High accuracy ultrasonic monitoring of electrochemical processes

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ABSTRACT

Ultrasonic testing (UT) can be used for non-intrusive corrosion monitoring. In this paper, we firstly show that UT is not only capable of monitoring wall-thickness losses, but can also be exploited for tracking electrodeposition processes. All ultrasonic measurements reported are in agreement with analytical predictions and optical surface profile measurements. Since UT is highly sensitive to the coupling conditions and the relative acoustic properties of substrates and deposited materials, it can become an effective tool for studying the interface phenomena in which dissolution and deposition compete. Examples of these include passivation layer formation and scale deposition which are corrosion-inhibiting electrochemical processes.

1. Introduction

The monitoring of corrosion processes can help to control plant operating conditions in order to mitigate adverse effects. Ultrasonic testing (UT) with permanently installed transducers has been widely used for component wall-thickness loss monitoring [1–4]. Compared to conventional techniques such as weight loss measurements [5,6] and electrochemical measurements [7–9], UT does not require probes to make direct contact with electrolytes or to access the interiors of closed vessels. Also, it measures wall-thickness losses directly without the need for assumptions about the corrosion reactions that are taking place and the surface area over which they are occurring.

Electrodeposition is an important technique in the manufacturing industry. In previous work, an acoustic sensor was designed for monitoring the thicknesses of electrodeposited films through measuring the time delays of acoustic waves travelling in electrolytes [10]. The approach only indicates the presence of additional materials but does not confirm the integrity of the bonding conditions between deposited materials and substrates. In this paper, a more direct ultrasonic technique for monitoring the thickness increases during electrodeposition, which makes use of shear waves travelling in substrates, is firstly presented. The laboratory system that was used has a thickness measurement repeatability of 20 nm. The quality of ultrasonic deposition monitoring depends on the mechanical coupling conditions and the relative acoustic properties of substrates and deposited materials. Through an experiment in which both corrosion and the deposition of corrosion products took place, it is demonstrated that UT measurements do not capture build-up of loosely attached porous substances and only track underlying wall-thickness losses. This shows that UT, which only measures well adhered materials, is suitable for both structural integrity assessment and the study of corrosion inhibition phenomena such as passivation layer formation and scale deposition.

2. Experimental procedures

Fig. 1(a) shows the system that was used for carrying out the experiments in this work. On one side of a 10 mm thick mild steel (BS970:1983:080A15) sample, a simple 12 × 1 × 0.25 mm³ piezoelectric strip transducer (PZT27, Meggitt, UK) and a 1/3 DIN Pt1000 resistance temperature detector (RTD) (Alphatemp Technology, UK) are permanently adhered by epoxy resin. The epoxy resin for adhering the RTD is thermally conductive. A reaction chamber is sealed to the other side of the sample by means of an O-ring. Electrolytes, which are circulated through the chamber by a pump at 0.03 L/min, come into contact with the sample via a circular opening with a diameter of 22 mm. Constant electric currents/potentials were supplied by a potentiostat across the sample and the cathode inserted in the chamber. Further details about the experiments are given in Table 1. Note the sample and the cathode are not restricted to steel and zinc, which were chosen only for the purpose of demonstration.

The piezoelectric transducer operates in pulse-echo mode. The excitation signal, which is a 5-cycle Hanning-windowed sinusoidal toneburst with a central frequency of 2 MHz, is sent to the transducer via an arbitrary function generator (AFG). The transducer excites an antiplane shear wave that travels across the sample before being reflected towards the transducer by the back-wall of the sample (i.e. the metal/liquid interface) [1]. The permanent bond between the transducer and the sample eliminates front-wall echoes. Since liquid does not support

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shear loading, the shear wave reverberates only within the sample, resulting in full-amplitude reflections from the back-wall and thus a high signal-to-noise ratio. Also, there will not be any ultrasonic interaction with the reaction chamber which may lead to additional echoes that overlap with the back-wall echoes. The back-wall echoes are turned into a continuous electric signal, which is then amplified by 40 dB and digitised by an oscilloscope.

An electric signal that corresponds to the back-wall echoes acquired from the sample is displayed in Fig. 1(b). The remnant thickness of the sample $D$ can be calculated by

$$ D = -\frac{v_s}{2}(T_2 - T_1) $$

(1)

where $T_1$ and $T_2$ are the times-of-flight (ToFs) of the first and the second wave packet, and $v_s$ is the ultrasonic shear velocity. It can be inferred from Eq. (1) that the precision of thickness calculation is determined by how accurately ToFs are measured and how exactly shear velocities are known.

The procedure for obtaining an accurate ToF measurement is as follows.

1) 300 consecutive signals are recorded and averaged.
2) The averaged signal is filtered by a 5th-order Butterworth band-pass filter with cut-off frequencies at 1.6 and 2.4 MHz.
3) The filtered signal is up-sampled to 800 MHz.
4) The up-sampled signal is auto-correlated.
5) The peaks in the auto-correlation correspond to the ToFs of wave packets. The exact locations of the peaks are determined by gradient based linear interpolation.

In steel, shear velocity decreases by approximately 0.6 m/s for every 1 °C of increase in temperature [1]. For the 10 mm thick sample, this is equivalent to a measurement uncertainty of 1.8 μm. The relationship between temperature and shear velocity can be found according to the following steps.

1) Temperature and ToF measurements are acquired simultaneously for 24 h at 1 min intervals.
2) The ToFs are converted into shear velocities according to Eq. (1).
3) The equation that describes the relationship is obtained via linear regression.

The calibration curve between temperature $\Gamma$ (°C) and shear velocity $v_s$ for the steel sample used in this work is given by

$$ v_s = -0.64081\Gamma + 3259.5 $$

(2)

Temperature measurements, and the thicknesses reconstructed with and without temperature compensation are shown in Fig. 1(c). The moderate temperature variation reflects the typical environmental condition in which the UT experiments were conducted. When a constant shear velocity of 3250 m/s is assumed, the thickness measurements vary as a function of temperature. In contrast, when shear velocities are determined based on the temperature measurements, the

### Table 1. Electrochemical setups of the UT experiments.

| Experiment | Anode          | Cathode       | Electrolyte | Load  |
|------------|----------------|---------------|-------------|-------|
| 1: Galvanostatic forced corrosion | Steel sample | Steel insert | 3.5% w/v NaCl | 25 mA |
| 2: Electrodeposition | Zinc insert    | Steel sample  | NH₄Cl 12% w/v | 50 mA |
| 3: Potentiostatic forced corrosion | Steel sample  | Steel insert  | 20% w/v NaCl 10⁻⁶ M NaOH (pH 8) | 1.1 V |
|            |                |               | ZnCl₂ 2.5% w/v | 100 mA |

| Electrolyte | Load  |
|-------------|-------|
| NaCl 3.5% w/v | 25 mA |
| NH₄Cl 12% w/v | 50 mA |
| ZnCl₂ 2.5% w/v | 100 mA |
| 10⁻⁶ M NaOH (pH 8) | 1.1 V |
| 10⁻⁴ M NaOH (pH 12) | 1.1 V |

Fig. 1. (a) Laboratory system for the UT experiments. A piezoelectric strip transducer permanently bonded on a steel substrate is shown (the arrows indicate the polarisation direction of anti-plane shear waves). (b) An ultrasonic signal acquired in pulse-echo mode from the system. (c) Temperature (red), and uncompensated (blue) and compensated (black) thickness measurements. The true thickness of the sample is 9.95 mm (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
thickness measurements match much more closely with the actual thickness of the sample. The standard deviation of the thickness measurements taken in the first hour is 23 nm. Over 24 h, it degrades to 47 nm due to the greater temperature fluctuation.

Ultrasonic thickness measurements were compared to analytical predictions based on Faraday’s law of electrolysis [11] and to optical surface profile measurements. According to Faraday’s law, the thickness change of a finite area due to forced corrosion or electrodeposition (oxidation or reduction reactions) can be calculated by

\[ \Delta D = \pm \frac{Mt}{nFA} \]  

where \( F \) is Faraday’s constant, \( M \) and \( \rho \) are the molar mass and the density of the material that is lost or gained, \( n \) is the number of the electrons that are lost or gained per atom, \( A \) is the area of the reaction surface, \( I \) is the applied current, and \( t \) is the elapsed time. In the experiments conducted, \( n = 2 \) for both the oxidation of iron and the reduction of zinc.

The optical profile scan of a reaction surface is obtained by a white light interferometer (TMS-100 TopMap Metro.Lab, Polytec Ltd, Germany) according to the following procedure.

1) A corrosion/deposition surface is placed within the aperture of the scanner.
2) The exposure time and the scan speed are set by an automated routine.
3) The scan is performed across the height variation of the corrosion/deposition surface.
4) The result of the scan is post-processed using the software supplied by the manufacturer:
   a. Blank pixels are filled in by a median filter;
   b. Outliers are eliminated by a spike removal algorithm;
   c. The plane is translated and rotated such that the area outside the reaction surface lies on \( z = 0 \).

To compare with ultrasonic thickness measurements, optically measured surface profiles are converted into mean thickness changes. Due to the positioning uncertainty of the piezoelectric transducer and the measurement uncertainty of the white light interferometer, both the mean thickness change of the full corrosion/deposition surface and that of a concentric circle with a diameter of 12 mm (i.e. the length of the transducer) are calculated and displayed as error bars.

Finally, the procedure for conducting an UT experiment is summarised below.

1) An electrolyte is prepared and left to equilibrate under ambient conditions for 12 h.
2) The back-wall of the sample is finished with 1 \( \mu \)m diamond particles. The reaction chamber is attached to it.
3) The pump is switched on to circulate the electrolyte through the reaction chamber.
4) The acquisition of ultrasonic and temperature measurements is initiated.
5) The application of an electric current/potential begins after 30 min of data acquisition.
6) The reaction surface is scanned by a white light interferometer.

### 3. Results and discussion

Experiment 1. The capability of UT to track micron level thickness changes is demonstrated by two galvanostatic forced corrosion experiments with applied DCs of 25 and 50 mA. As illustrated in Fig. 2, the ultrasonically measured wall-thickness losses are in excellent agreement with the analytical predictions, and fall well within the error bounds of the mean thickness changes derived from the independent optical surface profile measurements.

Experiment 2. The ultrasonic monitoring of electrodeposition processes is presented through the electrodeposition of zinc onto steel with applied DCs of 50 and 100 mA. Fig. 3 shows that the ultrasonic measurements of the micron level thickness increases match very well with the analytical predictions and the optically measured thickness changes. Since the zinc layers were strongly adhered to the steel sample and the acoustic impedance mismatch between zinc and steel is very small, the transmitted waves were able to penetrate the steel/zinc interface with little loss of energy, before being reflected by the zinc/liquid interface.

Experiment 3. Further potentiostatic forced corrosion experiments were conducted in pH 8 and pH 12 conditions with an applied potential of 1.1 V. In both cases, the deposition of porous corrosion products was visually observed, but the corrosion products did not adhere to the sample very strongly and could be easily washed off under the tap. As shown in Fig. 4, the ultrasonic measurements resemble the optical measurements that were taken after the corrosion products had been washed off. This suggests that the transmitted waves did not travel into the loosely deposited corrosion products and were reflected by the thinned-down back-wall of the sample.
Fig. 4(b) and (c) shows that the corrosion in the more alkaline condition led to the formation of a larger amount of oxide which is known to be corrosion-inhibiting. The passivation effect of the oxide is evident in Fig. 4(a) through the reduction in corrosion rate. The fact that the corrosion in the more alkaline condition was initially faster is due to the higher concentration of OH\(^{-}\) ions which resulted in a more conductive electrolyte. However, this soon became overshadowed by the passivation effect of the oxide.

The two extreme scenarios – electrodeposition and the deposition of porous oxide – highlight the sensitivity of UT to the adhesion quality of electrochemical products. The experimental results clearly demonstrate that UT is an effective tool for monitoring changes in the integral thicknesses of metal substrates and well adhered materials. If the adhesion is poor, UT will only measure the thickness of the substrate. This makes UT a promising laboratory tool for studying not only electrodeposition, but also corrosion inhibition processes which involve passivation layer formation and scale deposition.

4. Conclusion

In this paper, the capability of UT to monitor micron level thickness changes has been demonstrated. This certainly allows for more convenient and more accurate process control of corrosion and electrodeposition. The ultrasonic thickness measurements of the steel sample in the three sets of corrosion and electrodeposition experiments were validated by analytical predictions and independent optical measurements. The observation that UT is sensitive to the bonding conditions between substrates and deposited materials contributes to better understanding of surface electrochemical processes in which the formation of passivation layers and scales with micron and sub-micron thicknesses is important.

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