Antifouling and anticorrosive prevention with ceramic coatings on offshore structures for renewable energy

D.S. Sanz, S. García, A. Trueba, G.A. Esteban, D. Boullosa-Falces

Abstract— **In the past, ships, port facilities and offshore platforms dedicated to the exploitation of fossil resources were the only man-made structures that were exposed to seawater, currently the exposed structures are extended to all those used in the field of renewable ocean energy sources, such as waves, tidal flows or oceans streaming and offshore wind energy. Therefore, this study highlights the need for offshore structures to consider the choice of ceramic coatings in the field of surface treatment and marine corrosion control without neglecting another of the main problems that affects structures in contact with seawater, which is the phenomenon known as biofouling. This study evaluated differences in the total of seawater biofouling attached on coated paints and ceramic coatings in carbon steel for offshore structures. All three different ceramic coatings were made of incorporating active ceramic particles against biofouling as titanium, cobalt and manganese. The results of the investigation showed that the Mn–Fe-based coating had the best antifouling properties at the end of the experimentation, although there was no significant difference in the biofouling attached during the two years of exposure, but great differences were shown with respect to the antifouling paints. Biofouling adhesion resistance was greatest when a coating thickness of 300 μm was used and when the substrate surface roughness (Ra) was 0.245 μm. On the other hand, the results showed a progressive degradation of the antifouling paint coatings, which meant an exponential increase of biofouling adhered to the samples, but not in ceramic coatings during the experimentation.**

Keywords—**Ceramic coating, biofouling, low roughness surface, corrosion, antifouling.**

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I. INTRODUCTION

The global shift towards cleaner and more sustainable energy sources has given rise to offshore renewable energy as a significant and promising solution [1]. As the demand for electricity continues to grow and concerns over climate change intensify, harnessing the power of wind and waves in the vast expanses of the world's oceans has become a significant focus for governments, researchers, and energy companies alike [2]. Offshore structures for renewable energy refer to the specially designed platforms, installations, and infrastructure deployed in offshore locations to capture and convert the abundant natural resources available at sea into usable energy. These structures typically support the generation of renewable energy through two primary sources: offshore wind and wave/tidal power [3].

The construction and installation of offshore structures for renewable energy pose unique challenges compared to their onshore counterparts [4]. The harsh marine environment, including strong winds, corrosive saltwater, and dynamic ocean conditions, requires engineering solutions that can withstand these forces while maintaining the integrity and longevity of the structures. Innovations in materials, design, and maintenance techniques are continually evolving to address these challenges and ensure the reliable operation of offshore renewable energy systems [5].

Seawater is a complex solution composed of water molecules (H_2O) and dissolved salts, predominantly sodium chloride (NaCl), followed by magnesium and calcium salts [6]. It exhibits unique characteristics, including a slightly alkaline pH, and serves as a crucial habitat for diverse marine life, supporting their biological activity through the provision of nutrients, oxygen, and a stable environment [7]. However, these distinct characteristics of seawater have undesirable consequences for structures in contact with it, particularly in terms of corrosion and the adhesion of biofouling organisms [8]. On the one hand, corrosion is the process of material degradation caused by chemical and electrochemical reactions with the surrounding environment [9]. It leads to the gradual deterioration of a material, resulting in loss of structural integrity and functionality. On the other hand, biofouling refers to the attachment and build-up of living organisms, including microorganisms, plants, algae, and animals, on surfaces that are submerged or in contact with water [10]. These organisms form a self-produced polymer matrix known as a biofilm, which can also contain inorganic components like salts and corrosion products [11]. When any metallic surface is in contact with seawater, it quickly becomes colonized by a diverse range of microorganisms [12]. These biofilms contribute to microbial biofouling and can lead to the accumulation of larger organisms, causing macro-fouling. The primary constituents of biofouling are polysaccharides and water, with the specific composition of the polysaccharides varying depending on the species involved. Common oligosaccharides found in biofouling include glucose, mannose, galactose, xylose, and others [6].

The relationship between biofouling and corrosion is interconnected, as both phenomena can influence and promote each other [13]. Biofouling has the potential to initiate corrosion processes, and in turn, corrosion can create conditions that facilitate biofouling. Consequently, studying and considering both parameters together is essential to gain a comprehensive understanding of their combined effects [14]. A coating that is showing very acceptable results in this regard in the long term are ceramic coatings, furthermore, it is important to note that the material in question does not contaminate or release harmful substances into the marine environment through leaching or other means [15].

Among the array of antifouling properties exhibited by ceramic coatings the main ones are their ability to maintain a low roughness level. Surfaces with a smooth and low initial roughness make it challenging for biofouling organisms to adhere and grow on the surface and the low contact angle which creates a challenging environment for organisms to attach and adhere to the surface during the early stages of adhesion [16].

In this study, an experiment was conducted to assess the antifouling (AF) effectiveness of a ceramic coating when exposed to seawater in a static condition over a duration of two years. The ceramic material was applied using electrophoretic deposition to create a conformal coating through a high temperature process. It is a versatile and widely used method to apply coatings to various materials, including metals, ceramics, polymers, and composites [17]. The primary objective was to reduce biofilm adhesion on the surface and investigate how the newly coated surface affected the composition and structure of the resulting biofilms.

II. MATERIALS AND METHODS

A. *Research area*

Santander Bay, particularly the breakwater jetty of the Molnedo Dock, was selected as the ideal location to install the experimental samples. This decision was made based on the advantageous abiotic and biotic conditions that occur in port environments. By conducting the study in this setting, the researchers aim to replicate the most challenging experimental conditions from the perspective of biofouling development. Additionally, the proximity of the location to the Biofouling laboratory of the University of Cantabria played a significant role in the selection process.

B. *Experimental phase*

The primary objective of this study was to assess the behavior of three different ceramic coatings in comparison with two conventional paint coatings (Intersleek 1001 and Intersleek 970) in preventing marine biofouling on carbon steel surfaces. To apply these coatings, the method of electrophoretic deposition was used. Table I shows the composition of the three ceramic coatings.

The samples were subjected to visual examinations and monthly tests following the guidelines outlined in ASTM D790. The study aimed to evaluate both the coatings' ability to resist fouling by marine organisms and their effectiveness in protecting against corrosion. Separate investigations were conducted for each aspect.

Steel structures located in coastal and offshore areas are classified as C5-M and must meet specific requirements for protective paint systems according to ISO 20340. Before applying the coatings, the surfaces of the samples were thoroughly cleaned by blasting to achieve the desired levels of surface roughness (Sa2.5 or Sa3) and cleanliness as specified in the ISO 8503 and ISO 8501 standards. The paint coatings were applied with a total thickness of 300 μm.

TABLE I
CERAMIC COATING COMPOSITION

Elements (%)	Blue (Co)	White (Ti)	Black (Mn-Fe)
O	57.81	58.24	59.70
Si	23.79	19.08	21.59
Na	8.09	9.47	7.19
Al	0.92	3.73	1.79
K	3.78	2.27	1.43
Ti	3.29	5.44	1.12
Co	2.34	-	-
Mg	-	0.77	-
P	-	1.01	-
Ca	-	-	1.42
Mn	-	-	1.26
Fe	-	-	4.09
Cr	-	-	0.45

To enhance adhesion and safeguard the substrate against corrosion, dense metallic under-layers were deposited using high velocity air-fuel spray processes. The samples were cleaned using FreeBact20 and sterile water, air-dried, and photographed before being placed in seawater.

The mass of the samples was averaged monthly following the guidelines of ASTM D6990-05 to evaluate the weight variation of the adhered biofouling. The experiment spanned a duration of two years, during which the samples were immersed in shallow marine environments at a depth of 0.6 m. Additionally, the temperature and chemical parameters of the seawater were measured monthly throughout the experiment thus evaluating its influence on biological development.

III. Results and Discussion

Aligning with the findings of [14], the initial surface roughness of antifouling coatings holds significant importance in inhibiting the attachment of biological organisms to the surface. Fig. 1 shows the surface topography of the three types of ceramic coatings.

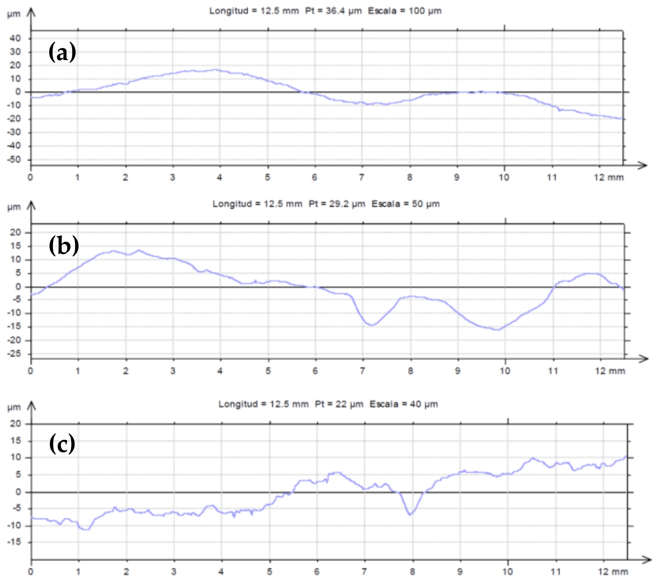

Fig. 1. Surface topography of the three ceramic coatings: a) Co-based enamel, b) Ti-based enamel and c) Mn–Fe-based enamel.

The data extracted from Fig. 1 reveals that the cobalt-based ceramic coating exhibits a roughness measurement of 0.245 µm, the titanium-based ceramic coating has a roughness measurement of 0.189 µm and the Mn–Fe-based ceramic coating presented a roughness measurement of 0.437 µm. Therefore, the presence of extremely low roughness values created a challenging environment for organisms to adhere to the coating surface in the initial stages.

Fig. 2 presents a quantitative representation of the weight changes observed in the experimental ceramic samples as a result of biological growth at the conclusion of the 12th and 24th month, respectively, of exposure in the marine environment.

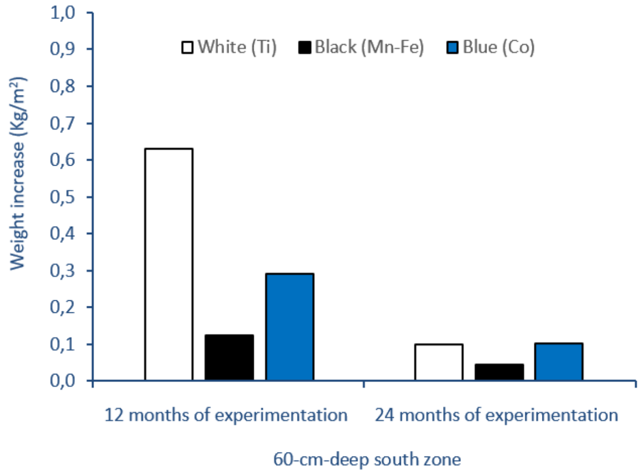

Fig. 2. Quantitative analysis of weight-based biological growth on three different ceramic coatings samples.

The weight of the ceramic coatings was observed to be lower in month 24 compared to month 12 of exposure. This can be attributed to the continuous detachment and development of biofouling on the ceramic coating. Furthermore, by month 24, the abiotic factors became less favourable for biological growth, contributing to the reduced weight of the coatings.

In relation to the commercial paints, a gradual deterioration of the paint was observed. However, it is worth noting that during the initial year of exposure, the paints exhibited better results compared to the ceramic coatings. Nevertheless, significant degradation occurred, leading to the convergence of data between the paints and ceramic coatings at month 24. In simpler terms, while the performance of paints worsened over time, the ceramic coatings maintained relatively consistent values throughout the experiment.

Figure 2 illustrates the accumulation of biofouling on coatings infused with titanium, manganese and cobalt resulting in values of 0.63, 0.12, and 0.29 Kg/m2, respectively, after twelve months of exposure and 0.17, 0.08, and 0.18 Kg/m2, respectively, after twenty-four months of exposure.

Upon the conclusion of the experimentation, a thorough visual inspection was conducted on the samples coated with ceramic enamel. Remarkably, no evidence of corrosion was observed, thus validating the enduring and highly effective protection provided by the ceramic enamel against marine corrosion.

IV. Conclusion

The research findings have conclusively demonstrated that ceramic coatings serve as an effective and long-lasting solution against both marine corrosion and biological adhesion. The primary mechanism behind their antifouling properties lies in the inherent low roughness exhibited by ceramic glazes, which significantly hinders organism adhesion. Furthermore, the specific chemical composition of ceramics has shown varied effects on the antifouling performance of the coatings. Notably, the manganese-based ceramic coating exhibited a remarkable 125% reduction in biofouling compared to the cobalt-based coating and an impressive 112.5% reduction compared to the titanium-based coating after two years of exposure in a marine environment.

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