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Antifouling and Anticorrosive Protection of Renewable Energy Marine Structures with TiO_2-Based Enamel

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ABSTRACT: Biofouling is a significant problem that affects renewable energy marine structures (REMS), such as wind turbines and those designed for wave or tidal energy exploitation. Marine organisms, including algae, barnacles, and mollusks, attach themselves to the surface of these structures, which can lead to reduced efficiency and increased maintenance costs. In addition, biofouling can also cause corrosion, which can compromise the structural integrity of the offshore platforms. To combat this problem, several methods have been developed, including anti-fouling coatings, physical methods, and biological methods. Each method has its advantages and disadvantages, and the most effective solution often depends on the specific type of fouling and the location of the offshore structure. Effective biofouling prevention is essential for the safe and efficient operation of offshore structures and the protection of marine ecosystems. To prevent the spread of invasive species, an innovative ceramic coating has been designed and tested in accordance with ASTM-D3623 procedure. The investigation results revealed that, after four years of experimentation in a real environment, the biofouling growth observed in the splash zone of the antifouling paint was 129.76% higher than that of the titanium-based ceramic coating and it is expected that this difference will continue to grow over time.

1 INTRODUCTION

Biofouling and corrosion are two related but distinct phenomena that can have significant impacts on various types of materials, structures, and equipment, especially those that are exposed to water or other aqueous environments like renewable energy marine structures (REMS). Biofouling refers to the accumulation and growth of microorganisms, such as bacteria, algae, and other marine organisms, attach and grow on surfaces in contact with seawater [3,11]. This can occur in a variety of settings, from marine vessels and offshore structures to water treatment facilities and industrial equipment [4]. These microorganisms can associate in a self-produced polymer matrix called biofilm, a thin layer of organic material which can serve as a substrate for the attachment and growth of larger organisms called macro-organisms, resulting in macro-fouling, such as barnacles and mussels [7,15]. This polymer matrix can also include inorganic components, such as salts and/or corrosion products [2]. Over time, the biofilm can grow and become thicker, eventually leading to the formation of a full-fledged community of marine organisms on the surface. The formation of marine biofouling can be influenced by a variety of factors, such as water temperature, nutrient availability, water flow, and the composition of the surface itself [6]. For example, surfaces that are smooth and free of imperfections may be less prone to biofouling than rough or irregular surfaces. Similarly, water with high levels of nutrients, such as nitrogen and phosphorus, may promote the growth of biofilms and the attachment of larger organisms [12].

Corrosion, on the other hand, refers to the deterioration of a material due to chemical or electrochemical reactions with its environment. This can occur in many different forms, such as rusting of metal, cracking of concrete, or steel degradation [17]. Corrosion can be caused by a variety of factors, including exposure to oxygen, moisture, acids, and salts. In the harsh marine environments, the presence of saltwater and other corrosive agents can accelerate the rate of corrosion and cause significant damage to structure over time [1]. Corrosion in marine structures can have a range of negative impacts, including reduced efficiency and performance, increased maintenance costs, and even safety risks. For example, corrosion can weaken the structural integrity of an offshore platform, increasing the risk of failure or collapse [18]. Corrosion can also cause leaks and other failures in pipelines and other infrastructure, leading to environmental damage and operational downtime. Preventing or mitigating corrosion in marine structures is therefore a crucial goal for the offshore renewable energy industries and their applications. This can be achieved through a variety of methods, such as using corrosion-resistant materials, applying protective coatings, and implementing corrosion monitoring and maintenance programs. Effective corrosion prevention and control measures can help to ensure the safe and reliable operation of marine structures and equipment, while reducing costs and minimizing environmental impacts [8].

Biofouling, or the accumulation of marine organisms on REMS, can result in substantial economic losses due to several factors such as obstructed sensors, added weight and thickness/rugosity to devices, and decreased structural integrity and performance [3]. Key macrofouling organisms are responsible for these negative impacts. Microfouling and macrofouling organisms can also cause corrosion, which is a significant economic impact [20]. Microbiologically influenced corrosion (MIC) occurs when anaerobic marine microorganisms induce or accelerate corrosion, and macrofouling can facilitate MIC by creating oxygen-depleted conditions under the macrofoulers where microbial communities can grow. Some macrofoulers can also promote localized corrosion by adhering or perforating substrata. During maintenance, coating damage caused by attached organisms can further accelerate corrosion [12].

The relationship between biofouling and corrosion is complex, as the growth of microorganisms on a surface can accelerate or exacerbate corrosion [10]. This is because microorganisms can produce acidic substances that can eat away at the surface, and also provide a surface for corrosion-inducing agents to attach and accumulate. Therefore, preventing or mitigating biofouling is an important strategy for controlling corrosion, and vice versa so that both parameters should be studied in parallel [20]. Antifouling (AF) and anticorrosive protection are important factors in the maintenance and longevity of marine structures, in this way, titanium-based enamels can provide effective antifouling and anticorrosive protection for these structures [16].

Titanium-based enamels are coatings that contain titanium dioxide (TiO_2) as the main pigment. TiO_2 is a naturally occurring substance which has excellent properties such as high refractive index, opacity, and resistance to UV [13]. When applied to marine structures, titanium-based enamels form a smooth, hard surface that is resistant to adhesion and growth of marine organisms due to its unique surface chemistry and physical properties. Specifically, the surface of titanium exhibits a high degree of hydrophilicity, meaning that it has a strong affinity for water molecules. This hydrophilic property prevents the attachment of organic molecules, which is the first step in the formation of biofilms and the subsequent growth of larger fouling organisms [21]. In addition, the surface of titanium-based coatings also has a unique microstructure which creates a thin layer of titanium oxide that inhibits the adhesion of marine organisms by creating a barrier that prevents their attachment. On the other hand, the vitreous structure of ceramic glazes provides the coating with a smooth surface, with an average roughness height of 0.189 μm [13], which makes it difficult for microorganisms to adhere and facilitates their detachment when a wave crashes into them [14]. One of the advantages of titanium-based enamels is that they are environmentally friendly and do not contain toxic substances, such as copper or other heavy metals, which can be harmful to marine life. In addition, these coatings have been found to be highly durable and long-lasting, even in harsh marine environments [19].

Currently, there are many obstacles that limit the use of ceramic enamel as a protective coating for steel structures. Traditional methods of applying the coating, such as dipping and wet spraying, are not practical for large objects except for certain items like chemical reactors and panels [22]. Additionally, a sintering process is required to strengthen and vitrify the coating, but this can cause unwanted changes to the structure and strength of certain materials like light alloys and tempered steels, as well as distortion and warping of the coated objects. In recent years, thermal spray technology has emerged as a promising alternative for applying ceramic coatings to a wide range of materials and surfaces. This process involves heating ceramic particles and then propelling them at high velocity onto the surface to be coated [9]. This method offers several advantages over traditional methods, including the ability to coat large and complex surfaces, the ability to tailor the coating to specific requirements, and the ability to achieve a high-quality coating with minimal distortion or warping of the underlying material. In this context, the application of ceramic coatings using thermal spray has become an increasingly popular solution for a range of industrial applications. The biggest challenge in achieving high-quality, corrosion-resistant ceramic enamel coatings through thermal spraying is the presence of voids, gaps, microcracks, and entrained gases between the flattened droplets. These imperfections are caused by the rapid cooling of the material after it's been sprayed. Despite successful lab-scale development of thermal spray glass coatings for a variety of metallic and ceramic substrates, these limitations have, up to now, prevented widespread adoption of the technology in industrial applications [13].

In this study, an experiment was conducted to assess the effectiveness of a titanium-based ceramic coating in preventing biofouling and corrosion in seawater, and the results were compared to those obtained from a commercially available antifouling paint Intersleek 1001. The main goal was to reduce the adhesion of biofilm to the surface and investigate how the newly coated material affected the composition and structure of the biofilm. This research is particularly important for the antifouling field because it involves a new environmentally-friendly technology that can improve efficiency and productivity of offshore renewable energy marine structures.

2 MATERIALS AND METHODS

2.1 *Area of study*

The Biofouling Research Group of the University of Cantabria conducted the study on biological growth in a natural environment at Molnedo's Dock breakwater jetty (43º 27.713′ N, 03º 47.541′ W), located in the Bay of Santander in Cantabria, Spain. The research was conducted with the authorization of the Santander Port Authority for experimental activities. The bay opens to the Atlantic Ocean through the Cantabrian Sea and is located near the Biofouling laboratory "Emilio Eguía" at the E.T.S. de Nautica of the University of Cantabria, making it an ideal location for the experiment. Furthermore, the areas near the ports typically have the most conducive abiotic and biotic conditions for biological growth. Therefore, the chosen location for the study represents the most restrictive condition possible, as the results of biological development would likely be much lower in open waters.

2.2 *Preparation and characterization of experimental samples*

To apply the titanium-based ceramic coating, electrophoretic deposition by thermal spray technique was used over a carbon steel surface (A569/A569M6, 3 mm thick by 200 mm x 300 mm). ISO 20340 states that steel structures in coastal and offshore areas are exposed to high levels of salt, and as a result are classified as C5-M. Therefore, they require a protective paint system that meets certain minimum requirements. To prepare the surface for painting, it was cleaned using a blast cleaning process to achieve a final surface roughness of either Sa2.5 or Sa3 (according to ISO 8503) and cleanliness (ISO 8501). Once the surface was cleaned, dust and blast abrasives were removed to ensure a clean surface with a rating not exceeding 2 according to ISO 8502-3. For the first coat application, the metal surface was completely dry, clean, free from oil/grease, and had the specified roughness and cleanliness.

In order to achieve thinner coatings and lower deposition rates, atomistic deposition processes were used to apply titanium-based ceramic coating. Initially, a dense metallic under-layer was deposited between the functional ceramic topcoat and the substrate using the high velocity air-fuel spray process, which utilized compressed air instead of oxygen. The purpose of this step was to protect the substrate from corrosion and improve the adhesion strength of the ceramic enamel top layer. The use of HVAF torches was found to be an effective method of depositing watertight metallic coatings with low flaw capacity, resulting in even higher particle velocities and lower particle temperatures. The paint coating applied had a total thickness of 600 µm.

Ceramic coatings and autorelease paints exhibit similar anti-fouling properties. The antifouling action of enamels is mainly based on four pillars: the chemical composition, the surface roughness, the contact angle (CA) and the thickness of the coating. The studied ceramic coating has titanium dioxide as one of its key components. Figure 1 shows the chemical composition of the ceramic coating. The use of titanium in the composition of the coating also provides enhanced strength, durability, and resistance to high temperatures.

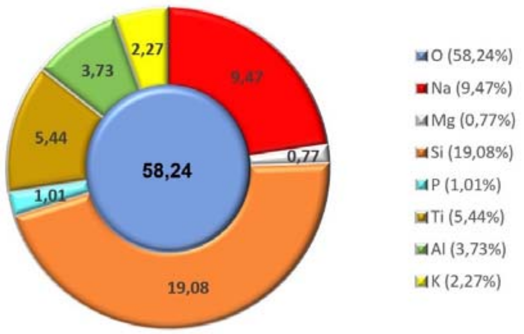

Figure 1. Titanium-based ceramic coating composition.

Once the titanium-based ceramic coating was applied to the experimental samples, the surface roughness and the degree of hydrophilicity were checked according to ASTMD7490-13. Figure 2 shows a graph of the roughness spectrum measured on the x-axis of the sample. The measurements were taken three times on the x-axis and three times on the y-axis, so that the arithmetic mean of the six measurements equals 0.188 µm. On the other hand, three measurements of the drop angle were taken to confirm the degree of hydrophilicity of the sample. The results of the measurement are presented in Table 1.

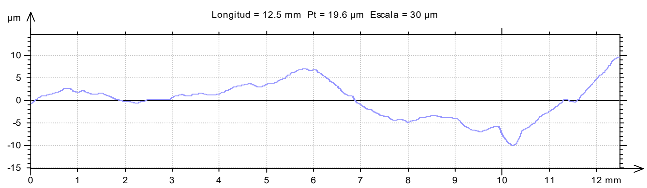

Figure 2. Titanium-based ceramic coatings surface finish metrology.

Table 1. Distilled water drop contact angle.

Nº	Contact angle (˚)	Adjustment error µm	Volume µl	Area mm²	eight mm
1	25.5	1.55	9.53	29.27	0.673
2	21.2	1.15	6.16	24.55	0.514
3	25.8	1.84	7.64	25.06	0.630
M	24.1		7.78	26.29	0.606

2.3 *Experimental phase*

Once the ceramic coating characterization was completed and verified, the experimental stage began on October 6, 2018, introducing the samples into the Santander Bay water. According to ASTM D 3623-78a, the samples were introduced in the splash zone with a south orientation, and at a depth of 60 cm with a north and south orientation. The experimental phase lasted four years and in it the samples mass was measured once a month to later calculate the increase in mass with respect to the initial weight. In addition, three test samples covered with Intersleek 1001 paint were introduced under identical experimental conditions to compare the results. On the other hand, monthly measurements of water temperature were taken to assess its impact on biological development.

Before the experimentation began, samples were weighed to determine their initial weight. After the experimentation, their weight was measured again and compared with the initial weight to determine if there were any changes in weight. To ensure accurate measurements, both the specimens coated with titanium-based coatings and the specimens coated with Intersleek 1001 paint were washed to remove any biofouling. This ensured that the weight measurements were not affected by any external factors and provided reliable data for the study of possible corrosion.

3 RESULTS AND DISCUSION

Figure 3 shows the quantitative evolution of the weight increase of the samples exposed in a real marine environment over a span of four years. Furthermore, the aforementioned data is overloaded onto a bar chart that visually depicts the seawater temperature during the course of the experiment. As shown in Figure 3, the highest values of seawater temperature occur in the summer months, while the lowest values are reflected in the winter months, in fact, February 8, 2020, recorded the lowest seawater temperature value (11.9ºC), whereas the highest temperature value (21.6ºC) were observed on August 9, 2021.

Regarding the growth of biofouling in the splash zone, it was observed that the titanium-based ceramic coating showed significantly higher biological growth than the antifouling paint during the first nine months of exposure, in fact, the performance of the paint was commendable, even for an autorelease paint that was tested under static conditions, and it was in this month of experimentation when the ceramic coating exhibited a much greater difference in mass increase compared to the paint. In fact, the biofouling attached to the ceramic coating was 276.32% more than that attached to the Intersleek 1001 paint, making the difference in growth between the two quite substantial. From the eleventh to the fourteenth month, the investigation showed that the antifouling paint experienced mass increase values slightly below zero, meaning that at this point in the investigation, some of the paint had disappeared, which subsequently affected its antifouling performance. The graph in Figure 3, specifically in the "south splash zone," indicates that the growth of biofouling on the ceramic coating is strongly linked to the temperature of the seawater, as also exemplified by the research conducted by [5]. During the summer months, there was a higher increase in mass, while the increase was lower during the winter months. The growth pattern was observed to be stable and cyclical, with very similar values between the same months of 2020, 2021, and 2022. The highest value of biofouling was achieved on August 9, 2021 with a mass increase of 222.0 g. However, the behavior of the Intersleek 1001 paint was very different and, coinciding with [7], the increase in biofouling gradually increased, reaching much higher values in the last year of experimentation. In fact, the biofouling increase in the antifouling paint was 129.76% greater than in the titanium-based ceramic coating in the last month of experimentation and it is expected that this difference will continue to grow over time.

Regarding the results obtained in the experiment 60-cm-deep south zone and 60-cm-deep north zone, a much lower biological development can be seen compared to the splash zone in both antifouling coatings. Although there is a direct relationship between temperature and biofouling growth, it is much weaker than the relationship observed in the splash graph. Towards the end of the experiment, it was found that in the 60-cm-deep south zone and 60-cm-deep north zone, the titanium-based ceramic coating experienced 141.85% and 69.41% less mass increase, respectively, compared to the Intersleek 1001 paint.

After the experimentation was completed, the samples were cleaned and their weight was compared to their initial values. It was observed that the three samples that were protected with titanium-based coatings maintained a weight very similar to their initial weight, indicating their ability to resist corrosion. However, the samples coated with antifouling paint showed a decrease of 16.2%, 21.3%, and 19.5% in mass in the south splash, 60-cm-deep south and 60-cm-deep north zones, respectively. This decrease in weight was due to two factors. Firstly, certain layers of the paint came off in some areas of the samples, and secondly, beginnings of corrosion were seen on some edges of the samples.

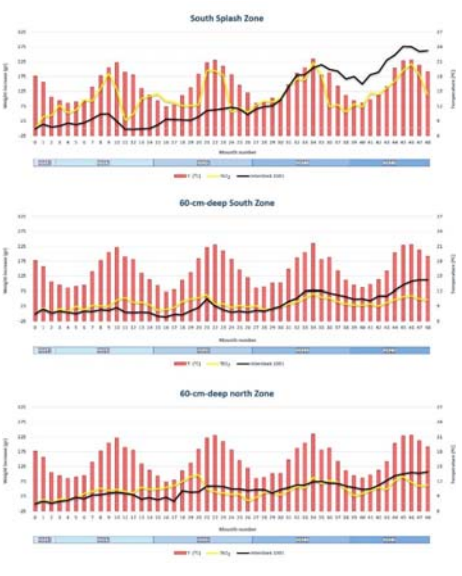

Figure 3. Relationship between the mass increase of ceramic coatings and the temperature of seawater over time.

4 CONCLUSIONS

This study focused on analyzing the anti-fouling properties of a titanium-based ceramic coating and comparing it with a reference antifouling paint coating. Following a span of four years within a natural environment that fostered evolution and biological diversification of species, the behavior of both coatings was examined, and the extent of biofilm buildup was quantified. The results showed that the ceramic coating exhibited excellent properties in preventing biological adherence. The properties that influence the biofouling resistance of the ceramic coating include its roughness, which impedes initial adhesion and promotes the detachment of biofouling communities, furthermore, the contact angle of the coating also plays a role, as a hydrophilic surface hinders the initial adhesion of biofouling. While the contact angle loses its impact once the initial settlement of organisms has occurred, the detachment of the biofouling, resulting from the low roughness of the surface, re-establishes the relevance of the contact angle, thereby establishing a direct relationship between both parameters. The antifouling and anticorrosive functionality of ceramic coatings is also based on diverse AF additives to reject biofouling adhesion, in this sense, titanium has shown excellent behavior.

In addition, a clear correlation has been observed between seawater temperature and biological growth in titanium-based ceramic coatings, whereas the development of organisms in the control antifouling paint was more gradual, with a less pronounced sensitivity to temperature variations. Upon completion of the experiment, it was found that the ceramic coating had achieved a reduction in biofouling mass increase of 126.76%, 141.85%, and 69.14% as compared to the antifouling paint in the splash south zone, 60-cm-deep south zone, and 60-cm-deep north zone, respectively.

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