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Original scientific paper

Digital holographic reconstruction detection of localized corrosion arising from scratches

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Abstract: In this study, electrochemical methods and the digital holographic reconstruction technique were combined to detect the localized scratch-induced corrosion process of Alloy 690 in 0.50 mol dm^{-3} H_2SO_4 containing 0.10 mol dm^{-3} NaCl. The numerical reconstruction method has been proved to be an effective technique to detect changes of solution concentration. One can obtain direct information from the reconstructed images and capture subtle more revealing changes. It provides a method to detect localized corrosion arising from scratches.

Keywords: digital holography; numerical reconstruction; Alloy 690; scratch corrosion.

INTRODUCTION

Alloy 690 is one of the most widely used nuclear materials and its corrosion has been studied for many years.[1–6] Localized corrosion is of particular interest because it can lead to a fast and fatal failure in engineering structures. Various experimental techniques have been employed to study localized corrosion, such as atomic force microscopy (AFM),[7] the acoustic emission technique (AET),[8] the optical interferometry technique (OIT),[9] electrochemistry impedance spectroscopy (EIS),[10] the electrochemical noise (EN)[11] technique, *etc*. Calvo *et al.*[12] examined *in situ* the localized corrosion of tinplate with a line scratch immersed in H_2SO_4 solution by the scanning electrochemical microscopy (SECM) and indicated that the current over the scratch was markedly increased. However, it takes about 30 min to capture one image by SECM, during which time the surface status of the sample could change.

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There is another method to study localized corrosion. In the 1990s, Habib[13–15] studied pitting corrosion by holographic interferometry. The method can be also used in microscopic structure measurements,[16] biology[17,18] and other fields. Li[19] investigated the pitting corrosion of aluminum induced by chloride ions by holographic microphotography. Using the in-line digital holography[20], an amplitude-contrast and phase-contrast image of the specimen can be obtained simultaneously, which can yield useful information during electrochemical measurements. Yuan[21] introduced carrier-wave-recording into experiments and reconstructed the holograms, which can capture more revealing subtle changes. Digital holographic reconstruction can be applied to visualize the two-dimensional distribution of a concentration change at an electrode/solution interface.

The experimental principle is based on the relationships between the phase difference of an object wave ($\Delta\Phi$), the refractive index of the solution (Δn) and concentration (Δc). Generally, several components are present in a solution. Thus, the net refractive index is the summation of the effect of the concentration of each species. The relationship is:[22]

$$\sum_i \Delta c_i = \sum_i k_i \Delta n_i = \frac{\lambda_0}{2\pi d}\sum_i k_i \Delta\Phi_i \quad (1)$$

where k_i is the concentrative refractivity ; λ_0 is the wavelength of the laser light and d is the geometrical path length where the refractive index variation exists. Thus, the measurement of concentration change can be transformed into the information of phase variation. Details about numerical reconstruction can be found in the literature.[21]

Electrochemical techniques, such as linear polarization and AC impedance spectroscopy[23–24] have been widely used to estimate the rate of general corrosion, but they suffer a major limitation in the measurement of the localized corrosion rate and distributions. In this study, an electrochemical technique and the digital holographic reconstruction method were combined to study localized corrosion arising from scratches. The results revealed that the method can be used to detect localized corrosion induced by scratches.

EXPERIMENTAL

Electrochemical system

An electrochemical cell consisting of a three-electrode system[20] was used. The working electrode was Alloy 690 (59.50 % Ni, 29.02 % Cr, 10.28 % Fe, 0.30 % Mn, 0.33 % Ti, 0.16 % Al, 0.018 % C, 0.31 % Si, 0.015 % Co, 0.01 % Cu and 0.009 % P) provided by the Electric Power Research Institute (EPRI). The counter electrode was a platinum sheet and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary tip set at 2 mm from the working electrode surface.

The entire working electrode was sealed in a glass tube with a thin layer of epoxy resin, leaving the end exposed to the solution. An electrode having two scratches is shown in Fig. 1a, while the electrode used for comparison having no scratches is shown in Fig. 1b. Both electrodes had the same area (0.046 c m^2). The scratch is 100 µm in width and 120 µm in depth. The working electrode material was cut from bulk material using an electric spark and polished with 1.5 µm alumina paste. After ultrasonic cleaning in acetone, the samples were electropolished in methanol containing 30 % nitric acid.

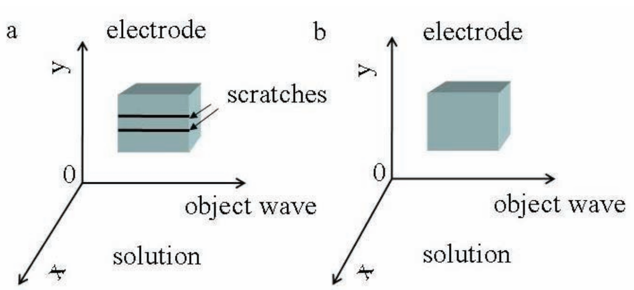

Fig. 1. The scheme of the electrode location. The *x*-axis is in the horizontal direction from the electrode surface toward the bulk electrolyte; the *y*-axis is in the vertical direction parallel to the surface of the electrode. The object wave and the scratch have the same direction.

In the experiments, the scratch-making device was self-made and it included a frequency converter, a straight-in feed electric engine, a scratching table and some conical heads. By adjusting the frequency converter to 10 Hz, a scratching speed of 9 mm/s was obtained. The geometry of the scratches was determined by the geometry of the conical heads. The conical head was fixed at the end of a micrometer and the scratching procedure was fixed in order to produce similar scratches.

To perform the *I*-*t* measurement, a polarization curve survey was first performed. All electrochemical measurements were measured using a CHI660B at room temperature. In this experiment, all potentials are referred to SCE.

Holography recording system

The measurement setup of the holographic recording system is shown in Fig. 2. The He–Ne laser with a wavelength of 632.8 nm is split by a beam-splitter into two beams, a reference wave and an object wave. Each beam is enlarged to a diameter of ≈ 50 mm by a beam ex-

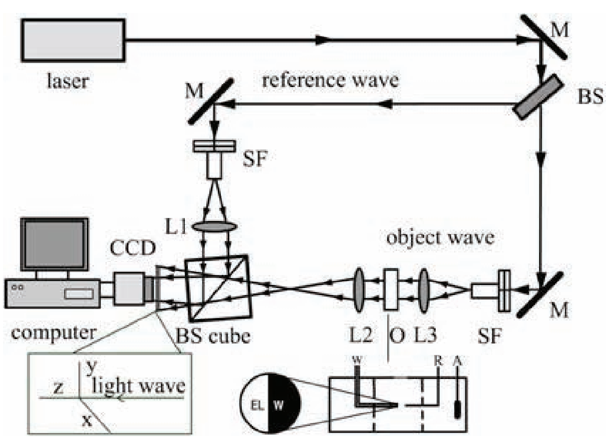

Fig. 2. Experimental setup of the digital holography recording system: M, mirrors; BS, beam-splitter; SF, spatial filter; L1, L2 and L3, lenses; O, object; BS Cube, beam-splitter cube; W, working electrode; R, reference electrode; A, counter electrode; EL, electrolyte.

pander including a spatial filter. The object wave, which carries the information of the electrode/solution interface, is combined with the reference wave by a beam-splitter cube. Thus, the two beams can interfere and produce a series of interference fringes. A Sony DSR-PD150P camera was used to record the interference fringes. The camera produces a standard CCIR video signal at 25 frames per second and the minimal phase difference detected was about 0.1 rad.

RESULTS AND DISCUSSION

The polarization curve and *I-t* curve of Alloy 690 in 0.50 mol dm^{-3} H_2SO_4 containing 0.10 mol dm^{-3} NaCl solution at room temperature are shown in Figs. 3 and 4, respectively. In Fig. 4, some different time points were selected to reflect the corrosion process.

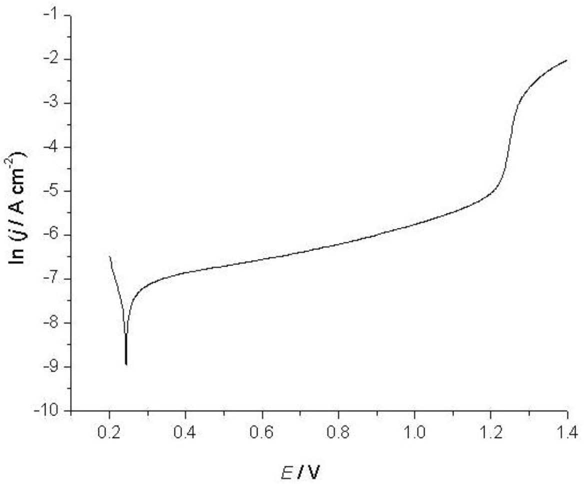

Fig. 3. The polarization curve of Alloy 690 in 0.50 mol dm^{-3} H_2SO_4 containing 0.10 mol dm^{-3} NaCl, recorded at 10 mV/s.

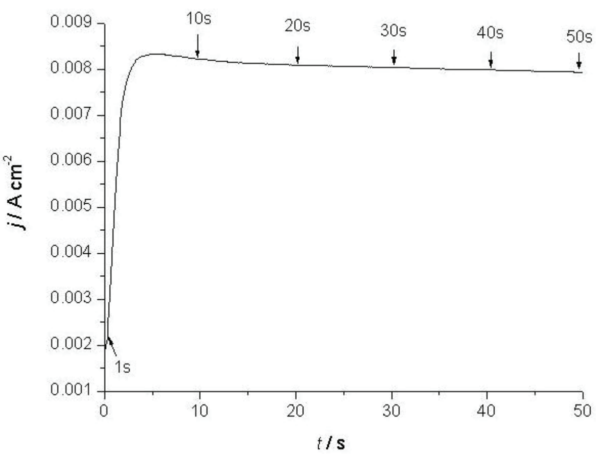

Fig. 4. The *j-t* curve of Alloy 690 in 0.50 mol dm^{-3} H_2SO_4 containing 0.10 mol dm^{-3} NaCl, with the potential controlled at 1.26 V.

Holograms were recorded simultaneously by the CCD camera and analyzed by the Fourier method[25–26] to abstract the information of phase difference. The Fourier analysis[27] method consists of Fourier transform, band-pass filtering and counter Fourier transform. The reconstructed images are shown in Fig. 5. In the images, the left part is the electrode, the right the solution and in between is the interface. The larger is the value of the phase difference (*z*-axis), the more intense is the concentration change. The green area indicates that the phase difference was zero or nearly zero. The phase differences are positive with increasing concentration changes from yellow to red. In the electrode area, the green level remained constant. In Fig. 5, the concentration change was very slight at 1 s. With passing time, two obvious yellow areas appeared at the electrode/electrolyte interface, which indicated that in both areas there were larger phase differences

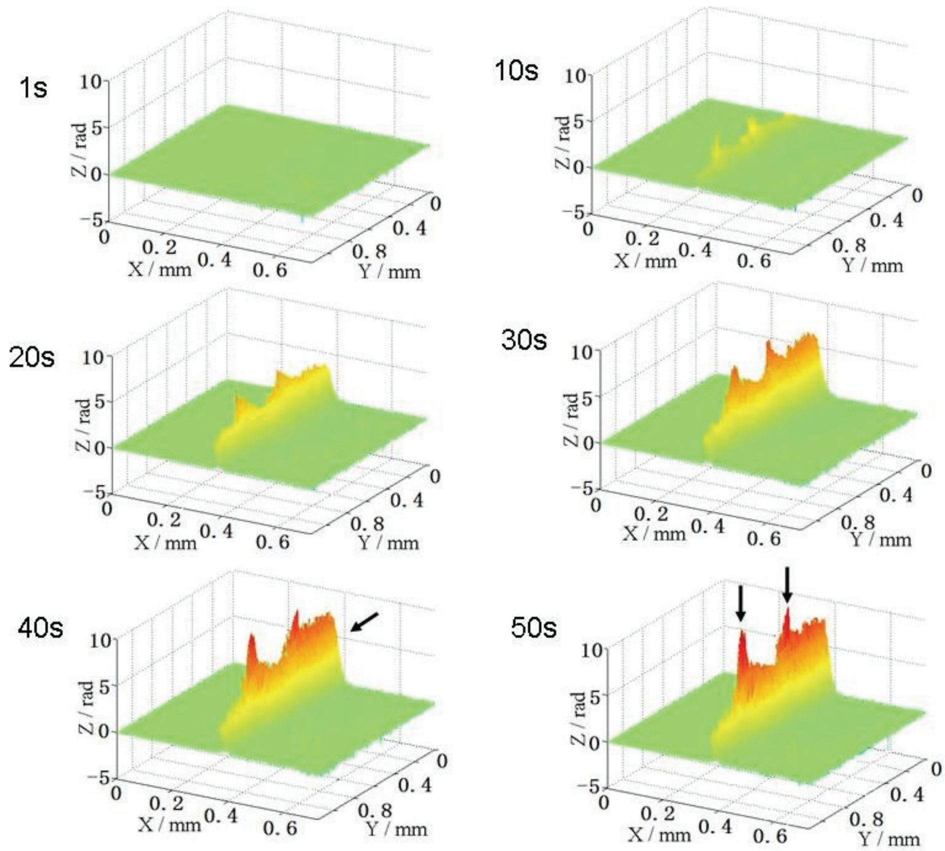

Fig. 5. Reconstructed three-dimensional images of the electrode/solution interface obtained at different times, shown in Fig. 4, for the scratched electrode. The *x*-axis is in horizontal direction from the electrode surface toward the bulk electrolyte while the *y*-axis in vertical direction is parallel to the surface of the electrode. The *z*-axis shows the phase changes.

than in other parts. The trait can be clearly seen in Fig. 5 at 50 s which has two prominent peaks (the position of the arrows). Because of the gravity,[28] the ions moved to the bottom of the electrode, hence the concentration at the bottom varied more greatly. In Fig. 5 at 40 s, the arrow indicates the bottom of the electrode.

To contrast to the above results, an electrode of the same size, but with no scratch, was used to detect the corrosion. The electrode schema is shown in Fig. 1b and the test conditions were the same as for the above measurements. From the reconstructed images shown in Fig. 6, the concentration changes at the electrode/electrolyte interface were well-proportioned. It can also be seen that the concentration at the bottom of the electrode increased markedly (see the arrow in Fig. 6 at 50 s).

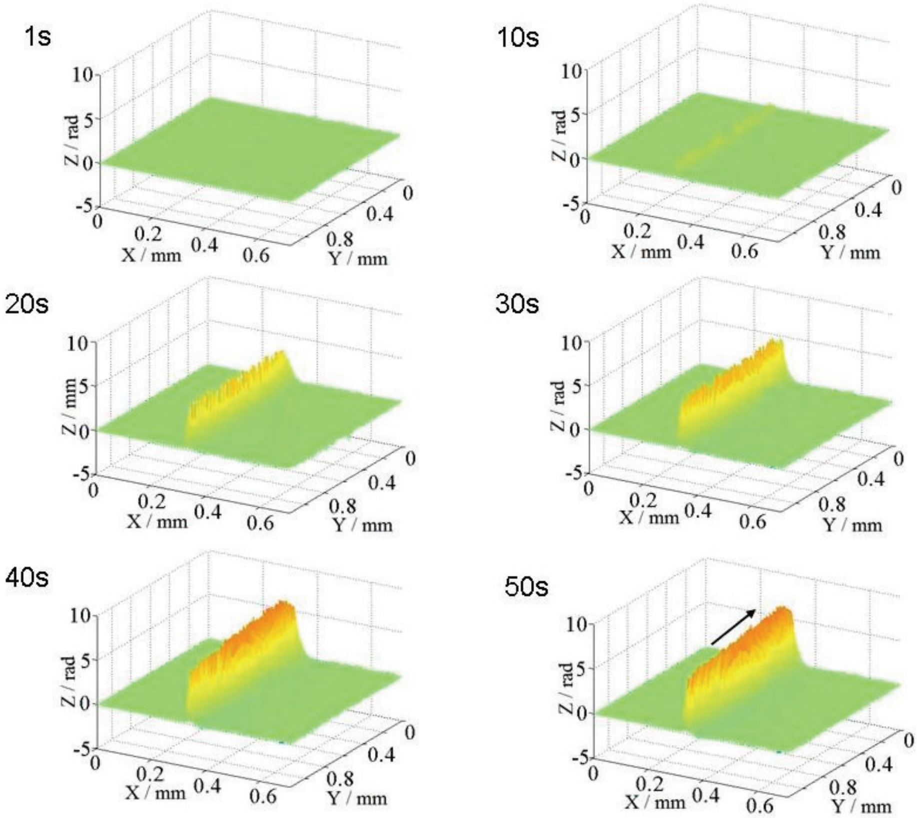

Fig. 6. The reconstructed three-dimensional images of the electrode without scratches during the electrochemical test. The meanings of the *x*-axis, *y*-axis and *z*-axis were the same as those in Fig. 5.

By comparing Figs. 5 and 6, it is clear that the increase of the concentration in the two peak areas was due to the existence of the scratches. The scratches can be viewed as defects on the metal surface. When localized corrosion occurs, the corrosion over the scratches will be more severe, which can lead to the more dramatic increase in the concentration.[28] The larger concentration changes can induce major changes the phase differences. Hence, two prominent peaks are evident in Fig. 5. As can be seen from the results, the method effectively enables the detection localized corrosion due to the scratches.

CONCLUSIONS

A numerical processing method for digital holograms was proposed to study the scratch corrosion of Alloy 690. Digital holographic reconstruction was applied to visualize the two-dimensional distribution of the concentration change at the electrode/solution interface. The reconstructed images provide visual results and more useful information about the change in concentration at the interface can be obtained from the results. The method was able to evidence that corrosion over the scratch was more significant than over the unscratched areas. The reconstructed images supplied more visual information for a better analysis and understanding of the dynamic processes of concentration change in the solution.

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ИЗВОД

КОРИШЋЕЊЕ ДИГИТАЛНЕ ХОЛОГРАФСКЕ РЕКОНСТРУКЦИЈЕ ЗА ДЕТЕКЦИЈУ ЛОКАЛИЗОВАНЕ КОРОЗИЈЕ ИЗАЗВАНЕ ОГРЕБОТИНАМА

LIANG WANG[1], SHENHAO CHEN[1,2], BOYU YUAN[3], FANJIANG MENG[2], JIANQIU WANG[2], CHAO WANG[2,4] И LIANG LI[4]

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У раду су комбиноване електрохемијске методе и техника дигиталне холографске реконструкције у циљу детекције локализованог корозионог процеса легуре 690 који је индукован огреботинама у раствору 0,50 mol dm^{-3} H_2SO_4 и 0,10 mol dm^{-3} NaCl. Показано је да је нумеричка реконструкција ефикасна техника за детекцију промена у концентрацији раствора. На основу реконструисаних слика могуће је добити директне и јасне информације из деликатних промена концентрације. Ово представља методу за детекцију локализоване корозије изазване огреботинама површине.

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