “effective” nearest neighbor distance (NND) of 17.3 μm taken as the average distance between an inclusion and its five closest neighbors. The model alloys had inclusion NNDs ranging from near infinity for the MnS inclusion-free alloy to 8.0–27.2 μm at low, intermediate, and high sulfur contents. Upward potential scans were conducted at 1 mV/s in 0.05 M NaCl (pH 6.8) at 47 °C after polishing to a 1 μm surface finish in a diamond polishing suspension. Epit was determined at the potential at which the rising current permanently exceeded 10 μA. The rotation rate of the electrodes was controlled using a rotating disk apparatus to control the solution phase diffusion boundary layer thickness (δ). Boundary layer thickness was estimated from the Levich equation and approximate values were verified as a function of rotation rate via studies of the oxygen reduction reaction on inert electrodes such as platinum and copper [31]. The lateral diffusion length of aggressive species is estimated to be within a factor of two of the diffusion boundary layer thickness controlled by the Levich Equation. For typical solution values, 10−2−10−4 RPM produces 5–50 μm diffusion boundary layer thicknesses vs. 100–200 μm produced by stirring. The Levich equation is well within the laminar regime for smooth small electrodes at zero to 10⁴ RPM [31] and ORR studies confirm this. Laminar flow behavior and applicability of the Levich equation has even been reported at 10⁴ RPM on small, smooth electrodes. Larger electrodes have a greater risk of becoming turbulent, in this case the quoted boundary layer thickness would be uncertain. However, it should be recognized that the same phenomena may effect pitting

2. Methods

Experimental studies were conducted using both commercially available AISI 316 stainless steel (0.13% C, 0.31% Co, 18.18% Cr, 0.38% Cu, 1.75% Mn, 2.40% Mo, 12.25% Ni, 0.016% S, 0.35% Si, balance Fe in wt.%) supplied in the form of 250 μm wire, an MnS inclusion “free” model alloy (containing a few oxide inclusions) as well as three similar model stainless steel alloys (10.01–10.13% Ni, 16.29–17.78% Cr, 2.08–2.26% Mo, 0.06–1.11% Si, 0.0035–0.0058% C, 0.02–1.87% Mn, and balance Fe in wt.%) all supplied in the form of 6.35 mm diameter rods. These contained distinctly different sulfur contents (0.0068, 0.016, and 0.075 wt.% S) producing a range of inclusion densities and spacings. The commercial stainless steel wire was mill-annealed and the model alloys were annealed in an argon environment at 1050 °C for 1 h and air cooled.
under turbulent flow but just in a less well controlled manner. The pitting potential ($E_{\text{pit}}$) was determined at different rotation rates (0, 5000, and 10,000 RPM). Metastable pitting behavior was investigated in a series of one hour potential holds conducted at various potentials near $E_{\text{pit}}$ under both stagnant conditions and at high rotation rates [29].

The spatial proximity of inclusions and metastable pits were determined before (inclusions) and after (inclusions and pits) potentiostatic experiments on the commercial AISI 316 stainless steel wire using Ripley's point pattern analysis (PPA) techniques [22,32,33]. Inclusions and pits were located using optical microscopy by detecting black dots on the electrode surface. The discrete x–y locations of inclusions and pit sites were determined from optical micrographs using image analysis software. The majority of inclusions on the commercial AISI 316 stainless steel surfaces were found to be between 0.3 and 3 μm in diameter. The minimum threshold size for pit detection was set to 3 μm to distinguish between inclusions and pits. The resulting pit site locations were inputted into a computer program that determined the Ripley's PPA results and, thus, the spatial proximity.

A pitting model was used to study metastable pitting patterns associated with cooperative interactions [23,34]. The core of this model is a memory function that determines a new local pit generation rate depending on local environmental and electrochemical changes that can promote or suppress pitting interactions [22,23]. The competing processes of local ohmic potential shielding vs. local aggressive species accumulation and subsequent inclusion damage are contained in this 2-dimensional model. The model used here differs from that applicable for homogeneous surfaces [21] in that pitting occurs stochastically only at randomly distributed inclusion sites. Subsequent local pit generation rates were decreased at nearby inclusion sites based on ohmic potential shielding or increased based on aggressive solution enhancement and subsequent surface damage within the diffusion lengths calculated dynamically during each time step. The conditions were varied between low, intermediate, and high initial pit generation rates, simulating either low or high applied potentials such as those near $E_{\text{pit}}$. Moreover, accumulation of aggressive species was mediated by changing the solution phase boundary layer thickness, simulating stirred conditions, which controlled transport of aggressive pit reaction products away from the metal-corrosive solution interface into the bulk solution. Changes in boundary thickness, in turn, changed the extent of lateral diffusion of aggressive species relative to inclusion spacing [34]. This key diffusion length was compared to the NND associated with inclusions. The critical pit generation rate causing explosive growth and clustering of pit sites, $w_{\text{critical}}$, was determined by systematically increasing the initial pit generation rate, $w_0$, at selected fixed inclusion NNDs and diffusion boundary layer thicknesses until cooperative pit spreading occurred.

### 3. Results

The statistically significant median values of $E_{\text{pit}}$ for the commercial 316 stainless steel (NND = 17.3 μm) in NaCl solution increased with rotation rate from +0.488 to 0.571, and, finally, to 0.685 V_{SCE} (volts vs. saturated calomel reference electrode) corresponding to no rotation ($\delta = 125$ μm), 5000 RPM ($\delta = 8.9$ μm), and 10,000 RPM ($\delta = 6.3$ μm), respectively (Fig. 1a). An explosive growth in the number of metastable pit sites/mm² was also seen with increasing potential as the applied potential approached the $E_{\text{pit}}$ even though the additional potential increase was small (closed symbols in Fig. 1a) [5,21]. Moreover, pit sites transitioned from spatially random to clustered as $E_{\text{pit}}$ was approached (Fig. 1a open symbols). However, $E_{\text{pit}}$ (taken as the potential associated with the current rise), the critical transition potential associated with explosive growth in metastable pit sites (Fig. 1a), as well as the critical potential at which pit sites became clustered were all shifted to more positive potentials upon stirring as the diffusion boundary layer thickness, $\delta$, decreased. In fact $E_{\text{pit}}$ was suppressed until +0.685 V_{SCE} when the rotation rate was 10,000 RPM. Moreover, the number of metastable pit sites decreases significantly with increasing rotation rate under otherwise identical conditions at selected potentials near $E_{\text{pit}}$, such as when held at +0.4 V_{SCE}.

Potentiostatic tests on commercial stainless steel reinforce these findings as shown in Fig. 1b–e. At potentials such as +0.3 V_{SCE}, far below the critical transition potential as shown in Fig. 1a and b, very few pit sites initiate under both stagnant and rotating conditions and pit sites (black dots in Fig. 1b) are randomly distributed as shown by $L_2$ vs. distance PPA curves (Fig. 1d) [33]. At slightly higher potentials (+0.375 V_{SCE}), electrodes in stagnant solutions exhibit many more pits (Fig. 1c), and more pit interactions and pit clustering occur as shown by PPA peaks with cluster radii on the order of tens of micrometers (Fig. 1e). Applied potentials +0.4 V_{SCE} that begin to approach the critical potential and $E_{\text{pit}}$ produce bursts in current (current spikes indicate metastable pitting) and strong clustering of pits under stagnant conditions, as shown in Fig. 2a–c. A rapid rise in the current is observed after a period of time and continuous metastable pit spikes are observed indicating strong cooperative interactions between pit sites (Fig. 2a). In contrast, the degree of cooperative interactions is reduced and the current–time series showed fewer and fewer clustered metastable pit current spikes when the solution was stirred at 5000 RPM ($\delta = 8.9$ μm) as shown in Fig. 2d–f. Explosive bursts in current are not seen and only weak pit clustering occurs upon stirring (Fig. 2d–f) at +0.4 V_{SCE}. PPA curves indicate that the degree of pit clustering is reduced (Fig. 2c vs.f) under

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[1] Another version of this model considers pitting at open circuit. In this version, the ohmic potential is taken to spread across entire electrodes and is a dominant effect compared to chemistry change – the same phenomena are still observed. However, spreading over entire electrodes is not seen.
was decreased below the nearest neighbor distance a rapid
decrease in the number of metastable pits occurred in con-
junction with a decrease in the degree of clustering to val-
ues less than zero, as shown in Fig. 3. The potential at
which a transition from random to clustered behavior
occurs (degree of clustering equal to zero) was found to
directly correspond with the measured $E_{pit}$ taken from
the rapid current rise, as shown in Fig. 4.

A related trend is found when a series of alloys with dif-
ferent NNDs between inclusions are tested at a fixed rota-
tion rate. $E_{pit}$, the transition potential associated with pit
clustering and the potential associated with explosion in
pit events was determined. An example is shown in Fig. 5
with a controlled rotation rate of 1000 RPM and solution
phase diffusion length of 19.8 mm. $E_{pit}$ increased abruptly
when the inclusion density was reduced from 3000 inclu-
sions/mm$^2$ (NND = 16.7 $\mu$m) to 2000 (NND = 20.5 $\mu$m)
or lower.

Spatial pitting model results are strikingly similar to
experiments. There is a strong potential effect, a stirring
effect, and a NND effect when model surfaces were given
different inclusion densities. The dependence on potential
captured in the model is associated with increased initial
pit generation rates. The model indicates that metastable
pitting events are randomly distributed at low pit genera-
tion rate (equivalent in the model to low applied potential).
As the generation rate is increased (representing increasing
applied potential near $E_{pit}$) clustering or aggregation of pit
sites occurs at low analysis radii closely matching experi-
mental results [34]. At high generation rates, bursts in cur-
rent and clustering occur over very large distances indicating
that strong interactions are occurring across electrode surfaces [34]. In addition, there is a strong depen-
dence of explosion of pitting events and clustering on the
diffusion boundary layer thickness. Specifically, decreasing
the diffusion boundary layer thickness, simulating an
increased stirring rate, suppresses both significant bursts
in current and strong interactions indicated by pit site clus-
tering which now only occurs at very small cluster radii. Pit
site clustering was greatly suppressed by stirring despite the
same initial pit generation rate that triggered a growth of
pit sites across an entire electrode surface under stagnant
conditions. These model results are interesting because
the model contains no provision for current rise due to sin-
gle pits; the current rise is solely due to spreading of meta-
stable pitting. Moreover, a similar effect of inclusion
spacing was seen. Pitting events occurred randomly (iso-
lated current spikes) and did not lead to explosive growth
when inclusion densities were low (1678 mm$^{-2}$) for a given
pit generation rate and fixed diffusion length as seen in
Fig. 6a. However, interactions and explosive growth in pit-
ting events occurred when the inclusion density was
increased (1831 mm$^{-2}$) and the NND was decreased for
the fixed diffusion length and initial pit generation rate
(Fig. 6b). The crucial role of inclusion density and NND
is further confirmed in Fig. 7. In these model simulations,
the inclusion density was decreased and NND increased

otherwise identical conditions. Here, the effective lateral
diffusion length was reduced from 125 $\mu$m at no rotation
to 8.9 $\mu$m at 5000 RPM stirring rate. As the rotation rate
was increased the diffusion boundary layer thickness was
decreased until it was smaller than the defect nearest near-
neighbor distance of 17.3 $\mu$m in this stainless steel. This is sup-
ported by the data of Fig. 1a. When the diffusion length is
reduced further to 6.3 $\mu$m compared to a defect NND of
17.3 $\mu$m, pit events are suppressed even at potentials of
$+0.45 V_{SCE}$. As the diffusion boundary layer thickness

Fig. 1. Pitting of commercial 316 stainless steel (NND = 17.3 $\mu$m) in
0.05 M NaCl (pH 6.8) at 47 °C after potentiostatic holds for 3600 s at
rotation rates and potentials indicated. (a) The average number of
metastable pits/mm$^2$ (closed symbols) after 1 h exposure at the rotation
rates indicated and degree of pit site clustering (open □ symbols) under 0
rotation rate at various constant potentials. A positive degree of clustering
when >0 indicates statistically confirmed clusters of pits. The location of
pit sites indicated by black dots on commercial 316 stainless steel
potentiostatically held for 1 h at (b) +0.3 $V_{SCE}$, (c) +0.375 $V_{SCE}$ at 0
rotation rate. PPA results for pit sites after potentiostatic experiments at
(d) 0.3 $V_{SCE}$ and (e) 0.375 $V_{SCE}$. When the position of the experimental $L_2$
vs. analysis radius data increases to values above the lower and upper
boundaries associated with random behavior, pit site clustering is statistically
confirmed [33] as seen in (e).
for a 50 μm diffusion length. The critical generation rate required to trigger interactions was determined by running the pit model at monotonically increasing pit generation rates, \( w_0 \), (similar to an upward potential scan as in Fig. 3) until explosion of cooperative pitting was forced. The critical potential associated with the critical generation rate, \( w_{\text{critical}} \), increased significantly when the NND increased from 26.7 μm to >47.5 μm for a fixed diffusion length of 50 μm as seen in Fig. 7. This trend is in excellent agreement with experimental data (Fig. 5).

4. Discussion

\( E_{\text{pit}} \) is often viewed to be controlled by initiation and stabilization of pits, but not often viewed to be controlled by interactions between pits [30]. Passive alloys may exhibit pitting potentials whether they have a large array of inclusion type defects, a few large defects or a limited number of small defects, suggesting the interactions are not always the case. For instance, inclusion-free sputter deposited high purity Fe–Cr alloys can be forced to pit at high potentials because such conditions may be required to form and maintain the aggressive solution composition within the pit [35]. Thus, the theory of cooperative spreading as an alternative explanation for \( E_{\text{pit}} \) might apply best to alloys with arrays of inclusions.
The importance of arrays of inclusions vs. the largest inclusions can be examined via stirring rate studies. $E_{\text{p pit}}$ is known to be dependent on rotation rate \cite{36,37}. The rotation rate dependence was explained by a reduction of the diffusion boundary layer thickness which increased the removal rate of corrosion products when considering a single pit site \cite{36,37}. The rise in $E_{\text{p pit}}$ (Fig. 1a) could be explained by either the diffusion length vs. NND theory, advanced here, or by the stirring effect associated with maintenance of the critical chemistry in single pits. However, the theory of stir-induced dilution involving a single large pit does not explain the rest of the behavior in Fig. 1a–e involving pit explosion and clustering, nor the pitting behavior of the model alloys with various inclusion densities reported in Figs. 3–5. Each of these model alloys contains a few similar large Mn(Fe,Cr)S inclusions. Therefore, these few large inclusions should have produced similar median pitting potentials according to the single pit theory (i.e., weakest link theory) in all model alloys as long as $E_{\text{p pit}}$ was controlled by stabilization of single pits instead of initiation and spreading. Similar $E_{\text{p pit}}$ values were not observed for all model alloys and $E_{\text{p pit}}$ increased considerably when the diffusion length decreases below the NND as shown in Fig. 5. This alternative view is supported by the model results, which considers NND but not inclusion size or stable pit propagation (Figs. 5 vs. 7).

The role of cooperative interactions between pits formed at an array of inclusions in producing a threshold potential was investigated by looking at the spatial distribution of pitting sites in the vicinity of $E_{\text{p pit}}$. Explosive growth in the number of metastable pits that occurred and clustering of pit sites, taken as evidence of spatial interactions, also occurred at a critical potential closely correlated with $E_{\text{p pit}}$ as shown in Fig. 4. At this potential, cooperative interactions occur with greater intensity than at more benign conditions causing explosive growth in the number of metastable pits by a cooperative critical phenomenon \cite{21}. Explosive growth in pit sites does not occur at low potentials $+0.3 \text{ V SCE}$ (Fig. 1b and d). Cooperative interactions do not trigger enough additional pitting at nearby inclusions when only a few sites initiate pits. Eligible sites are too far apart to trigger subsequent explosive lateral growth of pits. The behavior begins to change when the potential is raised to near $E_{\text{p pit}}$. At $+0.375 \text{ V SCE}$ the number of metastable pits begins to increase (Fig. 1c and e) and clustering of pits occurs. At potentials $+0.4 \text{ V SCE}$ (Fig. 2a–c). If cooperative interactions occur at great enough intensity to trigger spreading of pits, then the spatial proximity of metastable pit sites becomes highly clustered, as seen in Figs. 1a, e and 2c. $E_{\text{p pit}}$ correlates directly with the onset of cooperative interactions at the potential at which a transition from random to clustered behavior occurs, as shown in Figs. 4 and 8. At potentials higher than $E_{\text{p pit}}$, cooperative interactions occur with great enough intensity to spread pits across entire electrodes.
and cause an abrupt increase in anodic current. These experimental results strongly suggest that an intense increase in cooperative spreading of metastable pits and a transition from random to clustered behavior provides an additional explanation for the events occurring at $E_{\text{pit}}$.

Stirring raised $E_{\text{pit}}$, shifted the onset of explosive increases in the number of pit sites to higher potentials (Fig. 1a), and suppressed the transition from randomly distributed to highly clustered spatial distributions of pits when inclusion NND was fixed (Figs. 2 and 8). Pit clustering was suppressed and $E_{\text{pit}}$ was increased (Fig. 1a) when the experimental diffusion length was decreased from 125 $\mu$m to 8.9 or 6.3 $\mu$m given the NND of 17.3 $\mu$m in the commercial stainless steel. Similarly, when the diffusion length was set at 50 $\mu$m and the NND was increased from 26.5 to 47.8 $\mu$m in the model, a greater rate of pit initiation rate, $w_{\text{crit}}$, was required to force cooperative interactions (Fig. 7). Increases in $w_{\text{crit}}$ are analogous to raising the potential or $\text{Cl}^-$ level (i.e., aggressiveness to promote more pit events) [38,39]. Similarly, $E_{\text{pit}}$ increased significantly when the actual NND decreased below a diffusion length of 50 $\mu$m. When the distance between susceptible sites (NND) is larger than the lateral diffusion length, then aggressive species will not be transported in high enough concentration to cause sequential initiation at nearby sites. However, sequential initiation at neighbor inclusions occurs when the lateral diffusion length is greater than the nearest neighbor distance. Both diffusion length variations at a fixed inclusion spacing (Fig. 1) and variation in inclusion spacing at a fixed diffusion length (Fig. 5) support this hypothesis. Such inhibition of interactions can be overcome by raising the potential under highly stirred conditions which brings about the needed level of cooperative spreading. High pit initiation rates create the chance for near simultaneous initiation at adjacent inclusions which halves the diffusion length. Local aggressive solution formation at many sites simultaneously eventually forces cooperative interactions to occur with great enough intensity to cause widespread pitting even at high stirring rates.

In summary, the critical potential associated with cooperative interaction, explosive growth in pitting, and $E_{\text{pit}}$ are all raised by increasing the defect spacing compared to the diffusion length. These findings may be applicable to many passive materials such as stainless steels [40], Al [41–43], Ta [44], and Ti [45,46]. Pitting occurs in these materials at metallurgical defect sites that form an array that can be damaged by local solution chemistry. This alternative explanation for critical potentials can be used to design materials that are more intrinsically resistant to widespread pitting and at least one critical potential. Conventional corrosion mitigation strategies in corrosion-resistant materials include addition of expensive alloying elements such as Cr, Mo, Ni and W in solid solution. These both improve the passive film properties and stop the growth of pitting corrosion in the alloy beyond single large pit initiating inclusions and constituent particles [30]. Other approaches include use of amorphous metallic glasses that minimize the presence of the metallurgical defects to suppress both initiation and propagation [47]. However, these methods are expensive and not practical for every application. This paper identifies a different approach for the design of corrosion-resistant alloys. Increasing the spacing between pit initiating defect sites, beyond a characteristic lateral diffusion length, can be used as a method to significantly raise the overall pitting resistance by promoting higher critical potentials for at least one of the important stages of pitting.

Fig. 7. Average critical pit generation rate, $w_{\text{crit}}$ required to force explosive pit growth vs. model inclusion density from simulations at a fixed diffusion length of 50 $\mu$m. The pit generation rate, $w_{\text{crit}}$, was increased monotonically at each inclusion density until explosive pit growth occurred. Error bars indicate the standard deviation from 10 replicate simulations. $w_{\text{crit}}$ increases significantly when the NND distance increases from 26.5 (1200 mm$^{-2}$) to greater than 47.8 $\mu$m (<400 mm$^{-2}$). Note the similarity to the trend as in Fig. 5.

Fig. 8. The normalized area beneath $L_2$ vs. applied potential determined after 1 h potentiostatic metastable pitting experiments on AISI 316 stainless steel in 0.05 M NaCl at 47 $^\circ$C (pH 6.8). When $L_2 > 0$, pit clustering is confirmed statistically.
This can be accomplished without total elimination of all defect sites and can be implemented at much lower cost to conventional materials by control of sulfur levels, or appropriate chemical pretreatments or thermal surface treatments that remove some defects and change remaining defect spacings. This practical strategy to improve pit corrosion resistance has been used, but may be best explained by the alternative mechanism proposed here [48–51].

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