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Antifouling properties of different Plasma Electrolytic Oxidation coatings on 7075 aluminium alloy

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ABSTRACT

In this work the antifouling properties of different Plasma Electrolytic Oxidation (PEO) coatings produced on samples of 7075 aluminum alloy were studied and compared with those of samples treated with more commercial treatments, such as traditional anodizing and painting, and untreated ones. After the treatments, the different samples were characterized through scanning electron microscope (SEM) observations. The antifouling tests were carried out immersing the different coated samples in the Piave river for a month, collecting one sample series every week. After the immersion test, to evaluate the colonization by microalgae, the samples were investigated through stereomicroscope, inverted light microscope, and SEM. Results showed that the addition of silver/copper particles in the electrolyte does not modify the PEO process, obtaining thick and adherent coatings that contain particles both inside and outside of the pores. As regards the antifouling properties, surface PEO treated with copper particles exhibited a good effect inhibiting the colonization by microalgae.

1. Introduction

The appearance of aluminum alloys as an alternative material in boat and ship constructions is related to the 1960's (Holtyn, 1966) and, since then, aluminum is recognized as an advantageous material in shipbuilding by marine engineers and naval architects. In particular, it finds application in small boats as police or patrol boats, fishing vessels, fire boats or fast passenger vessels as catamarans (up to 400 passengers) in Europe, North America and especially in Asia (Allan, 1997). The lightweight, superior mechanical properties and corrosion resistance of aluminum alloys has dictated their use in many of these applications. Using aluminum, naval architects can design ships and boats with high-speed capability, long life, high payloads and low maintenance costs, as well as a high recycle value (Holtyn, 1972). The low density of aluminum, combined with high strength, toughness, and corrosion resistance, allow vessel designers to achieve weight savings of 15–20% over steel or composite designs (ASM International, 2017a; ASM International, 2017b). Weight savings equate to higher speed, increasingly demanded for vessels such as ferries, patrol boats, military craft, hydrofoils, fishing vessels, cargo vessels, leisure craft, and work boats. The weight saving improves the ship stability allowing design of narrower ships (Brown, 1999). However, aluminum structures in marine environment suffer of some corrosion problems especially connected with fouling (Davis, 1999).

Biofouling is a common problem on man-made objects submerged in the waters throughout the world (Satheesh et al., 2016; Wang et al., 2016). The biofouling growth on a substrate in the aquatic environment is a complex process, which consists in the first moments in a binding of glycoproteins, polysaccharides and proteoglycans, dissolved in the water, followed by an initial biofilm formation, constituted by bacteria, protozoa, and microalgae, through the secretion of adhesive extracellular polymeric substances (EPS) (Mejdandžić et al., 2015). The colonization proceeds with the final settlement of invertebrate larvae and algal spores (Wahl, 1997; Maki, 2002).

Biofouling on submerged surfaces in the marine environment has considerable ecological and economical importance, besides particularly serious implications for shipping, offshore aquaculture, and coastal industries (Gerhart et al., 1988; Armstrong et al., 2000; Cassé and Swain, 2006; Qi et al., 2008; Patil and Anil, 2015). The effects are mainly due to the loss of productivity in aquaculture (De Nys and

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Guenther, 2009) or increased costs of fuel to shipping, as well as the costs associated with ongoing prevention, management and control (Callow and Callow, 2002; Jackson, 2008). Therefore, the use of antifouling coatings in the marine environment has a long history. In particular, often organic coatings containing metallic species working as antifouling species are produced (Tang and Cooney, 1998; Chambers et al., 2006). The majority of tin-free antifouling paints currently available contain copper (Cao et al., 2011).

Organic coatings containing copper are already described in literature and the mechanism of action as antifouling compound is due to release of copper ions (Nirvan et al., 1982; Moreton, 1986; Callow, 1990; Del Amo et al., 1990; Ashraf and Edwin, 2016).

Moreover, even though the high cost of silver prevents its extensive application, the antifouling properties of organic coatings containing silver, as well as silver nanocomposites, have been recently studied (Neser and Kacar, 2010; Liu et al., 2014; Szabóa et al., 2014; Selim et al., 2015). Elementary silver, in detail, is believed to function as antimicrobial either as a release system for silver ions or as contact-active material (Ho et al., 2004).

Nowadays, one of the most promising techniques to produce coatings that can improve the corrosion resistance of aluminum alloys is the Plasma Electrolytic Oxidation (PEO) (Song and Atrens, 2003). PEO, also called 'Microarc Oxidation (MAO), is a relatively novel surface modification derived from traditional anodizing, but working at higher current densities and potential. This treatment produces a protective oxide ceramic coating on the metallic surfaces (Jiang and Wang, 2010; Li et al., 2013). Many works can be found in literature regarding the improved corrosion performances by PEO coated aluminum alloys in different environments (Hossein and Mehdi, 2014; Xiang et al., 2015; Venugopal et al., 2016). However, no works in literature exist regarding the antifouling properties of PEO coated samples even though, as reported above, the use of aluminum alloys in marine environments is widespread.

In this study the behavior of this new coating in a natural environment like Piave river was studied for the first time, with particular attention whether the coating can improve corrosion or antifouling properties of the aluminum alloy. This study represents a preliminary survey focused mainly on the antifouling effects of the PEO treatment.

In fact, the antifouling properties of different PEO coatings produced on samples of 7075 aluminum alloy, immersed in the estuarine Piave river for four weeks, were investigated through the analyses of the microalgal coverage developed on the substrates. In particular, coatings without additives and coatings containing silver or copper particles, incorporated in the PEO coatings directly during the production process, were tested. Moreover, different substrates without PEO (uncoated sample, an abrasive blasting sample, a conventionally anodized sample, and a sample with a commercial antifouling painting) were also tested as a comparison.

2. Materials and methods

2.1. PEO coating preparation

The different coatings were all produced on 7075 aluminum alloy. The nominal composition of the alloy is reported in Table 1.

Before PEO treatment, the samples were polished following standard metallographic techniques and then degreased using acetone through ultrasound. The PEO electrolyte was constituted by an aqueous alkaline solution with 5 g/l of NaOH and 25 g/l of Na_2SiO_3.

Table 1
Chemical composition of 7075 aluminum alloy.

Al%	Mg%	Zn%	Cu%	Others%
90.7	3.1	4.1	0.9	1.2

The plasma electrolytic oxidation process was carried out using a TDK-Lambda DC power supply of 300 V/8A capacity. During the treatment, the sample worked as anode and the cathode was a carbon steel mesh immersed in the electrolyte. The treatments were performed maintaining a constant current and letting the potential free to vary. The current density used was 0.3 A/cm^2 and the treatment lasted 5 min.

Among the coated samples, traditionally anodized ones were also tested as comparison. For this treatment, it was used a current density of 0.016 A/cm^2 for 25 min in a solution of sulfuric acid 20% using a lead cathode. The temperature of the electrolyte was maintained constant at 18 °C by a thermostatic bath. Other samples were painted: painting was performed sandblasting the samples and laying on the samples first one primer coat of epoxy resin and then two coats of white antifouling painting.

The silver and copper powders were appositely synthesized by hydrometallurgical processes and had average dimension of 0.5 μm and 3 μm respectively, as can be observed in Fig. S1.

These powders were added directly into the electrolyte during the treatments. The concentration of copper and silver in the coatings are respectively 0.8 mg/cm^2 and 0.3 mg/cm^2. Moreover, on the PEO treated samples, a sealing treatment was performed by immerging the samples into boiling water for 15 min.

The samples with copper or silver powders into the coatings were sealed using water added with other copper or silver powders, in order to increasing the amount of particles on the surfaces of the coatings.

After all the samples were coated, one per type was accurately characterized. To achieve this, the samples were first washed with deionized water and ethanol and dried with compressed air. The cross-sections of the treated samples were then cut and mounted in epoxy resin and polished with standard metallographic technique. Both the surface and the cross-section of treated samples were examined by a Cambridge Stereoscan 440 scanning electron microscope (SEM), equipped with a Philips PV9800 Energy Dispersive X-ray Spectroscopy (EDS), to evaluate the morphological features, the thickness of the coating and the elemental composition. The phase analysis was carried out through a Siemens D500 X-ray diffractometer using a nickel-filtered Cu Kα radiation source (λ = 0.15405 nm).

2.2. Antifouling test

After the characterization, seven types of samples, in quadruplicate, were prepared to perform the test for the evaluation of the antifouling properties of the coatings. During the test, all of replicated samples were completely immersed at the 40 cm depth in the Piave river.

The sampling site selected for the test (45.582065 N; 12.652398 E) is near to the river mouth, where the river is deep and tidal action is present. However, the test was performed in late spring, when the river flow is enough to prevent the ascent of the salt wedge. Every week, one series of samples was collected so up to four weeks and fixed with formalin neutralized with hexamethylentetramin. Moreover, the water pH and temperature were measured at every sampling. The test site and physical data are reported in Fig. 1.

2.3. Assessment microalgal colonization

At the beginning, fouling colonization was observed by a Zeiss Stemi 2000-c stereomicroscope. Moreover, to estimate the qualitative microalgal composition, the blocks were scraped by a blade into distilled water and the scraped material was then concentrated in a settling chamber. The microflora samples were observed at a Leitz Diavert inverted microscope. Microalgae were identified using standard keys, in particular for diatoms Peragallo and Peragallo (1897–1908), Hustedt (1930–1966), and Van der Werff & Hulls (1957–1974) were used as reference.

In addition, observations at scanning electron microscope were carried out to identify small microalgae, not detectable at light