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Experimental investigation of galvanic corrosion: Comparison between SVET and immersion techniques

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ABSTRACT

In this work, two experimental techniques: (a) scanning vibrating electrode technique (SVET) and (b) immersion technique are used to calculate the corrosion rate of two galvanic couples, AE44 (Mg alloy) – mild steel and AE44 – AA6063 (Al alloy). The maximum corrosion rate estimated from these two widely different experimental techniques is found to be in a good agreement for both couples considered here. The maximum corrosion rate of AE44 in AE44 – mild steel couple is found to be approximately five times higher than that in AE44 – AA6063.

1. Introduction

Galvanic corrosion is one of the major hurdles in the use of magnesium (Mg) and its alloys in automotive applications. Although Mg is the lightest structural material, which helps in light weighting the automobile, it is very prone to galvanic corrosion when used along with aluminium (Al) or steel. This is due to a significant potential difference between Mg and Al, or Mg and steel, as can be seen in the galvanic series [1]. There are several techniques available in order to estimate the corrosion rate of an individual alloy (not in a galvanic scenario) such as potentiodynamic polarization [2–6], weight loss method [2–6], hydrogen evolution measurement [4–6], etc., to name a few. But these techniques cannot be readily extended to estimate the corrosion rate of a galvanic couple. The corrosion rate in a galvanic scenario can be estimated by overlaying the polarization curves of the individual components of a galvanic couple using the mixed potential theory [7–12], or by using zero resistance ammeter (ZRA) technique [11–13]. There is, however, no standard technique to calculate the corrosion rate of a galvanic couple where the individual components of the couple are in direct physical and electrical contact. As a result, quantification of galvanic corrosion damage is challenging. Direct physical contact between the individual components of the couple is important in order to eliminate the effect of IR drop at the junction of the couple [7], but is not captured in the above mentioned literature on galvanic corrosion. In this work, we use the scanning vibrating electrode technique (SVET) and the immersion technique to calculate the maximum corrosion rate of a galvanic couple, which address some of the shortcomings of the earlier approaches.

SVET has been used in the past to investigate the galvanic corrosion behaviour. Isaacs [13] investigated the galvanic corrosion behaviour of antimony–tin soldered and lead–tin soldered copper using SVET, and found that the antimony–tin soldered copper is more susceptible to localized corrosion whereas lead–tin soldered copper is found to be passive. Simoes et al. [14] studied the galvanic corrosion of an iron–zinc cell using SVET and scanning electrochemical microscopy (SECM). They have mapped the negative and positive ionic current densities over the iron and zinc surfaces, respectively, and have reported the effect of probe-to-sample distance on the ionic current density. The magnitude of ionic current density was reported to be increasing with decrease in the probe-to-sample distance. The SECM technique provided complimentary information about the concentration of chemical species involved in the corrosion process. Simoes et al. [15,16] extended the use of SVET and SECM to investigate the mechanism of cathodic protection of an Al substrate by an Mg-rich coating. The sacrificial protection offered by Mg to the Al substrate was reported to have prevented pit nucleation and decreased the anodic activity at the pre-existing pit as shown by the evolution of pit activity captured using SVET. Souto et al. [17] reported the use of SVET to investigate the progress of the electrochemical reactions involved in iron–zinc galvanic corrosion and concluded that the cathodic reaction is the rate determining step in the overall corrosion process. Murer et al. [18] investigated galvanic corrosion between pure Al and Al4%Cu alloy using SVET and microcapillary electrochemical cell, and found that their finite element simulations are in agreement with the experimental results. In all the above mentioned work, the

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individual components of the couple are not in physical contact with each other, though they are in electrical contact. Hence, the current density variation capturing peak current densities at the junction (interface) of the couple has not been reported so far in literature. Simoes et al. [15] reported that the separation (of 2 mm) between the individual components of the couple is important due to significant hydrogen evolution. In this work, we perform SVET measurements on a galvanic couple where the individual components are in good physical and electrical contact, and in the presence of severe hydrogen evolution particularly in the vicinity of the junction.

The SVET output is sensitive to the various parameters used in the experiments, such as the probe-to-sample distance, as shown by Simoes et al. [14]. Akid and Garma [19] performed a calibration study to investigate the effect of operating parameters such as the time constant, the probe scan rate, the vibration amplitude, and the probe-to-sample distance on the SVET output. In this work, the effect of the probe scan rate, which controls the data acquisition time, has been brought out while holding the time constant, the vibration amplitude, and the probe-to-sample distance constant. The paper is organized as follows: sample preparation and the principle of operation of the SVET and the immersion techniques are discussed in Section 2. This is followed by Section 3 where the effect of the probe scan rate on the SVET output is discussed. The maximum corrosion rate estimated from the SVET and the immersion technique is then compared for two galvanic couples followed by Section 4.

2. Experimental

2.1. Materials, chemicals and sample preparation

In this work, we investigate the corrosion behaviour of two galvanic couples, AE44 (Mg alloy) – mild steel and AE44 – AA6063 (Al alloy). The sample preparation of the galvanic couple is very critical, as the two dissimilar materials need to be in very good electrical contact with each other. In order to achieve this, two sheets of the dissimilar materials of 10 mm × 20 mm size were first ground at the edges, held tightly using a vice and wrapped with Teflon tape and then hot mounted. It should be noted that Teflon tape works well in hot mount, when compared to other adhesive tapes such as scotch tape. After hot mounting, it was polished and electrical contact between dissimilar materials was checked using a multi-meter. For the SVET experiments, the galvanic couple was machine polished using Struers™ polishing machine, where it was first ground using 320 grit silicon carbide paper for 1 min, followed by MD Largo polishing cloth and 9 μm diamond paste suspension for 5 min, followed by MD Dac polishing cloth and 6 μm diamond paste suspension for 8 min, followed by MD Mol polishing cloth and 3 μm diamond paste suspension for 5 min, and finally by MD Chem polishing cloth and colloidal silica suspension for 3 min. The couple was then provided with a rear end electrical connection for the SVET experiments. For immersion experiments, it was ground using silicon carbide paper of 320 grit, followed by 600 grit, 800 grit, 1000 grit, and finally followed by 1200 grit. Electrolyte solution of 1.6 wt.% sodium chloride was used for all experiments in this work.

2.2. SVET experiments

SVET is an AC technique which measures the potential difference between the two extremes of vibration of the probe (across vibration amplitude) due to ionic current flow in the electrolyte solution. The SVET instrument manufactured by Uniscan Instruments, UK, (Model: Scanning Electrochemical workstation 370) was used in this work. The corrosion behaviour of a freely corroding (i.e. no external potential applied) galvanic couple was investigated using a setup, schematically shown in Fig. 1(a). The test specimen of the galvanic couple was connected to the working electrode (WE) of the potentiostat. The standard calomel electrode was used as the reference electrode (RE) and was connected to RE and the counter electrode (CE) of the potentiostat. The RE was also connected to V_{in} of the electrometer, which provided a stable potential against which the potential difference was measured in the electrolyte solution [20].

In the SVET experiment, a polished galvanic couple was fixed in a tri-cell and leveled using a high precision spirit level. Electrical connections were made as discussed above. The magnitude of the current density was reported in literature [14,19] to increase with a decrease in the probe-to-sample distance. Hence it was important to keep this distance at the lowest value practical, after considering the vibration amplitude. In this work, the scanning probe was placed within 50 μm distance from the sample surface, considering that the vibration amplitude was 30 μm. The probe was first brought down as close as possible to the surface as shown in Fig. 1(b), and then moved 50 μm upwards as shown in Fig. 1(c). The distance between the probe tip and its mirror image in Fig. 1(b) and (c) confirmed that the probe was placed within 50 μm distance from the surface. In order to optimize the signal, the probe was placed precisely at the junction of the couple. About 900 mL of the electrolyte solution was poured into the tri-cell and the signal was conditioned so that the vibrating probe output follows a sinusoidal waveform. After signal optimization, various parameters such as X and Y scan widths, X and Y μm per point, scan rate, full scale sensitivity and output time constant were specified, as reported in Table 1 for the various SVET experiments. The effect of the probe scan rate on the SVET output is discussed in detail in the next section.

A typical SVET output is shown in Fig. 2(a) in the form of an area scan, where 18 mm of distance in the x-direction and 1 mm of distance in the y-direction were scanned. It is represented in terms of the potential difference and the colour bar in Fig. 2(a) indicates its range measured during the scan. The current density can be calculated from the SVET output [21] as,

$$j = -\sigma \frac{\Delta E}{A} \tag{1}$$

where j is the current density in A m^{-2}, σ is the conductivity of the electrolyte solution which is 2.5 S m^{-1}, ΔE is the potential difference across the vibration amplitude in V, and A is the vibration amplitude. It should be noted that in Eq. (1) the conductivity of the electrolyte solution is assumed to be a constant. This was measured before and after the SVET experiment in order to confirm the above assumption, and the increase in conductivity was found to be marginal (less than 0.4%). It was also confirmed that there was no difference in the conductivity values, when measured closer to the galvanic couple and in the bulk solution.

Corrosion rate, C_R, can be calculated from current density using Faraday's law as follows,

$$C_R = \frac{M}{zF\rho} j \tag{2}$$

where M is the atomic mass, z is the electron number, F is the Faraday constant and ρ is the density. Eq. (2) is reported in literature in various forms [22–24]. We have used SI units and the various parameters used in Eq. (2) are as follows: F is 96485.34 C mol^{-1}, M is 26.82 g mol^{-1}, z is 2, ρ is 1820 kg m^{-3} for the corroding constituent of the galvanic couple (AE44), and C_R is in m s^{-1}.

2.3. Immersion experiments

A ground galvanic couple, which was prepared and hot mounted as discussed earlier in this section, was freely suspended