ENHANCED METHODOLOGY FOR APPLYING PROTECTIVE ZINC COATINGS ON COMPLEX CONFIGURATION PARTS

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The modification of carboxymethyl cellulose (CMC) with acrylic acid enhances its chemical properties, significantly improving its application as an additive in zinc plating processes. Unlike its role as a binder in other applications, modified CMC is employed here as an electrolyte additive, promoting uniform zinc deposition on complex geometric parts. This study explores the advantages of using modified CMC in zinc electroplating, demonstrating its impact on coating consistency and corrosion resistance, with implications for improving the longevity and performance of zinc-coated parts in harsh environments.

Introduction

Zinc coatings are essential for protecting metal surfaces, especially in environments exposed to high humidity, seawater, or chemical pollutants [1]. The sacrificial nature of zinc in cathodic protection allows it to corrode instead of the underlying steel, thus extending the longevity of metal components in various industrial applications. However, achieving a consistent zinc coating on complex surfaces presents challenges due to variations in coating thickness and the formation of microcracks. These imperfections can compromise the protective capabilities of the zinc layer, necessitating the exploration of effective additives to improve the coating's quality. Among the various compounds studied, carboxymethyl cellulose (CMC) has been invested as a promising additive for enhancing zinc coating performance in electroplating applications.

Carboxymethyl cellulose, a cellulose derivative known for its film-forming, binding, and water-retentive properties, is widely used in industrial settings to stabilize solutions and improve surface coatings. CMC's structure, featuring carboxyl groups, allows it to interact with metal ions, enhancing the adhesion and cohesion of zinc coatings on metal substrates [2-4]. This interaction contributes to the stability of the zinc layer, reducing the likelihood of microcracks and increasing the coating's durability.

Recent studies reveal that modifying CMC, such as by incorporating acrylic acid groups, can amplify its effects. Modified CMC improves the ionic conductivity of electrolytes in comparison with CMC, enhancing the distribution of zinc ions on the substrate. This increased conductivity is particularly beneficial for electroplating on intricate shapes, resulting in coatings that are more uniform and less prone to structural flaws.

An essential factor in zinc electroplating is the formation of a fine, uniform crystal structure [1]. Coatings with larger crystals are generally more brittle and prone to cracking, diminishing their protective properties. Research demonstrates that CMC can reduce the average crystal size of zinc deposits, resulting in a denser, more compact coating. Studies show that increasing modified CMC concentration in the electrolyte reduces the crystal size, with the smallest crystals observed at 1,0 wt % CMC. This refined microstructure not only improves the coating's aesthetic quality but also enhances its mechanical stability and corrosion resistance [1].

This reduction in crystal size is attributed to CMC's influence on the electrochemical environment. By enhancing polarization, CMC promotes controlled nucleation of zinc ions during plating, resulting in a finer grain structure. Consequently, the coating is smoother, more uniform, and less susceptible to flaws [4-6].

For zinc coatings, strong adhesion to the substrate is critical to prevent delamination and enhance durability in corrosive environments. Studies confirm that CMC, particularly in modified forms, significantly enhances the adhesion strength of zinc layers. The carboxyl groups in CMC form complexes with zinc ions, creating a more stable bond between the zinc coating and the substrate. This strengthened adhesion is valuable in industries where long-lasting protection is required, such as in automotive, marine, and construction applications [7,8].

Thus, CMC in elecytolytes enhances the corrosion resistance of zinc coatings by promoting a denser, less porous layer that serves as a more effective barrier against corrosive agents. Studies using salt spray tests and other corrosion assessments have shown that coatings with modified CMC additives resist corrosion for significantly longer durations than those without such additives. This added corrosion resistance is essential for applications where metal surfaces are frequently exposed to corrosive environments, as it increases the overall longevity of coated parts [2,3]

The influence polarization of Zn deposition plays a crucial role in achieving high-quality zinc coatings, especially for complex-shaped parts where achieving uniform thickness and coverage is challenging. Complex configurations, with intricate geometries and varying surface areas, demand a carefully controlled deposition process to ensure consistent coating thickness and to prevent issues like edge buildup or bare spots [6-8]. In zinc plating, influence polarization refers to the additional voltage required to sustain the deposition current. For complex parts, this phenomenon becomes even more significant as different areas may experience varying levels of polarization, leading to uneven zinc deposition. Ensuring uniform zinc coating on complex parts requires careful control over polarization to avoid irregularities, achieve even thickness, and prevent common issues such as peeling or insufficient coverage in recessed or intricately shaped regions. Simple Electrolytes (typically comprising basic zinc salts like zinc sulfate or chloride) can result in higher polarization effects, especially on complex parts [6]. These electrolytes lack complexing agents to help maintain a steady ion concentration near the cathode, leading to faster depletion of zinc ions in certain areas [7, 8]. This results in concentration polarization, which is even more pronounced on complex surfaces, as varying distances from the cathode cause differential deposition rates across the part.

The outcome is often uneven coating thickness, with a tendency for thicker deposits on protruding areas and thinner (or even bare) deposits in recesses or tight corners. Complex electrolytes, on the other hand, include additives and complexing agents [8]. These agents form complexes with zinc ions, improving ion mobility and creating a more stable ion concentration at the cathode. For complex-shaped parts, this means a more consistent deposition rate across all surfaces. Recent studies reveal that CMC and modifying CMC, such as by incorporating acrylic acid groups, can amplify complexing effects. Thus electrolytes may provide fewer issues with thickness uniformity, especially on hard-to-reach areas

The integration of CMC and modifying CMC in zinc plating electrolytes holds substantial potential for diverse industries requiring durable and corrosion-resistant coatings. Zinc coatings are essential for corrosion resistance, and the quality of these coatings directly impacts the durability and performance of parts used in industries such as automotive, aerospace, and electronics.

Experimental

This study investigates the modification of carboxymethyl cellulose (CMC) with acrylic acid to enhance its application as an electrolyte additive in zinc electroplating. The main objective is to assess how modified CMC contributes to uniform zinc deposition on parts with complex geometries, improving coating consistency and increasing corrosion resistance. In this study, a few electrolyte solutions were prepared: a control solution without CMC and an experimental solution with CMC and CMC modified by acrylic acid.

The chosen electrolyte was a chloride electrolyte with the following composition:

- $ZnSO_4$: 215 g/L
- Na_2SO_4: 80 g/L
- $Al_2(SO_4)_3$: 30 g/L
- CMC or CMC modified by acrylic acid

To conduct the experiment, steel samples with varying geometries were prepared by standard cleaning and surface activation processes. Electroplating was carried out at a current density of 0,5–5,0 A/dm² using both control and experimental electrolytes. Multiple deposition cycles were performed to compare coating performance on smooth and complex surfaces. After plating, the samples were analyzed microscopically to assess coating uniformity, and coating thickness was measured using optical microscopy. Additionally, corrosion resistance tests were conducted in a salt spray chamber, evaluating the time to corrosion initiation according to ASTM standards.

Results and Discussion

This study examines the effects of modified and unmodified carboxymethyl cellulose (CMC) as additives in zinc plating electrolytes, with a focus on their impact on ionic conductivity. The results on Figure 1 demonstrate that the addition of CMC reduces ionic conductivity relative to a baseline electrolyte without additives.

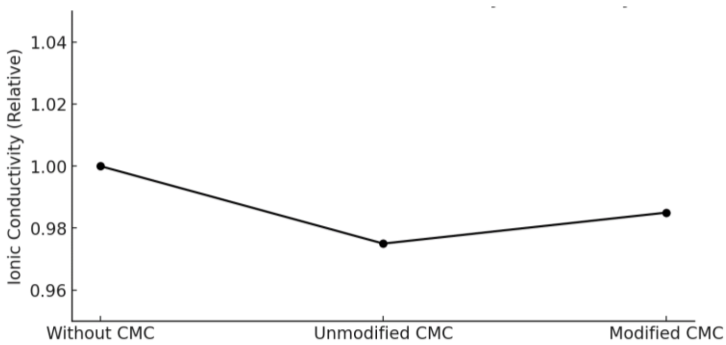

Figure 1 – Effect of CMC on ionic conductivity in electrolyte for zinc deposition

Unmodified CMC significantly decreases ionic conductivity, likely due to increased solution viscosity or ionic interactions that hinder ion movement, resulting in a relative conductivity of approximately 0,98. In contrast, modified CMC produces a smaller reduction in conductivity, maintaining a relative value close to 1,00, suggesting improved compatibility with the electrolyte and less disruption of ion mobility. These findings indicate that modified CMC offers a potential advantage over unmodified CMC in electroplating applications where maintaining higher ionic conductivity is beneficial for efficient and uniform zinc deposition.

In the work we investigate the impact of modified and unmodified carboxymethyl cellulose (CMC) as additives in zinc plating electrolytes, focusing on their effectiveness in controlling crystal size and improving coating uniformity. The study investigates the effect of modified CMC concentration on crystal size in zinc coatings. For this purpose, deposition was conducted in solutions with varying CMC concentrations. The deposition process was carried out at a temperature of 25°C and a current density of 2 A/dm². After deposition, the crystal size was determined using a metallographic microscope. The results on Figure 2 demonstrate that modified CMC significantly reduces the average crystal size in zinc coatings, achieving a minimum size of approximately 1,5 μm at a concentration of 1,0 wt.%, which suggests a more uniform and dense coating structure. At higher concentrations, up to 1,6 wt.%, the modified CMC maintains smaller crystal sizes than the baseline, indicating stability in the crystalline structure. In contrast, unmodified CMC shows a less pronounced effect, with crystal size reduction plateauing around 2,0 μm at concentrations above 1,2 wt.%. These findings indicate that modified CMC is a more effective additive for achieving fine-grained, uniform coatings, particularly beneficial for complex geometries, whereas unmodified CMC offers limited control over crystal size. The study highlights the potential of modified CMC to enhance the quality and consistency of zinc electroplating, offering improved coating properties in demanding applications.

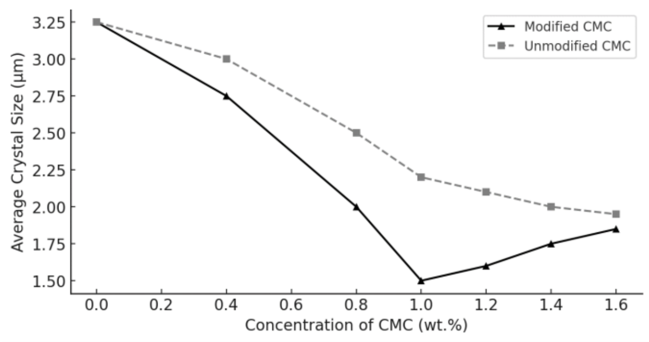

Figure 2 – Average crystal size of zinc layer vs. concentration of CMC

To investigate the covering and dispersing abilities of electrolytes, solutions with different types of CMC were examined. Specifically, three solutions were prepared: a control solution (without CMC), a solution with unmodified CMC (1,0 wt.%), and a solution with modified CMC (1,0 wt.%). For the experiment, a two-cathode cell was used, with cathodes positioned at different distances from the anode. To assess the impact of CMC type, the thickness of the zinc deposit on the distant electrode was analyzed. Thickness measurements were taken with a micrometer at three points on each sample. The target thickness of the deposited coating was 10 μm. As shown in figure 3, the coating thickness on the distant electrode in the cell without CMC is 6 μm, with unmodified CMC – 7,5 μm, and with modified CMC – 9 μm.

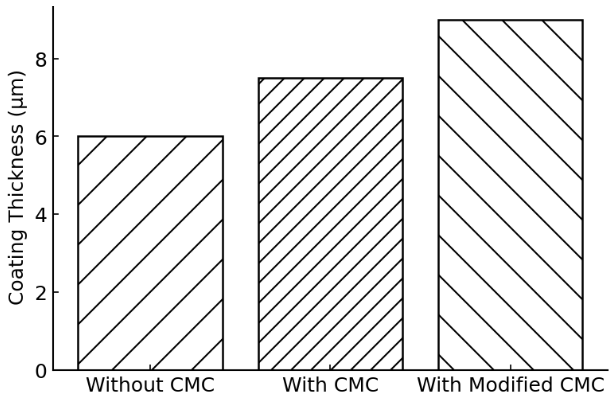

Figure 3 – Coating thickness of cathode in electrolytes of Zn deposition.

This indicates that modified CMC promotes the formation of a denser and more uniform coating. This increase demonstrates an improvement in the electrolyte's covering and dispersing properties, which positively affects the uniformity of the zinc coating. One of the important characteristics of coatings is their adhesion to the metal substrate. It has been established that the addition of CMC improves the adhesion of the zinc layer due to complex formation with metal ions, which provides even more stable bonding. Additionally, the increased viscosity of the electrolyte with CMC promotes a more uniform distribution of zinc ions, reducing the risk of microcrack formation. Thus, CMC helps to form a dense, durable coating, proving its effectiveness as an additive for enhancing adhesion.

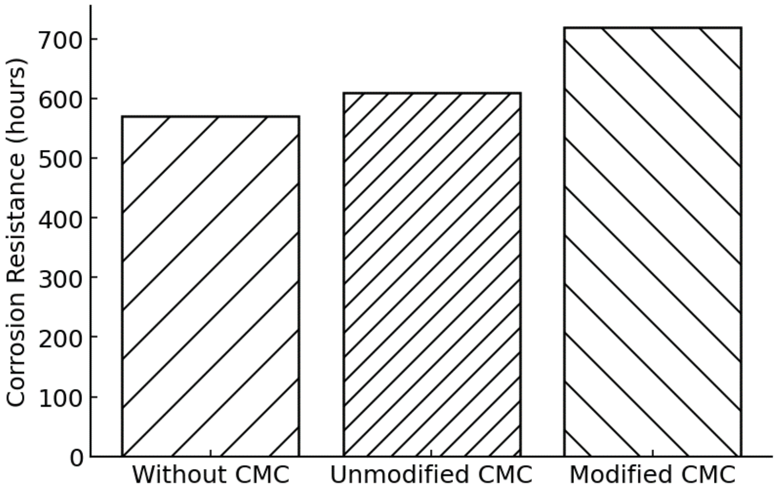

Figure 4 – Corrosion resistance of samples with Zn coating obtained in electrolyte with different additives

The corrosion resistance of the coatings was evaluated in a salt spray chamber according to ASTM B117 [9]. Three types of samples were prepared: a control sample, one with unmodified CMC, and one with modified CMC (carboxyl groups). As shown in Figure 4, the coating with unmodified CMC exhibits corrosion resistance of 610 hours, which is somewhat higher than that of the control sample (570 hours). The coating with modified CMC withstands corrosion for 720 hours, indicating an improvement in protective properties due to the modified structure of CMC.

Conclusion

CMC, particularly in its modified forms, has proven to be a highly effective additive in zinc plating electrolytes for parts with complex geometries. Its benefits include enhanced adhesion, reduced crystal size (achieving a minimum average of 1,5 μm at 1,0 wt.% concentration), increased thickness uniformity, and improved corrosion resistance, with modified CMC-coated samples exhibiting up to 720 hours of corrosion resistance compared to 570 hours for the control. These improvements contribute to high-quality zinc coatings ideal for demanding applications. The addition of CMC in electrolytes has the potential to significantly enhance the durability and performance of zinc coatings, making it a valuable asset for industries requiring long-lasting protective metal finishes.

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