Pitting corrosion behavior of metal materials and research methods

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Abstract. Pitting corrosion occurs easily in metal pipelines containing corrosive media, which leads to premature failure of pipelines, oil, gas and water leakage, and increases the risk of environmental pollution. In this paper, the conditions of metal pitting, several nucleation mechanisms, growth and repassivation processes of metal metastable pitting are summarized. Corrosion electrochemical measurement technology can reflect the behavior characteristics of metal materials in the process of corrosion. The application of pitting of metal materials in the medium is introduced by using such electrochemical measurement techniques as polarization curve, electrochemical impedance spectrum, electrochemical noise and scanning electrochemical microscope.

1. Introduction

Pitting corrosion is also known as pinhole corrosion, which has a small diameter and deep depth. Pitting corrosion pits nucleate on a microscopic scale, and cause metal and alloy failure through failure mechanisms such as perforation and stress corrosion cracking. Corrosion pits are always covered by corrosion products and cannot be found in time, and detection is difficult. Therefore, pitting corrosion is one of the most destructive forms of corrosion in metal [1]. Pitting corrosion includes three stages: pitting nucleation, metastable pitting growth and repassivation, and steady-state pitting. The factors affecting pitting corrosion mainly include chemical composition, microstructure characteristics, a second phase, grain size and other physical states of the metal, as well as environmental factors such as temperature, pH value and corrosive medium, etc., which all have a great influence on the corrosion resistance of the metal [2]. Pitting corrosion is an important factor that restricts the service time and integrity of oil and gas pipelines [3], so pitting resistance has become a feature of many metal components and structural design. To have a deeper understanding of the initiation and growth process of metal pitting, the forming conditions of metal pitting, the nucleation stage of metal pitting and the research methods of metal pitting are briefly discussed in this paper.
2. **Pitting conditions**

1) Passive metal materials and metal surfaces covered with passivation films, metal non-metallic inclusions or surface coated with cathodic coatings are prone to pitting corrosion.

2) Pitting corrosion generally occurs in media containing corrosive ions, such as oxidizers and passivation solutions that also have active anions. Metals are particularly sensitive to the corrosive medium of halogen ions, and the order of action is Cl->Br->I-.

3) Above a certain anode critical potential, the current density suddenly increases and pitting corrosion occurs. This pitting corrosion potential is called the pitting corrosion potential or breakdown potential (E_b). The pitting potential reflects the difficulty of the surface passivation film being broken down and is the most important factor in the existence of pitting corrosion. For the polarization curve, the potential E_p corresponding to the passivation current is also called the protection potential. Pitting corrosion greater than E_b develops rapidly. Between E_b and E_p, the developed pits continue to develop, but no new pits are generated; less than E_p, pitting corrosion does not occur, so the higher the potential, the better the pitting resistance of the material it is good. The closer E_b and E_p, the stronger the repairability of the passive film [4].

3. **Pitting nucleation stage**

Pitting corrosion has a certain period of incubation before it occurs, and the duration depends on the type of metal and the type of corrosive environment. The incubation stage is a metastable stage. The growth of pitting pits mainly includes the nucleation and growth of metastable pores and the process of metastable pores transforming into stable pit.

3.1. **The process of pit nucleation**

Nucleation models may vary in different media environments. The main influencing factors leading to the initiation and propagation of pitting corrosion are: local chemical and mechanical damage of the passivation film, dissolved oxygen in the environment, pH value and chloride ion concentration. The nucleation model of pitting corrosion is classified into two categories, namely the passivation film damage model and the adsorption model [5].

3.1.1. **Passivation film destruction model.** In the solution medium, a passivation film formed by Cr/Fe oxide will be formed on the metal surface, and it has been in a dynamic process of passivation-destruction [6]. Due to the presence of inclusions, grain boundaries, dislocations and solute impurities in the metal, the surface of the metal is rough and uneven [7], the passivation film destruction theory believes that mechanical and chemical effects will break the weak parts of the passivation film [8]. When the active anions are adsorbed to the surface of the passivation film, because of the electrostatic repulsion between the ions of the same number, the interfacial tension at the solution interface is reduced. When the stress is large enough, the passivation film will break [9]. Also due to the presence of sulfur-containing inclusions in stainless steel, the alloy composition around it changes, resulting in the formation of chrome-poor areas [10]. In a solution containing the corrosive ions, metal poor chrome area will accelerate the dissolution, the sulfide inclusion is formed grooves, and change the surrounding environment, the environment of the local solution, sulfide inclusion dissolve itself can also occur, dissolve the product in the original position to form shell, sulfur forming block area, chemical properties of solution in the area of change, leading to the steel substrate is not stable, forming pitting nuclear [11].

3.1.2. **Adsorption model.** According to the adsorption model, the passivation film formed on the metal surface is not in a static state, but in a dynamic equilibrium between dissolution and repassivation. This theory holds that the competitive adsorption of active chloride ion with oxygen can cause pitting corrosion [12]. In the initial solution, the metal surface is covered with stable oxide ions formed by water. Since chlorine ion is more absorbent than oxygen ion and hydroxide ion, the chloride complex replaces stable oxide ions, and the passivation film here is destroyed and pitting formed [13].
3.2. Growth and repassivation of metastable pitting corrosion
All stable pits underwent metastable growth stages before stabilization. Due to the formation of passivation film on the metal surface, most of the metastable pitting pits will subsequently disappear [14]. Metastable pitting pits occur far below the pitting potential, and the passivation film on the stainless steel surface has been broken and repaired. After the formation of pitting nuclei, cations leave the surface of the passivation film and enter the solution. The adsorption of anions leads to the appearance of cation vacancies on the interface between the passivation film and the dissolution. Finally, the cation vacancies penetrate the passivation film and accumulate at the interface between the passivation film and the metal. The diffusion rate of vacancies in the passivation film is greater than the generation rate of cations at the interface between the passivation film and the metal, and the cation vacancies are concentrated here, resulting in the thinning of the passivation film. When the radius of the vacancy is larger than the critical size, stable pitting will be formed quickly. Other factors such as the size of active impurities, geometry and fatigue stress also lead to metastable pitting over steady-state pitting [15].

3.3. Transition from metastable pitting to steady-state pitting
Most metastable pitting corrosion will stop growing and occur repassivation, and some will develop into stable pitting corrosion obeying random law. After pitting, because the metal potential inside the hole is negative and the metal potential outside the hole is positive, the metal inside and outside the hole constitutes a microcouple corrosion battery, forming the area ratio of large cathode and small anode. Due to the high current density of anode, the corrosion hole is deepened with fast diffusion speed, and the iron ion and active anion in the hole are enriched continuously, and the dissolution is faster than before. Cathodic reaction occurs at the pits due to the presence of oxygen, and the pH value increases there. The iron ions in the pits combine with OH⁻ to form Fe(OH)₃ precipitates and scale deposits. The precipitate formed by CaCO₃ will block a part of the pits. The Cl⁻ exchange in the pore is hindered, and the concentration of Fe²⁺ and Cr³⁺ in the pore is increasing. In order to maintain electrical neutrality, chloride ions outside the corrosion hole migrate into the corrosion hole to maintain electrical neutrality, forming a soluble salt FeCl₃, so that the solution formed in the pit. The chloride ion concentration reaches 3-10 times of the overall solution. The hydrolysis of chloride in the pit produces more H⁺ and Cl⁻, which reduces the pH value inside and outside the pit, increases the acidity, and the pH is about 2-3. The anodic dissolution further increases, and the pitting corrosion continues to develop as an autocatalytic process. The result of autocatalysis and the high concentration of chloride in the pores aggravated the corrosion in the pores, and the corrosion pits continued to develop deep.

4. Pitting corrosion research methods
The research methods of metal pitting include electrochemical measurement and surface morphology analysis. Electrochemical method is mainly used to judge the change of electrode surface state through the change of electrochemical parameters, and surface morphology analysis technology is used to observe the corrosion state of electrode and judge the accuracy of electrochemical method. In recent years, electrochemical impedance, electrochemical noise, scanning electrochemical microscope, polarization curve and other techniques have been gradually applied in the evaluation of metal pitting performance, which makes the pitting research further and further developed.

4.1. Chemical immersion method
The chemical immersion method is mainly by immersing the metal material in a solution containing corrosive ions for a period of time. The morphology can be shown by weight loss and observing the metal material, and the pitting pit morphology, pit depth and size can be obtained. Since pitting corrosion is sensitive to the scratches on the surface of the material, it is necessary to carefully polish the surface of the sample with sandpaper when processing the sample to ensure that the sample surface is clean and tidy without scratches. The chemical immersion method is only a macroscopic characterization of the sample, and further research on the pitting mechanism of the sample is required, and an electrochemical measurement method is required.
4.2. Polarization curve measurement method
The polarization curve measurement method can not only be used to evaluate the sensitivity of pitting corrosion and measure the rate of pitting corrosion, but also to compare basic electrochemical characteristics such as the self-corrosion potential and self-corrosion current density of the sample in different solutions [16]. Polarization curve measurement methods include potentiodynamic polarization curve and potentiostatic polarization curve. The pitting rupture potential $E_b$ and the pitting protection potential $E_p$ can be obtained from the potential polarization scanning curve. The more positive the $E_b$ is, the stronger the pitting resistance is, and vice versa; $E_p$ reflects the passivation of the metal in corrosive media Ability, the more positive the $E_p$, the stronger the passivation ability of the metal. Potential-constant polarization refers to the change rule of corrosion current density with time measured at a given potential. From the potential-constant polarization curve, nucleation time, development speed and other parameters representing pitting corrosion characteristics of materials can be obtained. In general, the constant potential is slightly less than the pitting rupture potential.

4.3. Electrochemical impedance spectroscopy technology
Electrochemical impedance spectroscopy technology is mainly used to study the nucleation and development process of metastable pitting corrosion. Through the changes of electrochemical impedance parameters, there is a certain understanding of the formation and development of sample pitting corrosion. It is generally considered that the high frequency and low frequency of the passive metal are single capacitive reactance arc in the passivation state; the high frequency part is capacitive reactance arc during the pitting corrosion induction period, and the low frequency part is inductive reactance arc; when pitting corrosion grows steadily, the low frequency inductive reactance arc disappears and replaces it. It is the low frequency capacitive reactance arc, and the high frequency is still capacitive reactance arc.

The length of the induction period of pitting corrosion can be obtained from the Nyquist diagrams of different materials soaked for different time, and then the corrosion resistance of the pitting corrosion of the material can be known. Jia Zhi Jun [17] used potential scanning electrochemical impedance spectroscopy (DEIS) to study the pitting behavior of stainless steel in solutions containing Cl-. With the increase of the applied polarization potential, the passivation film on the sample surface increased. It is thick, and then undergoes the initiation of metastable pitting and the development of steady-state pitting. The pitting sensitivity increases with the increase of polarization potential. The impedance data shows that the passivation film is a double-layer structure. The outer layer is a porous layer, and the inner layer is a dense layer.

4.4. Electrochemical noise method
Electrochemical noise is the random non-equilibrium fluctuation phenomenon of electrochemical parameters such as electrode potential, current density and capacitance during electrochemical experiments. These nonequilibrium fluctuations reflect the nucleation of the pitting hole, the rupture of the passivation film and the repair of the passivation film. The occurrence and growth of pitting corrosion can be judged according to the variation characteristics of noise resistance $R_n$. Some scholars used electrochemical noise technology to measure the pitting growth process of 304 stainless steel in FeCl3 solution. Noise resistance $R_n$ fluctuated at a high level at the initial stage of immersion, and the samples showed passivation state. After 4-14 hours of immersion, $R_n$ decreased, and now the pitting induction period had entered. When the white noise appears in the low-frequency area, the potential suddenly drops and does not recover, and metastable pitting corrosion develops into steady-state pitting corrosion. When both electrochemical noise wave and noise resistance $R_n$ tend to be stable, pitting corrosion develops steadily and pitting pits are formed on the sample surface [18].

4.5. Scanning electrochemical microscope technology
Scanning electrochemical microscope (SECM) can be used to study the mechanism of metal pitting. SECM is an in-situ electrochemical measurement technology developed by scanning tunneling
microscope (STM) with a resolution between ordinary optical microscope and STM. SECM can detect current in solution or apply current between the microelectrode and the sample. Its biggest feature is that it can conduct real-time, on-site and three-dimensional observation of the research system. Because the redox current of the scanning microprobe has the characteristic of feedback, it is directly related to the composition of the solution, the distance between the microprobe and the substrate surface, and the indication characteristics of the substrate electrode. It has superior chemical sensitivity and can accurately monitor information on the microscopic scale of metal corrosion behavior.

González-García [19] used SECM technology for the first time to monitor the metastable pitting corrosion of stainless steel under the open circuit potential in Cl\textsuperscript{-} solution. The results show that the anodic current peak on the scanned image represents the current change in the oxidation reaction of Fe\textsuperscript{2+} diffused from the metastable pits on the probe, and the reduction reaction of dissolved oxygen occurs near the metastable pits in the solution, thereby promoting. After the oxidation of Fe\textsuperscript{2+}, the anode current peak shifts negatively to the cathode current peak. This is because the dissolved oxygen around the etch pit not only generates water, but also generates hydrogen peroxide that reacts with Fe\textsuperscript{2+}, which is detected by the probe. The Fe\textsuperscript{2+} oxidation current decreases, so SECM can simultaneously monitor metastable pitting corrosion and the cathodic reaction around the pits.

5. Conclusion
Metal materials are prone to pitting corrosion in media containing corrosive ions, destroying the integrity of the materials, shortening the service life of the metal materials, and causing huge economic losses. The development of electrochemical technology has greatly promoted the research in the field of corrosion. The application of electrochemical measurement methods and surface topography analysis techniques to study the pitting process of metal materials has great theoretical and practical significance for exploring the nature of corrosion. However, there are certain difficulties in dealing with some complex processes, which cannot be accurately analyzed. In the future, electrochemistry will also devote itself to more accurate analysis of the steps and principles of the corrosion process, in order to propose more practical methods to be applied to actual metal corrosion protection.

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References
[1] Tian W, Du N, Li S, et al. Metastable pitting corrosion of 304 stainless steel in 3.5% NaCl solution[J]. Corrosion Science, 2014, 85: 372-379.
[2] Akpanyung K V, Loto R T. Pitting corrosion evaluation: a review [C] //Journal of Physics: Conference Series. IOP Publishing, 2019, 1378(2): 022088.
[3] Tian W, Li S, Wang B, et al. Pitting corrosion of naturally aged AA 7075 aluminum alloys with bimodal grain size [J]. Corrosion Science, 2016, 113: 1-16.
[4] Jiang J, Liu Y, Chu H, et al. Pitting corrosion behaviour of new corrosion-resistant reinforcement bars in chloride-containing concrete pore solution [J]. Materials, 2017, 10(8): 903.
[5] Marcus P, Maurice V, Strehblow H H. Localized corrosion (pitting): A model of passivity breakdown including the role of the oxide layer nanostructure [J]. Corrosion science, 2008, 50(9): 2698-2704.
[6] Hoar T P, Mears D C, Rothwell G P. The relationships between anodic passivity, brightening and pitting [J]. Corrosion Science, 1965, 5(4): 279-289.
[7] Cui Zhifeng, Han Yichun, Zhuang Lijian, et al. Metal corrosion behavior and mechanism in Cl\textsuperscript{-} environment [J]. Corrosion and Protection in Petrochemical Industry, 2011, 28(4): 1-5.
[8] Kant R, Chauhan P S, Bhatt G, et al. Corrosion Monitoring and Control in Aircraft: A Review [M] //Sensors for Automotive and Aerospace Applications. Springer, Singapore, 2019: 39-53.
[9] Lei Yongyong, Zhang Hongyu. Summary of Metal Pitting Corrosion Behavior [J]. Total...
Corrosion Control, 2016, 30(8): 11-15.

[10] Bhandari J, Khan F, Abbassi R, et al. Modelling of pitting corrosion in marine and offshore steel structures–A technical review [J]. Journal of Loss Prevention in the Process Industries, 2015, 37: 39-62.

[11] Ryan M P, Williams D E, Chater R J, et al. Why stainless steel corrodes [J]. Nature, 2002, 415(6873): 770-774.

[12] Burstein G T, Pistorius P C, Mattin S P. The nucleation and growth of corrosion pits on stainless steel [J]. Corrosion Science, 1993, 35(1-4): 57-62.

[13] Pan Ying, Zhang Sanping, Zhou Jianlong, et al. Research progress in pitting nucleation process of metallic materials [J]. Equipment Environmental Engineering, 2010, 7(4): 67-70.

[14] Loto R T. Pitting corrosion evaluation of austenitic stainless steel type 304 in acid chloride media [J]. J. Mater. Environ. Sci., 2013, 4(4): 448-459.

[15] Akpanyung K V, Loto R T. Pitting corrosion evaluation: a review [C] //Journal of Physics: Conference Series. IOP Publishing, 2019, 1378(2): 022088.

[16] Shinde V P, Patil P P. A study on the electrochemical polymerization, characterization, and corrosion protection of o-toluidine on steel [J]. Journal of Solid State Electrochemistry, 2013, 17(1): 29-41.

[17] Jia Z, Du C, Li C, et al. Study on pitting process of 316L stainless steel by means of staircase potential electrochemical impedance spectroscopy [J]. International Journal of Minerals, Metallurgy, and Materials, 2011, 18(1): 48-52.

[18] Klapper H S, Goellner J, Burkert A, et al. Environmental factors affecting pitting corrosion of type 304 stainless steel investigated by electrochemical noise measurements under potentiostatic control [J]. Corrosion science, 2013, 75: 239-247.

[19] González-Garcia Y, Burstein G T, González S, et al. Imaging metastable pits on austenitic stainless steel in situ at the open-circuit corrosion potential [J]. Electrochemistry communications, 2004, 6(7): 637-642.