

A REVIEW: BEHAVIOR OF PITTING CORROSION IN MANUFACTURING FOOD EQUIPMENT

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REVIEW ARTICLE

ABSTRACT

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. The phenomenon of corrosion behavior studies is three elements include economic, safety and maintenance. Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced interring the material layer surface. It's considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Pitting corrosion can produce pits with open holes or covered with a semi-permeable capsule of corrosion products. In this review, we study about the pitting corrosion mechanism and stages in the manufacture food equipment metals in different conditions and environment.

Keywords: deterioration, cathodic reaction, NaCl electrolyte, environment.

علوان وآخرون

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مقالة: سلوك التآكل النقري في معدات تصنيع الاغذية

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المستخلص

التآكل هو تدهور أو تدمير المعادن والسبائك نتيجة التفاعلات الكيميائية أو الكهروكيميائية مع محيطها. دراسة ظاهرة سلوك التآكل تتضمن ثلاثة عناصر تشمل الاقتصاد والسلامة والصيانة. التآكل النقري هو نوع من انواع التآكل الموضوعي يكون على شكل ثقوب صغيرة والتي تنتج تجاويف تحت سطح المادة. ويعتبر هذا النوع أكثر خطورة و ضرر من التآكل العام، لأنه من الصعب اكتشافه والتنبؤ به وتجنبه عند التصميم. يمكن أن يظهر التآكل بشكل حفر ذات ثقوب مفتوحة أو مغطاة بكبسولة شبه نفاذة من منتجات التآكل. في هذا الاستعراض ، سيتم دراسة آلية حصول هذا التآكل ومراحل تقدمه في مختلف الظروف والبيئة في معدات تصنيع الاغذية.

كلمات مفتاحية: التدهور، الحماية الكاثودية، محلول كلوريد الصوديوم، البيئة.

INTRODUCTION

Pitting corrosion is one of the most difficult forms of corrosion to manage reliably. Chloride ion plays a big role in the corrosion process of structural steel, it's the most commonly encountered aggressive agent which causes pitting of many metals (1, 20, 24,). Resistance to pitting corrosion is a major engineering design feature of many structures and components, and despite this, and the wealth of surrounding knowledge, chloride induced pitting remains a major form of failure. Many, many variables are involved in the phenomenon; almost every feature of a metal/environment system has an effect on pitting. For example, the well-known phenomenon of chloride induced pitting of many metals is naturally a function of the chloride concentration and the temperature, quite apart from the identity, composition, and microstructural characteristics of the metal. In addition to the chloride concentration, however, the presence of most other components of the environment has an effect on the pitting characteristics as well. Even those ions which have no obvious chemical effect in the system can have a marked effect on pitting (14,27,28). One of the consequences of the sensitivity to the many variables is the difficulty in classifying true susceptibility or resistance to pitting. The pitting characteristics, one really needs to specify every possible component and feature of the system; if this is not done, it stands to reason that irreproducibility will result. Pitting in chloride solutions is often characterized by the so called pitting potential, and sometimes by the related re passivation or protection potential. There is a wealth of literature on these characteristic potentials and they form an important component of the knowledge of pitting. However, an important characteristic of pitting, at least in chloride solution, is the fact that pits can and do nucleate, and can even grow, at potentials below the pitting potential (4,5,11,15). The pitting potential, so often used to characterize pitting of metals and alloys, does not mark the boundary between pitting and no pitting at all. Convention frequently has it that passivity breaks down at or above the pitting potential; the recent evidence shows

that this must be regarded as erroneous, as discussed below

MECHANISM OF PITTING corrosion

The more conventional explanation for pitting corrosion is that it is an autocatalytic process. Metal oxidation results in localized acidity that is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electro migration of aggressive anions into the pit, Fig.1 (2). For example: when a metal is present in an oxygenated NaCl electrolyte, the pit acts as anode and the metal surface acts as cathode. The localized production of positive metal ions in the pit gives a local excess of positive charge which attracts the negative chlorine ions from the electrolyte to produce charge neutrality. The pit contains a high concentration of MCl molecules which react with water to produce HCl, the metal hydroxide, and H⁺ ions, accelerating the corrosion process. In the pit, the oxygen concentration is essentially zero and all of the cathodic oxygen reactions take place on the metal surface outside the pit. The pit is anodic and the locus of rapid dissolution of the metal (8). The metal corrosion initiation is autocatalytic in nature however its propagation is not. This kind of corrosion is extremely insidious, as it causes little loss of material with the small effect on its surface, while it damages the deep structures of the metal (18).The pits on the surface are often obscured by corrosion products. Pitting can be initiated by a small surface defect, being a scratch or a local change in composition, or damage to the protective coating. Polished surfaces display higher resistance to pitting. Pitting corrosion is an electrochemical oxidation-reduction process, which occurs within localized holes (cells) on the surface of metals coated with a passive film. Pitting corrosion is considered much more dangerous than uniform corrosion since its rate is 10-100 times higher. Pitting corrosion is highly accelerated if chloride, sulphate or bromide ions are present in the electrolyte solution. Stainless steels and other metals forming a passive oxide layers on their surfaces (Aluminum alloys, Copper alloys, chromium) in electrolytes and atmosphere are sensitive to pitting corrosion. Mechanism of

pitting corrosion is similar to that of Crevice corrosion: dissolution of the passivating film and gradual acidification of the electrolyte caused by its insufficient aeration (Oxygen penetration) (6). An initial pit may form on the surface covered by a passive oxide film as a result of the following: Mechanical damage of the passive film caused by scratches. Anodic reaction starts on the metal surface exposed to the electrolyte, the passivated surrounding surface act as the cathode. Particles of a second phase (non-metallic inclusions, intermetallic inclusions, metallic particles, Microsegregation) emerging on the metal

surface. These particles precipitating along the grains boundaries may function as local anodes causing localized galvanic corrosion and formation of initial pits. Localized stresses in form of dislocations emerging on the surface may become anodes and initiate pits. Non-homogeneous environment may dissolve the passive film at certain locations where initial pits form. In presence of chloride ions pits are growing by autocatalytic mechanism. Pitting corrosion of a stainless steel is illustrated in the figure 2 (14,16). Anodic

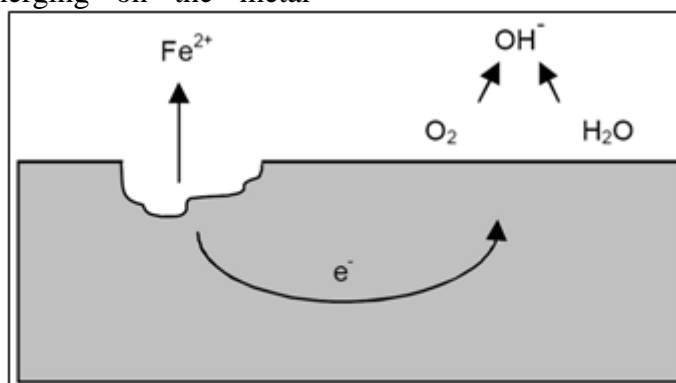
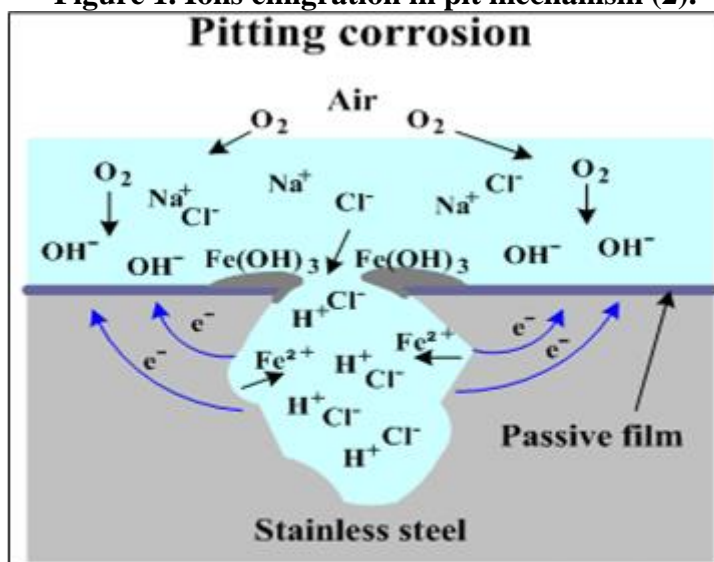


Figure 1: Ions emigration in pit mechanism (2).

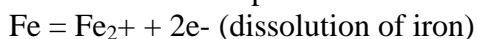
Figure 1. Ions emigration in pit mechanism (2).



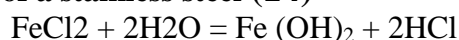
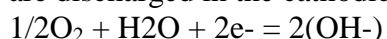
(14) Figure 2: Pitting corrosion of a stainless steel

Figure 2. Pitting corrosion of a stainless steel (14)

reaction inside the pit:



The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:



PH of the electrolyte inside the pit decreases (acidity increases) from 6 to 3, which causes further acceleration of corrosion process. Large ratio between the anode and cathode areas favors increase of the corrosion rate

Corrosion products ($\text{Fe}(\text{OH})_3$) form around the pit resulting in further separation of its electrolyte. Means of pitting corrosion control:

- Selection of appropriate material;
- Providing stirring of the electrolyte;
- Control of the electrolyte composition (PH, chloride ions);
- Corrosion inhibitors;
- Cathodic protection;
- Corrosion protection coatings.

Stages of pitting

There are various stages of pitting are discussed in order, from passive film breakdown, to metastable pitting, to pit growth. Any of these stages may be considered to be the most critical. For instance, once the passive film breaks down and a pit initiates, there is a possibility that a stable pit will grow. The full range of available spectroscopic and analytical techniques has been applied to the study of the structure and composition of passive films in a hope to predict and understand pit initiation (24). To those who prefer the surface science approach, for example, it is often assumed that alloying affects localized corrosion via changes in the composition and structure of the passive film. According to this view, pit growth is considered to be well understood and to offer little in the way of fundamental understanding of the phenomenon of pitting. On the other hand, others feel that pit growth is pivotal and often controls the pitting process, since pits will not initiate if they cannot grow at least for a short while (23). It is considered that the passive state is required for pitting to occur, but details of the passive film composition and structure play a minor role in the pitting process. This view is supported by the fact that many observations of pitting tendency can be fully accounted for by growth considerations. Furthermore, pit growth is critical in practical applications of failure prediction. Finally, the metastable pitting stage may be thought to be the most important since only pits that survive this stage become stable growing pits. Metastable pits exist on the edge of stability. Studies of metastable pits can therefore provide insight into fundamental aspects of pitting since both initiation and stability are key factors in metastable pitting (10, 25). The breakdown of the passive film and very

initiation of the pitting process is probably the least understood aspect of the pitting phenomenon. Breakdown is a rare occurrence that happens extremely rapidly on a very small scale, making direct observation extraordinarily difficult. The passive film is often drawn schematically as a simple inert layer covering the underlying metal and blocking access of the environment to the metal. The reality is, of course, much more complicated. Depending on alloy composition, environment, potential, and exposure history, this film can have a range of thickness, structure, composition, and protectiveness. Typical passive films are quite thin, and support an extremely high electric field (on the order of 10^6 to 10^7 V/cm). The passage of a finite passive current density is evidence of continual reaction of the metal to result in film thickening, dissolution into the environment, or some combination of the two. The view of the passive film as being a dynamic, rather than static, structure is critical to the proposed mechanisms of passive film breakdown and pit initiation. Theories for passive film breakdown and pit initiation have been categorized in three main mechanisms that focus on passive film penetration, film breaking, or adsorption, Fig. 3 (21, 22). These mechanisms are described below in terms of pure metal systems. As mentioned above, however, pits in real alloys are most often associated with inclusions or second-phase particles. Penetration mechanisms for pit initiation, Fig. 3a, involve the transport of the aggressive anions through the passive film to the metal/oxide interface where aggressive dissolution is promoted (18). Anion migration would be assisted by the high electric field in the film. The penetration mechanism is supported by the existence of an induction time for pitting following the introduction of chloride into an electrolyte. On the other hand, estimated induction times based on expected values of anion transport rates exceeded measured values by many orders of magnitude (9). Marcus and Herbelin found chloride present in passive films on Ni using careful XPS and radiotracer measurements (13). A critical concentration of chloride in the inner oxide portion of the passive film was associated with film breakdown and pit

initiation. Others, however, have found no evidence of chloride in passive films (3, 22). A related model for passive film breakdown is an outgrowth of the point-defect model developed by Macdonald and coworkers to describe passive film growth by the movement of point defects under the influence of an electrostatic field (7). The major point defects in an oxide film are assumed to be electrons, holes, and metal and oxide vacancies. Transport of vacancies across the film controls the film growth according to this view. The point-defect model has been used to explain pit initiation by assuming that aggressive ion (chloride) adsorption and incorporation at the outer surface of the barrier oxide layer results in the formation of cationic vacancies (12). These vacancies diffuse to the metal/oxide surface where they are annihilated by the oxidative injection of cations from the metal. However, if the flux of vacancies is larger than can be accommodated by oxidation, the vacancies will condense at the metal/film interface to form a void that is the first step in the pitting process according to this model. The point-defect model has been fitted to experimental data describing the statistical distribution of pitting potentials, the induction time for pitting, and the influence of alloying on the pitting potential (26). Interestingly, the pitting potential and induction time relate to pit stability and growth rather than pit initiation, since it is well known that metastable pits initiate at potentials far below the pitting potential and during the induction time prior to stable pit growth. Predictions from the point-defect model have yet to be compared to experimental measurements of the earliest stages of pit formation despite the fact that the model is based on phenomena occurring at the nanometer level (19). Other criticisms of the point-defect model have focused on the handling of the electrode potential and its role in influencing vacancy concentration and migration (17, 15). Adsorption theories of initiation, Fig. 3b, were first based on the notion of competitive

adsorption of chloride ions and oxygen. It is now known that the passive film is at least several monolayers thick rather than just an adsorbed oxygen layer. However, aspects of the adsorption model are still relevant. For instance, exposure of Fe to chloride and other halides caused thinning of the passive film based on XPS measurements, even under conditions where a pit had not formed, as a result of what was described as catalytically enhanced transfer of cations from the oxide to the electrolyte (22). On the other hand, another study using SIMS found that there was no difference in oxide thickness on Fe samples pre passivated in borate solution and then galvanostatically anodized at $5\mu\text{A}/\text{cm}^2$ in solutions with or without Cl^- (3). Interestingly, no Cl^- was found to be incorporated into the oxide during this treatment either. When thinning occurs locally because of some local adsorbed species, the local electric field strength will increase, which may eventually lead to complete breakdown and the formation of a pit (9). Pit initiation by a film-breaking mechanism, Fig. 3c, considers that the thin passive film is in a continual state of breakdown and repair (17, 19). Mechanical stresses at weak sites or flaws resulting from electrostriction and surface tension effects may cause the local breakdown events, which rapidly heal in nonaggressive environments. In fact, the background passive current density may come from a summation of many such breakdown and repair events. In chloride-containing solutions, however, there would be a lower likelihood for such a breakdown to heal because of the inhibition of re-passivation by chloride. The film-breaking model really involves initiation based on pit growth stability. It assumes that breakdown will always occur, albeit at a rate that depends on many factors related to the passive film properties. However, according to this model, breakdown will only lead to pitting under conditions where pit growth is possible.

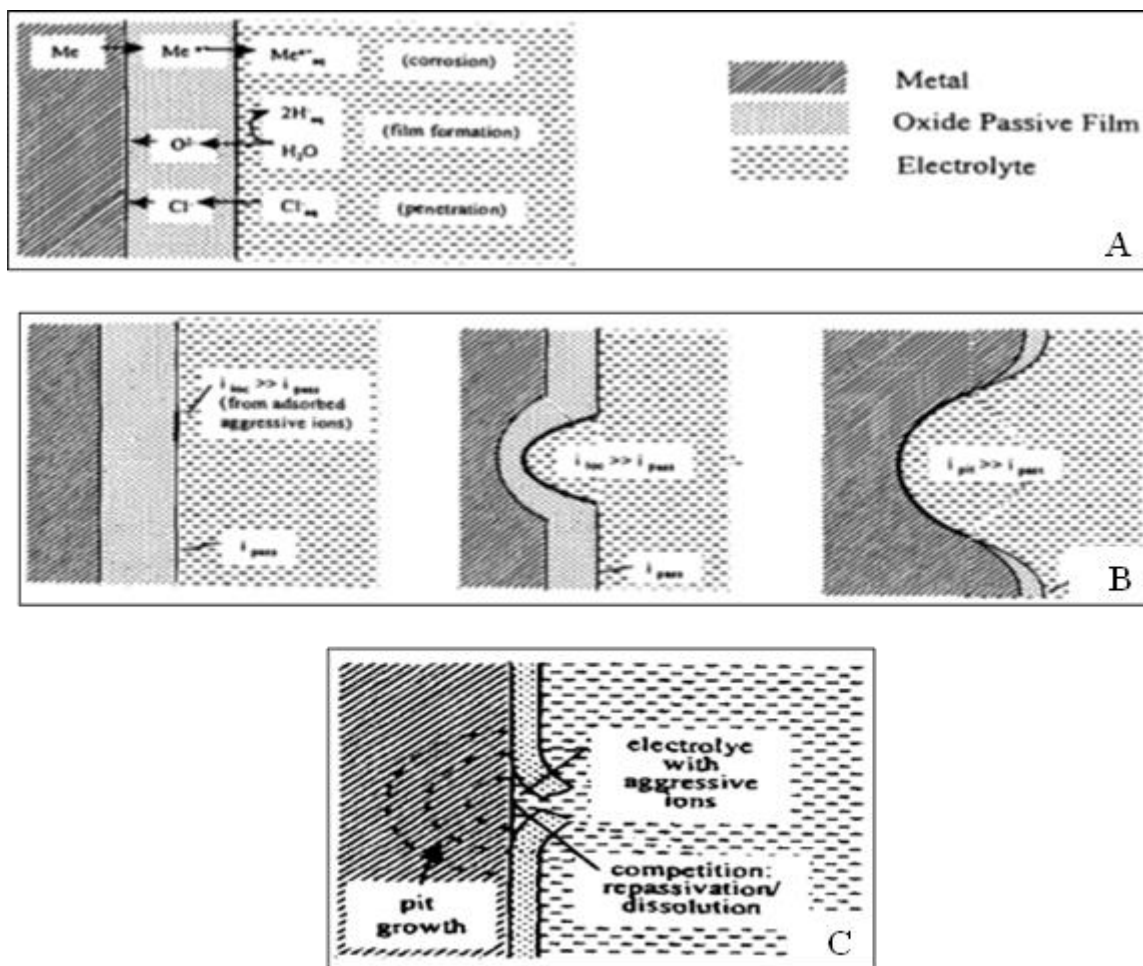


Figure 3. Schematic diagrams representing pit initiation by (a) penetration, (b) adsorption and thinning, and (c) film breaking (17).

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