Effect of Seawater Droplet Spreading Factor on Electrochemical Properties of Carbon Steel Surface Postprint

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Abstract

The wire beam electrode technique (WBE) was employed to investigate the corrosion behavior of carbon steel surfaces beneath seawater droplets. The results demonstrate that as corrosion time prolongs, the cathodic and anodic current values under the droplet gradually decline and eventually stabilize. A comparison of current distribution on carbon steel surfaces beneath seawater droplets of various sizes reveals that smaller droplets induce more severe corrosion and are more prone to forming asymmetric electrochemical zones. The concept of a droplet spreading factor is proposed. The investigation finds that with increasing droplet spreading factor, the average current density exhibits an exponential increase, while the maximum anodic current density and the standard deviation of anodic current density increase linearly, indicating enhanced corrosion intensity.

Full Text

Influence of Spreadability Factor of Seawater Droplets on Electrochemical Characteristics of Carbon Steel Surfaces

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Abstract

The corrosion behavior of carbon steel beneath seawater droplets was investigated using the wire beam electrode (WBE) technique. Results demonstrated that both anodic and cathodic currents beneath the droplets gradually decreased with increasing corrosion time before eventually stabilizing. Comparative analysis of current distributions beneath seawater droplets of varying sizes revealed that smaller droplets induced more severe corrosion and were more prone to forming asymmetric electrochemical zones. This study introduces the concept of droplet spreadability factor and investigates its influence on corrosion intensity. The average current density increased exponentially with increasing spreadability factor, while the maximum anodic current density and standard deviation of anodic current density increased linearly, indicating enhanced corrosion intensity.

Keywords: failure and protection of materials, atmospheric corrosion, wire beam electrode, spreadability factor

Introduction

Due to surface energy effects, electrolyte films adsorbed on metal surfaces do not distribute uniformly but rather form droplets of various sizes. These droplets create the necessary conditions for electrochemical corrosion and represent a critical factor influencing initial atmospheric corrosion behavior. Consequently, a thorough understanding of droplet phenomena is essential for investigating the early stages of atmospheric corrosion.

Previous research on metal corrosion beneath electrolyte droplets has yielded significant insights. Wang et al. [1] employed atomic force microscopy to study the relationship between corrosion rate and droplet size for pure iron beneath sulfuric acid droplets, finding that the average corrosion rate during initial stages decreased with reducing droplet size. Tsutsumi et al. [2] investigated the pitting corrosion mechanism of 304 stainless steel beneath $MgCl_2$ droplets under constant humidity conditions, demonstrating that pitting probability decreased with reductions in both droplet diameter and height. Jiang et al. [3-5] introduced the concept of the three-phase boundary line and theoretically confirmed the role of liquid-phase distribution in the cathodic processes of metal corrosion.

Given the unique dimensions of droplets, researchers have designed micro-scale reference and counter electrodes for electrochemical studies. Dubuisson et al. [6, 7] utilized dual platinum wire electrodes to study corrosion of galvanized steel beneath NaCl and Na_2SO_4 droplets, revealing that corrosion rates increased significantly when droplet height was less than 800 m, but showed minimal change above this threshold. Jiang et al. [8] employed a custom Ag/AgCl reference electrode to investigate the electrochemical corrosion mechanism of steel beneath chloride-containing droplets, identifying distinct anodic and cathodic zones—anodic regions primarily in the center, cathodic regions at the edges, with corrosion products forming between them to create a characteristic corrosion product ring. Micro-electrochemical techniques such as the scanning Kelvin probe (SKP) have also proven valuable. Zhang et al. [9] used scanning Kelvin probe reference electrode technology to study potential distribution characteristics during corrosion induced by inorganic salt particle deposition in vapor environments, observing volcano-shaped non-uniform potential distributions at salt deposition sites under elevated relative humidity. Tang et al. [10] investigated micro-area electrochemical parameter distribution characteristics on Q235 steel surfaces beneath NaCl droplets.

However, these studies employed large-area metal electrodes, which cannot capture the electrochemical characteristics at different positions, particularly current distribution information, thereby limiting research depth. The wire beam electrode (WBE) technique, developed over the past two decades, is a micro-electrochemical method that applies integral principles using a series of regularly arranged electrode wires to represent the entire electrode surface. This technique provides distribution information for electrochemical parameters across the electrode surface and serves as a powerful tool for investigating localized corrosion. Currently, Muster et al. [11] have studied the influence of droplet characteristics on zinc atmospheric corrosion, finding that current densities were essentially consistent across different droplet sizes (1-10 L) but varied significantly with NaCl concentration. Wang et al. [12] used WBE to investigate localized corrosion of 304 stainless steel in NaCl solutions, observing non-uniform current distributions with anodic current peaks primarily at droplet edges and noting that localized corrosion intensified with increasing droplet size.

Our research group has developed a WBE measurement and control system based on PXI modular instruments in the LabVIEW environment and applied it to various heterogeneous corrosion studies [13-17]. Carbon steel is one of the most widely used metallic materials. In marine atmospheric environments, different-sized droplets form on metal surfaces containing various inorganic salts, with particularly high NaCl concentrations that exert more severe destructive effects on carbon steel. Therefore, this study employs the WBE technique to investigate current distribution patterns on carbon steel beneath seawater droplets, examine the influence of droplet size on corrosion, and explore the effect of droplet spreadability factor on corrosion characteristics.

Experimental Methods

1.1 Electrode Preparation A wire beam electrode was fabricated by arranging 1.2 mm diameter A3 carbon steel wires in an 11$×$11 matrix and sealing them with epoxy resin. The individual carbon steel wires were insulated from each other with a spacing of 0.3 mm [Figure 1a: see original paper]. Prior to experiments, the WBE surface was progressively polished with 400#, 1000#, and 2000# waterproof abrasive paper, cleaned with ethanol, blow-dried with cold air, and stored in a vacuum desiccator for 24 hours. Seawater used in experiments was clean seawater collected from the Qingdao coastal area.

1.2 Experimental Setup The experimental apparatus is illustrated in [Figure 1b: see original paper]. The WBE was placed in an artificial climate chamber with environmental relative humidity controlled above 95% using a solution of the same concentration, and electrochemical tests were conducted at (20$±$1)°C. Seawater droplets of different volumes were applied to the WBE surface using a microsyringe, followed by measurement of the galvanic current distribution across the electrode surface.

1.3 WBE Testing The current distribution measurement system comprised NI PXI-1033, PXI-2532, and other modules [13-15, 18, 19]. Before measurement, all wires were short-circuited together to ensure free electron flow between different steel wires, analogous to electron transfer between local anodes and cathodes in bulk electrodes. During measurement, the 121 wires were sequentially disconnected, and the galvanic current between each individual wire and all remaining short-circuited wires was measured. The entire measurement process was controlled by LabVIEW 8.5 software, and experimental data were processed using Surfer 8.0 to generate current distribution maps at different corrosion times.

1.4 Corrosion Morphology Observation A stereo optical microscope was used to photograph droplet states at different time intervals, enabling determination of droplet radius, height, and corrosion conditions on the carbon steel surface.

Results and Discussion

2.1 Corrosion Behavior Beneath Seawater Droplets [Figure 2: see original paper] presents current distribution maps on carbon steel surfaces beneath a 50 L seawater droplet at various corrosion times. Positive values represent anodic current, negative values represent cathodic current, and color intensity indicates current magnitude. The dashed line encloses the droplet area, while the x- and y-coordinates correspond to different wires in the electrode array.

The current distribution beneath the droplet is non-uniform, with the droplet center serving as the anodic zone and the periphery as the cathodic zone, exhibiting typical Evans ring phenomena [19]. The varying thickness of the electrolyte film beneath seawater droplets creates oxygen concentration gradients that drive localized corrosion. The thinnest film at the edges facilitates rapid oxygen diffusion, promoting the cathodic oxygen reduction reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Conversely, the thickest film at the center limits oxygen diffusion, resulting in anodic dissolution: $Fe - 2e^- \rightarrow Fe^{2+}$.

The current distribution patterns evolve through distinct stages. At 10 minutes of corrosion, two prominent anodic current peaks appear in the droplet center with the deepest coloration, while cathodic zones at the edges also show intense coloration, indicating maximum corrosion intensity. During this initial stage, the steel surface lacks rust layer coverage, and strong electrode activity combined with oxygen depolarization intensifies the anodic reaction at the center. At 30 and 60 minutes, the number of anodic current peaks increases while their intensity decreases slightly, suggesting that oxygen consumption reduces central oxygen content and diminishes corrosion intensity. After 90 minutes, oxygen diffusion reaches equilibrium, and the sizes of anodic and cathodic zones stabilize. At 300 minutes, anodic current peaks persist beneath the droplet with essentially unchanged shape but significantly reduced intensity, while cathodic zones decrease markedly. Both anodic and cathodic current absolute values decline to approximately 0.2 A. At this stage, rust layers have essentially covered the entire droplet area, inhibiting both metal anodic dissolution and cathodic oxygen reduction, thereby rendering corrosion beneath the droplet more uniform.

To quantify the relationship between corrosion extent and time, the variation of average anodic current density with corrosion time was measured. Average anodic current density, defined as the ratio of total anodic current to anodic area, reflects corrosion intensity beneath droplets. As shown in [Figure 3: see original paper], the average anodic current density beneath a 50 L seawater droplet decreases with increasing corrosion time, with the most significant decline occurring during the first 60 minutes, indicating most intense initial corrosion. After 90 minutes, the values stabilize, suggesting that corrosion beneath the droplet reaches a relatively steady state, consistent with the results presented in [Figure 2: see original paper]. Thus, corrosion intensity beneath seawater droplets gradually decreases with time before eventually stabilizing.

2.2 Influence of Droplet Size on Current Distribution [Figure 4: see original paper] illustrates current distribution maps on carbon steel surfaces beneath seawater droplets of different sizes. Droplet size significantly impacts electrochemical distribution patterns. As shown in [Figure 4a: see original paper], beneath a 10 L droplet, only one primary anode is observed, and its location is not centered but rather adjacent to the cathodic zone, forming an asymmetric electrochemical region that does not conform to the Evans model. Smaller droplets more readily form asymmetric electrochemical zones with adjacent anodic and cathodic regions [11]. Electrochemical/chemical models of droplets indicate that the Evans ring model (center anode, edge cathode) applies only to large droplets, as shorter diffusion paths in small droplets prevent oxygen depletion from cathodic reactions, eliminating distinct differences between anodic and cathodic positions.

For droplets ranging from 25 to 150 L, the electrochemical distribution conforms to the Evans model, with the center as the anodic zone and the periphery as the cathodic zone, though major anodic points tend to be closer to cathodic regions. As droplet size increases, both anodic and cathodic zones expand, but current intensity decreases. In neutral seawater, oxygen reduction is the dominant cathodic reaction, and corrosion rate is primarily controlled by the cathodic reaction [6]. Increased droplet size raises droplet height and contact angle, reducing the rate at which O_2 reaches the metal surface and decreasing the diffusion-limited oxygen reduction current density [7], thereby lowering corrosion rate. In 150 L droplets, cathodic points appear in the center because non-uniform carbon steel surface conditions make defect sites more prone to anode formation, with other regions becoming cathodic and facilitating localized anode-cathode pairs.

2.3 Influence of Spreadability Factor on Electrochemical Properties

In surface chemistry, the dispersion degree of multiphase systems is commonly expressed by specific surface area, defined as the ratio of total surface area to total volume [23]. For a given volume, higher dispersion yields larger surface area and more pronounced surface effects. Consequently, interfacial effects become significant when substances are highly dispersed.

In atmospheric corrosion research, both droplet height and diameter influence metal corrosion. This study introduces the concept of spreadability factor to describe droplet spreading degree, using droplet projection area in place of total surface area. The spreadability factor is defined as: $A_0 = S_0/V$, where A_0 is the spreadability factor, V is droplet volume, and S_0 is the contact area between droplet and metal (i.e., droplet projection area). Different spreadability factors A_0 can be obtained by varying droplet volume.

[Figure 5: see original paper] shows the variation of spreadability factor with droplet volume, demonstrating that smaller droplet volumes yield larger spreadability factors, indicating greater electrochemical contact area per unit volume.

[Figure 6: see original paper] presents the variation of average anodic and cathodic current densities with spreadability factor, where average cathodic current density is defined as the ratio of total cathodic current to cathodic area. Both anodic and cathodic average current densities exhibit exponential growth trends with increasing spreadability factor, indicating that spreading degree significantly influences corrosion intensity—greater spreading degree yields higher corrosion intensity. Larger spreadability factors provide greater electrochemical contact area per unit volume, increasing the area participating in electrochemical reactions and thus intensifying carbon steel corrosion. Additionally, reduced droplet height accelerates oxygen diffusion to the metal surface beneath droplets, increasing corrosion rate and ultimately enhancing corrosion intensity.

Maximum galvanic current values partially reflect localized corrosion intensity. [Figure 7: see original paper] shows the variation of maximum anodic current density (i ,) with spreadability factor. The relationship between i , and spreadability factor is linear, with i , increasing linearly as spreadability factor increases, indicating intensified corrosion severity.

The standard deviation of galvanic current represents the degree of deviation from arithmetic mean values and is defined as S, reflecting electrochemical distribution heterogeneity. [Figure 8: see original paper] illustrates the variation of anodic current density standard deviation (S) with spreadability factor, showing that the standard deviation of anodic current density beneath droplets increases linearly with spreadability factor. This indicates that greater droplet spreading degree produces more heterogeneous electrochemical distribution on carbon steel surfaces.

Comparing [Figure 7: see original paper], [Figure 8: see original paper] with [Figure 6: see original paper] reveals that i , and S increase linearly with spreadability factor, while i increases exponentially. This demonstrates that corrosion intensity beneath droplets intensifies with increasing spreadability factor in an overall accelerating trend, rather than merely accelerating corrosion at specific locations, and suggests that corrosion beneath droplets becomes more uniform.

Conclusions

1. With increasing corrosion time, both anodic and cathodic current values beneath seawater droplets on carbon steel surfaces gradually decrease before eventually stabilizing.
2. For large droplets, corrosion beneath droplets follows the typical Evans ring model (center anode, edge cathode). For small droplets, asymmetric electrochemical zones form more readily, and smaller droplet size intensifies carbon steel corrosion.
3. Droplet spreadability factor significantly influences carbon steel corrosion. With increasing spreadability factor, average current density increases exponentially, while maximum anodic current density and standard deviation of anodic current density increase linearly, resulting in enhanced corrosion intensity beneath droplets.

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