Application mechanism and anti-corrosion measures of aluminum and titanium alloys in marine environment

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Abstract

With the rapid development of ocean engineering and ships, ocean engineering materials' corrosion resistance and portability are more prominent. This paper expounds on three aspects: (1) briefly describes the requirements and application of metal materials in ocean engineering. (2) corrosion mechanism of the ocean, corrosion resistance mechanism of aluminum, titanium, and its alloys in seawater. (3) Anti-corrosion measures of metals in the Marine environment. Currently, the research and development of Marine materials lacks the practice and application of low-carbon theory. Therefore, Marine environmental protection and low carbon has become an important development trend in various industries.

Keywords: Mechanism, titanium, aluminum, prevents, corrosion, measures

1. Introduction

The 21st century is known as "the Ocean Century". From the second half of the 20th century, the world's population and economy have expanded rapidly, and the energy demand has increased sharply. With the large exploitation of oil and gas and the continuous expansion of ocean resources development and space utilization, the corresponding offshore engineering has become one of the most rapidly developing projects in the past 30 years. Offshore engineering and deep-sea engineering have gone far beyond the scope of coastal engineering, and the basic science and engineering technology applied are also beyond the scope of traditional coastal engineering, thus forming a new type of Marine engineering. In addition, because the ocean is a strong, corrosive material, the requirements for ocean engineering materials are also very high. Chang Hui et al. wrote in the book *Ocean Engineering Titanium Metal Materials*[1] that ocean engineering materials meet the following requirements: (1) high strength, high specific hardness. (2)good toughness. (3)corrosion resistance fatigue resistance. (4)good process. (5)complete material varieties and specifications. (6) high recovery of materials.

China's ocean engineering materials are mainly used in the boat manufacturing industry and offshore oil and gas development. Common Ocean engineering materials include titanium, aluminum, copper, and other alloys, 304 and 316 stainless steel, etc. Compared with other metals, titanium, and aluminum have good corrosion resistance and are lighter. Therefore, Al, Ti, and their alloys are widely used in ocean engineering. Hemina et al. [5] said that in Russia, the United States, and China, titanium had been widely used in deep submersibles, underwater submarines, surface ships, ships and other bodies, seawater pipeline systems, superstructure and other components. Hu Hailiang et al. mentioned[2] that the shipbuilding industry at home and abroad is developing rapidly with the demand for lightweight ships. Due to the characteristics of low density, high strength, and strong corrosion resistance, it is widely used in ship manufacturing.

2. Mechanism

2.1 Corrosion mechanism of seawater

Seawater contains a large number of salts (Cl-, sulfate, carbonate. etc.........), dissolved oxygen, CO2, and microorganisms, and it is the most abundant natural electrolyte solution, so the seawater is highly corrosive. Seawater corrosion is typical of the electrochemical corrosion.

The factors that influence seawater corrosion are chemical (O2, Salt content, etc.), physical factors (flow rate, temperature, etc.), and biological factors. For metals that are difficult to passivate in seawater, the corrosion rate increases with the growth of oxygen content. Because of the large amount of Cl- in seawater, most metals have little anodic polarization blocks and high corrosion rates. And because the vast majority of metal corrosion is the depolarization process of oxygen (except Mg and its alloys), dissolved oxygen in seawater is the main factor affecting seawater corrosion. Sea water temperature increases, the diffusion rate of oxygen increases, the cathode and anode reaction accelerates, and the corrosion accelerates. With the salt concentration and the temperature increase, dissolved oxygen content decreases. Thus, the corrosion rate reaches a certain oxygen content. In addition, seawater's wave and flow rate accelerate oxygen diffusion, leading to accelerated metal corrosion. The attachment of animals, plants, and microorganisms in the ocean will cause the oxygen concentration difference inside and outside the attachment layer to cause battery corrosion. It may also damage the protective layer of the metal surface and accelerate the corrosion.

Different ocean environments can lead to different corrosion rates. As shown in Figure 2-1, in the atmospheric zone (more than 2m above sea level), the humidity is higher than the inland and has the salt spray of aerosol, so the speed of corrosion is greater than the inland. The splash zone (0-2m above sea level) can be bitten by the waves, which leads to the damage of the protective film, and the oxygen depolarization will promote metal corrosion in the splash area. The corrosion rate in the tidal zone is also fast but lower than that in the splash zone. The total immersion zone is divided into three regions, and the dissolved oxygen concentration is high in the shallow sea, so it is the most severe in the three regions, followed by the medium deep sea, and the corrosion rate of the abyssal area is the slowest in the three regions. Moreover, the corrosion rate is relatively slow because the sea mud zone is affected by bacterial corrosion and contaminated soil accumulation corrosion.

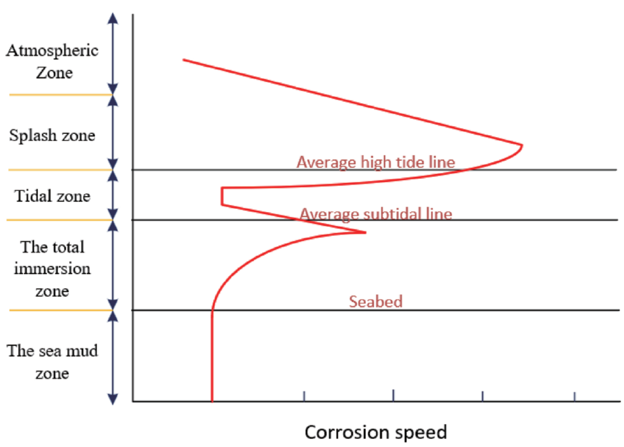

Figure 2-1 Comparison of corrosion velocity in different ocean regions

2.2 Application mechanism of aluminum and titanium

2.2.1 Application mechanism of aluminum

Firstly, aluminum has a better corrosion resistance because it can produce a dense oxide film on its surface (Al2O3); this oxide film can effectively prevent water and other harmful substances from infiltrating the aluminum surface, thus reducing the corrosion of aluminum. In addition, Hu Hailiang[2]mentioned alumina also has electrical conductivity, which not only can effectively prevent electrical corrosion but also can absorb electrical charges to prevent the positive charge from accumulating to the aluminum surface to effectively prevent the corrosion brought by the charge, to prevent the corrosion of aluminum. However, the oxide film of aluminum alloy is unstable in seawater; it will cause local corrosion.

In addition, aluminum alloy is widely used in ships because of its physical properties; the strength of the aluminum alloy is high (equivalent to steel), good plasticity, can be processed into a variety of profiles, and because the density ratio is lower than that of steel, its density is 2.7g / cm3(the density of the steel is 7.85g / cm3), so ships made of aluminum alloy are lighter.

2.2.2 Application mechanism and improvement method of titanium

First, titanium has very good seawater erosion and erosion resistance. Chang Hui et al.[1] mentioned, although the titanium electrode potential is low, titanium has easy passivation (because of its low blunt potential, the critical passivation current is small); its passivation is more than Al, Cr, Ni, and stainless steel; titanium also has strong blunt stability, the blunt potential area has 20V, not easy to produce passivation, and the passivation film is not damaged by chloride ion and has good self-healing (when it was broken can quickly automatic repair and form a new passivation film). Titanium's natural corrosion potential in 25°C seawater is higher than copper, which is about + 0.09V (SCE), so titanium has good seawater corrosion resistance in seawater.

In addition, titanium has no cold brittleness, and titanium equipment can work in cold areas such as deep sea low-temperature areas; titanium has no magnetic properties, improving the anti-magnetic interference ability.

Sun Jing et al. [3]mentioned that although titanium and its alloys have good corrosion resistance, its wear resistance is poor. In corrosion medium in long-term wear condition (such as Marine engineering key components), if the surface passivation film repair speed is slower than the damage speed, it will lead to the material body being destroyed, easily cause sudden failure, lead to huge economic losses and even casualties, this kind of situation in the condition of the extremely harsh ocean environment is the most obvious. Table 2-1 shows Sun Jing et al. [3] mentioned the different surface modification methods used by Chinese and foreign researchers to improve the wear resistance of titanium and titanium alloy.

Table 2-1 Different surface modification methods for improving the wear resistance of titanium/titanium alloys

researcher	method	conclusion
Deng Kai et al.	by performing a micro-arc oxidation of the TC11 titanium alloy, N+Injection, DLC multilayer film, and other methods and testing	Friction coefficient and wear are reduced, and the DLC method
Vladimir et al.	the TC4 titanium alloy was tested by W-DLC treatment, HVOF coating treatment, and ion injection	The W-DLC method has the best corrosion and wear resistance
He Qian et al.	Cr Si N / SW nanomultilayers with different modulation periods were prepared on TC4 titanium alloy surface and tested.	The lowest corrosion wear rate at the modulation period is 45nm
Jiang Luyao et al.	the Ti6Al4V alloy with coaxial fine crystal tissue and sheet α organization was obtained and tested by controlling the friction processing process	Isoaxial fine crystal tissue Ti6Al4V alloy has a low wear rate and friction coefficient, and its tissue characteristics have optimal corrosion and wear resistance.

3. Corrosion protection measures or techniques

3.1 Reasonable selection of materials

The selection of materials (structural materials) generally should have a certain strength, plasticity, impact toughness, and corrosion resistance.

3.2 Electrochemical protection technology

The electrochemical protection methods include the cathodic protection method with applied current and the cathodic protection method with sacrificial anode. The cathodic protection method is the external cathodic polarization of the protected metal to reduce or prevent metal corrosion. The cathodic protection method of the sacrificial anode refers to connecting a more negative metal to the protected metal as the anode, which forms a large battery with the protected metal in the electrolyte solution and is a method of cathodic polarization of the protected metal.

3.3 Thermal spraying technology

Zhang Wei, Jin Xi, et al. [4]mentioned thermal spraying technology to heat metal or non-metallic materials to high temperature to melt or semi-melt, and then spray the paint to the surface of the ship at high speed through spraying equipment, forming a uniform, dense protective layer. This protective layer can effectively isolate water, oxygen, and other corrosive media, thus delaying the corrosion process on the ship's surface and extending the ship's service life. Thermal spraying technology can handle various materials; the thermal spraying layer has high adhesion, density, and wear resistance and can withstand the harsh ocean environment and complex stress state. Thermal spraying technology can achieve thicker coating to provide more powerful protection performance with high production efficiency and can achieve rapid and continuous coating to reduce production costs. However, thermal spraying technology also faces some challenges in the field of ships, such as the oxidation, combustion, or decomposition of the coating to reduce the performance of the coating or may cause harmful toxic gas or dust during the spraying process.

3.4 Organic coating technology

Zhang Wei, Jin Xi, et al. [4]wrote that organic coating technology refers to the use of organic materials as the main component of the coating technology; its main principle is to use the excellent corrosion resistance of organic materials to form a protective layer on the surface of the ship. Its main materials include acrylic acid, epoxy resin, polyurethane, and other organic materials; these materials have excellent corrosion resistance and coating properties and can form a dense protective layer to avoid the ship's surface by seawater, climate, and corrosion media erosion. Organic coating technology is easy to construct; the coating thickness is easy to control and suitable for all shapes and sizes. However, after a long time of seawater erosion or different forces, some coatings will be decomposed, and their decomposition products will affect the ocean environment and the survival of ocean life.

Table 3-1. Role of various organic coatings

polyurethane coating	polyurethane	excellent corrosion resistance, chemical resistance, and heat resistance	prevent ships from erosion by seawater and chemical media
acrylic coating	acrylic resin	excellent corrosion resistance, UV resistance, and water resistance	avoid ship erosion by seawater, climate, and corrosive media
epoxy coating	bisphenol-A epoxy resin	Excellent acid and alkali resistance, corrosion resistance, and chemical resistance, with strong mechanical strength and wear resistance, environmental protection	prevent erosion from seawater and chemical media; reduce wear

4. Conclusion (conclusion + Outlook)

Aluminum and its alloys have good corrosion resistance, but its passivation film is unstable in seawater and will produce local corrosion. Titanium has good seawater erosion resistance and strong acid and alkali corrosion resistance, but its corrosion resistance is low, which can be improved by the surface modification method. Metal in seawater can be used for corrosion protection by reasonable material selection, coating protection, and electrochemical protection.

In developing various anti-corrosion materials and protective measures, a large amount of CO2 may be produced. Although seawater can absorb CO2, over time, if seawater absorbs excessive CO2, it will make the PH value in the ocean decline, leading to the acidification of seawater, affecting the survival of ocean life. Therefore, "low carbon" is the first consideration of researchers in developing materials.

At present, the concept of low carbon in engineering and material research in China is not mature enough, so it is necessary to deepen the understanding of the low carbon concept, only paying attention to the performance of the material but also the effect of it on the environment is not enough. For example, whether the organic coating covered outside the metal has been washed or corroded for a long time, whether the decomposed products adversely affect ocean or ocean life, and whether the preservative pigment on the ship is free of lead and chromium. In conclusion, material research and engineering development should focus on environmental protection and low-carbon applications and strive to build a sustainable development model of green, environmental protection, and ecological civilization. Clear waters and green mountains are gold and silver.

【Reference】

[1] Chang Hui. Liao Zhiqian. Wang Xiangdong. *Ocean engineering of titanium metal materials* [M]. Beijing Press of Technology.2017:9-11.

[2] Hu Hailiang. Research on the application of aluminum alloy in ships and Ocean Engineering [J]. Ship Science and Technology, 2023,45 (04): 45-48.

[3] Sun Jing, Qi Yuanjia, Liu Hui et al. Progress on corrosion and wear of titanium and titanium alloys in marine environment [J]. Material protection, 2020,53 (01): 151-156.

[4] Zhang Wei, Jin Xi, Zuo Hongxin, etc. Analysis of new corrosion protection technology on Marine ships [J / OL]. Biochemical industry: 1-7 [2023-07-27].

[5] Hai Minna, Huang Fan, Wang Yongmei. On the titanium and titanium alloy application in Marine equipment [J]. MetalWorld, 2021 (05): 16-21.