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The application of Biomimetic superhydrophobic materials in anti-corrosion on metal surface：a review

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Abstract

Metals, such as steel, magnesium, aluminum, and copper are important materials and are widely used in industry. However, they have a low resistance from corrosive gases and solutions, causing wastes of natural resources and damages to infrastructures. In this review, the basic theories of biomimetic superhydrophobic material, cause and effects of metal corrosion, and some successful cases of biomimatic superhydrophobic material application on anti-corrsion on metal surface are shown, showing a promising future of industrial application of this kind of material.

Keywords

Anti-corrosion, superhydrophobic.

1. Introduction

Various of different phenomena are shown by the nature that are worthwhile for humans to do research on. People research and utilize those phenomena in improving living conditions and quality of productions, generally called bionics. Inspired by nature, including lotus leaves, feathers of birds, and legs of water skipper. Biomimetic superhydrophobic material, a kind of material that has superhydrophobicity is invented Superhydrophobic material with a low maintenance cost is widely used in many fields, such as daily-used products, public buildings, and even in national air defense.

The promising applications of superhydrophobic materials can be apparently observed in many fields, including garments, textiles, water pollution control, auto industry, oil-water separation, construction industry, pasturage, optical applications and even aerospace. The research and exploration of biomimetic superhydrophobic materials has attracted many experts in different fields due to its great importance. Besides, superhydrophobic materials were discovered quite early, whose theories was established systematically by the attribution of the research work of Wenze and Cassie in the 1930s and 1940s.

They found the relationship between microstructure of surface roughness and wettability. The surface of most solids is not smooth and flat, from the micro view of uneven fluctuations. In the better superhydrophobic cases, the liquid drops on the solid surface will not completely fill the concave surface of the rough solid surface, then there will be air between liquid drops and the solid surface, leading to the existence of gap full of air between liquid drops and the solid surface. Apparently, the contact interface between solid and liquid is considered as a mixing interface which owned solid-liquid interface and gas-liquid interface. The formula summarized by Wenzel and Cassie has become the model basis for the current study on different roughness or surface microstructure, indicating that the superhydrophobicity of materials is jointly determined by the surface energy of materials and their microscopic geometry and arrangement.

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Metals and their alloys are widely used in many different industrial zones, especially copper(Cu), iron(Fe), magnesium(Mg), and aluminum(Al). Metals have their distinctive advantages in industry uses, including Foundry capacity, weldability, forgability, heat treatment, cold bending, stamping, headforging, and machinability. However, they also have limits. Aggressive corrosion of metals is one of those limits. Corrosion of metal is defined as the Loss caused by redox reaction between metals and surrounding gases or liquids. the essence of corrosion is metals lose some electrons and are oxidized. Corrosion of metal can cause serious damage to buildings, facilities, and devices such as bridge collapse, pipeline cracking, and Electronic instrument malfunction. Many scientific techniques are proposed to prevent corrosion. For example, add anti-corrosion barriers on the metallic surface as a coating. Unfortunately, the metallic surface is still corroded due to the contact layer of metal/coating. Hence, the coating is required to possess the ability of water-proof and low interfacial tension. The biomimetic superhydrophobic materials can fulfill these conditions. In this review, the basic theory of biomimetic superhydrophobic materials and its application in anti-corrosion of metals would be shown.

2. Basic principles of Superhydrophobicity

2.1. Contact angle

The mutual wettability of solid and liquid, hydrophilicity and hydrophobicity, is generally characterized by the contact Angleθ of liquid and solid phases. FIG. 1a is a solid-liquid-gas three-phase diagram formed by liquid dripping on a solid surface. The gas-liquid interface tangent is made along the liquid-liquid interface at the contact pointθ of the three phases of solid, liquid and gas, and the included Angle 0 between the tangent and the liquid-solid interface is the contact Angle (as shown in FIG. 1a<3-4>).

According to Figure 1A, if the solid surface is completely smooth and flat, the shape of water droplets on its surface is determined by the interfacial tension originating from the three-phase contact surface of solid, liquid and gas. Besides, the Contact Angle 0 is easily calculated by Young's equation in Formula (1) :

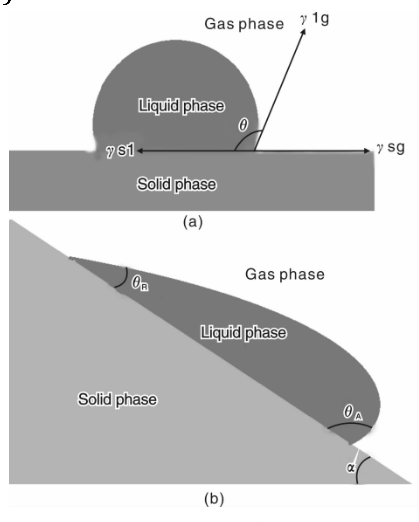

Figure 1:

the contact angle of liquid dropped on the solid surface and their interfacial energy (b) on the surface of the liquid in tilt solid rolling Angle, (b)rolling angle of liquid dropped on inclined solid surface

(1): $\cos\theta=\frac{\gamma_{sg}-\gamma_{sl}}{\gamma_{lg}}$

Type in γsg, γsl, and γlg represent the solid - gas and solid - liquid and liquid - gas interface free energy. The subscripts (sg, sl and lg) are the abbreviation of solid-gas, solid-liquid and liquid-gas, respectively. And the γ represents the free energy of different interface. The critical Angle degree of solid hydrophily is θ= 90, indicating that the solid surface is hydrophobic with θ> 90, then oppositely, it was hydrophilic. In general, the larger the contact Angle is, the stronger the hydrophobicity of the surface will be. Later, Cassie and Baxter improved the equation as shown in Formula (2):

(2)$\cos\theta'=f_1\cos\theta_1+f_2\cos\theta_2$

Where θ', in the experiments, represents the contact Angle of liquid with the rough surface, θ1and θ2 are the intrinsic contact angles of solid 1 and gas 2 for the same liquid, f1 and f2 represent the proportion of solid-liquid and gas-liquid contact surfaces on the composite interface. In addition f1+f2=1, and the rough surface is a composite interface which consists of solid and air.

Hence, the Cassie-Boxer equation in formula (2) can be simplified as formula (3):

$\cos\theta'=-1+f(\cos\theta+1)$

Where f refers to the area fraction of the solid with liquid, 1-f represents fraction of gas with liquid interface, and θ refers to the intrinsic contact Angle of solids.

2.2. Rolling angle

When the solid surface has a slope, the liquid can be rather static or rolling, this state can be interpreted with rolling angle that is the critical surface angle of inclination α at which a liquid droplet begins to roll on a solid surface as clearly illustrated in figure 2(b). A better hydrophobicity of the solid surface would be shown if the liquid's initial rolling Angle is smaller.

ON inclined surface, two different contact Angle θA and θB would be formed in the water frontier and rear when the water is moving under critical conditions. The hysteresis value of Contact Angle is easily calculated by the difference value of the two Angle, characterizing the solid surface's hydrophilic - hydrophobic state. The increasing of the lagged value of the contact Angle would decrease the rolling state of liquid. In conclusion, the hydrophobicity of solid surface is mainly affected by the rolling angle and contact angle. The increasing of contact and rolling angle would obviously increase hydrophobicity.

Appliance of Anti-corrosion superhydrophobic materials.

Corrosion of metals is now a global concern. It brings huge damage to economics and many wasted materials through deteriorating metal surface. Humidity, acidity, air pollution can all be factors that accelerate this procedure. At active (anodes) and less active (cathodes) areas, the corrosion process varied. In the former courses, an ionic current was generated in the solution due to the flow of metal cations into solution. For the latter one, the electronic current is produced in the metal due to the electrons from a metal moving to an acceptor, including oxygen (as another oxidant) or hydrogen ions. 2 main method are used to protect metal surfaces from corrosion: protective coatings and metal surface paintings[5]. However, these 2 general methods are not very effective due to the huge cost and low durability.

In the recent decades, superhydrophobic coating has been used on preventing metal corrosion due to its high self-cleaning capacity and high durability. In the following content, the application of superhydrophobic materials on the surface of common metals would be introduced.

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2.3. Cu

Copper owned much excellent abilities, including superior electrical conductivity, extraordinary thermal conductivity and mechanical machinability, fine outlook and ductility, which make it an important material widely used [6,7]. However, as an active metal, copper is easy to be corroded by aggressive anions, which is hard to be thoroughly solved through common methods. Under this circumstance, superhydrohobic coating is widely researched as a promising solution of corrosion problems of copper surface.

PeiPei Li, et al. were inspired by leaves of rose and lotus. Therefore, a composite coating formed by superhydrophobic silver-cuprous oxide/stearic acid (Ag-Cu2O/SA) was created on copper substrate using a simple solution immersion method, which owned little friction and fine anti-corrosion and anti-wear capacities. Correspondingly, the copper with coating can have resistance to abrasion and corrosion in engineering applications. This Ag-Cu2O coating after immersion enabled the copper surface to have a WCA angle over 150°, static WCA of 152.4° (the WCA angle on bare copper is 85.9°) that can last for four months within ambient environment, which shows the significance of this coating to applications on copper in industry usages. The one-step process was proposed to fabricate superhydrophobic copper surface by Huang, et al. Two copper plates were firstly immersed in a solution with dilute ethanolic stearic acid, which then was applied a voltage directly. Hence, the superhydrophobic surface of anode copper would be formed due to the reaction of copper and stearic acid solution. The copper stearate films with flower-like form and low surface energy covers the anode copper surface with water WCA Angle of 153±2 °, which, therefore, owned good rolling-off properties. Jingkun Liu, et al. prepared $Cu(OH)_2$ inorganic film for the Cu surface using an electrochemical anodization approach in their studies. Nanoneedles were modified with dodecylmercaptan to make them superhydrophobic. In addition, comparing to typical lubricant injected into surfaces, they used oil/hydrophobic nanoparticles as a composite fluid to inject superhydrophobic substrates. The anti-corrosion properties of superhydrophobic copper cladding and immersion surface were evaluated by electrochemical tests, seawater and sulfate reducing bacteria suspension. The results show that the oil-nanoparticle composite coating has good corrosion resistance that can be applied to Chemical engineering.

2.4. Al

As the amplest metal in the Earth's crust, Aluminum owned the ability of favored thermal conductivity, superior electrical conductivity, low specific gravity and barrier properties, and high specific strength, which, therefore, is widely used in Household goods, packaging, electrical facilities, shipping, construction, aircraft and defense applications. Over 40 million tons aluminum was produced annually.

Although aluminum has an inherent and continuous surface oxidizing layer (Al_xO_y), it is still acing the problems of corrosion from aggressive anions in solutions that have a PH value between 4 and 7<12>. Therefore, biomimetic super hydrophobic materials are used to prevent it from corrosion.

Based on the research results from Klein et al, the electrochemical and mechanical properties were investigated for superhydrophobic Aluminum substrates that has been modified by nano-silica and fluorosilane in the works of XianMing Shi, et al <13-14>. They measured the lotus leaf liked surface structure that has a WCA contact angle between 155°-158°. This research reveals the importance of defining the durability and reality of such modified aluminum substrate, showing the value of future applications and further research.

In Zhen Yang, et al.'s study, a stable superhydrophobic aluminum surface was prepared by laser ablation and surface chemical modification of (1,1,2, 24tetraethyl) triethoxysilane (Ac-FAS). The contact Angle reaches 160.6˚±1.5, with a rolling Angle of 3.0˚±1.0, which allow it to have good self-cleaning ability and long-term stability, and extraordinary chemical stability in acidic and alkaline solutions <15>. This aluminum superhydrophobic surface has high economical efficiency and durability, which may be a better choice for outdoor chemical engineering.

A simple method is proposed to prepare self-lubricating superhydrophobic layered anodic alumina (AAO) surfaces reported by Panneerselvam and Manickam, which has better corrosion resistance and is important for catalytic, aerospace and shipbuilding industries due to its resulting material that has a markedly reduced corrosion rate<16>.

2.5. Fe

Steel and its alloys are important and conductive engineering materials, which is a large component of our daily used tools and industrial facilities. It's widely used in construction, infrastructure, transportation, electrification, marine industry and so on. Annual global crude steel production exceeds 1.5 billion tons [17]. The difference among varies kinds of steel lies in the ratio of various chemical composition, mainly including carbon, copper, aluminum, iron, manganese, and tungsten. The properties of steel are greatly impact by the amount of alloying elements, involving hardness, ductility and tensile strength. For example, stainless steel was different with carbon steel in alloying elements content, hence both are considered as two main type of steel. To improve the efficiency of steel applications, superhdrophobic material is used to strengthen its corrosion resistance and durability in harsh environments.

N. Valipour Motalgh, et al. studied the preparation of superdouble hydrophobic coatings on stainless steel surface by using layer-structured materials with low surface energy. The layered structure was prepared by using SiO2 multi-layer coating, and the particle size of each layer was properly controlled. Also, Fluoropolymer compounds reduce the surface energy. The result of tests of maximum static contact Angle formed among DI water, ethylene glycol and fuel droplet on a preprepared surface confirms its superhydrophobic and superoleophobic properties of the coating surface. And those films have a satisfying durability while they are possible to be mass produced.<18>

Inspired by rose petal and coral, a bionic superhydrophobic coating with high corrosion resistance was prepared on galvanized steel (GS) surface by an one-step spontaneous deposition in ChongChong Zhong, et al.'s research. The results show that the surface is surrounded with layers of petal-like structures and even coral-like micro-nano structures, while having functional groups with low surface energy. The static water contact Angle of superhydrophobic coating is as high as 165±2.3 °. Electrokinetic polarization and electrochemical impedance spectroscopy (EIS) results showed that the superhydrophobic coating significantly improved the anti-corrosion property of GS sheets in 3.5% NaCl aqueous solution. The results of salt spray exposure showed that the effective inhibition of chloride ion penetration, demonstrating the potential of usage in chemical engineering<19>.

2.6. Mg

Magnesium is one of the most promising green engineering materials with the lowest weight used as base of building alloys. It has high thermal conductivity, fine impact resistance, good processability, and recyclability. Magnesium and its alloys have attracted great interests due to their potential applications in the automotive, aerospace and electronics industries [20]. In dry air, magnesium's high affinity to oxygen causes a thin layer of magnesium oxide to form on its surface. However, the hydration of oxidative layers lead to generation of a brittle $Mg(OH)_2$ layer of magnesium even under low relative humidity circumstance, which has weak adhesion to the metal[21]. In conclusion, magnesium would be easily corroded while applying in outdoor environments. Therefore, superhydrophobic coating become popular to be researched.

Inspired by petal, Ou etal. Fabricated a superhydrophobic surface covered with petal-shaped nanosheets through hydrothermal procedure. This kind of coating has a better anti-corrosion ability due to its hydroxide and oxide layers that act as barriers. In addition, it can associate

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with the covalent bonding of the hydroxide and oxide layers with perflfluoroothltriethoxysilane (PFOTES)<22>.

In Qing Jin, et al.'s study, a simple, environment friendly and low-cost method for fabricating a superhydrophobic and anti-corrosion (SAC) surface on AZ31B substrates(Al 2.500–3.500 %, Si 0.080%, Ca 0.040%, Zn 0.600–1.400 %, Mn 0.200–1.000 %, Fe 0.003%, Cu 0.010%, Ni 0.001%), a homogeneous and compact coating which was prepared by micro/nanostructured magnesium hydroxide can be grown on the substrate directly and then modified using stearic acid (STA), allowing the surface to have superhydrophobicity with the contact angle of 159°, a well corrosion resistant, and a high durability.

3. Conclusion

The basic theory describing superhydrophobic wettability is established by Young, Wenzel, and Cassie-Baxter. Biomimetic superhydrophobic materials have attracted a large quantity of attention for their unique properties and promising applications.

Corrosion of metals wastes resources and damages facilities. Metal surface corrosion has become a serious problem in Industry in recent decades. One of most significant utilization of superhydrophobic materials, currently, is to improve the corrosion resistance of these metals.

In this work, the corrosion resistance in terms of superhydrophobic materials on various metal surfaces is discussed: The persistent superhydrophobicity and corrosion resistance of these surfaces

The practical applications of persistent superhydrophobicity and corrosion resistance can meet industrial needs, showing a promising future in anti-corrosion applications in industry. Therefore, further research on this topic is considerably valuable and it will be done in the future decades.

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