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Incorporation of corrosion inhibitor in plasma polymerized allyl methacrylate coatings and evaluation of its corrosion performance

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ABSTRACT

By positioning the layer containing $Ce(dbp)_3$ close to the coating–metal interface, the effective use of the inhibitor is promoted, as the leaching out towards the metal surface is facilitated. The chemical nature of $Ce(dbp)_3$ did not undergo any significant change due to the plasma discharge. The coatings with $Ce(dbp)_3$ were compared with equivalent coatings without incorporated corrosion inhibitor and it was shown that $Ce(dbp)_3$ improved the corrosion performance when the coating was mechanically damaged. Optical evaluation of the coatings showed a significant decrease in the corrosion, especially in the area under the coating. However, the low corrosion resistance values obtained by electrochemical impedance spectroscopy indicate that corrosion was not inhibited all over the scribed area.

1. Introduction

Aluminum 2024 alloy is widely used in the aeronautical industry due to its high mechanical performance. However, the presence of intermetallic phases makes it very susceptible to localized corrosion [1]. An appropriate corrosion protection is therefore necessary for its successful use in engineering and commercial applications. A common technique to protect a metal from corrosion is the application of an organic coating. Such deposition provides passive protection against corrosion by creating a physical barrier between the surface of the metal and the environment [2]. However, if the coating is mechanically damaged, metal is exposed to the environment and corrosion is unavoidable. The incorporation of corrosion inhibitors in coatings offers an active corrosion protection mechanism as they hinder corrosion in areas where the coating has been mechanically damaged [3].

Plasma deposition is a versatile technique used for depositing a wide range of organic compounds on various substrates. Plasma deposition at atmospheric pressure has been recently developed and has the obvious advantage of avoiding all the technological requirements of vacuum technologies, which favors the scale-up for industrial application [4–6]. Several studies were published on the deposition of atmospheric plasma polymers used as protective coatings on metals. Lommatzsch and Ihde used atmospheric pressure plasma jet to deposit organosilicates on aluminum [7]. Bradley and Hammes deposited organic polymers by glow discharge polymerization and measured their electrical properties [8]. Stuart studied

the dielectric properties of plasma polymerized polystyrene [9]. Bardon et al. deposited organosilicate coatings using different plasma carrier gases and studied their anti-corrosion properties [10]. Merche et al. deposited styrene by different atmospheric plasma techniques on various substrates [11]. Batan et al. studied the difference on the chemistry between plasma deposited and wet silane coatings on aluminum [12].

Corrosion inhibitors are frequently used to slow down the corrosion. It is necessary to incorporate corrosion inhibitors in the protective coatings as their addition in the electrolyte is not always possible. Most commonly used corrosion inhibitors of the last decades are the chromates, which have high efficiency in aqueous media and are used for a wide range of metals and alloys. However, the high toxicity, the carcinogenic properties of Cr^{6+} and the consequent environmental hazards lead to a high demand for eliminating the use of chromates and turn to more environmentally friendly corrosion inhibitors [3,13,14].

Rare earth metal–organic compounds offer very good corrosion protection to AA2024 in chloride solutions with low environmental impact [15]. Therefore, they are potential candidates to replace the chromates. Matter et al. studied the corrosion inhibition of Ce compounds and the influence of the oxidation state. In this work, it was shown that Ce^{3+} has considerably higher corrosion inhibition effects compared to Ce^{4+} [16]. Zheludkevich et al. incorporated $Ce(NO_3)_3 \cdot 6H_2O$ in sol–gel coatings and studied them by means of electrochemical impedance spectroscopy (EIS) [17]. Birbilis et al. proposed the use of cerium(III) dibutyl phosphate $(Ce(dbp)_3)$ as a corrosion inhibitor. Phosphates hinder the corrosion by forming complexes on metal surfaces [15]. $Ce(dbp)_3$ inhibits oxygen reduction at the cathodic intermetallic phases and reduces the dealloying of the S-phase (Al_2CuMg) [15]. Scholes et al.
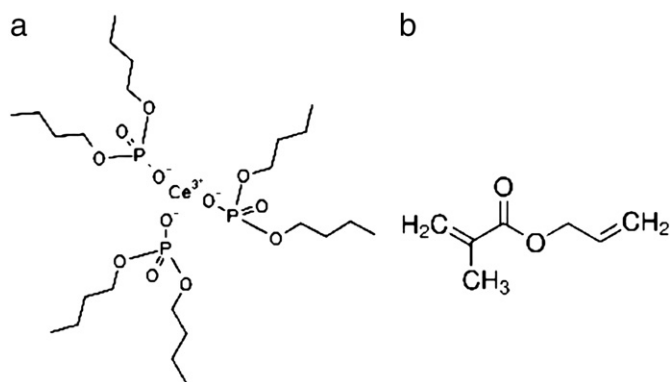
a b

Fig. 1. Chemical structure of a. cerium dibutyl phosphate and b. allyl methacrylate.

found that the dbp$^-$ adsorbs on Al surface, inhibits cathodic reactions on Al$_7$Cu$_2$Fe by the adsorption of Ce^{3+} and possibly dbp$^-$, and also on Al$_3$Fe by the oxidation and deposition of Ce^{4+} hydroxide as a passivating layer on the surface [18]. Garcia et al. studied the inhibition effect of Ce(dbp)$_3$ on AA2024 by means of electrochemical impedance spectroscopy (EIS) and energy dispersive X-ray spectroscopy. It is proposed that Ce^{3+} deposits on the cathodic sites while the phosphates cover the anodic sites of the corrosion area [19]. Mardel et al. incorporated Ce(dbp)$_3$ in epoxy–amine coatings and studied the Ce^{3+} the effect of the incorporated inhibitor in the corrosion performance of the coatings. A minor effect of the Ce(dbp)$_3$ in the chemistry of the epoxy–amine matrix was also observed [20].

The plasma deposition of several organic compounds has been thoroughly studied in the literature but according to our knowledge there are no studies dealing with the incorporation of corrosion inhibitors by plasma deposition. It is therefore a challenge to incorporate a corrosion inhibitor in plasma polymerized coatings without altering both its nature,

being stored as an active compound in the coating, and without significantly altering the general structure of the matrix [21,22]. In this work, allyl methacrylate (AMA) was used as precursor for the plasma deposited coatings. Prior studies showed that (AMA) has considerably high deposition rates and good retention of the ester functionality [23–25]. Then Ce(dbp)$_3$ was incorporated near the plasma polymer–metal interface which was found to be the more effective position for the incorporation of a plasma inhibitor. In these conditions, when the coating is mechanically damaged, the corrosion inhibitor is located closer to the metal and can more efficiently hinder the corrosion reactions. The inhibitor-free top layer restricts the leaching of the inhibitor from the top surface.

2. Experimental procedure

2.1. Materials

The coatings were deposited on a typical aeronautical AA2024-T3 aluminum alloy supplied by ThyssenKrupp Aerospace. Substrates were cut to 40 mm × 50 mm. Prior to the deposition, each substrate was mechanically polished up to 2200 grit to remove its superficial oxide and impurity layer. Argon of 99.99% purity was used as plasma gas. Allyl methacrylate (AMA) of 98% purity was obtained from Sigma-Aldrich (CAS no: 96-05-9) and used as precursor for the plasma deposition. Fig. 1 shows its chemical structure.

Ce(dbp)$_3$ (see Fig. 1) was not commercially available thus it was prepared in the lab based on the procedure described in the literature [18].

In order to spray the prepared Ce(dbp)$_3$ powder in the plasma discharge, it was suspended in a hexane/ethanol mixture. Hexane of 99% purity (80 ml) and ethanol of 99.9% purity (20 ml) were mixed by stirring and Ce(dbp)$_3$ 2.1 g was added. The mixture was stirred overnight, sonicated for at least 1 h and kept stirred until it was sprayed in the discharge. Due to the high amount and its low solubility (1 mM in aqueous
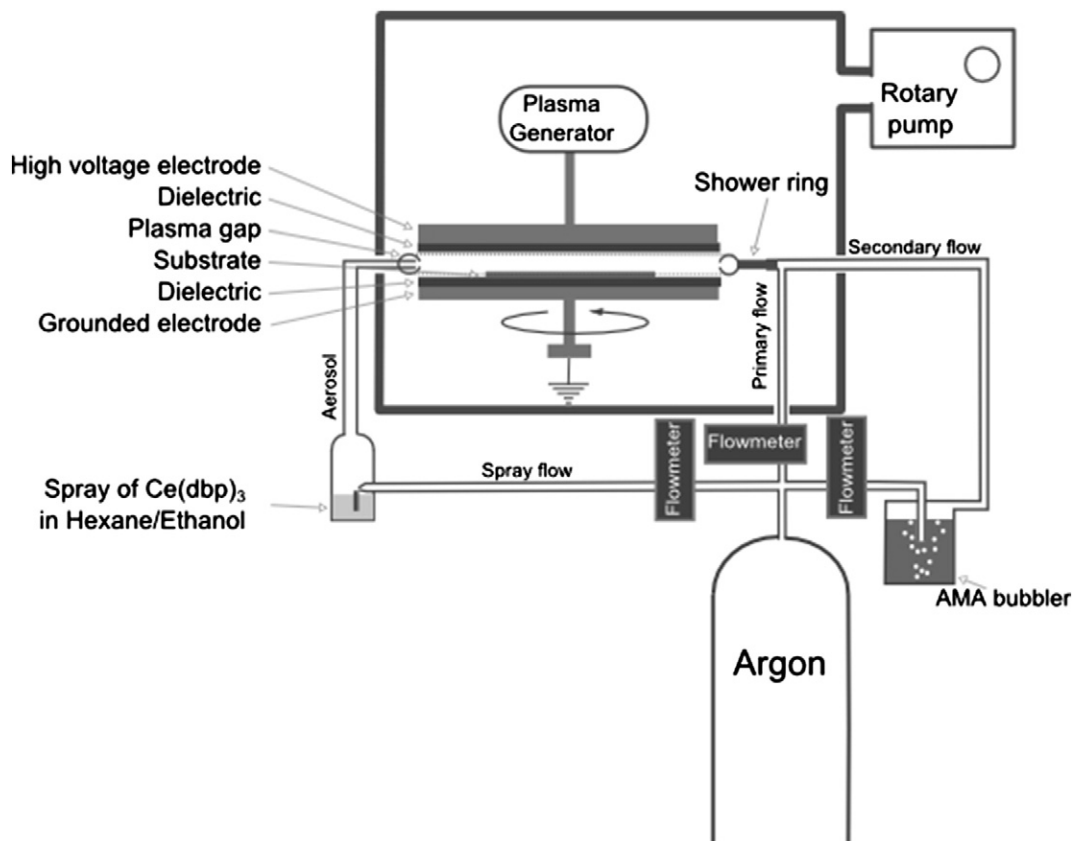

Fig. 2. Schematic diagram of the plasma deposition setup.