Anti-corrosion Coating Technology and Prospects for Offshore Wind Power Equipment

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Abstract

The marine environment (marine atmosphere, marine life, humidity) as nature's extremely harsh conditions, corrosion is very serious one of the environment, the long-term service state of offshore wind power equipment is very easy to cause serious corrosion. The application of anti-corrosion coatings plays an important role in slowing down and reducing the degree of attachment of marine organisms to the equipment and the degree of corrosion of the equipment. This paper discusses the corrosion of offshore wind power equipment, introduces the progress of relevant coating materials at home and abroad, and discusses the future research direction and development trend of offshore wind power equipment coating.

Keywords

Marine Anticorrosion Coatings; Offshore Wind Turbines; Conventional Antifouling Coatings; Environmentally Friendly Antifouling Coatings; Dacromet Technology; Graphene Anti-corrosion Coatings.

1. Current Status of Offshore Wind Farms

On 22 September 2020, during the 75th session of the United Nations General Assembly, China proposed to the world that it would increase its nationally owned contribution and adopt stronger policies and measures to achieve "carbon peak" by 2030 and "carbon neutrality" by 2060 [1]. The commitment to "carbon neutrality" will be honoured by 2060 [1]. Against this background of "peak carbon" and "carbon neutrality", the development of green energy has become a top priority in response to the national call. Wind power, as the fastest growing green energy technology in the world, has been popularised and developed by countries such as Germany, Spain, Denmark and the United States. At the same time, under such rapid development, people gradually realise the limitations of onshore wind energy. And offshore wind farms benefit from abundant wind energy resources, which have received great attention. Compared to land obstructions such as land, mountains and cities, the surface roughness of the sea water is low, the friction of the sea level is small, the flat surface of the ocean on the wind friction is significantly smaller, the wind speed is higher. Compared to land coasts and plains, offshore wind speeds are 20% higher and power generation can be increased by 70% [2]. The disadvantages of offshore wind farms are just as obvious as the advantages. Due to the special characteristics of the marine environment, the offshore wind power equipment in the ocean will receive damage from various factors such as marine organism attachment, electrochemical corrosion, temperature difference, etc. Therefore, the study of the corrosion of the equipment and the understanding of marine anti-corrosion coatings can effectively improve the working life of the equipment.

2. The Environment for Offshore Wind Power Equipment

Offshore wind power equipment is located in the complex situation of the marine environment, as shown in Figure 1[3] composed of offshore generator foundation, tower, blades, wind turbines are located in the following different environments: marine atmospheric zone, wave splash zone, seawater tidal zone, seawater full immersion zone and seabed sea mud zone.

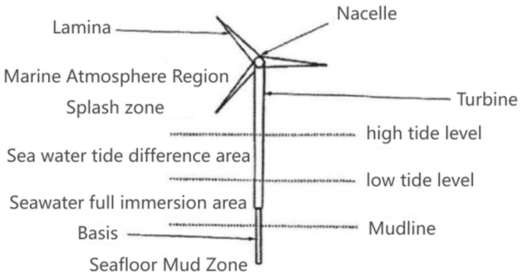

Figure 1. Schematic diagram of an offshore wind turbine[3].

2.1 Marine Atmosphere Region

The atmospheric zone is located above the splash zone in the atmospheric and coastal atmospheric zones. Exposed to the surface of the wind power equipment in this area will appear fine salt ion deposition, this is due to the air contains a large number of salts, humidity is very large, these sea salt particles will absorb the water molecules in the air and the metal surface to form a layer of liquid film, and dust, microbial deposition together with the role of corrosion.

2.2 Splash Zone

Splash zone is the average high tide line above the ocean splash can be wet location. In this area, metal materials repeatedly and continuously suffered from seawater wetting, and exposed to the air, in the high salt content, high oxygen content and seawater repeatedly impact the formation of abrasion - corrosion of the joint role of the three, the most serious corrosion.

2.3 Sea Water Tide Difference Area

Tidal range refers to the average high tide level and the average low tide level between the sections. Tidal zone corrosion is the most serious is also the above two tide, which is the role of oxygen concentration battery, oxygen-rich steel structure will become a cathode, oxygen-poor area of the rain to form anode, exacerbate the electrochemical corrosion of the region below the water line. In the tide difference area dry and wet alternation process metal suffers from ultraviolet radiation direct, resulting in corrosion.

2.4 Seawater Full Immersion Area

Full immersion area is located in the lower part of the low tide line, the region of seawater containing dissolved oxygen is very high at the same time the seawater temperature is also high. A large number of microorganisms adsorbed on the surface of metal materials to carry out metabolism, produce corrosive substances such as sulfur compounds, resulting in corrosion caused by marine biofouling, and at the same time, the seawater electrolyte is also continuing to corrode the structure [4].

2.5 Seafloor Mud Zone

The sea mud zone is mainly composed of seabed sediments, and the high salt content and low resistivity make the area form a good electrolyte, and although it is far from the sea level and the oxygen concentration is very low, the corrosion of metals is also higher than that of land soil. At the same time, the presence of sulphate-reducing bacteria (SRB), which can proliferate in sea mud, makes steel corrode tens of times faster than normal.

3. Anticorrosion Development

Comprehensive the above need to face the complex corrosion problems in the ocean, corrosion researchers at home and abroad have conducted a large number of corrosion experiments, but also got different corrosion-resistant effect of good protection programmes, such as cladding Monel alloy, titanium alloy, seawater-resistant stainless steel sheath method, but invariably, the price of these programmes is very expensive. Davy, a British chemist, experimented with the importance of cathodic protection for corrosion protection in 1824 and applied the technology for the first time. Since then cathodic protection technology began to develop rapidly in more than 170 years, has been widely used, and has become an indispensable corrosion prevention technology in all countries of the world, and has received general recognition in the field of corrosion and protection in the world [5]. However, the coating is prone to stripping under the action of cathodic current, and hydrogen embrittlement occurs in the protected metal.

Conventional antifouling coatings are mainly divided into base soluble antifouling coatings, abrasive antifouling coatings and self-polishing antifouling three kinds. In the middle of the 18th century, the researchers from the polymer medium will continue to release poisonous material in the ocean the nature of the traditional antifouling coatings can be developed around the coating to form a poisonous zone can prevent the marine organisms from attaching. Until today, domestic research on this coating has ranged from the initial selection of water-repellent polymers to control the rate of toxicant release, to the later use of magnesium soya-oleic acid with specific acrylic resin compounds. Foreign researchers, on the other hand, have developed from seawater-soluble resins to hydrolysable resins, and from metal-containing hydrolysable resins to non-metallic resins, with a great variety of hydrolysable resins [6]. However, with the gradual release of antifouling agents in the conventional type of marine antifouling coatings, its antifouling effect is weakened and can only last for 12-18 months. People are more concerned about the pollution of marine communities and the indirect damage to human beings than its anticorrosion aspects, so many countries and the International Maritime Organization (IMO) have explicitly banned the use of traditional marine antifouling coatings. In the mid-20th century, traditional antifouling coatings ushered in the development of the invention of organotin antifouling coatings, which has brought great economic benefits to marine corrosion prevention. The lipophilic and hydrophilic nature of the coordination groups of organotin ions was utilised to form an anti-fouling layer on the surface of an object to stop corrosion brought about by the marine environment. Even though organotin compounds can achieve broad-spectrum and highly efficient antifouling effect under low concentration conditions, it is still very harmful to living organisms, such as cellular energy use in the oxidative phosphorylation process is impaired, cellular immunity is impaired, and the central nervous system can cause cerebral leukoedema, and so on. To the human body will cause systemic poisoning, and even death. Although the use of organotin is also restricted by the legislation of coastal countries, but it is still contributing to the coating. Liu Sikui successfully prepared a three-component aqueous low-surface-energy antifouling coating using organosilicon emulsion as the film-forming agent, silane coupling agent as the curing agent, and organotin as the catalyst [7].

After IMO banned the use of organotin, cuprous oxide antifouling coatings began to replace organotin antifouling coatings, the mechanism of cuprous oxide is shown in Figure 2 [8], also using the decomposition of the coating, the resulting Cu^+ dissolved diffusion in the sea, the formation of a layer of the surface of the thickness of more than a dozen microns of the toxic micro-layer, in the Cu^+ in contact with marine organisms, it will be weakened by the metabolism of their role in coagulation of proteins, in this way, to achieve the effect of anticorrosion. In the final analysis, traditional anti-fouling coatings are used to kill marine organisms to achieve the effect of anti-corrosion, in the case of people's awareness of the protection of the marine environment continues to increase, many countries, the International Maritime Organisation has expressly prohibited the use of traditional marine anti-fouling coatings.

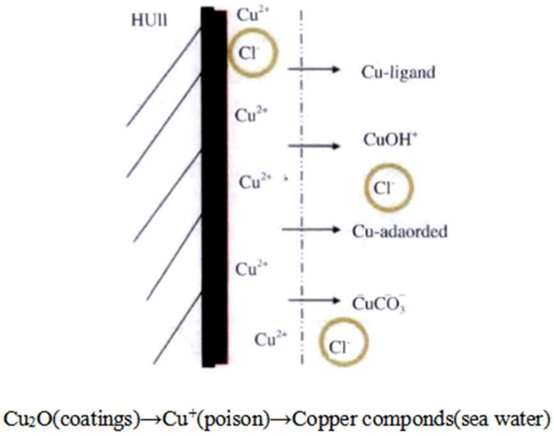

Figure 2. Mechanism of action of cuprous oxide antifouling coatings [8].

Conventional anti-fouling coatings are either restricted or banned, but every year the world suffers tens of billions of dollars in economic losses due to marine corrosion. The development of environmentally friendly marine antifouling coatings has become a top priority for corrosion prevention. The main categories of environmentally friendly marine antifouling coatings are shown in Table 1.

Table 1. Main categories of environmentally friendly antifouling coatings

categories	base	subcategories	Anti-corrosion mechanism
Low surface energy antifouling coatings	Low surface energy materials	Organosilicon, Organofluorine, Fluorosilicon	Low surface energy makes it difficult for marine organisms to attach to coated surfaces
Bionic coatings and natural antifouling agents	Antifouling agents that mimic the natural antifouling structure of marine organisms and are derived from living organisms	Bionic antifouling coatings,Natural antifouling agents	Bionic antiseptic
Nano antifouling materials	Nano-biofouling agents	Metals, Metal Oxides	Antifouling agents seep out to stop attachment of marine organisms

3.1 Low Surface Energy Antifouling Coatings

Compared with other anti-fouling coatings, low surface energy anti-fouling coatings rely on the physical properties of the coatings themselves to achieve anti-fouling effects, rather than releasing toxic substances. The low surface energy and low elastic modulus of low surface energy antifouling coatings can effectively target the adhesion mechanism of marine organisms on the surface of the coating: the biological secretion products are poorly infiltrated on the low surface energy surface, and the organisms can not grow on the surface, and the use of self-gravitation, the impact of the water flow, or the clean-up of auxiliary equipment can make the organisms come off from the surface in the way that tends to be peeled off. Marine organisms are dislodged mainly by stripping, non-planar shear and planar shear, among which stripping requires the least energy [9], and it is easier to remove the fouling. In order to achieve the above functions to achieve anti-corrosion and anti-fouling, the contact angle θ between the surface of the coating and water needs to be greater than 98°, or the surface energy is lower than 25 mJ/m2. The bond energy of the C-F bond in the fluorine-containing low-surface-energy coatings is larger than that of the C-H bond, and the electron cloud of the F atoms has a stronger shielding of the C-C bond than the H atoms, and moreover, the distribution of the electron clouds of the C-H bonds makes the substances containing the C-H bonds able to interact with the oil and dirt, while the electron cloud in the C-F bonds is stronger than that of the H atoms. In addition, the electron cloud distribution of C-H bond makes the substance containing C-H bond can interact with the oil, and the electrons in C-F bond are tightly bound around the nucleus, which makes the fluorine-containing compounds have low surface energy. For example, the surface energy of polytetrafluoroethylene, which has a high fluorine content, is about 20 mN/m [10]. It has been shown that the surface energy of resins such as perfluoroacrylates and perfluoromethacrylates can be reduced to less than 6 mN/m when $-(CH_2)_2-(CF_2)_n-F$ is attached to these resins, where $n > 10$ [11].

3.2 Bionic Coatings and Natural Antifouling Agents

In some marine organisms such as dolphins, whales, sponges, etc. also in order to avoid highly parasitic organisms such as barnacles and oysters, a special chemical is secreted or the attachment is inhibited by some special structures, both of which usually have low surface energy and have both hydrophobic and oleophobic properties. Although the antifouling mechanism is still being investigated, it is generally believed that the antifouling performance is related to the microstructure of the surface of these organisms, the bioactive molecules, the self-shedding of the surface layer, the secreted mucus and the hydrolytic enzymes, etc., [12]. The lotus leaf effect is a famous example of bionics in coatings. Dr Wilhelm Barthlott, a botanist at the University of Bonn, Germany, and his team studied the ultrastructure of the lotus leaf and found that there are many micron-sized endosperms and nano-substructures on its surface. As shown in Figure 3 [13], this special structure and water-repellent matrix makes it easy for water droplets to form a spherical shape and roll off the surface of the lotus leaf while carrying dirt particles, thus achieving self-cleaning.

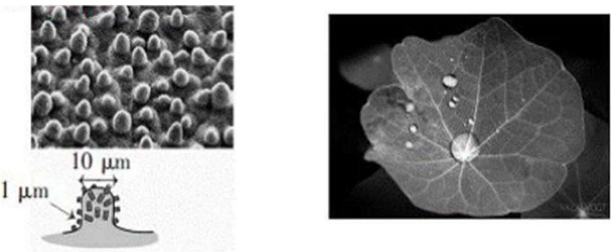

Figure 3. Surface microstructure of lotus leaves [13]

3.3 Nano-antifouling Materials

The application of nanomaterials to coatings can obtain advantages such as ageing resistance, peel strength and radiation resistance. Domestic research on silica nanomaterials in anticorrosive coatings is very intensive, and it was found that silica nanomaterials can improve the corrosion resistance, abrasion resistance, and hardness of coatings. Chen Yong, Li Ming et al [14] produced a composite coating of 4-fluorophenyl isocyanate-modified Es resin with the addition of modified SiO_2 nanomaterials, and this new type of coating has excellent anticorrosive properties with low surface energy and good adhesion.

Below are two coatings that are highly regarded for their performance in various aspects.

3.4 Dacromet Coatings

Dacromet coatings are commonly used in offshore wind energy components, and are a coating technique where a sacrificial anode is used to achieve protection of the target surface. The coating consists of a water-based zinc-aluminium coating solution composed of chromic anhydride, scaled zinc powder, flaked aluminium powder, reducing agent, dispersant, surfactant, pH adjusting agent and other additives, which is uniformly stirred and coated, and then dried and cured at a temperature of about 300°C to form a layer of Dacromet coating with corrosion-resistant properties. In the Dacromet coating, zinc and aluminium potential is lower than the steel substrate, the use of the principle of primary battery, to prevent corrosion of steel, compared with the traditional electroplating process, Dacromet is a "green plating", in the case of the coating thickness of only 4-8μm, its superb corrosion resistance is the traditional zinc plating, hot-dip galvanising or paint coating method 7-10 times more, its own process is also the same as the traditional zinc plating, hot-dip galvanising or coating method 7-10 times more. More than 10 times, its own process also determines that Dacromet has no hydrogen embrittlement phenomenon, and the heat-resistant temperature can reach more than 300℃, as well as the advantages of good bonding force and re-coating performance, good permeability, no pollution and public health. Hexavalent chromium ions contained in the coating will flow spontaneously when the coating is broken, and re-passivate with the Zn and Al and Fe substrates at the notch to prevent further corrosion. Dacromet uses chromic anhydride as a raw material, and during the preparation and use of diluent and subsequent drying, the operator will inevitably come into contact with hexavalent chromium, which is highly toxic and carcinogenic [15], so hexavalent chromium compounds do not comply with environmental standards.

3.5 Teflon Coating

Teflon PTFE, commonly known as "non-stick coating", is a synthetic polymer material that uses fluorine to replace all hydrogen atoms in polyethylene. This material almost does not bond with all substances, even if the coating is very thin also shows good non-stick properties, heat resistance to 300 ℃ for a short period of time, working at freezing temperatures without brittleness, high temperature without melting. The surface of Teflon coating is not stained with water and oil, and it is not easy to be stained with solution during production operation. If there is a small amount of dirt, it can be removed by simple wiping. However, Teflon coating belongs to organic materials, and has poor performance in abrasion resistance and UV resistance. Zhejiang University, Professor Dong Ze [16] team studied the silica-aluminium sol composite siloxane coatings, cured at 120 ~ 640 ℃ coating, measured at room temperature coating pencil hardness of 3H ~ 6H, the use of Pepsi cloth as a friction head, abrasion test machine friction number of times in the 2000 ~ 6,000 times to be worn through to expose the substrate. Iron black, carbon black, whisker silicon and other fillers added to the silica-aluminium sol composite siloxane coating for modification, and applied to the flat plate coating of the iron, its pencil hardness can be increased to 9H, but the number of rubbing times of the cleaning cloth was 5000 times to be rubbed through and exposed the substrate, mainly because of the limited thickness of the coating, resulting in the abrasion resistance is to be further improved.

4. Outlook for Anti-corrosion Coatings for Offshore Wind Power Equipment

For offshore wind power equipment needs to be in service as expected in the future under the changing environment of the complex sea, relying on the existing anti-corrosion coatings can not achieve the desired effect, the structure and performance of the existing coatings need to be optimised, and the following coatings have also become the main target of the research.

4.1 Chromium-free Dacromet Technology

Chromium-free Dacromet compared with the traditional Dacromet, without affecting its non-hydrogen embrittlement, high heat resistance, superb corrosion resistance and other advantages of the case of the coating does not contain chromium, to achieve a really harmless, environmentally friendly, green. 1990s France DACRAL developed 0.038μm/cm2 Dacromet coatings in the United States during the same period of the United States Metal Coatings International (Diamond Shamrock Corp Metal Coatings Dio) developed a "water-based chromium-free organosilicon zinc-aluminium coatings and painting technology" (cross-metal technology), which is also widely accepted as chromium-free.

China's citation of chromium-free Dacromet technology and research than foreign countries to late, and by the foreign core technology embargo, made of chromium-free Dacromet coating corrosion resistance is far less than foreign countries, compared with the corrosion resistance of chromium Dacromet also has a gap. In the face of this situation, domestic researchers put their efforts. Changzhou Jiemaitre Surface Technology Co., Ltd. developed the cross-metal does not contain Cr3+ and Cr6+ and has a variety of advantages of Dacromet, and at the same time to meet the EU 2 environmental requirements [17]. The research team of Zhang Xuming [18] from Northeastern

University found that by replacing chromic anhydride with silane coupling agent, organic resin and silane solution, the corrosion resistance of the coating was found to be up to the level of chromium Dacromet after neutral salt spray test. The team of Ji Liya [19] from Nanjing University of Aeronautics and Astronautics (NUAA) replaced chromic anhydride with silane coupling agent and molybdate, which was also found to be closer to chromium Dacromet in terms of performance after salt spray test.

Chromium-free Dacromet coating is an ideal anti-corrosion coating, removing the disadvantages of poor stability, high coating cost, energy consumption, more in the loss of passivation repair of hexavalent chromium, the coating will lose the self-repairing function, so it is difficult to truly replace the traditional Dacromet coating, and need to rely on the in-depth study of researchers. For passivation repair, chromium-free Dacromet technology future research direction in the use of organic passivators, inorganic passivators and inorganic-organic joint passivators to replace hexavalent chromium. Among them, in-depth study of inorganic-organic passivators, looking for better passivation system and a variety of passivation system mix to achieve high performance passivation is the most important.

4.2 Graphene Anti-corrosion Coatings

Graphene anticorrosive coating benefits from graphene in which carbon atoms in sp2 hybridised orbitals form a planar structure film of ortho-hexagonal 2D honeycomb lattice, with superb impermeability, chemical stability and electrical conductivity, etc., and its components are inorganic and non-toxic, and the ecology of the marine pasture is highly harmoniously integrated with that of the marine pasture, conducive to the health of the people and environmental protection, and it has been receiving a lot of attention in the field of offshore wind power in recent years. Shen Haibin [20] and other research teams found that the addition of graphene in epoxy zinc-rich coatings can significantly reduce the amount of zinc powder, as a solution to the traditional sacrifice of zinc powder corrosion, greatly enhancing the corrosion resistance of the coating can be widely used in the field of offshore wind power equipment. At present, China's graphene anti-corrosion coating research is in the initial stage, the research direction to prepare graphene into composite materials and added to the coating, worthy of graphene composite coating will have better corrosion resistance, adhesion and wear resistance.

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