The metastable pitting potential and its relation to the pitting potential for four materials in chloride solutions

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ABSTRACT

The metastable pitting potential for four materials, Q235 steel, X70 steel, pure iron and 316L stainless steel in chloride solutions were measured by slow scan potentiodynamic polarization. For the four materials, good linear relationship exists between the metastable pitting potential E_m and pitting potential E_b. The close relationship between the two parameters is attributed to the passivity of the metals in environments, which plays the key role in both the nucleation processes of metastable pitting and stable pitting. Higher passivity results in higher average pitting potential and larger difference between average E_b and E_m values.

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1. Introduction

Many researchers have observed that before pitting of metals and alloys some small current fluctuations occur, which are the results of the nucleation, growth and repassivation of metastable pits on the surface, and are defined as metastable pitting [1–6]. Many previous studies on metastable pitting corrosion focused on stainless steels and aluminum alloys. Stewart and Williams [7] studied the effect of inclusions on the early stage behavior of austenitic stainless steels and pointed out that the sulfur-rich inclusions dominate as pit nucleation sites and the lifetime of metastable pits is related to the size of the inclusion particles. The nucleation frequency and lifetime of metastable pits were both notably reduced after laser surface melting treatment. Burstein and Pistorius [8] investigated the effects of surface roughness on metastable pitting susceptibility of 304 stainless steel in Cl⁻ solution and the transition from metastable pitting to stable pitting corrosion. It was indicated that a rougher surface facilitates the incidence of metastable pitting substantially. The stable pitting potential decreases with the increase of surface roughness [9]. Rudd and Scully [10] measured the pitting potential and the current fluctuations of aluminium in solutions containing Cl⁻. The effects of six inhibitors on the repassivation process of pitting corrosion were compared. The inhibitors are effective in raising the pitting potential in the decreasing order: nitrate > phosphate > citrate > tartrate

> benzoate > acetate. Cheng et al. [11] studied the role of Cl⁻ in metastable pitting of A516 carbon steel using electrochemical noise method, and pointed out that the main role of Cl⁻ in pitting is to increase the breakdown chance of the passive film, rather than to inhibit the surface repassivation. Dong et al. [12] studied the roles of the inhibitors nitrite and TEPA on nucleation, growth and repassivation of pitting corrosion of Q345 carbon steel in synthetic carbonated concrete pore solution containing Cl⁻. It was concluded that the two inhibitors reduce the donor density in passive film, leading to a more positive film breakdown potential. Moreover, nitrite can decrease the size and density of pits, and results in quicker repassivation rate for both metastable pits and the broken passive film. Gupta et al. [13] reported the relationship between the metastable pitting rates and the hardness values of pure aluminium and several aluminium alloys. The increase in hardness was found to be proportional to the metastable pitting rate observed, and the metastable pitting rate tends to increase with the electrochemical heterogeneity of the alloys studied.

Generally, after stable pits occur, serious damage already exists on material surface. On the other hand, metastable pits usually develop into a few microns then repassivate, causing smaller damages on material surface. There are consistency and correlation between the behavior of stable pitting and that of metastable pitting [14]. The growth rate of a pit is controlled by the outward diffusion process of the species in the pit. If the acidity and the concentration of aggressive ions to keep dissolution in a pit cannot be maintained, repassivation would happen. When a pit has developed to the critical condition which can maintain continuous

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dissolution in the pit, the metastable pit would transform to a stable pit. Williams et al. [15] analyzed the current fluctuations during metastable pitting stage of stainless steel. The statistical relationship between metastable pitting and stable pitting was explored in order that a transition probability for the pit from metastable to stable propagation is derived. Frankel et al. [4] proposed a critical condition for a metastable pit to transfer to stable pit: the product of the dissolution current and the pit radial, *ir*, reaches 4 mA/cm, while Burstein et al. [2,16–18] suggested a pit stability product of 3 mA/cm. Trueman [19] reported that for 2024 aluminum alloy in NaCl solution, the critical value for a stable pit is 15–20 μC. Hudson et al. [20–22] explained metastable pitting in another way. They suggested that once a metastable pit forms, reactions in the pit produce aggressive species that move laterally away into the bulk. These species act on the film and weaken the protective layer. Under certain condition an "explosive autocatalytic grow" in the number of matastable pits may happen.

On a potentiodynamic polarization curve the potential corresponding to the first current peak may be called as metastable pitting potential [23], and the potential where continuous current increase starts is considered as the pitting potential. Although there were many studies on metastable pitting corrosion, studies on the nature and affecting factors of metastable pitting potential and the relation to pitting potential were seldom reported. Our previous work [23,24] investigated the influence of Cl^- and surface roughness on metastable pitting potential E_m and pitting potential E_b values of carbon steel and stainless steel. The results showed that the changes of E_m and E_b with Cl^- concentration follow similar tendency, and as the surface roughness decreases, both the nucleation rate and the peak current of metastable pits decrease, while the E_m and E_b potentials move in the positive direction. Therefore, it is reasonable to presume that there is internal relevance between the parameters E_m and E_b. However, more studies are required to understand the relation between the two important parameters. In this paper, potentiodynamic polarization curves of two carbon steels (Q235 and X70), pure iron and 316L stainless steel in solutions containing Cl^- were measured. The influence of measuring condition on metastable pitting potential was studied, the distribution characteristics of the metastable pitting potential E_m and the pitting potential E_b of the four materials were investigated, and the relationship between these two potentials was explored. A clear understanding of the relationship between E_m and E_b would be beneficial for the prediction about the occurrence of pitting corrosion.

2. Experimental

The test materials included Q235 steel, X70 steel, 316L stainless steel and pure iron. The purity of pure iron is more than 99.99%. The compositions of the other three steels are shown in Table 1.

The size of the specimens was 1 cm × 1 cm × 1 cm. The working surface of the electrode was manually abraded with 240, 600, 1000 grit silicon carbide papers successively, and cleaned with de-ionized water and alcohol. Then the samples were coated with epoxy resin after welding copper wire to one end, leaving an area of 0.16 cm² exposed to test solution.

Polarization measurements for the four materials were carried out in different solutions as follows: 0.1 mol/L NaCl solution (pH = 7.0) for 316L stainless steel, 0.5 mol/L $NaHCO_3$ solutions (pH = 8.2) with 0.1 mol/L and 0.15 mol/L NaCl for Q235 steel and X70 steel respectively, and 0.1 mol/L $NaNO_2$ + 0.1 mol/L NaCl solution (pH = 7.0) for pure iron. In above solutions the tested materials respectively showed typical metastable pitting behavior and the initial tiny current fluctuations may be clearly observed.

Potentiodynamic polarization curves of the four materials in the test solutions were measured using a CS350 electrochemical workstation (Corrtest Company, China). The polarization tests were begun at a potential 300 mV (vs. Ag/AgCl) below the open circuit potential, at a potential scanning rate of 0.2 mV/s in anodic direction until stable pitting happened. The data acquisition rate was 20 times per second and no data smoothing was applied. Because of the stochastic character of pitting corrosion, under each experimental condition twelve tests were run. The data from the parallel tests were statistically analyzed. A three electrode system was used in the test. The steel specimen worked as a working electrode, a platinum electrode functioned as a counter electrode, and the reference electrode was a Ag/AgCl electrode. All the tests were performed at ambient temperature.

To understand the effect of surface inclusions on pitting nucleation, for each material some samples were manually polished and the surface morphologies were observed with a scanning electronic microscope before and after polarization tests. Energy disperse spectroscopy (EDS) was used to discern the inclusions. The polarization tests were carried out in above described solutions and the polarization scanning rate was 0.2 mV/s until stable pitting occurred.

3. Results and discussion

3.1. The effects of measuring condition on metastable pitting potential

Fig. 1a shows a typical polarization curve of 316L stainless steel in 0.1 mol/L NaCl solution. As the potential increased, current fluctuations occurred and both the peak current and the number increased gradually. Because the background current fluctuated by a range of 0.02–0.03 μA/cm² (Fig. 1a and c), if the peak current of a fluctuation is less than 0.02 μA/cm², it may be confused with the background noise. Therefore, we selected 0.02 μA/cm² as the standard for initiation of metastable pitting. Since a current fluctuation is focused at a very small local site, the sample area may be ignored. Additionally, because the initial pit repassivates very quickly, we may simply use the peak current instead of the electric quantity. Therefore, when a current peak is 0.02 μA higher than the background, it is considered as a metastable pitting process. On a polarization curve the potential corresponding to the first 0.02 μA current peak is referred to as metastable pitting potential E_m, which is point C in Fig. 1a, and the potential from which the current increases continually is denoted as pitting potential E_b. Fig. 2 shows the polarization curves of Q235 steel, X70 steel and pure iron in the testing solutions and the E_m and E_b potentials were obtained in the same way.

The selected standard above was based on the resolution of the instrument and the signal to noise ratio. As the result the current peaks smaller than the selected standard would be neglected. In order to examine the influence of the current standard selection on the measurement of E_m potential, we selected 0.02 μA,

Table 1
The compositions of the steels (wt.%, balance Fe).

	C	Mn	P	S	Si	Ni	Cr	Mo	O	N
Q235	0.11	0.74	0.012	0.0028	0.13	–	–	–	0.010	0.0040
X70	0.063	1.29	0.010	0.0015	0.19	–			0.0026	0.0030
316L	0.021	1.05	0.031	0.02	0.69	12.4	17.61	2.29	–	–