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SHORT COMMUNICATION

Mapping the concentration changes during the dynamic processes of crevice corrosion by digital holographic reconstruction

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Abstract: The dynamic process of crevice corrosion during anodic dissolution of a crevice electrode in a 5.0 mmol dm⁻³ NaCl solution has been studied by digital holographic reconstruction. Digital holographic reconstruction has been proved to be an effective and *in situ* technique to detect the changes in the solution concentration because useful and direct information can be obtained from the three-dimensional images. It provides a valuable method for a better understanding of the mechanism of crevice corrosion by studying the dynamic processes of changes in the solution concentration at the interface of crevice corrosion.

Keywords: digital holography; crevice corrosion; numerical reconstruction; phase difference; concentration change.

INTRODUCTION

Crevice corrosion is a common and dangerous type of localized corrosion, which occurs within crevices or other occlusive areas on metal surfaces exposed to a corrosive environment. A crevice can be formed between metallic parts or a non-metallic part and a metallic part. For certain corrosive environments, especially in NaCl solution, crevice corrosion could be fatal to the metal.^{1–3}

Various experimental techniques and mathematical models have been presented to study crevice corrosion in the past few decades.^{4–8} Digital holography has been proved to be a versatile and rapid technique to detect concentration changes in a solution because of its non-contact, non-breakage and high precision. It has also been successfully applied in chemistry,⁹ biology^{10,11} and other

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fields. In our laboratory, experiments were performed by digital holography to study dynamic electrochemical processes.

The principle of the experiments were based on the relationship between the phase of an object wave ($\Delta\phi$), the refractive index of the solution (Δn) and solution concentration (Δc), which was formulated as:¹²

$$\Delta c = k_1 \Delta n = (k_1 \lambda_0 / 2\pi d) \Delta \phi \quad (1)$$

Thus, measurement of the concentration change can be transformed into measurement of the phase difference. In the present study, the phase difference was recorded on and stored in a computer in the form of holograms. After numerical reconstruction by the Fourier analysis method, the holograms were transformed into three-dimensional images. Details about numerical reconstruction can be found in literature.^{12,13} In this study, numerical reconstruction was used to study the process of crevice corrosion.

EXPERIMENTAL

Electrochemical system

The electrochemical cell consisted of a three-electrode system. A carbon steel electrode (0.17 % C, 1.18 % Mn, 0.008 % P, 0.008 % S, 0.04 % Cr, 0.04 % Mo, 0.27 % Si), 1.6 mm × 3.7 mm in size, with a central 0.1 mm wide crevice was used as the working electrode. The electrode was carefully sealed in a glass tube with a thin layer of epoxy resin, leaving only the surface area with the crevice exposed to the solution. The crevice was positioned parallel to the laser. A large sheet of platinum was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary tip set 2 mm from the working electrode surface. All potentials in the experiments were measured with respect to the SCE. The electrolyte was a 5.0 mmol dm⁻³ NaCl solution. The $I-t$ curve measurement was performed using a CHI660B electrochemical station. All experiments were performed at room temperature.

Holography recording system

The experimental setup of the in-line holographic recording system, which was described earlier,⁹ is shown in Fig. 1. The video signals were captured and stored in the computer. The

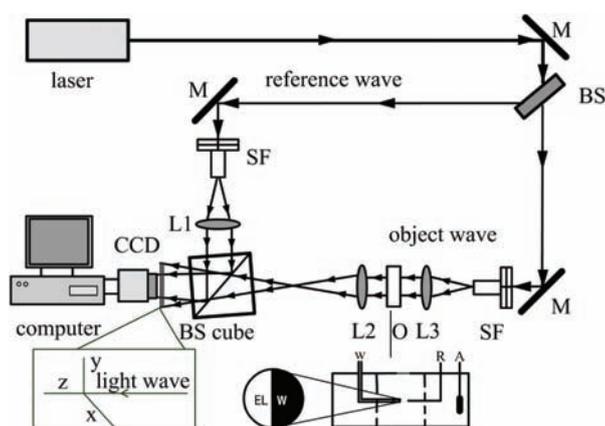


Fig. 1. Experimental setup of the in-line holographic recording system. M – mirror; BS – beam-splitter; SF – spatial filter; L1, L2 and L3 – lenses; O – object; BS Cube – beam-splitter cube; W – working electrode; R – reference electrode; A – counter electrode; EL – electrolyte.

holograms were processed by the reconstruction algorithm and the information was transformed into three-dimensional images.

RESULTS AND DISCUSSION

The $j-t$ curve of the crevice electrode in 5.0 mmol dm^{-3} NaCl solution at 0.20 V is illustrated in Fig. 2. The distribution of the phase difference in comparison with the starting time during the reaction corresponding to the points a–g in Fig. 2 are shown in Figs. 3a–3g, respectively. As shown in the images, the left sides are the solution parts and the right sides are the electrode parts, between which are the interfaces obtained by the edge detection algorithm. The color variation reflects the change of the concentration. A green area indicates that the phase difference, *i.e.*, concentration change, is zero or almost zero, while the yellow and red areas indicate that the phase differences are positive with the concentration changes increasing from yellow to red. The value of Z (phase difference) reflects how much the phase has changed. The larger is the value of Z (phase difference), the more evident are the color changes, that is to say, the more severely the concentration changes.

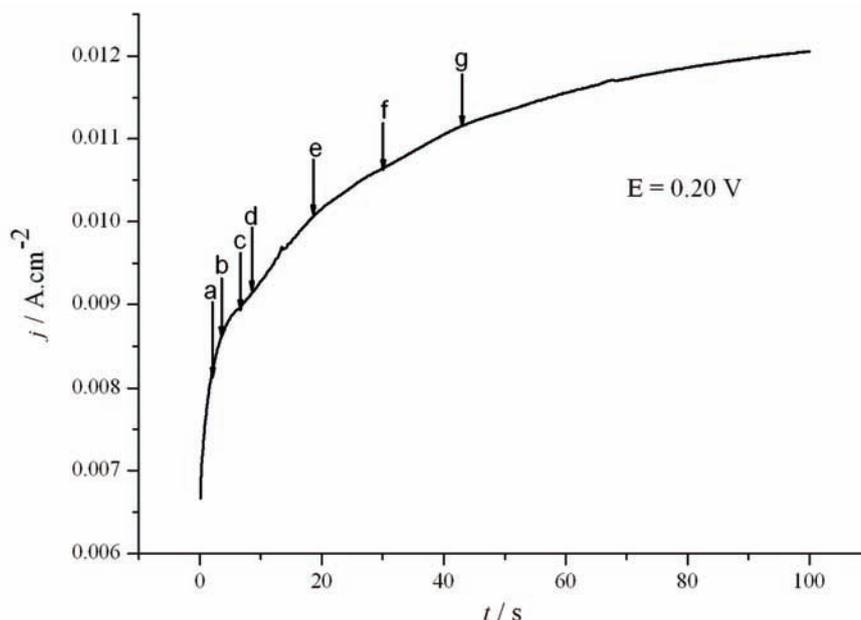


Fig. 2. The $j-t$ curve of the crevice electrode in 5.0 mmol dm^{-3} NaCl solution, with the electrode potential controlled at 0.20 V .

Figure 3a shows the distribution of the phase difference at 2 s , in which a change at the interface can hardly be seen. With increasing time, the appearance of a yellow area in Fig. 3b at a time of 4 s indicates that the concentration had increased. This change can be clearly seen in Fig. 3c at 6 s . It can also be observed

from Fig. 3c that the change of the concentration at the interface was not uniform and the concentration change at the crevice mouth is most obvious. This pheno-

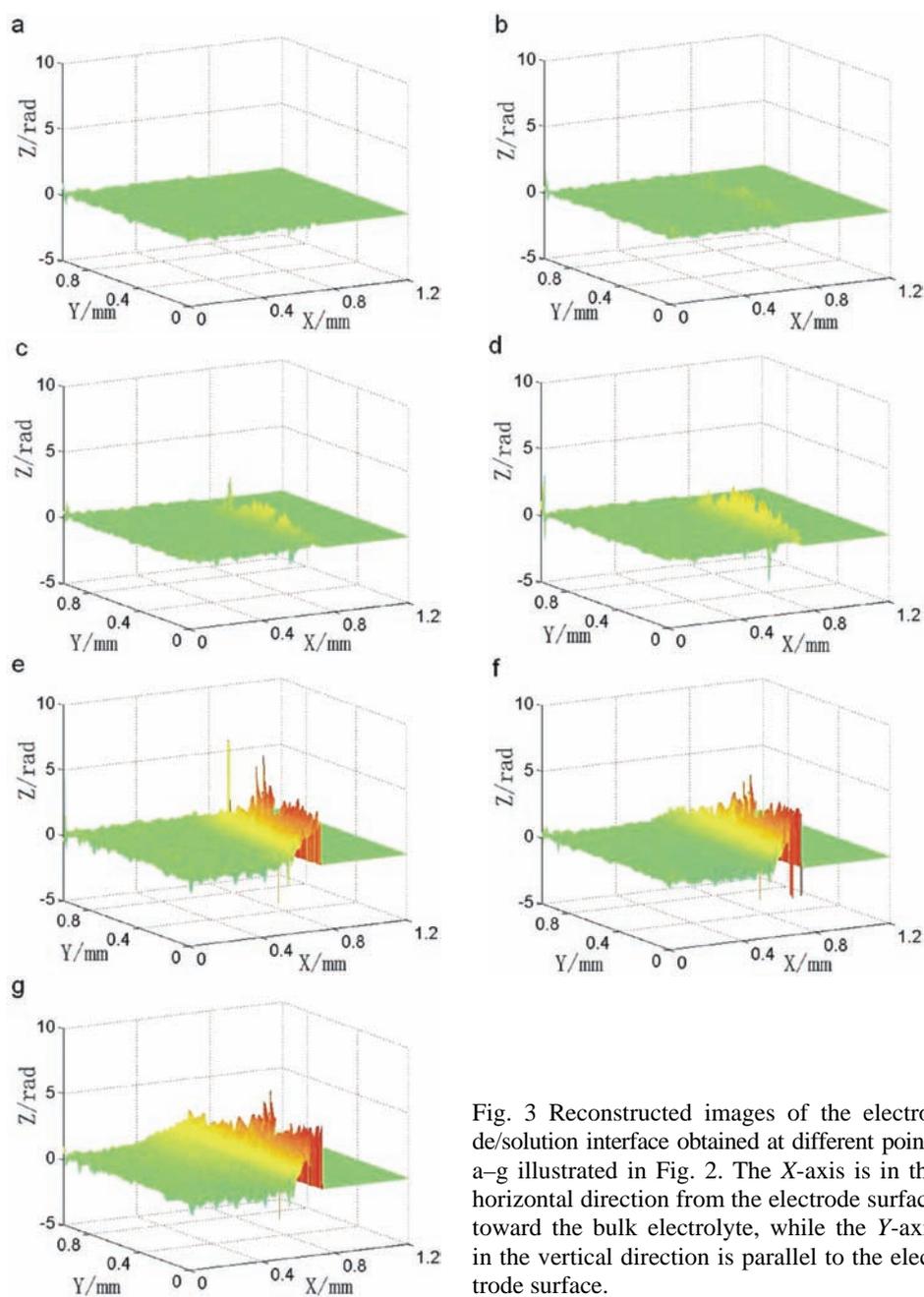


Fig. 3 Reconstructed images of the electrode/solution interface obtained at different points a–g illustrated in Fig. 2. The X-axis is in the horizontal direction from the electrode surface toward the bulk electrolyte, while the Y-axis in the vertical direction is parallel to the electrode surface.

menon becomes more visible in Fig. 3d at 8 s, with the first appearance of a red area at the crevice mouth, which indicates that phase difference or concentration continued increasing. The red area in Figs. 3e, 3f and 3g are very evident. This proves that many more ions had been produced in the crevice and transported out. Metal ions produced in the crevice moved to the bottom of the electrode because of gravity, which is in accordance with the red areas in Figs. 3e, 3f and 3g.

CONCLUSIONS

Digital holographic reconstruction was employed to study the change of the concentration at the interface of crevice corrosion. The reconstructed images provide visual results, from which more useful information about the change of concentration at the interface can be obtained. The results show that the changes of concentration at the interface are not uniform and that the concentration increase at the crevice mouth was the most obvious. The reconstructed images supply more visual information for a better analyzes and understanding of the dynamic processes of solution concentration change.

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ИЗВОД

МАПИРАЊЕ ПРОМЕНЕ КОНЦЕНТРАЦИЈЕ ТОКОМ ДИНАМИЧКОГ ПРОЦЕСА КОРОЗИЈЕ У ПУКОТИНАМА КОРИШЋЕЊЕМ ДИГИТАЛНЕ ХОЛОГРАФСКЕ РЕКОНСТРУКЦИЈЕ

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Динамички процес корозије у пукотинама током анодног растварања у раствору 5,0 mmol dm⁻³ NaCl праћен је дигиталном холографском реконструкцијом. Дигитална холографска реконструкција се показала као ефикасна *in situ* техника за детекцију промене концентрације, јер даје корисне и директне информације у виду тродимензионих слика. Она омогућава боље разумевање механизма корозије у пукотинама испитивањем динамике промене концентрације раствора уз површину пукотине.

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