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# Microelectrode Studies on the Pitting Corrosion Process of Stainless Steel

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Differing with the scanning microelectrode techniques<sup>[1]</sup>, which scan microelectrode closely to the interface of electrode/electrolyte and make electrochemical imaging in a lateral spatial resolution, the technique of microelectrode with a micron diameter is of very high time-resolution and ratio of signal/noise in electrochemical measurements. The microelectrode technique allows double-layer capacitance and background current for a microelectrode to be drastically reduced due to the exposed area of a microelectrode is usually 6~8 orders of magnitude lower than that of a conventional electrode with large-scale exposed area<sup>[2,3]</sup>. Microelectrode was recently developed as a new powerful electrochemical technique and widely used in the studies of electrochemical kinetics, electrodeposition, electroanalysis and batteries<sup>[4]</sup>. However, most of the microelectrodes was limited with the novel metals, such as Pt and Au, and only a little of work has reported on using microelectrode in corrosion research<sup>[5,6,7]</sup>. In the present work, the microelectrode technique was developed to study the initiation and propagation of pitting corrosion of 18/8 stainless steel. The insight into the dissolution process of inclusion defects at the anodic potential of active dissolution and the dynamic behavior of growth and ceases for the micropitting during its development was attained. Microelectrode technique may offer a numbers of advantages for further recognizing the mechanism of pitting corrosion: to catch the fast and weak signal in an early stage of pitting initiation because of extreme low in both of double-layer capacitance and background current for a microelectrode; to clarify the dependence of pitting nucleation on the inhomogeneous defects; and to follow the propagation process for a simulated single pitting corrosion.

## 1 Experimental

The microelectrochemical investigation was performed on a wire of A ISI 302 stainless steel with a diameter of 25  $\mu\text{m}$  (Goodfellow Metals). The schematic arrangement of micro-

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electrode was showed in Figure 1. The stainless steel wire of 20mm length was connected electrically to a copper wire of 0.5 mm diameter and 100 mm length, and then it was imbedded in glass tube of 3 mm inner diameter by an epoxy adhesives. The exposed surface of the microelectrode was mechanically ground with diamond paste to a mirror and rinsed with distilled water and ethanol. All solutions were prepared from reagent grade chemical and distilled water. In order to perform the electrochemical measurements with current range of  $10^{-10}$  to  $10^{-12}$  A, a homemade computer aided electrochemical measuring system was developed, and the good shielding and grounding circuit to suppress electromagnetic interference were arranged in the experiments. The three electrodes configuration was employed, in which the working electrode was microelectrode of stainless steel, the counter electrode was platinum foil and the reference electrode was saturated calomel electrode (SCE). The experiments were performed in the ambient condition.

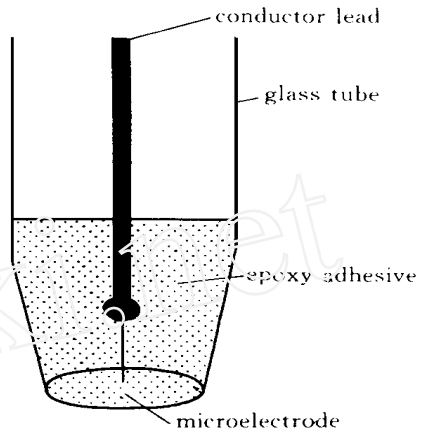


Fig 1 Schematic arrangement of microelectrode

## 2 Results and Discussion

### 2.1 Transient behaviors of passivity

Figure 2 illustrated a relationship of current and time obtained from a stainless steel microelectrode under the different anodic polarization at +0.2 V and +0.7 V (SCE) respectively in a solution of 1 mol/L  $\text{Na}_2\text{SO}_4$ . It was clear to note that there is a distinct current fluctuation of 2~6 pA for the stainless steel microelectrode during the anodic polarization in  $\text{Na}_2\text{SO}_4$  solution. The current transients were believed to be related directly to the events of micro breakdown, self-repairing and repassivation of the surface passive film of stainless steel. The dynamic passivity behavior for the competition of breakdown and repassivation remained obviously in the whole anodic process and varied with the environmental conditions. When the polarization potential was shifted from +0.2 V to +0.7 V (SCE), the peak current and background

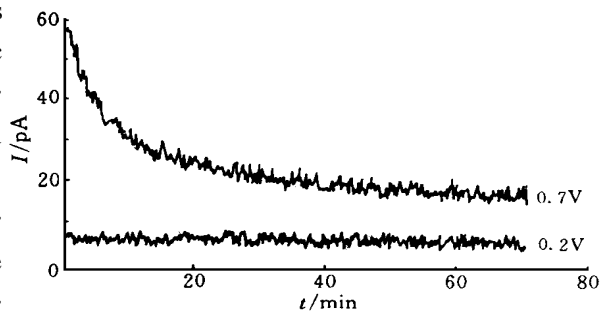


Fig 2 Relationship of current and time obtained from a stainless steel microelectrode under the different anodic polarization at +0.2 V and +0.7 V (SCE) respectively in a solution of 1 mol/L  $\text{Na}_2\text{SO}_4$

current increased, which meant that the tendency of passivity breakdown was strengthened. When +0.7 V anodic potential was applied to the microelectrode, the background current gradually decreased with time, and finally remained in a constant current level. No crevice corrosion was observed in the experiments.

It was also demonstrated that the local breakdown of passivity and micro pitting corrosion was possible to occur even in chloride-free solution. However, this kind of micro pitting corrosion was metastable one and usually cannot propagate to be a visible pitting corrosion under the experimental condition. The result indicated that addition of chloride to  $\text{Na}_2\text{SO}_4$  solution raised to a distinct increase of the peak current and the frequency of current fluctuation. Despite chloride plays a vital role in the initiation and propagation of pitting corrosion, chloride is not a unique necessary condition for inducing the local breakdown of passivity and micro pitting corrosion. For a commercial stainless steel, it usually contains many different kinds of defects and inclusions, which may dissolve and re-passivate, and result in a current fluctuation in its anodic process. In the experiment condition the dissolution and elimination of the corrosion active or non-active inclusions did not cause a visible pitting corrosion, but actually result in a modification on the surface of stainless steel.

## 2.2 Effect of inclusion defects

When a stainless steel electrode with large scale exposed area was controlled at -0.25 V (SCE), corresponding to its active dissolution potential, in 1 mol/L  $\text{Na}_2\text{SO}_4$  + 1 mol/L NaCl solution, an increase of the current for anodic dissolution was generally observed. In this condition the stainless steel had not attained to passivation, a more uniform dissolution on the whole surface increased with time. It was interesting to note from figure 3 that the current peak appeared at beginning of 1~2 minutes, and then some anodic current transients overlaid on the average polarization curve when a microelectrode of stainless steel was controlled at its active dissolution potential in the same solution. Obviously, the irregular current peaks appeared at the potential of active dissolution were attributed to the active dissolution of the defects on first layer of surface, and then continued exposure and dissolution of inclusion defects during the process of active dissolution for a stainless steel microelectrode. The irregular small current peaks can be sensed only for microelec-

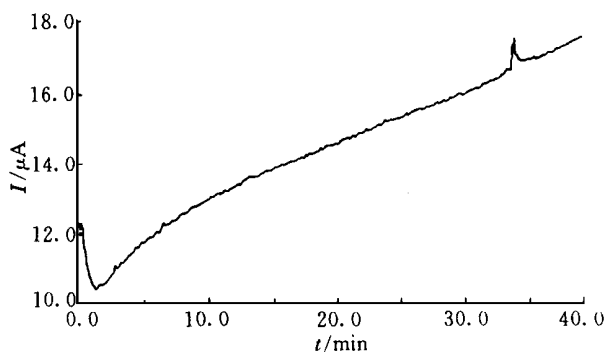


Fig. 3 Potentiostatic current-time curves for a microelectrode of stainless steel controlled at -0.25 V (SCE) and immersed in 1 mol/L  $\text{Na}_2\text{SO}_4$  + 1 mol/L NaCl solution

trode because of its extreme reduction of the background current. Accompanying with the further average dissolution of a microelectrode, the inclusion defects which distributed at random in stainless steel exposed and dissolved. The shape and value of the irregular current peaks were determined on the properties of inclusion defects, such as geometric size, chemical composition, electrochemical activities and etc.

## 2.3 Dynamic behavior of pitting propagation

Figure 4 illustrated a potentiostatic current-time curves for a microelectrode of stainless steel when controlled potential at 1.35 V (SCE) in 1 mol/L NaCl solution. It was indicated that there may exist four stages during the development of pitting corrosion: (i) the current sharply increased to the maximum and pitting corrosion occurred rapidly if the controlled potential was sufficient high; (ii) then the current immediately fell down and self-repassivation of pitting corrosion took place instantaneously; (iii) successively, a current fluctuation with higher amplitude and distinct frequency appeared for a period (about 1 hour), which was attributed to the competition of pitting growth and pitting cease; (iv) finally, the current fluctuation transferred to a small noise with lower amplitude, and pitting development was remained in a average rate as high as  $16.7 \text{ mA/cm}^2$ , approximating to the background baseline of the current fluctuation. It was evidenced that the development of pitting corrosion was a very complex dynamic process.

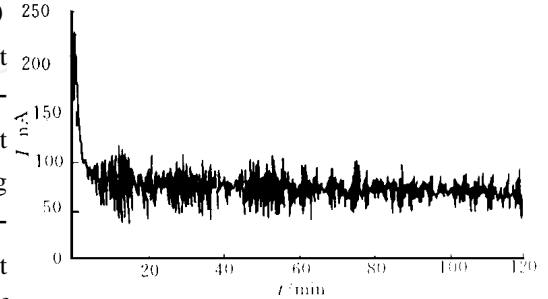


Fig 4 Potentiostatic current-time curves for a microelectrode of stainless steel controlled at 1.35 V (SCE) and immersed in 1 mol/L NaCl solution

An abruptly occurring of pitting corrosion will usually result in a sharp change for the micro geometric size and chemical environments in the micro location, due to the instantaneous reactions involving metal dissolution, hydrolysis, precipitation, and limited transportation between occluded location and bulk solution, and etc.<sup>[8,9]</sup> Therefore, the development of pitting corrosion is a dynamic competition process, and depended on the various chemical and geometric factors in pit position.

Based on a minimum double-layer capacitance and strongly elimination of current background for a microelectrode, the microelectrode technique is able to attain fast and fine information which is very helpful for further understanding initiation and propagation of pitting corrosion. Because the diameter of a microelectrode approximates to the size for a single pit it is also appropriate to perform a simulated study on the kinetic behavior for pitting development, and prevent from the mutual interference among the pits if a traditional electrode with a large scale exposed area used.

### 3 Conclusions

1) Microelectrode technique may offer a numbers of advantages for further recognizing the mechanism of pitting corrosion. It is useful to catch the fast and weak signal in an early stage of pitting initiation because of drastically low double-layer capacitance and background current for a microelectrode, to clarify the dependence of pitting nucleation on the inhomogeneous defects, and to follow the propagation process for a simulated single pitting corrosion.

2) The facts on electrochemical properties of the inclusion defects under potentiostatic controlled anodic active potential, and the complex dynamic behavior for pitting propagation have been obtained for the first time and discussed.

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# 微电极法研究不锈钢点腐蚀发生发展过程<sup>\*</sup>

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**摘要** 应用微电极法研究不锈钢点腐蚀发生发展过程, 首次获得不锈钢夹杂物缺陷在阳极活化电位的活性溶解信息和点腐蚀发展过程蚀点生长和消止两个相互竞争、不断发展的动态行为, 深化对夹杂物缺陷诱导点腐蚀的发生及点腐蚀发展过程机理的认识。实验表明, 应用微电极技术研究点腐蚀过程可具有若干明显特点: a. 由于界面双层电容和背景电流的大幅度降低, 有利于检测点腐蚀发生和发展过程快速、信号微弱; b. 可考察夹杂物缺陷的电化学活性及其诱导点腐蚀成核的重要作用; c. 可研究单孔点腐蚀发展的动态行为及影响因素。

**关键词** 不锈钢, 微电极, 点腐蚀, 机理, 研究方法

<sup>\*</sup> 国家自然科学基金资助项目