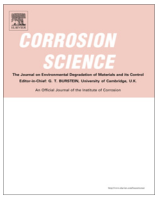
Corrosion Science 96 (2015) 1–5

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Letter

The effect of electrolyte layer thickness on electrochemical migration of tin

Xiankang Zhong [a,*], Guoan Zhang [b], Xingpeng Guo [b]

[a] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, School of Oil and Natural Gas Engineering, Southwest Petroleum University, Chengdu 610500, China
[b] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 22 March 2015
Accepted 19 April 2015
Available online 24 April 2015

Keywords:
A. Tin
C. Anodic dissolution

ABSTRACT

In this work, electrochemical migration behaviour of tin under electrolyte layers with different thicknesses was investigated using thin electrolyte layer method. The results show that the time to short circuit first increases and then decreases with increasing thickness of the electrolyte layer, the maximum value is present at 100 μm. Inductively Coupled Plasma Source Mass Spectrometer was employed to measure the local concentration of tin ions. The result shows that the lowest local concentration of tin ions is present at the 100-μm-thick electrolyte layer, resulting in a maximum value in the time to short circuit.

1. Introduction

Electrochemical migration (ECM) is an important phenomenon related to the failure of electronics. This process occurs when two oppositely biased and closely spaced electrodes are connected by a continuous electrolyte layer. Metal ions are produced at the anode and then migrate towards the cathode, where they can be reduced to metallic dendrite which then grows towards the anode [1]. As soon as the dendrite reaches the anode, the short circuit occurs and causes the failure of electronics. Therefore, ECM significantly compromises the reliability of electronics.

Based on the operating conditions, ECM can be divided into humid-ECM and wet-ECM [2]. Humid-ECM means that the migration proceeds under a thin and continuous invisible film of moisture, while wet-ECM represents that the migration proceeds under a visible layer of condensed water. Therefore, it can be considered that the essential of ECM is an electrochemical reaction under electrolyte layers with different thicknesses. Although the influence of different factors such as alloy element, bias voltage and corrosive media on ECM behaviour and mechanisms has been widely investigated [3–7], the effect of thickness of the electrolyte layer on ECM is still unknown.

A change in the thickness of the electrolyte layer affects some parameters [8], e.g., solution resistance and the transport of species which, subsequently, affect the electrochemical reaction rate such as anodic dissolution rate, diffusion rate and dendrite growth rate. Therefore, it is very significant to understand the effect of electrolyte layer thickness on ECM behaviour. However, there was no method for controlling and measuring the thickness of electrolyte layer accurately during the ECM test. That is why the effect of electrolyte layer thickness on ECM has never been studied before.

In our previous work [6,9], we proposed a new method for ECM research, i.e., thin electrolyte layer (TEL) method, which can be used to real time in situ study the ECM under an electrolyte layer with an accurately controlled thickness. In this work, the ECM of tin under electrolyte layers with different thicknesses was investigated using TEL method.

2. Experimental

Pure tin (>99.999 wt.%) with the dimensions of 2 × 5 × 10 mm was used in this work. Two identical tin electrodes, i.e., one as cathode and the other one as anode, were embedded in epoxy resin at 0.5 mm distance in parallel direction, as shown in Fig. 1a, insulated from each other with an epoxy resin layer between them. A copper wire was welded to the backside of each electrode to ensure electric connection. Before each test, the electrode surface was ground to 1200 grit with silicon carbide paper. Subsequently, the surface was rinsed with deionized water, degreased with acetone and dried in cool air.

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* Corresponding author. Tel.: +86 28 83032210.
E-mail address: zhongxk@yeah.net (X. Zhong).

http://dx.doi.org/10.1016/j.corsci.2015.04.014
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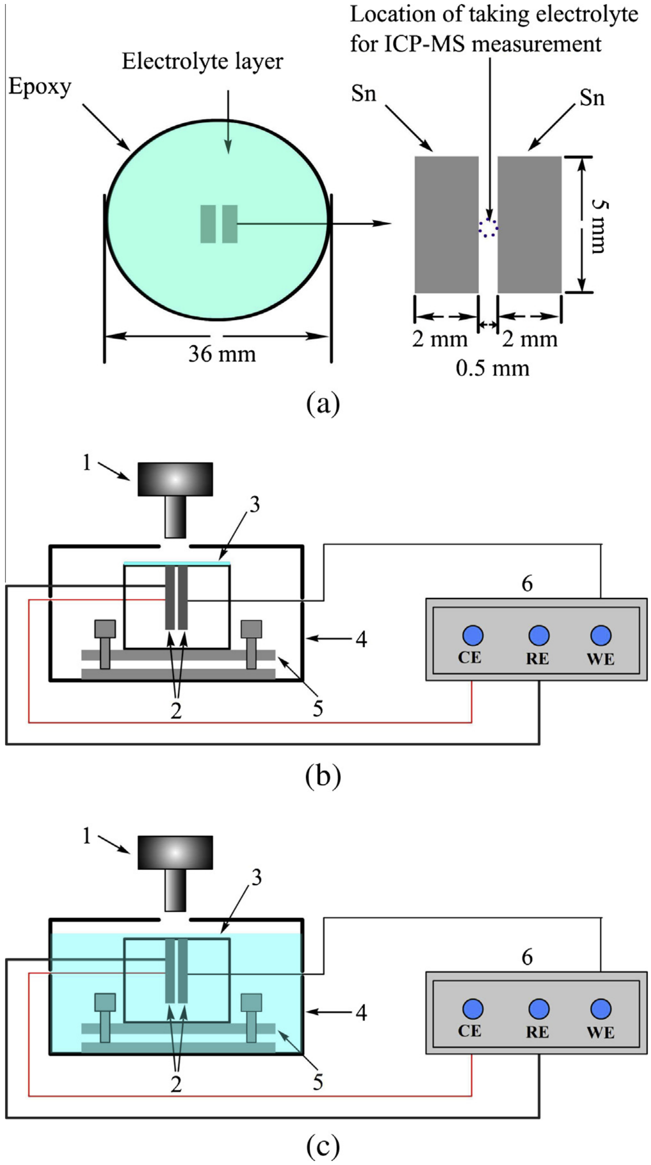

Fig. 1. (a) Top view of the electrode, and schematic diagrams of setups for electrochemical migration under thin electrolyte layer with different thicknesses (b) equal to or more than 100 μm and (c) less than 100 μm: (1) 3D microscope, (2) electrode, (3) electrolyte layer, (4) glass chamber, (5) horizontal stage and (6) potentiostat.

Then the pretreated electrodes were put into a glass chamber where there was a horizontal stage, which was leveled using a spirit level (Fig. 1b and c). If the thickness of electrolyte layer was equal to or more than 100 μm (100, 500, 1000 μm), a certain amount of electrolyte was placed on the electrode surface to form a continuous and smooth electrolyte layer (Fig. 1b). However, due to evaporation of the electrolyte and the action of surface tension, it is not technically feasible to get such a continuous and smooth electrolyte layer with a thickness less than 100 μm (30, or 70 μm) if the experiment set-up shown in Fig. 1b is used. Therefore, an improved set-up used for thicknesses less than 100 μm was proposed (See Fig. 1c). The same electrolyte as the electrolyte layer was continuously put into the glass chamber until an electrolyte layer was formed on the electrode surface. The thickness of the electrolyte layer was adjusted by adding electrolyte into the chamber or taking electrolyte out from the chamber using a syringe. In this case, the problems caused by evaporation and surface tension were avoided successfully. Nishikata et al. proposed a similar set-up which can form a thin electrolyte layer with a thickness merely 10 μm [8]. The thickness of the electrolyte layer was measured using a set-up consisting of a sharp Pt needle (Φ = 0.1 mm) with a Z-stage equipped with a micrometer. The detailed information and method of measurement were described elsewhere [10].

The electrolyte was 1 mM NaCl solution (pH6.7), which was prepared from deionized water (18.2 MΩ cm in resistivity) and analytical grade reagents. A CS350 electrochemical test system (Wuhan Corrtest, China) was used for ECM tests. A 3 V direct current (DC) bias voltage was applied across the two electrodes and the current flowing through the circuit was recorded simultaneously as a function of time. To check the reproducibility, all of the ECM tests were repeated at least five times. The local concentration of tin ions was measured by the Inductively Coupled Plasma Source Mass Spectrometer (ICP-MS, ELAN DRC-e, PerkinElmer America). The location of taking the electrolyte was at the centre of the electrode system shown in Fig. 1a. The local concentration measurement was repeated five times to guarantee reproducibility.

3. Results and discussion

During the ECM process, the ions produced by anodic and cathodic reactions will migrate under the electric field, e.g., OH^- produced by cathodic reactions will move towards the anode, and Sn^{2+} and Sn^{4+} produced by anodic dissolution will migrate towards the cathode where they can be reduced to metallic dendrite which then grows towards the anode [6]. Once the dendrite reaches the anode, the short circuit will occur. The time interval from the time when the bias voltage is applied across the two electrodes to the time when the short circuit occurs is defined as the time to short circuit (t_{sc}). Based on this definition, it can be considered that it will take less time for the dendrite growing from the cathode to reach the anode if the growth is faster.

Typical current density vs. time curves during the ECM test of tin under electrolyte layers with various thicknesses are shown in Fig. 2a. It is seen that the current density increases with increasing electrolyte layer thickness. As the thickness of electrolyte layer increases from 30 μm to 1000 μm, the current density increases from about 10^{-5} A/cm^2 to about 10^{-3} A/cm^2. This can be attributed to the fact that solution resistance decreases with increasing thickness of the electrolyte layer, accelerates the electrochemical reaction rate, hence an increase in current density. A sudden current density spike appears when the dendrites bridge the anode and the cathode, resulting in short circuit. Fig. 2b shows that the average t_{sc} first increases and then decreases with increasing electrolyte layer thickness, the maximum value is present at 100 μm. According to our previous work [6], the dendrite growth under thin electrolyte layer with 1 mM Cl^- can be mainly ascribed to the direct reductions of Sn^{4+} and Sn^{2+} as given by Eqs. (1) and (2).

$$Sn^{4+} + 4e^- \rightarrow Sn \tag{1}$$

$$Sn^{2+} + 2e^- \rightarrow Sn \tag{2}$$

Therefore, it is believed that the dendrite growth rate is determined by the concentration of tin ions (Sn^{4+} and Sn^{2+}) which are derived from the anodic dissolution during the ECM test.

Generally, the concentration of tin ions is in correlation with the volume of electrolyte and the amount of tin ions.