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Corrosion-resistant nanostructured super hydrophobic coating for MG-Alloys: A review

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Abstract

Due to their superior properties, magnesium (Mg) and its alloys are extensively used in many engineering applications, but corrosion limits their use. The degradation due to corrosion can be minimized using multifunctional water-repellent coating i.e., superhydrophobic coating (SHC). Many scientists and industrialists are working on fabricating such coating to get the desired product by optimizing many parameters like types, size, the concentration of nanoparticles, time of reaction, temperature, and the methods used to develop it. This paper reviewed the current research status to provide a clue or thought for beginning researchers to understand how corrosion is dangerous to Mg alloys and how SHC can be a potential solution to overcome corrosion problems. The rudiments of SHS with its wetting models and recent progress in the fabrication of SHC for Mg alloys are discussed.

Keywords: Magnesium, corrosion, contact angle, surface roughness, surface energy, superhydrophobic.

Introduction

Due to their outstanding physical and mechanical properties, magnesium and its alloys are becoming the frontier of biodegradable materials research[1]. It has excellent specific stiffness, low density, specific strength, and high strength/weight ratio, which have always been in demand for various industrial applications, especially in aerospace, transportation, electronic devices, biomedicine, and our daily lives [2]. Despite this, Mg and its alloys exhibit lower corrosion rates when exposed to atmospheric conditions than Al alloys and steels. Various factors, which include the alloy elements, the second phase distribution, the grain size, the orientation, the texture strength of the crystals, and crystal defects, contribute to the corrosion of magnesium alloys . The use of Mg and its alloys is limited due to corrosion. The nanostructured SHC may be a potential solution to mitigate corrosion problems as this coating will reduce the interaction of water droplets and an acidic corrosive environment with metal surfaces [3], [4], [5]. Natural plants like lotus, taro, and animal skin show hydrophobicity.

Generally, if the water droplet is rolling and bouncing off surfaces, the surfaces show much less CA hysteresis, called the nonwetting state, expressed by the Cassie model[6].

Corrosion-resistant mechanism of superhydrophobic coating.

Because of its unique anti-wetting property, SHC provides substantial corrosion protection for different metals used in industrial applications because this coating decreases the corrosion current density by several magnitudes[7], [8]. The mechanism of anti-corrosion behaviour of SHC on Mg alloys can be explained as follows: the SHC contains three layers (i) a rough layer with micro-nano order surface roughness [9] (ii) a low surface energy layer [10], [11], [12] (iii) the trapped air between the grooves in the SHS with the Cassie state [13], [14], [15][Fig 2]. All three layers significantly reduce the contact area and contact time of the corrosive element to contact with the metal surface.

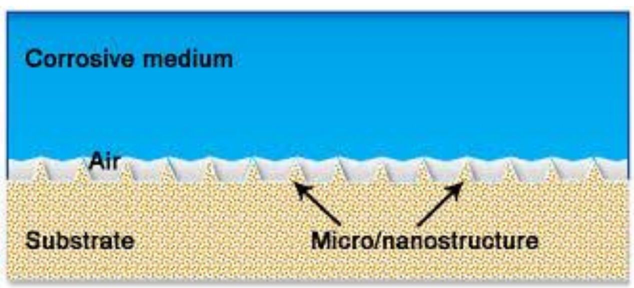

Fig 1: Mechanism of anti-corrosion using a superhydrophobic surface[16]**.**

The bare and SH-coated Mg surfaces indicate how SHC coating reduces the contact area and inhibits the metal from corrosion. The bare Mg shows high surface hydrophilicity and attracts corrosive ions, accelerating corrosion.

Fabrication Techniques for Corrosion-resistance Coating on Mg Alloys

Many scientists performed their experiments to develop the SHC for improving the corrosion resistance of Mg alloys by combining different techniques, especially bottom-to-top and top-to-bottom, and combining these two techniques. Dip coating is the simple and quickest method to create thin-film coatings. It is a procedure in which the material protected from corrosion is dipped in a liquid form in the container containing the anti-corrosion material. The substrate is dipped into the solution at a constant speed, which spreads automatically on the surface because of the impact

of different forces such as gravity, viscous drag, etc.

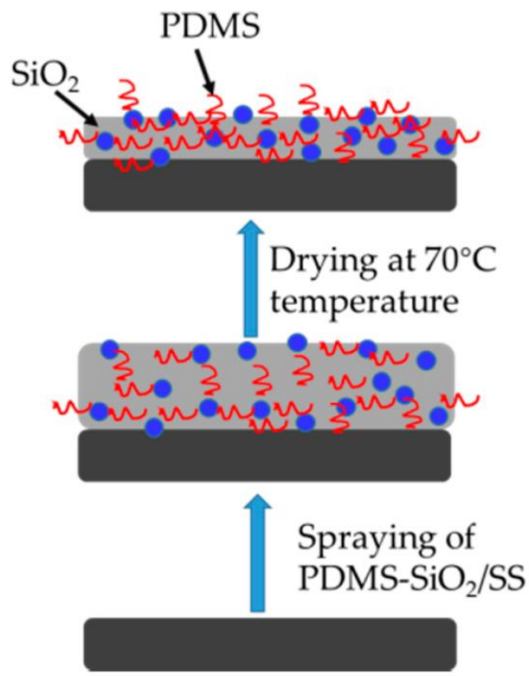

Fig 2. Schematic diagram of fabricating PDMS-SiO_2/SS[17]**.**

Jia et al.[17] fabricated polydimethylsiloxane modified SiO_2/organic silicon sol (PDMS-SiO2/SS) hybrid coating via a simple two-step modification route. They synthesized nanoparticles of PDMS-SiO_2 through a high-temperature dehydration reaction using silica and excessive PDMS. The NPs lapped with each other and formed a branch and tendril structure. The PDMS-SiO_2/SS hybrid coating exhibits a superhydrophobic performance with a maximum water contact angle of 152.82°. Meanwhile, the defrosted water droplets rolled off from the coated surface easily, which is a benefit for frost suppression during the next refrigeration cycle [Fig 2].

Xie et al. [18] developed PDMS/SiO_2-based corrosion-resistant SH coating on a magnesium alloy by the painting process. They used SiO_2 nanoparticles of sizes 40 nm and 50–250 nm to produce micro-nano structures. The type of nanoparticles and size significantly affect the hydrophobic character of the developed films as they are dominant in creating nano air pockets, preventing corrosive elements from interacting with the metal surface, and providing mechanical robustness. These coatings show good hydrophobicity as they maintain WCAs (138° -150° and 133° -153°) even after 50 sandpaper abrasion cycles. Moreover, they performed electrochemical experiments where the coating showed excellent corrosion resistance after analyzing the Tafel plots of (E_{corr}) and (I_{corr}) of the coated samples, and the scratch test/ pressure test was also performed to observe its strength.

Chemical etching has attracted scientists due to its low cost, required less time, less complex procedures, and ability to control parameters, shape, and substrate orientation [19]. A chemical etching process involves creating a rough surface on the Mg surface by reacting with a metal oxidant followed by low surface energy materials to get SH coating[20]. Yin et al.[21] used HNO_3 and $Cu(NO_3)_2$ mixed solution etched AZ31 alloy, which created a lotus-like structure. The developed surface was modified with KH-832, giving a high WCA 157.3° ± 0.5°. Wang et al. [22] They developed an SHS on the Mg alloy surface by chemical etching and self-assembly treatments. They observed that the oleic-acid-based SH coating showed a WCA of 155° on the developed surface due to low surface energy and a three-dimensional porous structure, which significantly improved the corrosion resistance behaviour of pristine Mg alloy.

A majority of magnesium alloys are developed using the hydrothermal process because of its simplicity, cost-effectiveness, high yield, and ease of control over crystal shape. This process involves placing the precursor in an autoclave at high temperatures and pressures and modifying it chemically. Hydrothermal methods cannot prepare coatings that need to cover large areas. A hydrothermal process was followed by stearic acid modification on Mg alloy for 6 hours. Li et al.[23] fabricated SH coating on Mg alloy. SHS was prepared by injecting lubricant oils into the micro/nanostructures to create slippery liquid-infused porous surfaces (SLIPS) that exhibit excellent superhydrophobicity due to continuous and homogenous liquid-infused surfaces. Due to the continuously infused lubricant replacing the trapped air in the micropores, the developed SLIPS exhibit better anti-corrosion properties. Thermally assisted healing properties of the SLIPS are superior to those of the SHS. Electrochemical deposition (also known as electroplating) gives the desired surface roughness to a conductive substrate by depositing thin coatings of ions or charged nanoparticles onto a solution. Its simplicity, ease of control, low cost, and scalability make it a popular technique for developing corrosion-resistant SHC. Currently, researchers are focusing on Ni-based coatings on Mg alloys, which are applied via electrodeposition and then modified with low surface energy. A magnesium, magnesium, and cerium nitrate hexahydrate solution containing myristic acid and cerium nitrate hexahydrate was electrodepose-deposited in ethanol within one minute by Liu et al. [24] observed a very good CA of 159.8° and a SA of less than 2° with the developed coating. Tests in 3.5 wt % solutions of NaCl, Na_2SO_4, $NaClO_3$, and $NaNO_3$ have shown that the SHS exhibits good anti-corrosion properties. The developed coating also demonstrates chemical and mechanical stability.

Application of the superhydrophobic coating

Due to low surface energy and special texture, superhydrophobic coating plays an important role in various industrial applications. We have discussed in detail how SHC is beneficial in preventing or reducing metals from corrosion by reducing the contact area of corrosive materials to interact with the metal surfaces[25]. The unique surface topography and low surface energy will also be helpful in anti-icing coating, drag reduction, anti-dust coating, anti-fogging, self-cleaning, antimicrobial, etc[26]. In SHSs, the air is trapped between the nanosize grooves, so trapped air is an obstacle between the water and material's surface [44], making the water droplets more spherical and simply slide off from the material's surface [27]. In all these cases, water has very little contact area with the substrate[26], [28], [29].

Conclusion

This paper concludes with the corrosion in Mg and its alloys and the various factors like the alloy elements, the second phase distribution, the grain size, the orientation, the texture strength of the crystals, and crystal defects affecting the corrosion. The losses due to corrosion, present solutions to prevent corrosion in the industries, SHS prevention technique, and past experimental approaches. The fundamentals and the mechanisms were also explained. To fabricate these SHCs, three approaches - bottom-up, top-down, and mixed methods are well known, and the recent advances to fabricate corrosion-resistant superhydrophobic coating with their characterization are also discussed.

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