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J. Serb. Chem. Soc. 73 (5) 561–568 (2008)

JSCHS-3738

Journal of the Serbian Chemical Society

JSCHS@tmf.bg.ac.yu • www.shd.org.yu/JSCHS

UDC 778.38+77.035:546.62+546.131-71

Original scientific paper

Investigation of the pitting of aluminum induced by chloride ions by holographic microphotography

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(Received 29 October 2007, revised 7 January 2008)

Abstract: Holographic microphotography was used to investigate the dynamic processes of pitting during anodic dissolution of aluminum in a solution containing chloride ions. The induction and the follow-up propagation processes of the pitting were observed in real-time. A simple model of the propagating process of the pitting was deduced from the result of the holograms of the Al/electrolyte interface. The results prove that holographic microphotography is a useful tool to study the dynamic processes of pitting.

Keywords: holography; pitting; aluminum; chloride ions.

INTRODUCTION

Passive films are easily formed on the surfaces of Al and its alloys in open air and solutions without aggressive ions. However, aluminum and its alloys are much more susceptible to pitting than other metals and a great variety of anions can bring about pitting, such as Cl^- , Br^- , etc.¹ The study of pitting corrosion is of particular interest and importance in many scientific and technological applications. Many techniques, such as radiotracer techniques,^{2,3} adsorption from solution onto powders,⁴ X-ray photoelectron spectroscopy (XPS),^{5–8} X-ray absorption spectroscopy (XAS),^{6,7} and Auger spectroscopy⁵ are used to investigate the pitting of Al and Al-alloys caused by chloride ions. Various theories on pitting corrosion have been formulated. It was proposed that the first step in the pitting process is the adsorption of chloride onto the oxide-covered surface due to attractive forces, mainly coulombic ones, and the induction of the adsorbent by the approaching ion.⁹ In neutral solutions, the oxide film on aluminum has a positive surface charge,¹⁰ and the adsorption of chloride ions is most likely favored on a positively charged oxide surface, as ion–ion forces are attractive in nature. This

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doi: 10.2298/JSC0805561L

adsorption process is further enhanced under an anodic potential. According to the point defect model (PDM) proposed by Macdonald *et al.*,¹¹ defects exist in the oxide film. The breakdown of the passivity of the Al electrode is caused by the adsorption of the chloride ions into the surface oxygen vacancies. There are still many problems concerning the pitting of Al and Al-alloys (such as deterministic factors in pit initiation), which need to be studied further.¹² Opinions differ on how the pitting is initially induced with the presence of aggressive ions and how the pits propagate. Answers to the above unsettled questions can cast light on the mechanism of the pitting. To observe *in-situ* the initiation and the propagation processes of pitting, new experimental methods are required.

Based on the principles of holographic interferometry techniques for measuring microsurface dissolution, Habib *et al.*¹³ developed a mathematical model and an optical corrosion-meter¹⁴ to characterize the electrochemical and mechanochemical properties of metallic materials, such as localized corrosion of stainless steel,¹⁵ and the anodic dissolution behavior of carbon steel in seawater, with and without inhibitor.¹⁶ It was proposed that holographs have many potential applications in the field of electrochemistry, which are yet to be explored.

Holographic microphotography was employed to study the dynamic processes during the electrodissolution of iron in sulfuric acid solutions.¹⁷⁻¹⁹ Recently, digital holography was used to study the anodic dissolution processes of an iron electrode.^{20,21}

In this study, holography was employed to observe *in situ* how the pitting is initially induced by chloride ions and how the pits propagate on the surface of an aluminum electrode.

EXPERIMENTAL

A three-electrode system was used. The working electrode, 1.8 mm×1.0 mm, prepared from aluminum of industrial purity (0.031 % Mn, 0.17 % Si, 0.01 % Cu, 0.29 % Fe, 0.05 % Zn) was carefully embedded in resin, and only the end of the Al specimen was exposed to solution. The specimen was polished with # 600 and # 1200 emery papers to a mirror-like surface and then washed with alcohol and double distilled water in an ultrasonic bath before each experiment. The counter electrode was a large platinum sheet. A saturated calomel electrode (SCE) with Luggin capillary tip set at 2 mm from the working electrode surface served as a reference electrode. All potentials reported here are referred to SCE. All electrolytes were prepared from analytical grade reagents and double distilled water. In each run, 50 ml of the tested solution was used. The electrochemical experiments were performed at room temperature with a CHI602A electrochemical station.

The dynamic processes of the electrode/electrolyte interface during the anodic dissolution of the electrode were videotaped synchronically by a Sony digital recorder. The holograms presented here were transferred from the digital videotape with the aid of a computer. The electrochemical cell and the light path are shown in Fig. 1. The working and the counter electrodes were placed horizontally, facing each other. For details of the procedures of holographic microphotography, previous publications can be referred to.¹⁷⁻¹⁹

Before the experiments in which the morphology of Al electrode was observed using a scanning electron microscope (FEI QUANT200-ESEM), the sample was first rinsed with anhydrous ethanol and then with double distilled water.

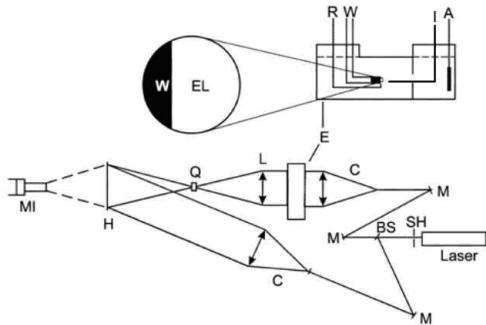


Fig. 1. Schematic diagram of the arrangement for holographic microphotography and the configuration of the electrochemical cell. SH – shutter; BS – beam splitter; M – mirror; C – collimator; L – imaging lens; Q – phase filter; H – holographic plate; MI – microscope; E – electrochemical cell; W – working electrode; R – reference electrode; A – counter electrode; I – chloride ion injection tube.

RESULTS

The $i - t$ curve of the Al electrode in 3.5 % NaCl solution at -0.55 V_{SCE} is shown in Fig. 2. The holograms of the electrode/electrolyte interface taken at different points illustrated in Fig. 2 during the initiation and the propagation of pits on the surface of the electrode in 3.5 % NaCl solution are displayed in Fig. 3.

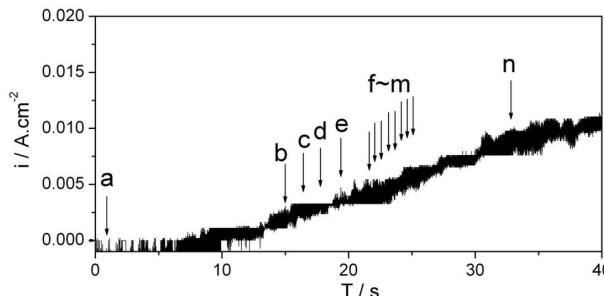


Fig. 2. The $i - t$ curve of the Al electrode in 3.5 % NaCl solution at -0.55 V_{SCE}.

Initiation of pitting

Figures 3a–3f correspond to points a to f in Fig. 2. Figure 3a exhibits the interface at the start of the electrodissolution of the Al electrode. The dark and bright fringes are straight and parallel to each other, indicating that there are concentration gradients at the electrode/electrolyte interface. However, after about 15 s of anodic dissolution of the Al electrode, as shown in Fig. 3b, the fringes bend at one point towards the electrode surface and then small trumpet-like fringes appear at other points (Figs. 3c–3e). The appearance of the fringe bend and trumpet-like fringes indicates that the concentration gradient at the electrode/electrolyte interface is no longer uniform. In other word, the concentrations are higher in the areas with trumpet-like fringes than elsewhere, which was caused by the initiation of pitting. About 4 s later than the hologram shown in Fig. 3e, one of the trumpet-like fringes had expanded (Fig. 3f). This indicates that the

pitting had entered the propagating process. These trumpet-like fringes appeared in many areas near the surface of the electrode, indicating that many pits were initiated. However, only some of the pits propagate (Figs. 3b–3e) while the others were repassivated.

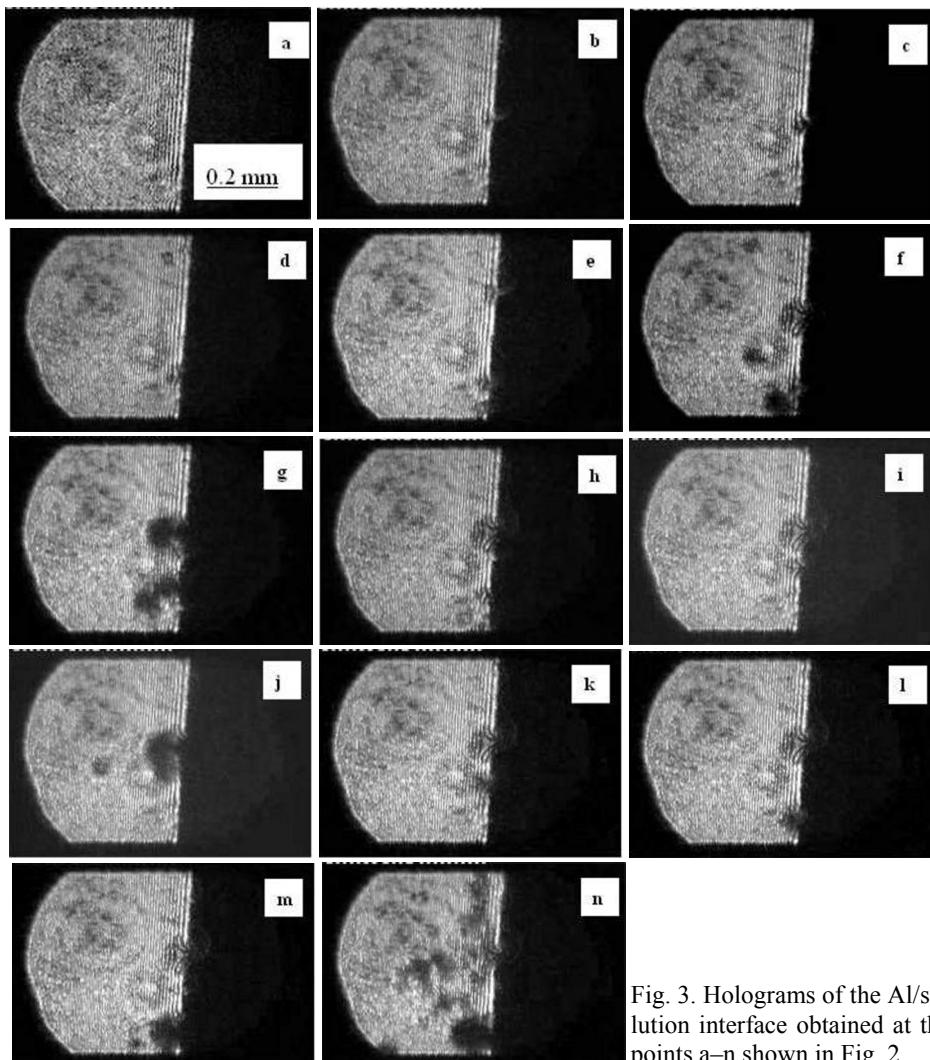


Fig. 3. Holograms of the Al/solution interface obtained at the points a–n shown in Fig. 2.

Propagation of pitting

After the trumpet-like fringes had expanded (Fig. 3f), corrosion products emerged in the local area (Fig. 3g). As these products diffused away from the surface of the Al electrode, more trumpet-like fringes appeared, indicating more pits were propagating, as shown in Figs. 3h and 3i. As the products re-emerge

(Fig. 3j), more and more pits propagate (Figs. 3k–3m), until the entire electrode is activated (Fig. 3n). Then the object wave was blocked by the quickly accumulated products, so the fringes could no longer be observed afterwards.

Surface morphology

After the electrochemical experiment (Fig. 2), an ESEM micrograph of the electrode was taken. Figure 4 shows pits with different diameters and depths, indicating that these pits were at different stages of the propagation processes.

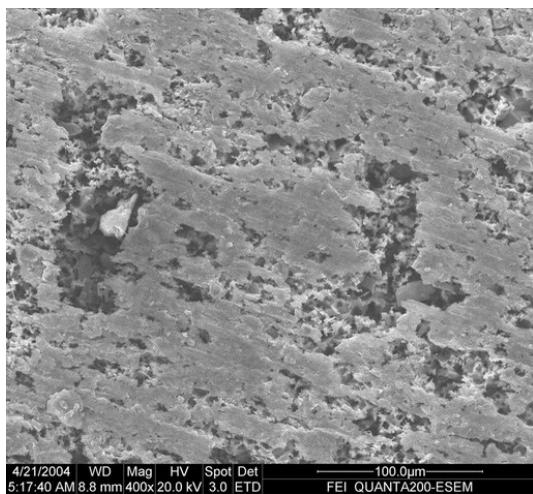


Fig. 4. An ESEM micrograph of the electrode after the experiment shown in Fig. 2.

DISSCUSSION

If the dark and bright fringes are straight and parallel to the surface of the electrode, there may be iso-concentration planes parallel to the electrode surface. C1, C2 and C3 in Fig. 5 show that there is a concentration boundary layer near the electrode surface. This concentration boundary layer caused a gradient of the refraction index. The actual imaging interferes with the reconstructed one on the holographic plate and fringes appeared whenever the following condition was satisfied:¹⁷

$$\Delta n = \frac{(2k+1)\lambda}{2d}$$

where Δn is the difference in the refractive index, d is the optical length over which the refractive index was different, λ is wavelength of the light and k is an integer representing the order of the fringe.

When light passes through different concentration planes, different Δn values will be produced. The dark or bright fringe is caused by different values of Δn .

However, if the dark and bright fringes are neither straight nor parallel to the surface of the electrode, there was no iso-concentration planes parallel to the electrode surface. Trumpet-like pits gradually emerged and expanded (from Fig. 3b

to Fig. 3n) along the fringes towards the electrode surface, indicating different periods of pitting. This can be explained as follows: the fringes bend because the concentration in the area is higher than that in other areas at the electrode/electrolyte interface. As the trumpet-like fringes appear (Fig. 3b), pits start to form on the surface of the electrode. The trumpet-like fringes expand with the increase of the concentrations in the local area, indicating that the pits propagate. As more and more pits propagate, the Al electrode is finally activated.

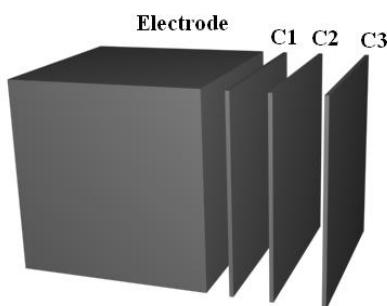


Fig. 5. Illustration of the iso-concentration plane during the general dissolution of the Al electrode.

In order to visualize better how the chloride ions attack the oxide film, a small amount of chloride ions was injected into the vicinity of the electrode surface during the anodic polarization of Al in neutral Na_2SO_4 solution, in which medium an oxide film is readily formed on the electrode surface. The $j - t$ curve of aluminum electrodes in 0.50 M Na_2SO_4 at -0.50 V_{SCE} is shown in Fig. 6. After 0.50 ml 3.5 % NaCl solution had been injected towards the surface of the electrode, the current increased rapidly.

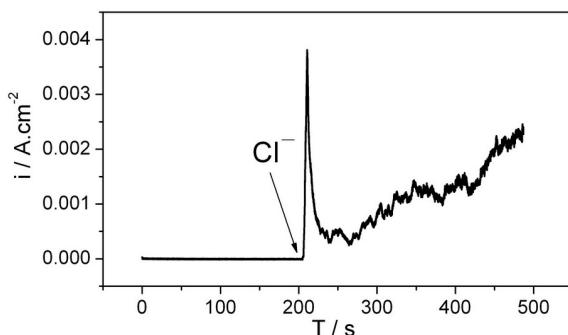


Fig. 6. The $i - t$ curve of the electrode in 0.50 M Na_2SO_4 at -0.50 V_{SCE} after injection of 0.50 ml 3.5 % NaCl solution near the surface of the electrode.

The anodic oxidation of aluminum in near-neutral solutions, e.g., Na_2SO_4 , leads to the growth of thin barrier-type oxide films, normally less than 50 nm thick.²² The first step in the pitting process is the adsorption of chloride on the positively charged surface.^{9,10} The adsorption of the anions leads to the generation of cation vacancies at the film/solution interface.¹¹ The oxide film with defects caused by chloride ions becomes mechanically stressed and damaged by

the pores and flaws, and finally, the passive film on the surface of the electrode is broken. As the pits on the surface of the Al electrode propagate, the current increases (Fig. 6).

According to the obtained results, a simple model of the propagating process of a pit was developed, as shown in Fig. 7. During the propagating process of a pit, both its diameter and depth develop synchronously, which is verified by the fact that there are pits with different diameters and depths shown in Fig. 4, and the trumpet-like fringes (Fig. 3) emerge and expand during different periods of the anodic dissolution of the electrode.



Fig. 7. Schematic diagram of the propagation process of a pit.

CONCLUSIONS

The bending of the fringes and the appearance of trumpet-like ones at the electrode/electrolyte interface indicate the initiation of the pitting, because the concentrations are higher in the pitting areas than elsewhere. The expansion of these trumpet-like fringes indicates propagation of the pitting.

A simple model of the propagation process of a pit has been deduced from the experiment results, and it was found that both the diameter and the depth of a pit develop synchronously.

Acknowledgement. This work was supported by the Natural Science Foundation (No. 05KJB150130 and 06KJB150108) of the Jiangsu Education Committee of China, the Jiangsu Qing-Lan Project of China (QL200616), the Chinese National Science Fund (No.20573069) and Special Funds for the Major State Basic Research Projects (No.2006CB605004). The Project was also sponsored by SRF for ROCS, SEM of the P. R. China.

ИЗВОД

ИСПИТИВАЊЕ ПИТИНГ КОРОЗИЈЕ АЛУМИНИЈУМА ИЗАЗВАНЕ ХЛОРИДНИМ ЈОНИМА КОРИШЋЕЊЕМ ХОЛОГРАФСКЕ МИКРОФОТОГРАФИЈЕ

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Холографска микрофотографија је коришћена за испитивање динамичких процеса питинг корозије током анодног растварања алуминијума у раствору хлоридних јона. Почетак и развој питинга праћени су у реалном времену. На основу холограма границе фаза алуминијум/електролит изведен је једноставан модел развоја питинга. Резултати потврђују да се холографска микрофотографија може успешно користити за испитивање динамичких процеса питинга.

(Примљено 29. октобра 2007, ревидирано 7. јануара 2008)

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