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High accuracy ultrasonic monitoring of electrochemical processes

Fangxin Zou*, Frederic B. Cegla

Non-Destructive Evaluation Group, Department of Mechanical Engineering, Imperial College London, London, SW7 2AZ, UK

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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 $12 \times 1 \times 0.25\ mm^3$ 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 anti-plane 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

* Corresponding author.
E-mail addresses: f.zou11@imperial.ac.uk (F. Zou), f.cegla@imperial.ac.uk (F.B. Cegla).

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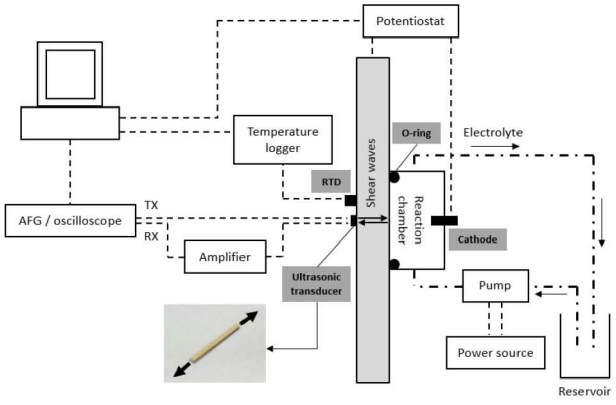
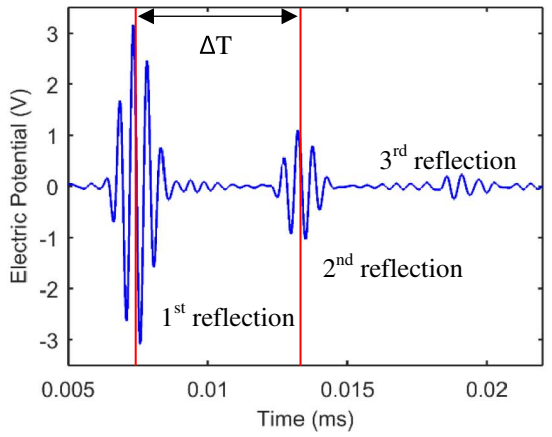


(a)



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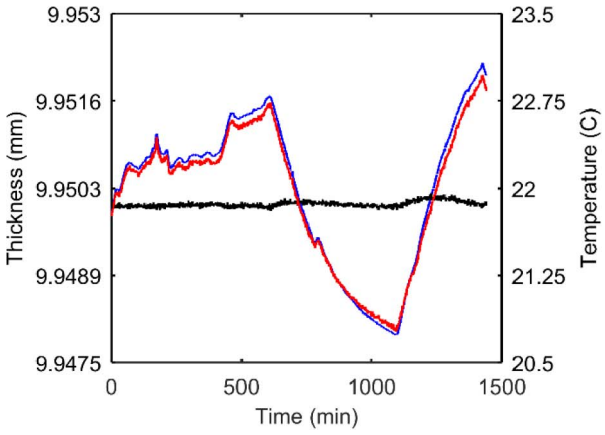

(c)

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.)

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

Table 1
Electrochemical setups of the UT experiments.

	Anode	Cathode	Electrolyte	Load
Experiment 1: Galvanostatic forced corrosion	Steel sample	Steel insert	3.5% w/v NaCl	25 mA 50 mA
Experiment 2: Electrodeposition	Zinc insert	Steel sample	12% w/v NH_4Cl 2.5% w/v $ZnCl_2$	50 mA 100 mA
Experiment 3: Potentiostatic forced corrosion	Steel sample	Steel insert	20% w/v NaCl 10^{-6} M NaOH (pH 8) 20% w/v NaCl 10^{-4} M NaOH (pH 12)	1.1 V

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

$$D = \frac{(T_2 - T_1)v_s}{2} \quad (1)$$

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 Γ (°C) and shear velocity for the steel sample used in this work is given by

$$v_s = -0.64081\Gamma + 3259.5 \quad (2)$$

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