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Corrosion protection by microwave plasma-polymerized organic films

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الملخص

اجتذبت البلمرة بالبلازما اهتمامًا كبيرًا في الحماية من التآكل للعديد من السبائك المعدنية. تم تحضير الأغشية العضوية المبلمرة بالبلازما بنجاح بواسطة الترسيب الكيميائي للبخار المعزز بالبلازما و باستخدام التولوين كبادئة. القدرات الوقائية لأغشية التولوين كدالة لنسبة التولوين و غاز الارجون في محلول كلوريد الصوديوم تم قياسها بالطريقة الكهروكيميائية. ازدادت كفاءة الحماية مع انخفاض نسبة التولوين (60–15%)، وبالتالي انخفاض في معدل التآكل السنوي لأغشية التولوين. ثم الحصول على أعلى كفاءة وقائية وهي 65٪ عند 15٪ من نسبة التولوين. توضح هذه الدراسة أن أغشية التولوين يمكن استخدامها في تطبيقات الحماية من التآكل للعديد من الركائز المعدنية المختلفة وسبائكها.

Abstract

Plasma polymerization has attracted considerable interest in the corrosion protection of metallic alloys. Plasma polymerized organic films were successfully prepared by plasma-enhanced chemical vapor deposition using toluene as the precursor. The protective abilities of toluene films as a function of toluene-Ar gas ratio in a 3.5 wt.% NaCl solution was characterized by the electrochemical method. The corrosion protective efficiency of plasma-polymerized toluene films increased with decreasing the toluene ratio (60-15%). Thus the corrosion rate of aluminum alloy coated with toluene films decreased. The highest protective efficiency was 65% at a 15% toluene ratio. This study shows that the toluene films have the potential to be used in corrosion protection applications of metallic substrates and their alloys.

Keywords: Plasma polymerization, organic films, corrosion protection, aluminum alloy.

Introduction

The fabrication of novel materials and the development of techniques for thin films characterization lead to a broad interest in science and technology. The polymer thin film offers potential development in organic material science. Among many techniques used to deposit polymer thin films, plasma enhanced chemical vapour deposition (PECVD) has been gaining importance for the last several years as a tool to modify material surfaces [1-6]. It is a unique technique for fabricating polymer films from a variety of organic materials. The obtained films are pinhole-free and highly cross-linked. Owing to the excellent properties of the plasma polymerized films, they have attracted considerable interest in various fields of scientific research and technology [7]. There is a significant difference in the mechanisms of polymerization between the conventional methods of polymerization and plasma polymerization [8, 9]. While chemical reactions in conventional polymerization, such as radical or ionic polymerization, are highly specific and, in most cases, predictable, the chemical reactions in plasma polymerization are generally very complex and involve multiple reaction pathways, resulting in the formation of a diverse range of species [10].

Corrosion is the degradation of material properties due to interactions with their environments, and corrosion of most metals is inevitable. It can be mitigated by many methods, such as coatings, cathodic protection, materials selection, chemical inhibitors, and environmental change. Polymer coatings for corrosion protection of metallic surfaces such as magnesium, iron, steel, aluminum, copper, and their alloys have attracted considerable interest in the fields of research and industry. [11, 12]. Plasma enhanced chemical vapour deposition (PECVD) appears to be an important technology for the surface modification of metallic materials to increase their corrosion resistance [13]. The process is carried out at low pressure and low temperature, resulting in a polymerized film with a higher cross-linking density than conventional films. This study reports the effects of toluene content on the corrosion resistance of polymerized toluene films prepared by PECVD method.

Experimental approach

Polymer- like films were grown using plasma-enhanced chemical vapor deposition (PECVD) method. Figure 1 shows a schematic diagram of the low-pressure plasma reactor used for PECVD method. Plasma polymerization was carried out in a stainless steel vacuum chamber. The chamber 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 deposition process. Aluminum alloy (AA2024) substrates, with dimensions of (1.5×1.5) cm^2, were used to deposit the films. The film 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 microwave 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 10-100%. Potentiodynamic polarization measurements were carried out in a 3.5 wt.% NaCl solution at room temperature. Aluminum samples, both bare and coated with toluene film, 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).

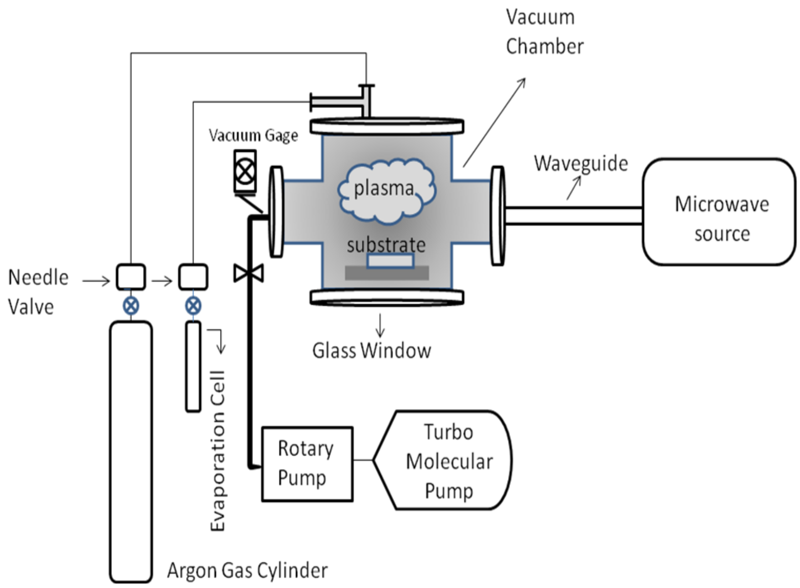

Figure 1. A schematic diagram of micro wave plasma reactor

Result and discussion

A toluene film was applied to the aluminum surface using low-pressure microwave plasma. All films were subjected to the same plasma treatment time of 25 min at room temperature. Ji et al. [14] 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. Figure 2 shows the typical potentiodynamic polarization behavior of bare 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 film [15]:

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

Where i_{corr} and i°_{corr} represent the corrosion current densities with and without the deposited film, respectively. The values were obtained by extrapolating the cathodic Tafel lines of the anodic and cathodic branches of the potentiodynamic curve [16-18]. 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 with lower anodic and cathodic reaction velocity [19]. 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 1 represents the corrosion properties of AA2024 alloy before coated with toluene film.

TABLE 1. Corrosion properties of as-received AA2024 obtained from potentiodynamic curve

E_{corr} (mV)	i^0_{corr} (μA / cm^2)	Corrosion Rate (mm / year)
-747	11.65 ± 0.05	o.13

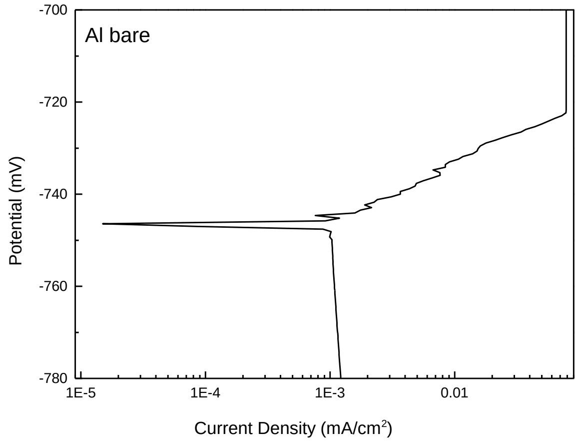

Figure 2. Potentiodynamic curve of AA2024-bare in 3.5 wt.% NaCl solution

The corrosion behavior of the aluminum alloy substrate coated with toluene films at various toluene/argon ratios is shown in Figure 3. The obtained results are summarised in Table 2.

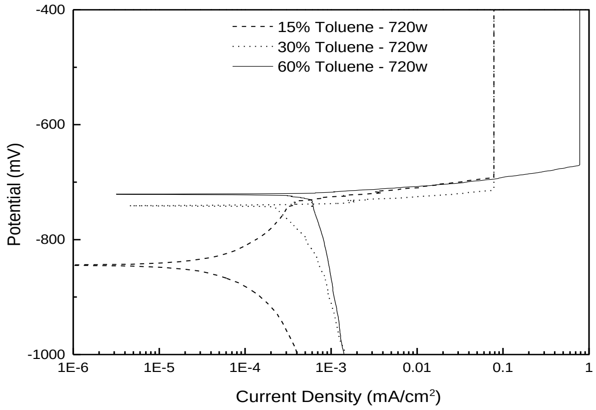

Figure 3. Polarization curves of AA 2024 electrodes coated with toluene films as a function of toluene / argon ratios

TABLE 2. Corrosion properties of aluminum electrode covered with toluene films with different toluene/argon ratios obtained from potentiodynamic curve

Toluene Ratio	E_{corr} (mV)	i_{corr} (± 0.05μA/cm^2)	P_i %	Corrosion Rate (mm / year)
15 %	-850	4.20	65.00	0.040
30 %	-745	4.22	63.80	0.046
60 %	-725	7.49	35.70	0.079

The results of the polarisation data show that the corrosion resistance of AA2024 alloy with toluene coating has increased to some extent. The i^0_{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. Conversely, the I_{corr} value of the coated sample was relatively lower. Similar results have also been reported for sol-gel Ceria coatings on the surface of AA2024 alloy [20]. As shown in Table 2, as the toluene ratio decreased, the protective abilities of films increased, and thus the corrosion rate decreased. A high protective efficiency of 65% was obtained at a 15% toluene ratio. The film turned to powder when the toluene ratio reached above 65%. The findings demonstrate that the toluene coating is effective for corrosion protection of the aluminum alloy. And that toluene ratio alterations showed a significant impact on the film's protective capabilities.

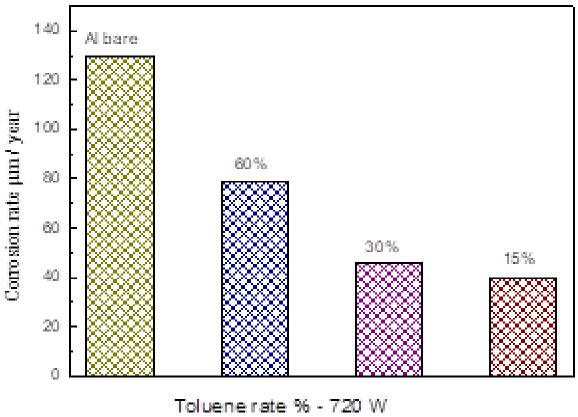

Figure 4. The corrosion rate of aluminum electrodes as a function of toluene ratio % at 720 W

Figure 4 shows the corrosion rate calculated from Table 1 and Table 2. As shown in Figure 4, the corrosion rate decreased in the presence of toluene film. The film deposited at 15% - 720 W showed an obvious reduction in its corrosion rate value, 40μm / year. This improvement in corrosion resistance was attributed to a toluene film that inhibits both anodic and cathodic reactions. The toluene films were densely packed and firmly linked, which suppressed oxygen reduction and diffusion of an electrolyte onto the aluminum surface. The presence of toluene coatings could significantly reduce aluminum's susceptibility to environmental corrosion.

Conclusion

The purpose of the current study was to investigate the effect of toluene-Ar gas ratio on the protective abilities of toluene films. Therefore a series of microwave plasma polymerized toluene films were successfully prepared using a simple plasma enhanced chemical vapor deposition method (PECVD). All films were deposited on aluminum alloy substrates at low pressure and room temperature. The results demonstrate that the toluene ratio alterations had a significant impact on the corrosion resistance of the films. An improvement in protective efficiency with reduction of toluene content was observed, where the highest value (65%) was obtained at a 15% toluene ratio. The proper flow of toluene during the plasma polymerization process may enhance the cross-linking in the film, hence improving the corrosion resistance. The existence of a high ratio of toluene monomer led to powder formation on the substrate surface.

References

[1] M. Ardic and A. Gifvars, "A study on the effects of the process parameters of polymerised HMDSO using RF-PECVD in corrosion protection applications," ed, 2017.

[2] J. Bowen and D. Cheneler, "The stability and degradation of PECVD fluoropolymer nanofilms," *Polymer Degradation and Stability,* vol. 160, pp. 203-209, 2019.

[3] Y. Fermi, M. Kihel, S. Sahli, and P. Raynaud, "Synthesis of nanopowders in a PECVD reactor from organosilicon precursor," *Phosphorus, Sulfur, and Silicon and the Related Elements,* 20.19

[4] Z. Krtouš, L. Hanyková, I. Krakovský, D. Nikitin, P. Pleskunov, O. Kylián, *et al.*, "Structure of plasma (re) polymerized polylactic acid films fabricated by plasma-assisted vapour thermal deposition," *Materials,* vol. 14, p. 459, 2021.

[5] D. Mitev ,E. Radeva, D. Peshev, M. Cook, and L. Peeva, "PECVD polymerised coatings on thermo-sensitive plastic support," in *Journal of Physics: Conference Series*, 2016, p. 012014.

[6] Y. Zhou, B. Rossi, Q. Zhou, L. Hihara, A. Dhinojwala, and M. D. Foster, "Thin Plasma-Polymerized Coatings as a Primer with Polyurethane Topcoat for Improved Corrosion Resistance," *Langmuir,* vol. 36, pp. 837-843, 2020.

[7] P. M. Martin, *Handbook of deposition technologies for films and coatings: science, applications and technology* :William Andrew, 2009.

[8] A. Grill, *Cold plasma in materials fabrication* vol. 151: IEEE Press, New York, 1994.

[9] D. Jung, H. Pang, J.-H. Park, Y. W. Park, and Y. Son, "Photoluminescence and Electroluminescence from Polymer-Like Organic Thin Films Deposited by Plasma-

Enhanced Chemical Vapor Deposition Using Para-Xylene as Precursor," *Japanese journal of applied physics,* vol. 38, p. L84, 1999.

[10] D. Thiry, S. Konstantinidis, J. Cornil, and R. Snyders, "Plasma diagnostics for the low-pressure plasma polymerization process: A critical review," *Thin Solid Films,* vol. 606, pp. 19-44, 2016.

[11] M. Ates, "A review on conducting polymer coatings for corrosion protection," *Journal of adhesion science and Technology,* vol. 30, pp. 1510-1536, 2016.

[12] A. A. Olajire, "Recent advances on organic coating system technologies for corrosion protection of offshore metallic structures," *Journal of Molecular Liquids,* vol. 269, pp. 572-606, 2018.

[13] P. Natishan, E. McCafferty, E. Donovon, and G. Hubler, "The use of surface modification techniques for the corrosion protection of aluminum and aluminum alloys," *Advances in coatings technologies for corrosion and wear resistance coatings,* 1995.

[14] Y. Ji, J.-H. Cho, and H.-S. Chae, "Surface modification of aluminum by toluene plasma at low-pressure and its surface properties," *Applied surface science,* vol. 280, pp. 518-522, 2013.

[15] D. G. Enos and L. L. Scribner, "The potentiodynamic polarization scan," *Solartron Instruments, Hampshire, UK, Technical Report,* vol. 33, 19.97

[16] K. Aramaki, "Protection of iron corrosion by ultrathin two-dimensional polymer films of an alkanethiol monolayer modified with alkylethoxysilanes," *Corrosion science,* vol. 41, pp. 1715-1730, 1999.

[17] K. Nozawa and K. Aramaki, "One-and two-dimensional polymer films ofmodified alkanethiol monolayers for preventing iron fromcorrosion," *Corrosion Science,* vol. 41, pp. 57-73, 1999.

[18] N. Tsuji, K. Nozawa, and K. Aramaki, "Ultrathin protective films prepared by modification of an N, N-dimethylalkylamine monolayer with chlorosilanes for preventing corrosion of iron," *Corrosion science,* vol. 42, pp. 1523-1538, 2000.

[19] J. Singh-Beemat, J. O. Iroh, and L. Feng, "Mechanism of corrosion protection of aluminum alloy substrate by hybrid polymer nanocomposite coatings," *Progress in Organic Coatings,* vol. 76, pp. 1576-1580, 2013.

[20] M. Zuo, T. Wu, K. Xu, S. Liu, D. Zhao, and H. Geng, "Sol–gel route to ceria coatings on AA2024-T3 aluminum alloy," *Journal of Coatings Technology and Research,* vol. 12, pp.2015 ,83-75 .