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Synthesis of Plasma-Polymerized Toluene Coatings by Microwave Discharge

Suleiman Musa Elhamali

Libyan center for plasma research, Tripoli, Libya

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Abstract: Plasma- polymerized coatings were successfully applied on aluminum alloy, AA2024, surface for corrosion protection. The plasma polymerization process was carried out by low pressure microwave plasma at room temperature. The effect of microwave plasma power on the corrosion resistance of polymer coatings was investigated using the potentiodynamic polarization technique. As the microwave plasma power increased, the relative protective efficiency increased. Polymer coatings on alloy surfaces suppressed both anodic and cathodic reactions. The increment in protective efficiency was due to a higher degree of cross-linking in the coating. These findings suggest that the toluene polymer coatings provide a considerable protection barrier for aluminum alloys.

تصنيع طلاءات التولوين المبلمرة بالبلازما بواسطة التفريغ الكهربائي بالموجات الدقيقة

الكلم ـات المفتاحي ـة :
الحماية من التأكل،
الترس ـيب الكيمي ـائي المعزَّز بالبلازما،
طلاءات التولوين.

المستخلص : قام الباحث بتطبيق الطلاءات المبلمرة بالبلازما بنجاح على سطح سبائك الألومنيوم (AA2024) لغرض الحماية من التآكل. ونُفِّذت عملية بلمرة البلازما بواسطة بلازما الموجات الدقيقة منخفضة الضغط عند درجة حرارة الغرفة. ولدراسة تأثير قدرة البلازما على مقاومة التآكل لطلاءات البوليمر استخدم الباحث تقنية الاستقطاب الديناميكي الفعال. ولوحظ أنه مع زيادة طاقة البلازمـا ازدادت كفـاءة الحمايـة النسـبية لهـذه الطلاءات. وجود الطلاءات البوليمرية على أسطح السبائك أدَّت إلى كبت التفـاعلات الأنوديـة والكاثوديـة. وجاءت الزيادة في كفاءة الحماية نتيجة ارتفاع درجة التشابك المتبادل لسلاسل البوليمر داخل هذه الطـلاءات. تشير هذه النتائج إلى أن طلاء بوليمر التولوين يوفر حاجز حماية كبير من التآكل لسبائك الألومنيوم.

INTRODUCTION

Aluminum and its alloys have excellent mechanical and physical properties for several applications. Because of the unique combination of high strength-to-weight ratio, makes it an ideal material for aerospace applications where weight reduction is considered (Abd El-Hameed & Abdel-Aziz, 2021). The aluminum alloy (AA2024) is one of the most important groups of aluminum alloys that widely used in satellites and space structures(Zuo et al., 2015). Aluminum alloys, on the other hand, are more susceptible to corrosion. This could limit its usage in aerospace industries, where harsh service environments are unavoidable. The most straightforward way to prevent corrosion is to coat the alloy surface to keep it from coming into contact with the environment. For protection, the surface is clad with Al-1Zn, which may reduce fatigue strength(Navas et al., 2015). In addition, Chromate conversion coatingsare commonly applied to aluminum alloy surface. However, the major concern with this coating is its toxicity(Yan et al., 2009). Polymer coatings

***Corresponding author:** Suleiman Musa Elhamali: *suleiman_hamali@yahoo.co.uk* , Libyan center for plasma research, Tripoli, Libya

for corrosion protection of metallic surfaces and their alloys have attracted considerable interest in the fields of research and industry(Ates, 2016; Olajire, 2018). Among recent techniques used to deposit polymer coatings on material surfaces, plasma enhanced chemical vapor deposition (PECVD) (Ardic & Gifvars, 2017; Bowen & Cheneler, 2019; Fermi et al., 2019; Krtouš et al., 2021; Mitev et al., 2016; Zhou et al., 2020). It is a unique technique for fabricating corrosion-resistant polymer coating from a variety of organic materials(Aramaki, 1999; Esbayou et al., 2018; Grundmeier et al., 2003; Jaritz et al., 2019; Natishan et al., 1995; Singh-Beemat et al., 2013; Wang et al., 1996). The obtained coatings are pinhole-free and highly cross-linked(Martin, 2009). In the current research, a polymer toluene coating was successfully deposited on an aluminum alloy substrate(AA2024) with good corrosion abilities.

The effect of microwave plasma power on the corrosion resistance of polymerized toluene coatings, prepared by the PECVD method, was studied systematically. Microwave plasma with high frequencies (2.45 GHz) was used to generate a glow discharge to initiate the plasma polymerization process.

MATERIALS AND METHODS

Polymer coatings were prepared using plasma-enhanced chemical vapor deposition (PECVD) method. Figure 1 shows a schematic diagram of the low-pressure plasma reactor used for PECVD. Plasma polymerization was carried out in a stainless steel vacuum chamber. The chamber was evacuated from atmospheric air to 10^{-5}Torr. Microwave plasma (0-900 W-2.45 GHz) was used to generate a glow discharge necessary to initiate the polymerization process. Aluminum alloy (AA2024), with dimensions of (1.5×1.5) cm^2, were used to deposit the polymer coatings.

The coating quality is directly impacted by the substrate conditions. To achieve a homogeneous, defect-free deposition, the substrates were cleaned using distilled water and acetone. Then they were exposed to Ar plasma in situ to create an oxygen-free surface and improve film adhesion. This process was carried out at 720 watt of Mw power and lasted up to 20 min. Toluene monomer was used as an organic precursor. The PECVD process was run at 100-800 watt, a deposition time of 10-25 minutes, and a toluene/argon ratio of 15%. A spectrometer analyzer was used to characterize the chemical composition of aluminum alloy. Potentiodynamic polarization measurements were carried out in a 3.5 wt.% NaCl solution at room temperature. Aluminum samples, both bare and coated with toluene coating, were connected with an isolated electric wire and all surfaces were painted with Lacquer 45, leaving only 1 cm^2 exposed to the electrolyte. The electrodes were immersed in the solution for 3 hours.The electrode's potential was then swept at 0.166 mV/s from a starting potential of -400 mV vs. E_{corr} to a final potential of 1000 mV vs. E_{corr}. The data acquisition and data analysis were performed using the ACM instrument's software (GILLAC-UK).

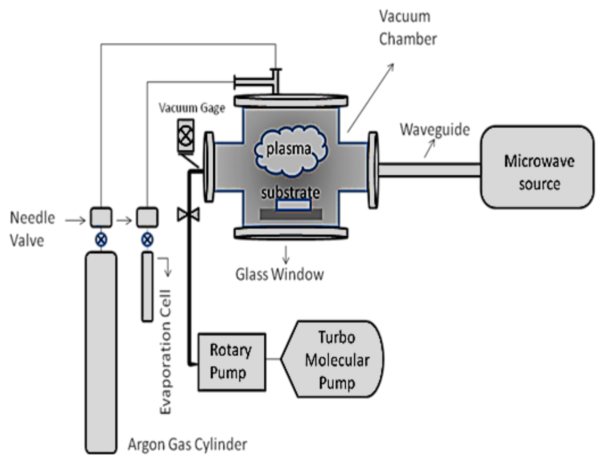

Figure: (1). A schematic diagram of micro wave plasma reactor

RESULTS AND DISCUSSION

The chemical analysis of aluminum alloy, AA2024, is shown in Table 1. A toluene coating was deposited on aluminum alloy surface using low-pressure microwave plasma. All coatings were subjected to the same plasma treatment time of 25 min at room temperature. Ji et al.(Ji et al., 2013)prepared toluene coatings on the aluminum substrate using RF discharge plasma. They reported that the increase in treatment time beyond 30 min led to the formation of a brown powder on the aluminum surface.

Table:(1). Chemical analysis of aluminum alloy (AA2024)

Element	Al	Cu	Si	Fe	Mn	Mg	Cr	Zn	Ti
Wt %	90	3.8	0.5	0.5	0.3	1.6	0.1	0.25	0.15

Figure 2 shows the typical potentiodynamic polarization behavior of as received aluminum alloy, AA2024, in a 3.5 wt. % NaCl solution. In the potential range investigated, the polarization curve displays three unique regions: the active (Tafel) zone, the active-passive transition region, and the limiting current region. The protective efficiency (Pi) and corrosion rate can be derived from the potentiodynamic polarization curve. The following formula was used to calculate the protective efficiency (Pi) of the coating(Enos & Scribner, 1997).

Protective efficiency (Pi)=100 x $(1 - i_{corr} / i^{\circ}_{corr})$ (1)

Where i_{corr} and i°_{corr} represent the corrosion current densities with and without the deposited coatings, respectively. The values were obtained by extrapolating the cathodic Tafel lines of the anodic and cathodic branches of the potentiodynamic curve(Aramaki, 1999; Nozawa & Aramaki, 1999; Tsuji et al., 2000).The slope of the cathodic and anodic branches of the polarization curve determines the anodic and cathodic reactions at the metal/coating interface. Higher slope values are associated withlower anodic and cathodic reaction velocity (Singh-Beemat et al., 2013).The corrosion rate was calculated using the following equation:

$$\text{Corrosion Rate} = (w \times A) / \rho \qquad (2)$$

Where w is the mass of material removed, A is the exposed surface area and ρ is the material density. Table 2 shows the corrosion properties of AA2024 substrate before coated with toluene coating.

Table:(2). Corrosion properties of as received AA 2024 obtained from potentiodynamic curve

E_{corr} (mV)	i^0_{corr} (μA / cm^2)	corrosionrate (mm/year)
-747	11.65±0.05	0.13

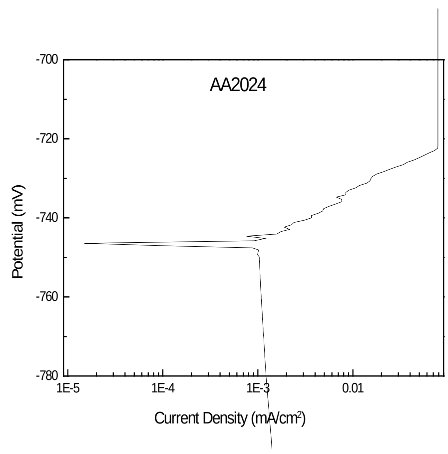

Figure: (2). Potentiodynamic curve of as received aluminum alloy, AA2024, in 3.5 wt.% NaCl solution

The i°_{corr} value of the bare sample increased due to the presence of Cl^{-1} ions in the immersion solution, resulting in severe localized corrosion on the sample surface. Similar results have been reported for sol-gel Ceria coatings on the surface of AA2024 alloy(Zuo et al., 2015).Figure 3 shows the corrosion behavior of the aluminum alloy substrates covered with toluene coatings at different microwave powers. Table 3 summarizes the data obtained from the analysis of each potentiodynamic curve. It clearly demonstrates that the coated samples exhibit a marked improvement in the protective abilities compared to the uncoated one. The I_{corr} values of the coated samples were relatively lower, compared to as received AA2024 alloy. Both the cathodic and anodic branches of the polarization curves were remarkably suppressed by coverage of the electrodes with the toluene coating. Yu et al. have reported that the densely packed toluene films on copper substrate can inhibit for the copper dissolution caused by diffusion of chloride ions to the copper surface(Yu et al., 2003).

Table:(3). Corrosion properties of aluminum electrodes covered with toluene coatings with different m.w. Powers at 15% toluene ratio

Power (watt)	E_{corr} (mV)	i_{corr}(±0.05 μA/cm^2)	P_i%	Corrosion Rate (mm/year)
720	-850	4.20	65.00	0.040
540	-737	4.30	63.00	0.047
360	-742	5.10	57.50	0.053

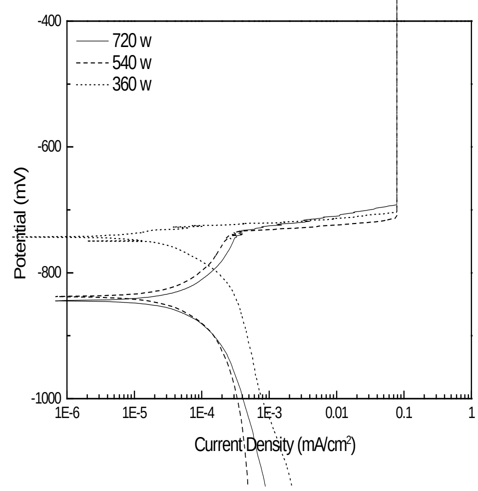

Figure: (3). Polarization curves of AA2024 coated with toluene films as a function of m.w. Power

With an increase in microwave power, the protective abilities of toluene coatings improved slightly. Highest protective efficiency of 65% was obtained at 720 watt. At a power of less than 360 w, the deposition process could not take place. Joo et al.(Joo et al., 2000) studied the Effects of plasma power on the properties of low-k polymer-like organic thin films deposited by PECVD method using the toluene as the precursor. Their results showed that when the plasma power is low enough, it cannot decompose the benzene ring in the toluene precursor. Yu et al.(Yu et al., 2003) reported that the protective abilities of toluene films, prepared by the PECVD method, increased with increasing RF power.

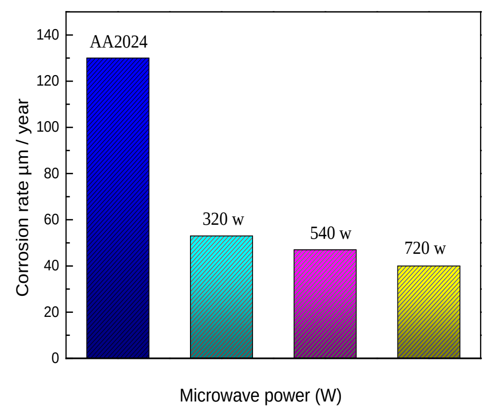

Figure: (4). Corrosion rate of aluminum alloy electrodes as a function of microwave power

Figure4 shows the corrosion rate calculated from Table 2 and Table 3. As shown in Figure4, the corrosion rate decreased in the presence of toluene coating. The coatings deposited at a 15% - 720 W showed an obviousreduction in its corrosion rate value, 40μm/year. This improvement in corrosion resistance was attributed totoluene coatings that inhibit both anodic and cathodic reactions. The toluene coatings were densely packed and firmly linked, which suppressed oxygen reduction and diffusion of an electrolyte onto the alloy surface. The presence of toluene coatings could significantly reduce aluminum's susceptibility to environmental corrosion.

CONCLUSION

Plasma polymerized organic coatings were successfully prepared using plasma enhanced chemical vapor deposition method.

The protective abilities of organic coatings as a function of microwave power were characterized by potentiodynamic polarization test. The presence of organic coatings suppressed oxygen reduction and diffusion of an electrolyte onto the alloy surface. The protective efficiency of the toluene coatings increased with increasing microwave power. The highest protective efficiency was 65% at 720 watts of microwave power. Toluene coatings with increasing microwave power had the higher degree of cross-linking, suggesting that better corrosion protection for AA2024 aluminum alloy.

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