Preparation and Properties of Thermally Sprayed Zinc-Aluminum Alloy Superhydrophobic Coatings (Postprint)

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Abstract

A zinc-aluminum alloy coating was deposited on Q235 steel plates via arc spraying technology, and a superhydrophobic film was constructed on the zinc-aluminum alloy coating surface through a stearic acid/ethanol surface modification technique. The wettability, surface morphology, and chemical structure of the coating before and after modification were characterized using a contact angle measuring instrument (OCA-20), scanning electron microscope (SEM), and intelligent Fourier transform infrared spectrometer (ATR). Electrochemical impedance spectroscopy and polarization tests were conducted on the zinc-aluminum coating before and after stearic acid surface modification using a three-electrode system electrochemical workstation (Solartron analytical). The results demonstrate that the thermally sprayed zinc-aluminum coating exhibits a micro/nano composite structure and displays hydrophilic properties before modification due to the high surface energy of the metal coating. After stearic acid surface modification, the static contact angle of the coating reaches 153.2°, with a sliding angle less than 10°. Infrared analysis reveals that the zinc-aluminum coating surface is composed of numerous hydrophobic hydrocarbon long chains, conferring superhydrophobic properties. Corrosion test results indicate that the modification treatment significantly enhances the corrosion resistance of the zinc-aluminum coating. The superhydrophobic film formed on the coating surface impedes the detachment and dissolution of corrosion products from interfacial electrochemical reactions, increases the charge transfer resistance, and reduces the corrosion current density, thereby improving the corrosion resistance of the coating.

Preparation and Properties of Superhydrophobized Sprayed Zn-Al Coating

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Abstract

A superhydrophobic Zn-Al coating was prepared by electric arc spraying technology followed by surface modification with stearic acid/ethanol solution. The surface wettability, morphology, and chemical structure of the Zn-Al coating before and after modification were characterized by contact angle measurement (OCA-20), scanning electron microscopy (SEM), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), respectively. The impedance spectra and polarization curves of the coatings were measured using an electrochemical workstation (Solartron Analytical) with a three-electrode system. The results show that the as-sprayed Zn-Al coating consists of irregular micro- and nano-sized alloy particles and pores, exhibiting clear hydrophilicity, which may be ascribed to the high surface energy of the metallic coating. After surface modification with stearic acid, the static contact angle of the coating reached 153.8° with a rolling angle less than 10°, because there existed a large number of hydrophobic long alkyl chains on the surface of the modified Zn-Al coating. In addition, the surface modification could significantly enhance the corrosion resistance of the Zn-Al coating due to the thin hydrophobic film playing an important role in suppression of the fall-off and dissolution of corrosion products on the Zn-Al coating, leading to increased charge transfer resistance and decreased corrosion current density.

KEY WORDS materials failure and protection, thermal spraying Zn-Al coating, surface modification, hydrophobicity, corrosion behavior

Introduction

Since Barthlott and Neinhuis revealed the mystery of the lotus leaf' s "self-cleaning" effect in the 1990s, numerous studies have investigated the preparation of superhydrophobic surfaces on various substrates. The key principle is that such surfaces consist of micro/nano composite structures or are modified with low surface energy materials. For example, Bae et al. used wire electrical discharge machining to create dual-scale sinusoidal patterns on aluminum alloy surfaces, achieving a water static contact angle of 156° and contact angle hysteresis less than 3°. Liu et al. fabricated boehmite needle-like micro/nano composite arrays on aluminum foil through etching, followed by stearic acid modification, resulting in a water static contact angle of 167° and rolling angle of 3°. Yu et al. electrodeposited Ni/P coatings with flower-like micro/nano structures on copper sheets, achieving a static contact angle of 155.5°. Lee et al. used polycarbonate templates and hot-pressing to create nanoscale cylindrical array structures on high-density polyethylene films, attaining a static contact angle of 165°.

However, these and similar preparation methods share a common drawback: complex experimental procedures, harsh conditions, and difficulty in scaling up for industrial applications. As a surface strengthening technology, thermal spraying offers high deposition efficiency, low cost, and most importantly, feasibility for engineering applications. Furthermore, thermal spray anticorrosion coatings have been widely used in modern industry and daily life, with their corrosion resistance properties having been thoroughly investigated. Among various thermal spray anticorrosion coatings, arc-sprayed Zn-Al alloys have found extensive application due to their excellent long-term protection capabilities and relatively low cost. Therefore, this study employs high-velocity arc spraying to prepare Zn-Al coatings with inherent micro/nano morphologies, followed by stearic acid modification to construct superhydrophobic surfaces, and investigates the hydrophobic mechanism and its influence on the corrosion behavior of Zn-Al coatings.

1 Experimental Methods

Q235 low-carbon steel specimens (3.5 cm × 1.5 cm) were ultrasonically cleaned in acetone, ethanol, and distilled water sequentially, dried in an oven, and then sandblasted to roughen the surface. The prepared specimens were fixed on a spraying fixture, and a Zn-Al coating was deposited using a high-velocity arc spraying system (Shanghai Xuma XM-400). The coated steel specimens were immersed in a 10 mmol/L stearic acid ethanol solution for a specified duration, then heated at 50°C. Finally, the modified coatings were rinsed with ethanol and distilled water, dried, and characterized. All reagents used were analytically pure.

The static contact angles before and after modification were measured using a contact angle goniometer (OCA20, Dataphysics, Germany) at room temperature. The rolling angle was measured by automatically tilting the sample stage. The water droplet volume was 3 L. The surface chemistry of the stearic acid-modified coating was characterized using a Fourier transform infrared spectrometer (ATR, Nicolet 6700, USA). Surface morphology was observed using a field emission scanning electron microscope (Quanta FEG250, FEI, USA). Electrochemical tests were performed using an electrochemical workstation (Modulab ECS, Solartron Analytical) with a three-electrode system, where the Zn-Al coated steel served as the working electrode, platinum as the auxiliary electrode, and saturated calomel electrode (SCE) as the reference electrode. The corrosion medium was 3.5 wt% NaCl solution, and the corrosion resistance of the coatings before and after modification was evaluated.

2 Results and Discussion

2.1 Surface Microstructure and Wettability of Zn-Al Coating

The morphology and initial contact angle of the arc-sprayed Zn-Al coating are shown in [Figure 1: see original paper]. The surface morphology [Figure 1a: see original paper] reveals that the arc-sprayed coating possesses a micro/nano composite structure. At higher magnification (inset in [Figure 1a: see original paper]), these structures consist primarily of molten micro/nano-sized granular or rod-shaped Zn-Al alloy particles stacked together. The contact angle measurement shows a water contact angle of 67.4° for a 3 L droplet on the as-sprayed surface [Figure 1b: see original paper], indicating hydrophilic behavior. The high surface energy of the Zn-Al alloy and its partial oxides causes the droplet to spread easily on the surface.

[Figure 2: see original paper] shows the relationship between the contact angle of the Zn-Al coating and immersion time in the stearic acid ethanol solution. The contact angle gradually increases with immersion time, reaching a maximum after 48 h and then decreasing with further immersion. For example, after 48 h immersion, the maximum contact angle of 153.2° is achieved, while after 72 h, the contact angle decreases to 151°, indicating that 48 h is the optimal immersion time for preparing superhydrophobic Zn-Al coatings.

The surface morphology of the Zn-Al coating after 48 h modification was analyzed by SEM [Figure 3a: see original paper]. The results show that micro/nano-scale flower-like structures grew on the modified Zn-Al coating surface. High-magnification SEM images reveal that each flower-like structure consists of several "petals." The contact angle measurement yields a value of 153.2° with a rolling angle less than 10° [Figure 3b: see original paper], demonstrating that the modified Zn-Al coating transformed from hydrophilic to superhydrophobic.

To analyze the wetting behavior, the Cassie-Baxter equation was applied: cos * = f(cos + 1) - 1, where * is the apparent contact angle on the rough surface, is the intrinsic contact angle, and f is the solid-liquid contact area fraction. The intrinsic contact angle of the polished Zn-Al coating was measured to be 86.3°, while the apparent contact angle after modification was 153.2°. Substituting these values into the equation yields f = 0.1009, indicating that approximately 90% of the water droplet’ s contact area is with air, while only about 10% is in direct contact with the solid surface.

2.2 Surface Chemical Composition of Zn-Al Coating

XRD analysis of the Zn-Al coating surface before and after stearic acid modification is presented in [Figure 4: see original paper]. Before modification, the coating consists primarily of metallic Zn and Al phases. After modification, the diffraction pattern shows noticeable changes, with several new peaks appearing in the 2 range of 5°-30° (shown in the magnified inset). These new diffraction peaks correspond to zinc stearate phase [15,16].

FTIR spectroscopy results of the coating surface are shown in [Figure 5: see original paper]. The stearic acid spectrum shows characteristic absorption peaks at 2918 cm^{-1} and 2849 cm^{-1} corresponding to asymmetric and symmetric C-H stretching vibrations of $-CH_2$ groups, and a peak at 1700 cm^{-1} for the -C=O group. The spectrum of the modified Zn-Al coating shows absorption peaks at 3600-3200 cm^{-1} attributed to Zn/Al-OH stretching vibrations. The peaks at 2918 cm^{-1} and 2849 cm^{-1} match those of stearic acid, while new peaks at 1538 cm^{-1} and 1398 cm^{-1} can be assigned to -COO-Al and -COO-Zn vibrational modes [17-20]. These results confirm that hydrophobic stearic acid hydrocarbon chains were successfully grafted onto the Zn-Al coating surface, forming a low surface energy superhydrophobic coating.

2.3 Corrosion Electrochemical Behavior

The impedance curves of the coatings before and after modification were fitted using equivalent circuits in ZSimpWin software, as schematically shown in [Figure 6: see original paper]. In [Figure 6a: see original paper], QCPE1 represents the superhydrophobic coating capacitance, Rc is the superhydrophobic coating resistance, and QCPE2 is the double-layer capacitance. In [Figure 6b: see original paper], QCPE1 represents the coating capacitance, Cdl is the double-layer capacitance, Rs is the solution resistance, and Rct is the charge transfer resistance in both circuits. Based on these results, the superhydrophobic Zn-Al coating shares the same interfacial properties as the unmodified coating except for the self-assembled hydrophobic molecular layer. The fitting errors for the impedance curves of the unmodified and modified coatings were 3.80$×10^{-4}$ and 2.3$×10^{-3}$, respectively, indicating that these equivalent circuits effectively represent the electrochemical behavior of both coatings.

The fitted Nyquist plots for the Zn-Al coating and superhydrophobic Zn-Al coating are shown in [Figure 7: see original paper]. In the high-frequency region, the impedance of the Zn-Al coating is greater than that of the superhydrophobic coating, while in the low-frequency region, the superhydrophobic coating shows significantly higher impedance. The high-frequency region corresponds to coating capacitance and resistance, suggesting that the self-assembled stearic acid film may be non-uniform and partially disrupts the passive layer, making it easier for the corrosive medium to contact the Zn-Al coating. The low-frequency region corresponds to charge transfer resistance (Rct) associated with electrochemical reactions. The fitted Rct values are 11.59 $\Omega \cdot \text{cm}^2$ for the unmodified coating and 159.2 $\Omega \cdot \text{cm}^2$ for the superhydrophobic coating, demonstrating that the superhydrophobic coating primarily functions at the interface electrochemical reaction stage by preventing the detachment and dissolution of corrosion products, thereby increasing charge transfer resistance and improving corrosion protection [21-23].

Potentiodynamic polarization tests were conducted in 3.5% NaCl solution for the Zn-Al coatings before and after stearic acid modification, with results shown in [Figure 8: see original paper]. The cathodic polarization curves show no significant difference before and after modification, both representing oxygen reduction processes with a corrosion potential difference of approximately 0.1 V. However, the anodic polarization curves differ markedly, with the stearic acid-modified coating exhibiting clear passivation behavior in the potential range of -1.0 to -1.5 V, indicating that the stearic acid molecular layer can further reduce the corrosion rate. Tafel analysis using Modulab ECS software shows that the corrosion current densities of the stearic acid-modified and unmodified Zn-Al coatings are 1.008$\times10^{-5}$ $\text{A} \cdot \text{cm}^{-2}$ and 2.567$\times10^{-5}$ $\text{A} \cdot \text{cm}^{-2}$, respectively, confirming that the stearic acid molecular layer indeed provides corrosion inhibition.

3 Conclusion

Superhydrophobic Zn-Al coatings were successfully prepared by modifying arc-sprayed coatings with inherent micro/nano composite structures using stearic acid. Micro/nano-scale flower-like structures formed on the modified surface, achieving a static water contact angle of 153.2° and rolling angle less than 10°. The improved hydrophobicity results from successful grafting of hydrophobic stearic acid hydrocarbon chains onto the Zn-Al coating surface through ethanol solution immersion, forming a low surface energy superhydrophobic coating. The modification treatment significantly enhanced the corrosion resistance of the Zn-Al coating because the stearic acid molecular layer on the coating surface hindered the detachment and dissolution of corrosion products, increased the charge transfer resistance, and thereby inhibited material corrosion.

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