

扫描复合微 pH 电极原位测量 局部腐蚀体系 pH 分布图象

林昌健¹ 骆静利² 孙海燕¹ 杜荣归¹

(¹ 物理化学研究所, 固体表面物理化学国家重点实验室, 厦门大学, 厦门 361005)

(² Alberta 大学化学和材料工程系, 加拿大)

摘要 金属点腐蚀是一种典型的局部腐蚀, 点腐蚀过程不仅与金属相组分、夹杂及表面状态等有关, 而且与许多环境因素密切相关, 其中在金属/溶液界面 Cl^- 浓度和 pH 的分布是影响金属点腐蚀发生、发展过程最为重要的微化学环境因素。研究点腐蚀过程中金属/溶液界面微化学环境对于了解点腐蚀机理及过程动力学具有重要的意义。本文首次研制成功复合型 IrO_2/Pt pH 电极, 复合微电极是 IrO_2/Pt pH 微探针和 $\text{AgCl}/\text{Ag}(\text{KCl})$ 微参比电极组成。实验表明, 复合型 IrO_2/Pt 微 pH 电极对 pH 值有良好的线性关系, 测量灵敏度高, 并可补偿局部腐蚀电位差异的影响, 能够原位检测靠近金属/溶液界面二维方向微区 pH 值的分布图象。结合微区电位分布测试仪测量了不锈钢点蚀过程, 金属/溶液界面二维方向微区 pH 值及其变化, 探索了点腐蚀发展过程机理。扫描复合型 pH 微电极可成为原位研究金属局部腐蚀发生、发展过程机理的一种重要方法。

关键词 扫描复合微 pH 电极, 原位测量, pH 分布图象, 局部腐蚀, 微化学环境

Scanning Combination Micro pH Electrode for In-Situ pH Imaging in the Localized Corrosion

Lin Changjian^{1*} Luo Jingli² Sun Haiyan¹ Du Ronggui¹

⁽¹⁾ *Inst. of Phy. Chem., State Key Lab. for Phy.*

Chem. of Solid Sur. Xiamen Univ., Xiamen 361005)

(Dept. of Chem. and Materials Engineering, Alberta Univ., Canada)

Pitting corrosion is a typical kind of the localized corrosions. The process of pitting corrosion is not only associated with the composition of alloy, structure, defects and surface conditions, but also related closely to the various environmental factors. The distribution of chloride ion concentration and pH at the interface of metal/solution are one of the most important environmental determinants to the initiation and development of pitting corrosion. In order to get further understanding the mechanism of pitting corrosion, it is necessary to study the chemical environments in micro area during the process of pitting corrosion. [1-5]

The measurements for the concentration of chloride ion and pH in the occluded area of pitting corrosion have been wildly carried out in recent years. Micro probes are frequently used for determining the chemical species related to corrosion inside pit, and other works are study the corrosion behaviors of metals in the stimulated pit solution^[6]. There are quite few reports on the in situ image of Cl^- and pH at the interface of metal/solution by using scanning micro probes. Lin^[6] obtained in situ images for the localized corrosion by developing scanning combination micro Cl^- probes. Using micro IrO_2/Ir electrode, Lewandowski^[8] determined pH distribution in the two dimensions during the corrosion process of mild steel in neutral solution.

It has been shown that a fair lineal relationship can be gained for the potential response of IrO_2 electrode to pH of solutions^[9,10]. However, if IrO_2 probe is far away from the reference electrode when imaging pH for localized corrosion system, it will be difficult to measure accurate pH distribution, due to the fact that the corrosion potential varies with different position on the same surface and different time during the corrosion process. The measured potential of IrO_2 electrode, E_{meas} , always contains two variables: 1. the potential response to pH at different locations, E_{pH} , and 2. the difference of corrosion potential at different position, E_{corr} , during the corrosion process. Therefore, we have:

$$E_{\text{meas}} = E_{\text{pH}} + E_{\text{corr}} \quad (1)$$

The more accurate pH image for localized corrosion system can be measured if only E_{corr} is compensated completely by combination of micro pH probe and micro reference electrode. In this work, The attempts was made to develop a scanning combination micro pH electrode and to examine its feasibility for study localized corrosion systems. The in situ pH image was measured and the behavior of pitting propagation was characterized for 18/8 stainless steel in neutral NaCl solutions.

The combination micro pH electrode has two compartments: one serves as the pH sensitive probe, and the other acts as the reference electrode. A heavy-wall, two barreled, 1.5/0.8 mm (o. d. / i. d.), 50mm long borosilicate glass capillary was pulled by a puller, under electrically heating, into a pointed-shape micropipette. The inside diameter for two tubes at tip is approximate 25 μm respectively. A platinum wire (Goodfellow) with 20 μm diameter and 25mm long was connected with a copper wire of 0.5mm diameter and 25mm long, and then was inserted into one of barrels. The epoxy resin was used to seal the gap between platinum wire and inside glass tube, and exposed platinum cross section at the tip. At the other end copper wire was sealed in the glass barrel by silicone rubber adhesive. One of the two barrels was filled with 0.1M KCl (agar) for Luggin bridge at the tip and the 0.1 M KCl for filling solution in the glass tube. Finally Ag / Ag-Cl electrode of 0.5 mm diameter and 60 mm long as a reference electrode was inserted into the glass tube, and the top was also sealed by silicone rubber adhesive to avoid the evaporation of KCl solution. A Pyrex glass tube (i. d. 3mm, 50mm long) was used as a holder to connect, by molten wax, two barrel glass with pH probe and reference electrode. The preparation of the combination micro pH electrode was operated with an optical microscope. The structure of the combination micro pH electrode was illustrated schematically in figure1.

The preparations of IrO_2 electrode have been extensively studied in electrolysis industries and electro-chromatic device. Electrodeposition of IrO_2 on a platinum tip was applied in this work. The typical solu-

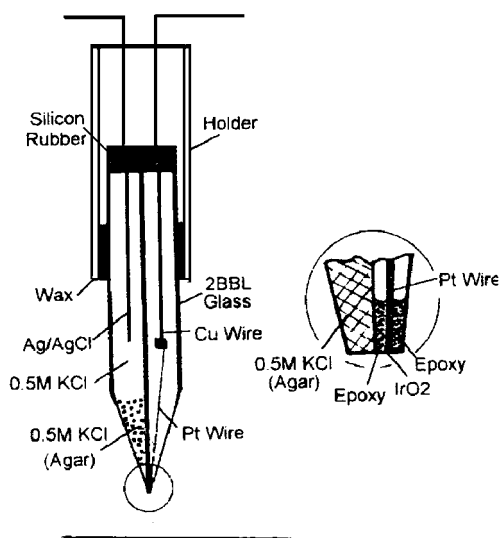


Fig. 1 Schematic structure of combination micro pH electrode

tion composition of electrodeposition^[11] is :

IrCl_3 1.5 g/l, H_2O_2 (30 wt %) 1 ml/l, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ 5 g/l, pH ~ 10.5, adjusted by K_2CO_3 . $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ is a complex compound of electrodeposition for finer plating and to avoid from precipitation of IrCl_3 in the solution. Addition of H_2O_2 in the solution may keep higher rate for the process of electroplating. The solution was prepared by chemical pure reagents and triply distillate water, and aged for one day before application. The electrodeposition of IrO_2 was carried out at 1.0 V (vs. SCE) for 30 min controlled by a micro current potentiostat. A IrO_2 coating with dark blue on the platinum tip as a pH sensor can be obtained for the combination micro electrode. A linear calibration curve was obtained for the combination micro electrode in the solutions with different pH. It was shown that the 70mV/pH curve slope is agreement with the theoretical consideration.

The experiments were carried out using commercial 18/8 stainless steel with a composition : (C 0.091, Si 0.85, P 0.041, Mn 1.38, Cr 18.40, Ni 9.55, wt %). The specimens were fabricated as a cylinder of 6 mm diameter and 20 mm high, and sealed in a Teflon holder epoxy. The testing surface of sample was mechanically

polished to a final with 0.5 μm diamond paste. After polishing, the specimens were degreased with methanol and cleaned several times with triply distilled water. The specimens were connected to a Teflon container through a screw. The specimen was installed onto the scanning stage of the measuring system^[12] with face upward. After carefully adjusting the tip of micro

pH electrode to be very closely (approximately 10 μm) to the specimen surface with an optical microscope, the test solutions of 0.1 M NaCl was added into the cell with a syringe. The electrode potential of the specimen was controlled at 0.3 V (vs. Ag/AgCl) by a micro

current potentiostat. Platinum wire was arranged in circles concentric with the specimen as a counter electrode to maintain an uniform polarization current on RE surface. The solutions in the cell were exposed to air at room temperature throughout the experiments.

Figure 3 is a pH image on the surface of 18/8 stainless steel in 3% NaCl solution when pitting corrosion occurring at 0.3 V potential (vs. Ag/AgCl). It is indicated that an acid chemical

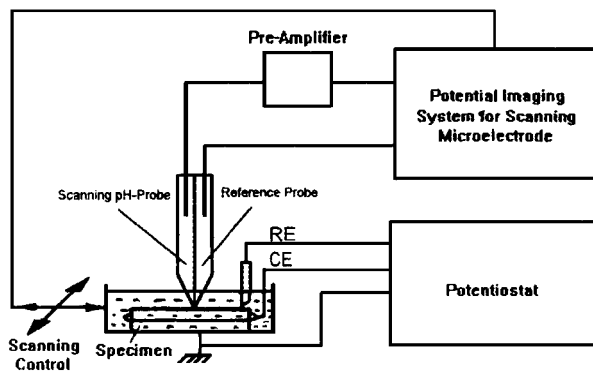


Fig. 2 Arrangement of the measuring system for imaging pH at the interface of metal/solution

environment at the vicinity of pit is setup , due to the pitting corrosion. The pH value at pit location is nearly 2 pH unit lower than that in the other location of passive surface. It was observed in the experiments that there was a uniform pH distribution at the interface of metal/ solution , when no active pitting corrosion happened on the surface of stainless steel. If the anodic polarization was dismantled , the occurred pitting corrosion ceased and pH image tended to become uniform quickly. With the development of pitting corrosion , the pH value of solution at vicinity of active pit decreased slowly (Fig. 3 a ,b) .

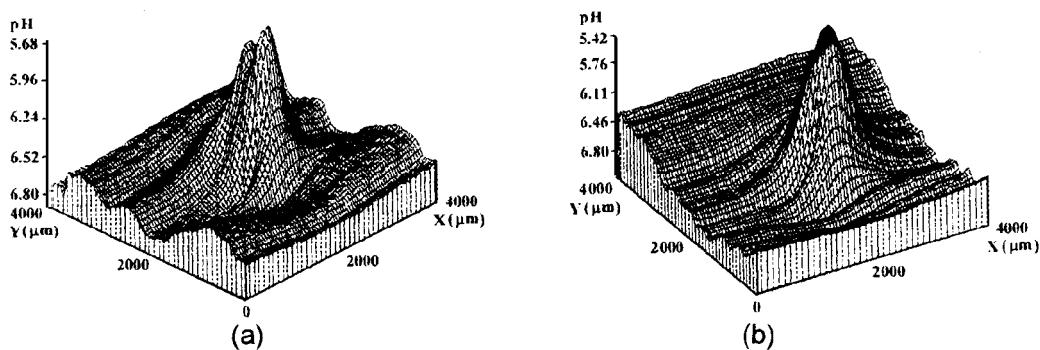


Fig. 3 pH image on the surface of 18/8 s. s in 3 % NaCl solution when pitting corrosion occurring at 0.3 V potential , at different time , (a) 5 min , (b) 10 min.

When pitting corrosion is happening on the surface of stainless steel in neutral NaCl solution , the corrosion reactions including metal dissolution and reduction of dissolved O_2 carry on at anodic and cathodic area respectively , and the hydrolysis reaction of the metal ions accompany around in anodic zone :



For 18/8 austenitic stainless steel , dissolved metal ions are mainly Fe^{2+} , Cr^{3+} and Ni^{2+} . The hydrolysis reactions of these metal ions make the pH value of local solution in vicinity of anode , pitting position , obviously reduction. Because of higher hydrolysis constant of Cr^{3+} and Ni^{2+} dissolved from stainless steel , and difficulty of mass transfer in the occluded geometrical condition , the pH of solution inside pit may drop to as low as $1-2^{[6]}$. The accumulation of H^+ from hydrolysis of metal ions consume by the both ways of evaporation of H_2 and diffusion to bulk solution through the pit mouth. That is why lower pH in vicinity of pit can be sensed when micro pH probe scanning over the surface of metal. Although reduction of O_2 may produce alkaline production at cathodic area , the pH of solution remain constant due to much larger area and free mass transfer in the cathodic area.

The scanning combination micro pH electrode is not only able to indicate accurate location of active pitting corrosion, but also able to monitor the process of pitting development. After local breakdown of passive film of stainless steel, the pitting corrosion initiates and nucleate to form metastable micro pitting. The metastable micro pitting may ceases to be repassivation or continues growth to form a visible pitting corrosion, depending on the condition of micro chemical environment in anodic zone. The in situ pH image can be used to characterize the dynamic process for pitting corrosion, which related to the nature of hydrolysis reaction of metal ion in anodic occluded area, geometrical condition of pits and extents of pitting propagation.

The combination micro pH electrode composed of IrO_2/Pt pH probe and $\text{AgCl}/\text{Ag}(\text{KCl})$ reference probe was designed and fabricated for the first time for the study of localized corrosion system. The combination IrO_2/Pt micro pH electrode is of linear relationship between the potential response and the measured pH of solutions, and is able to in situ image pH distribution at interface of metal/ solution by scanning the probe over the surface. The scanning combination IrO_2/Pt micro pH electrode can become a promising technique for in situ studying the mechanism of dynamic process for the pitting corrosion.

Key words Micro-combination IrO_2/Pt electrode, pH Imaging, localized corrosion.

Acknowledgment Financial support for the Natural Science Foundation of China and Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged.

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