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The role of electrochemical polarization in micro-droplets formation

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ABSTRACT

The effects of electrochemical polarization on the micro-droplets formation were investigated using microscope observation method and electrochemical polarization techniques.

It is found that cathodic polarization can initiate and accelerate the formation of micro-droplets, whereas anodic polarization can inhibit the micro-droplets formation, independent of metal type, electrolyte species, composition of air, and environmental humidity, indicating that the electrochemical polarization is the key condition for micro-droplets formation on metal surfaces. Based on above results, it is suggested that both the decrease of liquid/metal interface tension and the cooling of temperature of the three-phase-boundary area which are caused by cathodic polarization, may be the main reason for the micro-droplets formation.

1. Introduction

The micro-droplets formation on metal surfaces, an important phenomenon closely related to atmospheric corrosion, has been reported and investigated in recent years [1].

It was found out that micro-droplets could only form in a corrosive combination of metal and electrolyte droplet, namely, the metal substrate can be corroded for the primary-droplet, and appeared easier at higher relative humidities (RH), while lower RH and oxygen-free atmosphere were helpless for the micro-droplets formation [2,3].

It is known that micro-droplets form around the three-phase boundary which involves four different environments, i.e. gas (air composition and humidity), liquid, metal and liquid/metal interface. The liquid/metal interface can be affected by other three phases (corrosive media, corrodible metal and oxygen) except for RH which only provides water vapor. Accordingly, electrochemical condition of the liquid/metal interface plays a vital role in the micro-droplets formation.

In addition, since the three-phase boundary is a special area focalizing three kinds of interfaces and interfacial tensions and its state changes will cause interphase reactions and interphase mass transfer, it is also important for the micro-droplets formation.

To clarify the role of electrochemical characterization of liquid/metal interface in micro-droplets formation, the effect of electrochemical polarization on micro-droplets formation was systematically studied and its mechanism was discussed.

2. Experiments

2.1. Specimens and chemicals

Carbon steel (A3) and stainless steel (1Cr18Ni9Ti) plates of 10 mm × 10 mm × 3 mm were used as the specimen. The working surface was finally polished with 1200 grit SiC waterproof paper and diamond paste until a mirror smooth surface was obtained, and then cleaned by acetone and twice distilled water. Solutions were prepared from the analytical grade chemicals and twice distilled water. All tests were conducted at room temperature (~22 °C).

2.2. Experimental instruments and procedures

A two-electrode cell was used with a pair of identical metal sheets parallelly embedded in epoxy resin 100 μm apart with each other, as shown in Fig. 1A. Solution of 5–10 μL was dropped onto the intersection of two electrodes using a micro-syringe to form a primary-droplet and the primary-droplet will be polarized with a voltage applied to the two parallel electrodes.

In order to observe the micro-droplets formation in situ, a thin climate chamber was used as shown in Fig. 1B. The detail of humidity control method in this study was similar to that reported by Zhang et al. [3]. The processes of the micro-droplets formation were surveyed in situ with a laser confocal microscope (Bio-Rad MRC1024).

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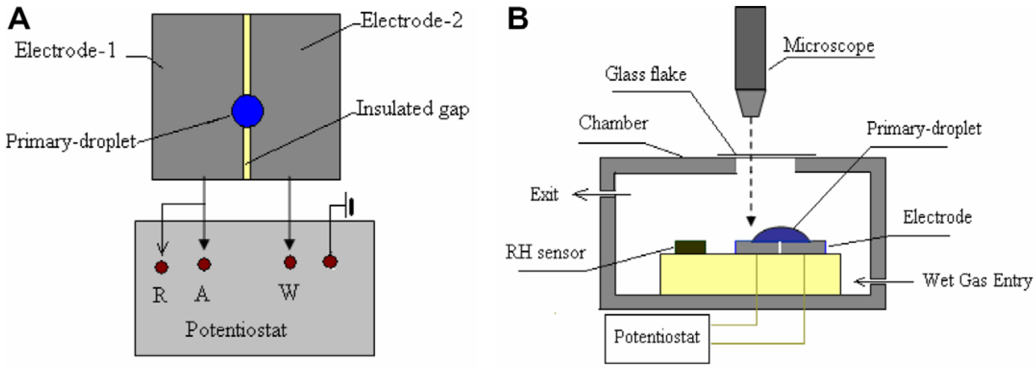

Fig. 1. Schematic diagrams of polarization setup and control air chamber for in situ observation of micro-droplets formation.

3. Results and discussion

3.1. Effect of cathodic polarization on the formation and spreading of micro-droplets

In our previous works [3,4], we found that a corrosive combination of metals and electrolyte droplets, containing oxygen atmosphere and higher RH could promote the formation of micro-droplets. However, it was also found out, provided that the primary-droplet was under cathodic polarization, the micro-droplets could form around the border of the primary-droplet even for the non-corrodible combination, indicating the important influence of electrochemical polarization on the micro-droplets formation. To clarify this effect, systematic investigation was performed.

3.1.1. In oxygen-free environment

When a primary-droplet of 1 M NaCl solution was put on the surface of stainless steel in pure argon atmosphere, no micro-droplets appeared in this environment. However, by exerting a potentiostatic polarization on electrode surface, it was obviously observed that micro-droplets appeared in the cathodic area, as shown in Fig. 2A, and the number of micro-droplets increased with increasing the cathodic polarizing potential. A similar result was also observed in pure nitrogen, as presented in Fig. 2B. In addition, although a large amount of tiny micro-droplets appeared on the cathodic area, there was no micro-droplets formation in anodic area.

The above results indicated that oxygen was not the necessary condition for the micro-droplets formation, whereas cathodic polarization may contribute a lot to the formation of the micro-droplets.

3.1.2. In lower RH environment

It was found that under natural condition, micro-droplets appeared only when RH was higher than the saturated relative humidity of primary-droplet at the same temperature [4]. However, by exerting cathodic polarization on metal surface, micro-droplets could form at lower RH. The formation of micro-droplets of NaCl solution on A3 steel surface at a potential of -600 mV at 32% RH was shown in Fig. 3A. From Fig. 3A we can see that even though the RH is much lower than the saturated relative humidity of NaCl solution (76% in the experiment), the micro-droplets still form in cathode. Similar behavior was also observed for NaCl droplet on stainless steel surface at a potential of −1570 mV, as seen in Fig. 3B.

These results indicated that higher RH was also not the necessary condition for the micro-droplets formation, while the electrochemical cathodic polarization played a vital role in the micro-droplets formation.

3.1.3. Non-corrosive combinations of metal and salt solution

In the previous papers [3,4], it was found that micro-droplets could not appear in the case of non-corrosive combinations of metals and salt solution, such as $MgCl_2$/A3, $CaCl_2$/A3, NaCl/SS and

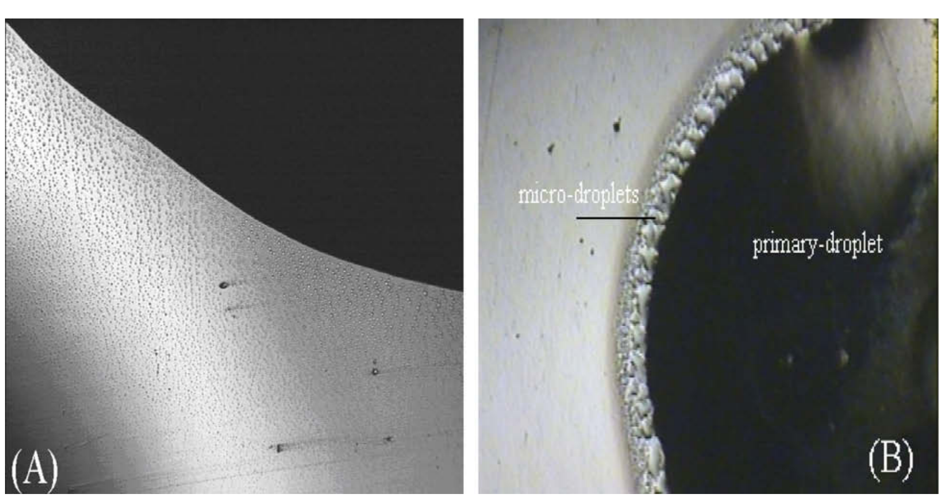

Fig. 2. In oxygen-free environment, micro-droplets formed under polarization for 1 M NaCl/SS. (A) In pure argon (95%RH, −1500 mV), (B) In pure nitrogen (85%RH, −1300 mV).