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Short communication

The comparison of the corrosion of ultrapure iron and low-carbon steel under NaCl-electrolyte droplets

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ABSTRACT

The corrosion of ultrapure iron under deliquesced NaCl particles was compared with that of low-carbon steel. The critical droplet size for corrosion to occur was larger for ultrapure iron (150–200 μm) than that for low-carbon steel (40–100 μm) indicating a lower corrosion propensity for ultrapure iron. Polarization experiments performed under NaCl micro-droplets showed that ultrapure iron had passivation-like behavior and a pitting-like potential of $\sim 1.69 V_{\text{SCE}}$ compared to $\sim 0.4 V_{\text{SCE}}$ for low-carbon steel. The disparity was attributed to a more homogenous and protective iron oxide film on ultrapure iron as compared to that on low-carbon steel.

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1. Introduction

The deposition of salt particles on metal surfaces plays a vital role in marine atmospheric corrosion. Marine aerosols (mainly NaCl) are primarily generated from sea spray, which is produced by ocean and coastal wave action. The aerosols can be carried far inland by wind and induce corrosion. Above the critical relative humidity (CRH), hygroscopic salt absorb moisture from the environment and form salt droplets, which can substantially accelerate the corrosion of metals.

Extensive research has been conducted on the corrosion of metal surfaces caused by deliquesced salt droplets [1–8] and pre-deposited salt droplets [9–13]. Recent work has been conducted to study the corrosion initiation on carbon steel induced by both laboratory [14–21] and naturally [22] deposited NaCl particles. Corrosion initiation and propagation on carbon steel under NaCl droplets and the related electrochemistry were investigated in great detail [8–16]. For droplets less than a critical size of approximately 40–100 μm [15,21], corrosion did not initiate. Polarization experiments showed that the steel substrate had passivated under relatively small droplets, with a pitting potential at approximately 0.4 V_{SCE} [18]. Under droplets larger than the critical size, corrosion always initiated from slag-based inclusions and then propagated

into the surrounding area by the active corrosion of the steel substrate, which is the normal expected behavior for low-carbon steel in aerated chloride environments [15].

To investigate the effect of surface oxide film on the droplet corrosion on carbon steel, the present study compares NaCl particle-induced corrosion on low-carbon steel and ultrapure iron. Ultrapure iron was selected because it is similar to plain carbon steel but contain less and smaller inclusions than that in carbon steel, which is believed to result in a more homogeneous and protective iron oxide film. Both droplet corrosion initiation and micro-droplet polarization experiments were conducted. The reason why small micron-sized droplets were studied in this work was because these conditions are relevant to corrosion in the field.

2. Experimental

Specimens with a thickness of 2 mm were cut from an ultrapure iron rod (D = 5 mm, 99.99%), and were then mounted in epoxy resin. The specimens were subsequently ground with 180, 400, 1200 grit SiC grinding paper; polished with 9.0, 3.0, 1.0 μm polycrystalline diamond suspensions (METADI SUPREME, BUEHLER); and finished with a MASTERPOLISH polishing suspension (alumina + colloidal silica, 0.05 μm) (BUEHLER). The specimens were then ultrasonically cleaned in reagent-grade alcohol; rinsed with ultrapure water (18.0 $M\Omega\text{ cm}$); dried under warm air; and kept in a dry box (1% RH) for 5 days prior to conducting experiments. The 1018 carbon steel samples (C: 0.15–0.20 wt.%, Mn: 0.60–0.90 wt.%, P: 0.035 wt.%, S:

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0.04 wt.%, Fe: balance) were prepared following the same procedure as pure iron.

Two approaches were employed to deposit salt particles onto the sample surfaces. The first approach involved using an ultrasonic humidifier (ETS, model 5462) and a saturated NaCl solution made of analytical grade NaCl and ultrapure water (18.0 MΩ cm). The samples were exposed to the mist produced by the humidifier for 2 s, and then were dried in a dry box (1% RH) to obtain fine salt particles ($D \approx 1\text{--}10\ \mu\text{m}$). The second approach was the manual deposition of salt particles using a tiny probe ($D \approx 10\ \mu\text{m}$) and a stereomicroscope. Grounded NaCl particles ($D \approx 2\text{--}100\ \mu\text{m}$) were placed on sample surface using the tiny probe with the assistance of static electricity. The samples with pre-deposited NaCl particle(s) were then placed in a custom-made humidity chamber with humidity maintained above 80% RH [15].

The polarization experiments were conducted with a combination electrode with a tip diameter of approximately 2–5 μm [18] using an EG&G model 273A potentiostat. The combination electrode is composed of a custom made Ag/AgCl reference electrode housed in a borosilicate glass capillary fabricated using a micropipette puller (P-97, Sutter Instruments) and a Pt-wire counter electrode. The tip of the combination electrode was a glass micro-capillary similar to that used for the Ag/AgCl reference electrode. The combination electrode was mounted to a computer-controlled 3D manipulator to facilitate positioning it into the micron-sized droplets.

The samples with the combination electrode positioned in the NaCl droplets were stabilized at open-circuit potential (OCP) for 2 min before scanning at a rate of 10 mV/s. Notice that it is theoretically impossible to obtain the true pitting potential of a material using such a high scan rate (i.e., non-steady state) [23] and a very small sample area [24]. However, instead of defining the true pitting potential and obtaining corrosion rates, the present work aims to compare the electrochemical responses of pure iron and carbon steel under micron-sized NaCl droplets, which help to differentiate the protectiveness of the oxide films on the two types of materials. The relatively high scan rate was selected to reduce the experiment duration in order to avoid significant increase in the droplet size (possibly due to moisture absorption) and changes in droplet chemistry. The high (> 10 mV/s) scan rate has been used in a similar configuration: the micro-capillary cell, to avoid significant changes in the droplet chemistry during polarization [25,26]. Multiple droplet polarization experiments were conducted to confirm repeatability, while only representative curves are shown herein. More details about experimental procedures can be found in previous publications [15,18].

3. Results and discussion

3.1. Droplet corrosion

NaCl particles ranging from 3 to 40 μm in diameter were obtained using the ultrasonic humidifier with a 2 s exposure. This resulted in a density of approximately 125 salt particles per square mm. After deliquescence in a humidified environment (80–85% RH), the NaCl-electrolyte droplets ranged from approximately 9 to 106 μm in diameter. The majority of the NaCl-electrolyte droplets (>95%) could not initiate corrosion on ultrapure iron even after 6 h of exposure; whereas, corrosion initiated under other droplets in time spans as short as 3 min. Similarly, a manually-deposited NaCl particle (Fig. 1a1, $D = 45\ \mu\text{m}$) which transformed to a droplet with a diameter of 132 μm (Fig. 1a2) in the humid environment could not induce corrosion on ultrapure iron after 6 h of exposure (Fig. 1a3). Additional experiments showed that corrosion did not generally initiate under NaCl-electrolyte droplets with diameter

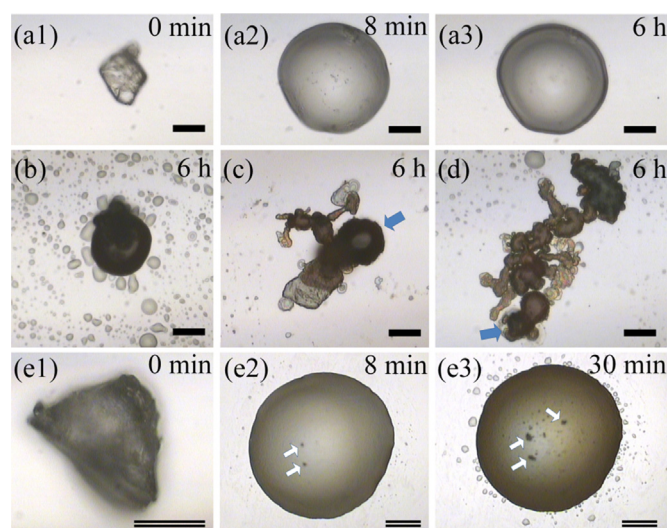


Fig. 1. (a) A manually deposited NaCl particle that could not initiate corrosion on ultrapure iron after 6 h in high humidity; (b–d) corrosion caused by small NaCl particles deposited using a humidifier; and (e) a large NaCl particle ($D = 123\ \mu\text{m}$) that transformed to a droplet of 401 μm in diameter which induced corrosion on ultrapure iron. The arrows in (c) and (d) indicate the locations of the original droplets. The arrows in (e2) and (e3) point to corrosion initiation sites. Single-line scale bars (a–d) are 40 μm , and double-line scale bars (e) are 100 μm .

smaller than approximately 150–200 μm . However, when a very large number of salt particles were deposited on the ultrapure iron surface (≈ 125 particles per square mm) using the ultrasonic humidifier, corrosion was observed on a few of the smaller droplets. It was hypothesized that the high density of salt particles increased the probability that a small droplet would settle on a slag-based inclusion. Fig. 1b–d shows some rare cases of corrosion on ultrapure iron where the NaCl-electrolyte droplets were small ($D = 56\text{--}72\ \mu\text{m}$). In these droplets, corrosion initiated quickly and in some cases spread to large areas in the form of filiform corrosion (Fig. 1c and d). Similar filiform corrosion phenomenon has been observed on pure iron [27] and steel [15,28] exposed to NaCl droplets. Secondary droplets were also seen around the corroded regions (Fig. 1b–d). The formation of secondary droplets around the main droplets has been reported in the NaCl particles-induced corrosion of metals such as zinc, steel, and copper [3,29,30]. The driving force for the formation of secondary droplets was believed to be the potential difference between the central anodic and the peripheral cathodic regions of the main droplet [3,4,31]. When large NaCl-electrolyte droplets ($D > 200\ \mu\text{m}$) formed on ultrapure iron, corrosion initiated within approximately 3 min under the large droplets with corrosion pits primarily in the center of the droplet area, as an example shown in Fig. 1e.

The continuity of surface oxide films grown on ultrapure iron and low-carbon steel can be affected by the presence of microstructural precipitates (Fig. 2). Both low-carbon steel and ultrapure iron contain slag-based inclusions, and low-carbon steel also contains iron carbide (Fe_3C). Since many slag-based inclusions ($D < 20\ \mu\text{m}$) exist in low-carbon steel [15], the iron oxide film on low-carbon steel (Fig. 2a) would have more disruptions at inclusion sites compared to that on ultrapure iron (Fig. 2b) which has less and smaller slag-based inclusions. Hence, the critical droplet size below which corrosion rarely initiates is smaller for low-carbon steel (40–100 μm) [9] compared to ultrapure iron (150–200 μm). This is because it takes a larger region on ultrapure iron to contain an inclusion (that can induce corrosion) compared to low-carbon steel [15,21]. However, corrosion could initiate under droplets smaller than critical droplet size if the droplet region contains an inclusion. Although this would be a rare occurrence, it was observed in

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