

Bioactive Ceramic Coating Solution for Offshore Floating Wind Farms

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ABSTRACT: Biofouling is a natural phenomenon that consists of the accumulation of living organisms on an artificial surface submerged or in contact with water like Offshore platforms. This study highlights the need for offshore floating wind farms structures to consider the choice of material used in offshore applications to minimize microbial-associated and corrosion problems. For this purpose, differences in the total of seawater biofouling attached on two coated paints and three ceramic coatings in carbon steel for offshore structures were evaluated and compared. All ceramic coatings were made of incorporating, by electrophoretic deposition, active ceramic particles against biofouling as copper, silver, zinc and titanium. This experiment consisted of testing ceramic coatings and conventional paints in a real environment with high biological activity and at the same time in a shallow marine environment for a period of 1 year, which provided positive comparisons with the standard system (ASTM-D3623) for using in protecting offshore marine structures.

1 INTRODUCTION

Corrosion is defined as the chemical or electrochemical reaction of a metal or an alloy with its environment whose consequences have become a major problem in offshore environments due to extreme operating conditions and the presence of aggressive corrosive elements. In the design of any metal structure, it is extremely important to consider the corrosion resistance that it offers since it represents the difference between trouble-free long-term operation and costly downtime. Steel structures situated above the seawater in the so-called atmospheric zone are in a high corrosivity category, with a corrosion rate in the range of 80 - 200 μm per year [6]. The most used method in the prevention of external corrosion is to cover the exposed surfaces with a high-efficiency coating. In the case of offshore structures, the conventional approach consists of using polymeric coatings, but this method requires

periodical maintenance that includes a number of challenges associated with the physical environment in which the work takes place. Thus, i.e., the application of coating systems for offshore steel towers in modern facilities can cost up to 15 to 25€/m, depending on the work conditions and on the coating systems. Repairs of the corrosion protection can be from 5 to 10 times more expensive and total cost can easily rise to more than 1,000 €/m² [11, 13].

Offshore floating wind farms structures act as artificial reefs, supporting an undesirable accumulation of marine life by offering habitat for microorganism, algae, fish and in-vertebrates. Biofouling is defined as the adhesion and accumulation of biotic deposits on submerged or wetted surfaces, and the deposits consist of organic components, such as microorganisms, plants, algae, or animals, associated in a self-produced polymer matrix called a biofilm, which can also include inorganic

components, such as salts and/or corrosion products [4]. These biofilms cause microbial biofouling and can also result in the accumulation of macro-organisms, resulting in macro-fouling [10]. Biofouling consists primarily of polysaccharides and water. The components of polysaccharides vary depending on species but typically include repeating oligosaccharides such as glucose, mannose, galactose, and xylose, among others [9]. The effects caused by biofouling and corrosion are closely related to each other since biofouling may induce corrosion, but corrosion may also induce biofouling. Therefore, it is necessary to study both parameters in conjunction. Nowadays, chemically active antifouling paints with biocides or non-stick fouling release coating is practically the only method of fouling control. Today there is still debate regarding the most optimal coating systems for offshore structures [12, 15]. The service life of anti-fouling paints is defined by the coating thickness and has a considerable environmental impact besides from continuously maintenance operations due to limited life cycle and durability [17]. While control of corrosion for shipping is an enormous market, dynamic performance coatings for ships are the subject of intense development by paint companies and other researchers and specific needs of this sector are intensely cost sensitive [18]. Antifouling paints used in floating offshore structures require periodic maintenance. This maintenance is carried out in dry dock, with its respective costs of inactivity and transport, since an in-situ maintenance is difficult and expensive. For this reason, it is required a long term solution to corrosion and biofouling and coating systems used for shipping are too short lived to be entirely suitable. Current antifouling paints for floating offshore structures use similar formulations that are used in the shipping industry and rely either on biocides that gradually leach out of the coating (damaging surrounding ecosystems and only providing a limited time period of effective bio-activity) or on so called 'self-polishing' systems that require a certain water velocity to remove accumulated growth (unsuitable for static structures). At present, apart from the marine coating solutions, the corrosion protection is accomplished by coupling a less noble (i.e., more electronegative) metal in the structure. Sacrificial anodes can provide added protection in immersed regions, the problem is that they are costly to install and re-place and provide no protection in splash and tidal zones where corrosion is most severe. Organic paint coatings have limited lifetimes (<10 years) before needing substantial maintenance and repair [19]. The main problem with a conventional marine coating is the rapid corrosion of the underlying steel in potential areas that have lost protection due to scratching, etc. For this reason, the offshore industry tries to detect new needs to implement new solutions to overcome the challenges of current painting systems in terms of durability associated to corrosion protection, mechanical resistance and fouling avoidance. A novel alternative that is showing competitive results for similar and harsh environments are related to ceramic enamel coatings which have an excellent chemical and abrasion resistance due to their sintered vitreous structure.

Ceramic materials are attractive materials due to their characteristics like high chemical resistance, wear resistance, thermal resistance and corrosion resistance [16]. Ceramic materials have this unique performance. For example, ceramic tiles are coated with ceramic glaze layers to provide an easy to clean, wear resistant and high aesthetic surface. Ceramic coatings are used for instance in the protection of airplane turbines, where ZrO_2 is applied by Thermal spray; also chemical reactors are protected with a ceramic enamel coating. The advantage of ceramic enamel coatings is the capability to tailor the properties of the vitreous matrix with other oxide and functional particles [2].

Nowadays, there is two kinds of ceramic coatings: enamels or glazes and both are made up of a mixture of molten glass and diverse additives. The molten glass can have diverse compositions, being made up of oxides like SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , K_2O , CeO_2 , MgO , ZnO , CaO , ZrO_2 , TiO_2 and adhesion promoters for metal surface like, CoO_2 , NiO , Fe_2O_3 , MnO ; the characteristic that a glass can be adjusted in composition allows modelling their final properties, like thermal expansion coefficient, melting point, chemical resistance and biofouling adhesion. Ceramic coatings can be modified by addition of raw materials like quartz, titanium oxide, zircon silicate or ceramic pigments to adjust to the metal type and final application product [5]. At present the use of ceramic enamel to protect metallic structures has been limited by many factors. For example, conventional slurry application techniques (e.g. dip coating, wet spraying) are not suitable for large parts except for chemical reactors and panels. Even more importantly, a sintering thermal treatment is needed to consolidate the coating, that could be incompatible with some engineering materials (e.g. light alloys, quenched and tempered steels, etc.), as they would bring about unacceptable microstructural changes accompanied by a loss of mechanical strength apart from warpage and distortion of the coated items.

The electrophoretic deposition processes encompass a family of coating deposition techniques characterized by the use of a high-velocity and/or high-temperature gas stream to project softened/molten droplets of the coating material towards the substrate. Whilst the droplets may attain very high temperatures (hence, even refractory coating materials can be processed), the substrate remains relatively cold as it is rapidly scanned by the gas+droplets stream along typical raster patterns [8]. A large variety of coating/substrate material combinations is therefore possible; in particular, ceramic enamels can be sprayed [1] onto relatively cold substrates, thus avoiding overheating, microstructural alterations and distortions. Moreover, thermal spraying techniques are applicable to large structures and, with due adjustments, they are portable for on-site work [14]. The main problem to obtain tight, corrosion-resistant ceramic enamel coatings by thermal spraying resides in the typical voids and gaps between the flattened droplets (lamellae), microcracks within the lamellae (due to their rapid cooling after deposition), and entrained gases. These limits have, up to now, hindered the industrial uptake of thermal spray glass coatings which have been developed and validated at lab-scale

for a variety of applications on metallic and ceramic substrates [3].

The experiment carried out for this study evaluated the antifouling (AF) action of a ceramic coated statically exposed to the seawater. The conforming of the ceramic materials was carried out by electrophoretic deposition. The aim was to minimise the biofilm adhesion on the surface and study the effect of new coated in composition and structures of the biofilms produced. The scientific relevance of this research in AF is very highlight because it involves a new environment friendly technology against biofouling to improve efficiency and productivity in offshore floating wind farms structures.

2 MATERIAL AND METHOD

2.1 Area of study

The study area chosen for the research was the breakwater jetty of the Molnedo Dock (43° 27.713' N, 03° 47.541' W) after the authorization was granted by the Santander Port Authority for experimental activities to the Biofouling Research Group of the University of Cantabria on September 23, 2020.

2.2 Preparation of samples

The conforming of the three different ceramic materials will be carried out by electrophoretic deposition over carbon steel (A569/A569M6, 3 mm thick by 200 mm x 300 mm) which will be visually examined and tested once a month according to ASTM D790. Table 1 shows a comparative table with the elements of the three ceramic coatings used in the investment. During the study, not only were the antifouling properties against biofouling verified, but their protection against corrosion was also verified, so the two studies were carried out in parallel.

Table 1. Ceramic composition adjustment.

Coating	Base Material A-569									
	Elements (%)									
	O	Na	Al	Si	K	Ti	Co	Mg	P	Ca
Blue glaze BK	57,81	8,09	0,92	23,79	3,78	3,29	2,34	-	-	-
White glaze	58,24	9,47	3,73	19,08	2,27	5,44	-	0,77	1,01	-
Black glaze	63,36	7,63	1,92	22,91	1,52	1,18	-	-	-	1,51
Light Grey paint Coating	Intersleek 1001									
Dark grey paint Coating	Intersleek 970									

According to ISO 20340, steel structures for coastal and offshore areas are classified as C5-M (due to the high salinity) and should be coated where minimum requirements for protective paint systems. In this way, before coating application, the sample surface was blast cleaned in order to get a final surface roughness of Sa2.5 or Sa3 (ISO 8503) and cleanliness (ISO 8501). After blast cleaning (not exceed rating 2 of ISO 8502-3), dust and blast abrasives were removed from the surface. For the application of the first coat, the metal surface was completely dry, clean, free from oil/grease, and had the specified roughness and cleanliness. The paint coating applied had a total thickness of 300 µm.

The atomistic deposition processes were the method used for the application of ceramic coatings to get lower deposition rates and thinner coatings. Firstly, it was the deposition of dense metallic underlayers between the functional ceramic topcoat and the substrate by the high velocity air-fuel spray process using compressed air instead of oxygen. The goal of this is to protect the substrate from corrosion and enhance the adhesion strength of the ceramic enamel top layer. HVAF torches proved to be a viable means of depositing watertight metallic coatings with low flaw capacity generating even higher particle velocities and lower particle temperatures. In addition, following the manufacturer's instructions, a coating with a biocide free silicone coating (Silicone FR) were applied to carbon steel specimens. Finally, before sample's installation in seawater, they were cleaned with FreeBact20 (AquaFix, Satsjbaden, Sweden) and sterile water and airdried, and also photographed.

According to the standard specifications of the American Society of the International Association for Testing and Materials (ASTM), the surface topographies of the samples were denoted. Table 2, 3, 4, 5 and 6 show a comparison between the initial state of the samples and the final chemical composition of the experiment. Their surface roughness values were measured using a surface roughmeter (Mitutoyo, SurfTest SJ-201 Series) in accordance with the guidelines established in the standard ASME/ANSI B46.1-2009.

Table 2. Sample 1 assayed.

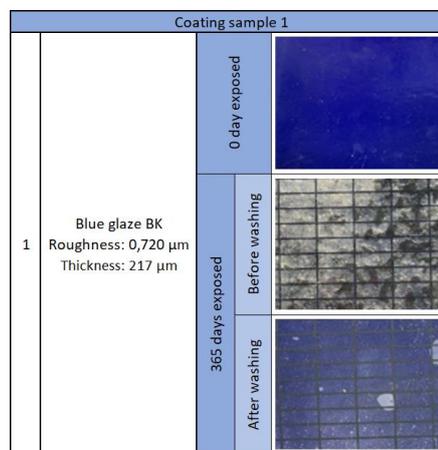


Table 3: Sample 2 assayed.

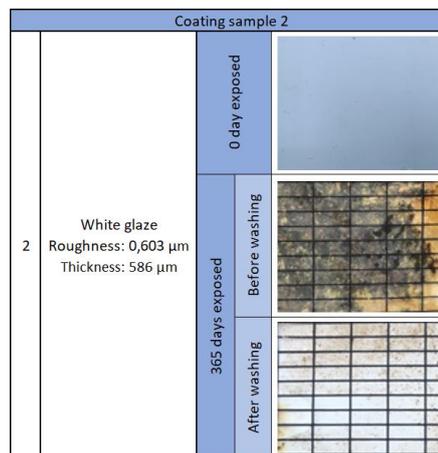


Table 4. Sample 3 assayed.

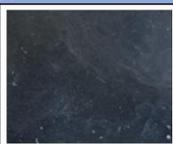
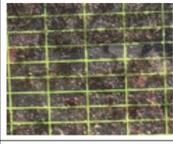
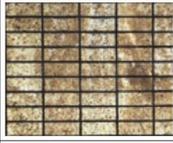
Coating sample 3				
3	Black glaze Roughness: 0,893 μm Thickness: 307 μm	0 day exposed		
		365 days exposed	Before washing	
			After washing	

Table 5. Sample 4 assayed.

Coating sample 4				
4	Light grey paint coating Roughness: 70 μm Thickness: 300 μm	0 day exposed		
		365 days exposed	Before washing	
			After washing	

Table 6. Sample 5 assayed.

Coating sample 5				
5	Dark grey paint coating Roughness: 72 μm Thickness: 300 μm	0 day exposed		
		365 days exposed	Before washing	
			After washing	

2.3 Biofouling assessment

The experiment tested and analyzed the behaviour of three ceramic coatings compared to two conventional paint coatings, all of them over carbon steel, against marine biofouling. Samples, with same geometry, were submerged during 365 days in the shallow marine environments, at a depth of 0.5 m.

At the end of the experiment, samples were analyzed in the laboratory as follows: i) Measurement of barnacle adhesion strength in shear as follow ASTM D5618-94. This test method covers the measurement of barnacle adhesion in shear to surfaces exposed in the marine environment, ii) analysis

quantitative and qualitative of biofouling on sampled surfaces and analysis optical by microscope of biofouling as qualitative analysis.

The standard practice for evaluating biofouling resistance and physical performance of marine coating system ASTM D6990-05 establishes a practice for evaluating degree of biofouling settlement on and physical performance of marine coating systems when panels coated with such coating systems are subjected to immersion conditions in a marine environment.

2.4 Experimental setup

Sample's installation in sea water was carried out on 06 February 2020 and were exposed until 06 February 2021 in realistic conditions of exposure of the submerged zones in the breakwater jetty of the Molnedo Dock. Samples were checked monthly by visual inspection following the ASTM D 3623-78a and roughness measurements were taken every two months.

Temperature of seawater were measured once a month during the experiment period. The chemical parameters of seawater were measured once a month during the experiment period.

3 RESULTS AND DISCUSSION

AF technologies for marine applications are of large interest mainly due to the economical and environmental benefits. Table 2 shows the antifouling performance of three ceramic coating in comparison with two convectional paint coating after being exposed for a period of 12 months in natural seawater. The development of a biofilm is influenced by the properties of the substratum, and it has been observed that biofilms develop more quickly and attain a greater biofilm thickness on rougher surfaces [9]. The sample coating No. 1 was covered by 85% of hard fouling organisms after 365 days and produced at 22% losses of AF coating on the surface. Furthermore, it was fouled by 13% of filamentous, 27% of barnacles, 40% of algae and 20% biofilm. The sample coating No. 2 was covered by 78% of biofouling organisms and produced at 25% losses of AF coating on the surface. Furthermore, it was fouled by 18% of filamentous, 20% of barnacles, 32% of algae and 30% biofilm. The sample coating No. 3 was covered by 90% of biofouling organisms and produced at 19% losses of AF coating on the surface. Furthermore, it was fouled by 15% of filamentous, 4% of barnacles, 29% of algae and 52% biofilm. The sample coating No. 4 was covered by 100% of biofouling organisms and produced at 76% losses of AF coating on the surface. Furthermore, it was fouled by 17% of filamentous, 5% of barnacles, 25% of algae and 53% biofilm. The sample coating No. 5 was covered by 95% of biofouling organisms and produced at 74% losses of AF coating on the surface. Furthermore, it was fouled by 20% of filamentous, 3% of barnacles, 27% of algae and 50% biofilm. Analyzing these parameters, coating No. 2 had the best antifouling release performance under static conditions.

The samples coating No. 4 and No. 5, silicon-based, produced the depletion and leaching of these silicon-based biofouling as the surface wears out, leading to changes in the surface chemical composition (eventually also topography) and lowering of the AF performance. This explains why the coatings No. 4 and No. 5 did not have long durability and high AF performance levels all through the coating life-cycle.

4 LIFE CYCLE ASSESSMENT

In a life cycle assessment (LCA), biofouling adhesion on ceramic coatings is compared to the equivalent adhesion on conventional paints. The LCA study consists of four stages under the ISO 14040 guidelines:

Stage 1: This experiment consisted of testing ceramic coatings and conventional paints in a real environment with high biological activity and at the same time in a shallow marine environment for a period of 1 year, which provided positive comparisons with the standard system (ASTM-D3623) for using in protecting offshore marine structures. To compare the different ceramic coatings with conventional paints, the samples were extracted once a month to check their weight, the variation in roughness of the fouling layer, and photograph them.

Stage 2: In this step, inventory analysis gives a description of materials used in the ceramic coating elaboration, which appear in table 1.

Stage 3: Ceramic coating systems may provide a long life-time due to their high biocorrosion-erosion resistance and excellent coating adhesion to steel surface, together with non-degradation (UV resistance) and non-lixiviation of materials during their whole life-time, so they may be a more durable and environmentally friendly solution than the currently used biofouling protection systems.

Stage 4: The results of the study shows that the antifouling performance of the ceramic coating No. 2, had the best antifouling release performance under static conditions. In comparison with two convectional paint coating after being exposed for a period of 12 months in natural seawater. The results are explained in detail in the section 2 "Results and discussion".

5 ECONOMIC ASPECTS

A 30% of failures in ships and other marine equipment are consequence of marine corrosion, with an annual cost of over \$1.8 trillion [7]. The result of these studies has shown that ceramic coatings offer distinct advantages for long-term corrosion protection over conventional coatings for marine service. This factor makes it possible to substantially reduce the maintenance of the structure and avoid dry-docking in the case of floating structures. The cost of one dry-docking can be as high as \$0.2M to \$0.7M. Dry-docking can also adversely affect the flexibility of operational schedules by taking offshore structure out of service.

Ceramic coating is applied by Thermal spray. One method to estimate the cost of thermal spray application method is per square inch. It can range from under \$1 to spray some lower cost materials to more than \$50 for higher value components with expensive coatings. Ceramic particles are a relatively inexpensive material, which makes this coating economically viable.

6 CONCLUSIONS

The results of this study indicate that biofouling is extensive and formed by a diverse group of microorganisms in coatings with different compositions. Therefore, the addition of different compositions into glass of coating affects the number and species of microorganisms attached to the surface.

One of the factors that directly affect microorganism's development on coating surface is its roughness, thus maximizing the negative consequences of biofilm accumulation. The low roughness offered by ceramic coatings hinders biological adhesion, as has been demonstrated in the marine field tests carried out for a year, even under static conditions. The functionality of ceramic coatings is based on antifouling efficiency relies on low adhesion strength and diverse AF additives to reject biofouling adhesion. The ceramic coatings with suitable compositions are recommended to the offshore anti-biofouling applications.

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