

Plasma-polymerised coatings used as pre-treatment for aluminium alloys

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Abstract

The pre-treatment of aluminium alloys prior to painting or adhesive bonding is an essential technology in many industrial sectors (e.g. aerospace industry). However, the pre-treatments used on the substrates, which are vital to ensure reliable long-term performance, often comprise a range of environmentally objectionable chemicals, such as solvents and chromates, some of which are carcinogenic. The plasma deposition of thin coatings on aluminium, which exhibit strong interfacial bonding, could be an alternative to the traditional chromate-based treatments. It is envisaged that in a single plasma reactor, plasma cleaning, etching and deposition could provide a complete preparation cycle before painting, avoiding the use, handling and disposal of hazardous materials. In the present work, the corrosion behaviour and adhesive joint performance of plasma-coated Alclad AA2024-T3 alloy were investigated. The coatings were deposited from hexamethyldisiloxane monomer (HMDSO) in a capacitively coupled RF plasma reactor. The same evaluations were carried out on specimens painted with an epoxy primer after coating deposition. The coatings conferred protection against corrosion and provided a good interface for strong, durable adhesive bonds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma polymerisation; Aluminium alloy; Adhesion; Corrosion

1. Introduction

Painting and adhesive bonding of aluminium are essential technologies in many industrial sectors and a successful process depends upon the generation of a strong and stable interface between an organic layer and the surface consisting of naturally formed metal oxide. This is particularly important in the aerospace industry. Pre-treatments, which leave the metal with a film structure that is stable and compatible with the organic layer, are vital to reliable, long-term performance and have been used for decades. However, proven pre-treatments involve the use of environmentally objectionable chemicals, such as solvents and chromates.

Growing concern about the environmental impact of traditional wet chemical methods of pre-treatment has generated interest in ecologically cleaner vacuum-based plasma technology.

The use of plasmas for thin film coating deposition has been widely researched. The deposition of coatings for the purpose of corrosion protection has received some attention, which until recently principally focussed on steel surfaces [1–7], although the protection of non-ferrous metals has also been studied with copper [8] and aluminium [9–12]. One of the main advantages of plasma is the complete enclosure of the process, within a vacuum chamber, enabling the ready disposal of the process gases. Scale up from the laboratory is often considered an issue but the plasma equipment market is mature and plasma equipment manufacturers can meet the demands of deposition at the industrial scale [13].

The plasma deposition of thin film coatings on aluminium, which exhibit strong interfacial bonding, could provide an alternative to the traditional chromate-based treatments. Such a plasma process could also include cleaning/etching. A complete preparation cycle, prior to painting or bonding, might be achieved in a single chamber without the handling and disposal of hazardous

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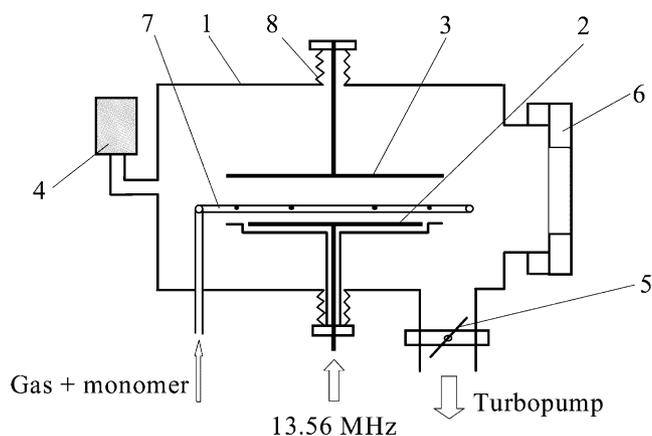


Fig. 1. Diagram of the plasma discharge chamber, where: 1-vacuum chamber; 2-powered electrode 3-grounded electrode; 4-capacitive pressure gauge (baratron) 5-butterfly valve; 6-vacuum door with viewport; 7-gas shower ring; 8-bellows translational stage.

materials. The process is also amenable to real-time monitoring and control.

In the present work, electrochemical impedance spectroscopy (EIS) and scanning Kelvin probe (SKP) measurements [14–16] were used to evaluate the corrosion behaviour of plasma-coated Alclad AA2024-T3. The adhesion properties were assessed by wedge cleavage tests. The monomer was hexamethyldisiloxane (HMDSO) and add-gases such as O_2 , N_2 , H_2 and Ar were employed. Plasma coatings from HMDSO and O_2 have proven to be effective primer coatings for adhesion promotion to aluminium [17]. The corrosion properties of these coatings have yet to be commented upon. Replacement of O_2 by another gas, e.g. N_2 , H_2 or Ar will significantly alter the chemistry of the deposition process and may produce improved protective coatings.

A capacitive radio frequency (13.56 MHz) plasma discharge was employed in this research. Such discharges have been extensively studied over the last three decades. The discharge used herein has an important advantage of scalability [18] cf. microwave discharges previously employed for aluminium plasma coating [9].

The corrosion resistance of specimens painted with an epoxy primer, after coating deposition, was also evaluated by SKP measurements, as well as by testing in a salt spray cabinet. In addition, X-ray photoelectron spectroscopy (XPS) has provided information on the chemical nature (e.g. functional group composition) of the plasma-coatings.

2. Experimental

2.1. RF deposition rig

A 21-litre stainless steel vacuum chamber plasma reactor was used (Fig. 1). Plasma was maintained by a 13.56 MHz RF capacitive discharge. The bottom-pow-

ered electrode was 160 mm in diameter and the grounded counter-electrode was 200 mm in diameter. Both electrodes could be shifted vertically using the bellows 'translational' stages. This option was used for setting the inter-electrode distance (typically 70 mm during deposition runs) and for loading samples through the side quick access vacuum door. The pumping system consisted of an EXT250 turbomolecular pump with a pumping speed 240 l s^{-1} and an E2M40 mechanical pump, with displacement $42.5 \text{ m}^3 \text{ h}^{-1}$. The turbopump was constantly purged by a 30 sccm flow of nitrogen, for protection of the pumps bearings from monomer vapour condensation. The control system of the rig was based on the MKS Instruments integrated control system 146C. It provided pressure readings from the baratron and the cold cathode pressure gauges, setting the gas flow by a mass-flow controller and regulating the processing pressure by means of a throttle valve. The hexamethyldisiloxane (HMDSO) monomer flow (1.3 sccm) was controlled through its partial pressure by regulating the metering valve on the monomer line.

2.2. Deposition procedure

The deposition substrate was an aluminium alloy, 2024-T3 Alclad and, prior to plasma deposition, all the samples were wiped by tissues with acetone. Samples were then placed on the powered electrode.

The vacuum chamber was pumped down to a base pressure of $(5-10) \times 10^{-6}$ torr by the turbopump. The plasma processing consisted of two stages: pre-treatment and deposition. During the first stage the aluminium samples were cleaned in Ar or Ar/ H_2 plasmas for 5 to 15 min at 80 mtorr discharge pressure with a -700 V self-bias on the powered electrode. The RF generator power was 185 W.

The gas mixture used for coating deposition was prepared by introduction of the add-gas into the chamber (O_2 , N_2 or H_2 at a flow of 30 sccm; or Ar at 20 sccm). The pressure in the chamber was set to 30 mtorr by the throttle valve. Then HMDSO vapour was added with its partial pressure being regulated by the metering valve in the monomer line. The gas mixture total pressure was in the range 31–35 mtorr.

The deposition process was conducted typically at a RF power of 11 W with the self-bias voltage in the range -190 to -150 V . Some experiments were conducted at higher power (65 W) leading to self-bias voltages of -500 V . The deposition step was carried out until a coating of 200 nm had been deposited on the sample substrate. The time required for this varied from 5 to 20 min, depending on the partial pressure of HMDSO and the RF power. The coating thickness was measured in situ by optical ellipsometry, which is not described in this publication.

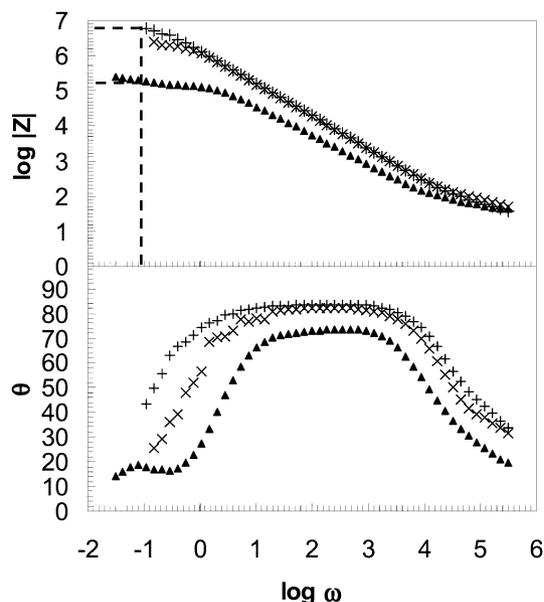


Fig. 2. Impedance plots for untreated Alclad 2024-T3 after different times of immersion in 0.5 M NaCl solution: + = 1 day, × = 7 days and ▲ = 60 days.

A minimum of two samples from each deposition batch was painted with a chromate-free epoxy primer (ADAF 37079).

2.3. Corrosion tests

Electrochemical impedance spectroscopy measurements were made in 0.5 M NaCl solutions. Untreated Alclad 2024-T3 was also tested. The experimental set-up for these tests comprised a 1250 Frequency Response Analyser and a 1286 Electrochemical Interface (both from Solartron/Schlumberger) controlled by a PC-compatible computer that also performed the data acquisition and processing. The behaviour of each sample was followed from the moment of immersion up to 60 days, allowing for the detection of the first corrosion spots (pits, for unpainted samples or delamination for painted samples). A minimum of two samples, prepared under the same conditions, were tested, in order to evaluate the reproducibility of the results.

A scanning Kelvin probe was used in order to assess the homogeneity of the plasma coatings and to check for the presence of delaminated areas in painted specimens. In order to get the high humidity conditions needed for these experiments, they were carried out in an environmental chamber.

Salt spray tests were performed according to ASTM standard B117-95.

XPS analyses were undertaken on a VG CLAM 2 XPS.

2.4. Adhesion tests

Structural adhesive joints need to be strong and durable, displaying both high initial strength and resistance to longer-term degradation when exposed to stress and moisture. In order to assess durability, the wedge cleavage test was used. Chromic acid anodising (CAA), simple abrasion (DG+GB) and an adhesion promoter (γ -GPS) were used as control treatments. The specimens were 25 mm wide, 3.2 mm thick and tested according to ASTM 3762-79 at 50 °C, 96% relative humidity. The adhesive used was an aerospace epoxy film adhesive, FM[®]-73, cured at 121 °C according to the manufacturer's instructions.

3. Results and discussion

3.1. Electrochemical Impedance Spectroscopy

Impedance spectra obtained for different immersion times in a 0.5 M NaCl solution for untreated Alclad 2024-T3 and for one of the samples of plasma-coated Alclad 2024-T3 are shown in Figs. 2 and 3, respectively. The results for the untreated alloy are identical to others reported previously for this type of alloy [19].

The impedance behaviour was very similar in the plasma-coated samples. Thus, in order to compare the performance of the different types of plasma coatings in terms of corrosion resistance, a practical criterion was developed.

From the literature [20] it is known that the onset of pitting corrosion is followed by a change in the shape

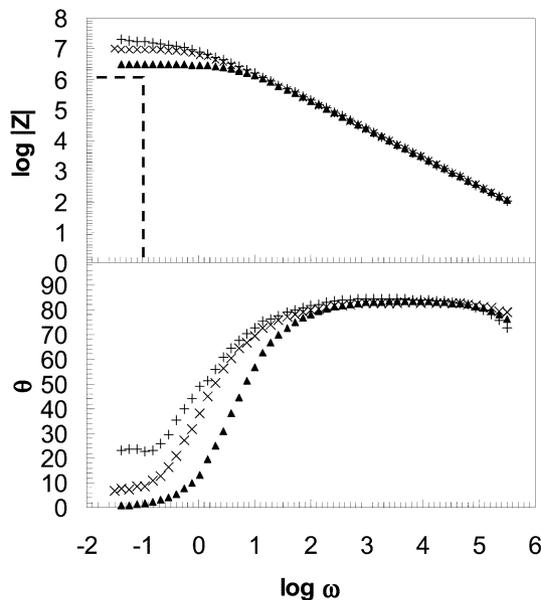


Fig. 3. Impedance plots for plasma-coated (HMDSO+O₂) Alclad 2024-T3 at different times of immersion in 0.5M NaCl: + = 1 day, × = 7 days and ▲ = 60 days.

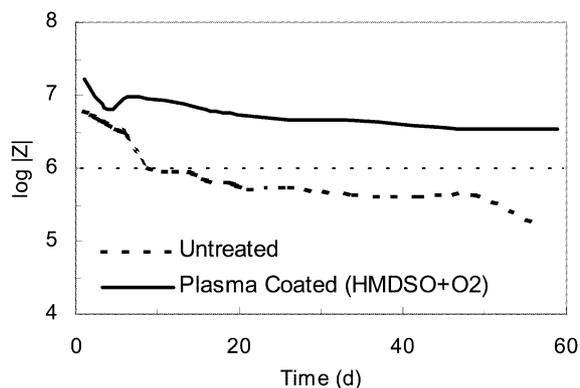


Fig. 4. Plot of $\log |Z|_{\omega=0.1}$ vs. immersion time for untreated and plasma coated Alclad 2024-T3.

of the Bode plots (Fig. 2). In the phase angle vs. $\log \omega$ plot, a new time constant appears in the low frequency range, whereas a decrease in the low frequency limit of $\log |Z|$ is noticed in the $\log |Z|$ vs. $\log \omega$ plot. Thus, the value of $\log |Z|$ taken at a fixed angular frequency of $\omega = 0.1 \text{ rad.s}^{-1}$ is a useful measure of the corrosion susceptibility.

In this study, a threshold of $\log |Z|_{\omega=0.1} = 6$ was set. When this parameter was below 6, it was taken to indicate that the specimen under study was displaying pitting corrosion. It was taken that samples had a good resistance to pitting corrosion if $\log |Z|_{\omega=0.1}$ was ≥ 6 after 7 days of immersion in 0.5 M NaCl solution.

Fig. 4 presents the results obtained for the same two samples in Figs. 2 and 3 as plots of the $|Z|_{\omega=0.1}$ vs. time for immersion in 0.5 M NaCl solution. According to the above practical criterion both samples display good resistance to pitting corrosion, with $\log |Z|_{\omega=0.1} \geq 6$ after 7 days of immersion.

However, the untreated sample fails for an immersion time of 9 days, whereas the plasma-coated specimen resists pitting corrosion for more than 60 days.

The presence of intermetallic precipitates in the alloy enhances the initiation of localised corrosion. The precipitates may be anodic (Al-Cu-Mg) or cathodic (Al-Cu-Mn-Fe-Si) relatively to the aluminium matrix, thus inducing the initiation of pitting corrosion in or around the precipitates [21–24]. The plasma coated samples are supposed to have a film covering the whole surface, which avoids the establishment of galvanic-induced pitting.

The importance of the add-gas used in the deposition was evaluated by comparing samples coated using the gas mixtures of HMDSO + H₂ and HMDSO + O₂. These mixtures were used in the same proportions, and the results are presented in Fig. 5. Although the best results from the adhesion tests (not shown), were obtained with samples prepared from mixtures of HMDSO + O₂, the use of HMDSO + H₂ mixture lead to higher corrosion

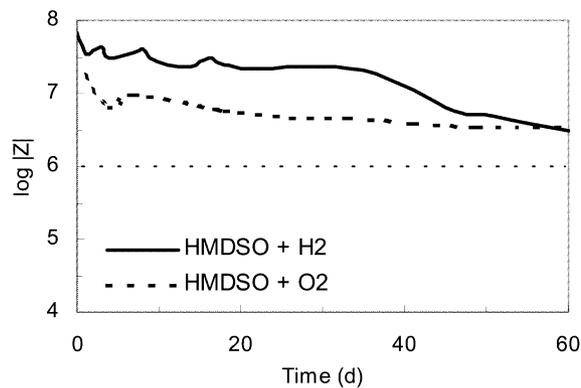


Fig. 5. Effect of the add-gas—Plot of $\log |Z|$ vs. time.

resistance, but this enhanced resistance disappeared for longer immersion times. The reason for the differences in performance between the specimens produced with the above gas mixtures is not fully understood but the presence of oxygen is thought to be responsible for a severe oxidation of the coating, which loses its organic character [17].

In order to evaluate the effect of the plasma pre-treatment, the results obtained from samples coated with HMDSO + H₂ are presented in Fig. 6. Both samples were pre-treated with Ar as described above, but the duration of the pre-coating step varied from 5.5 min (short pre-treatment) to 15.5 min (long pre-treatment).

The duration of the pre-treatment was found to strongly influence the speed of coating deposition. Heating of the substrate occurs during pre-treatment and a hotter substrate produces a denser and thinner coating. However, as can be seen from Fig. 6, long pre-treatment has a deleterious effect on the corrosion resistance. Surface roughness could increase with long pre-treatments, which in conjunction with the fact that the coating is thinner can leave peaks of the surface uncovered.

The RF bias had a strong effect on the deposition rate: at -500 V the rate was $36.4 \text{ nm}\cdot\text{min}^{-1}$ whilst at

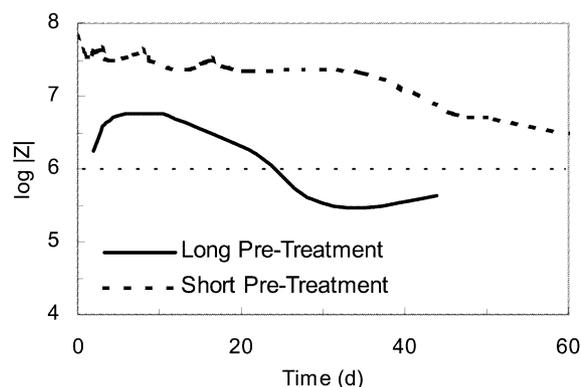


Fig. 6. Effect of the pre-treatment for samples coated with HMDSO + H₂—Plot of $\log |Z|_{\omega=0.1}$ vs. time.

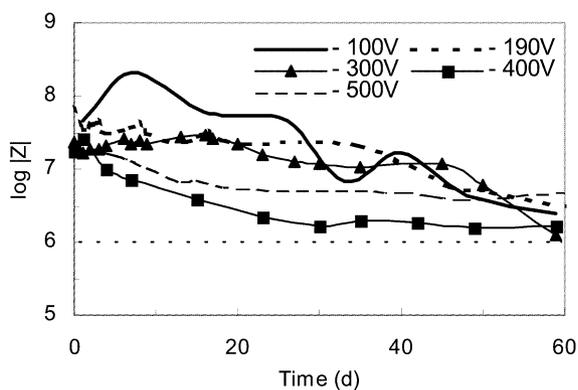


Fig. 7. Effect of the RF bias for samples coated with HMDSO + H₂ – Plot of $\log|Z|_{\omega=0.1}$ vs. time.

–100 V it was only $7.3 \text{ nm}\cdot\text{min}^{-1}$. Although the high RF bias is attractive since it shortens the process time, it produced coatings, which were much inferior in corrosion resistance (Fig. 7). This may be caused by high intrinsic stresses in the plasma-polymeric films, which arise due to surface bombardment, by energetic ions accelerated by the bias voltage.

As shown in the above figures, good corrosion resistance is seen in all the plasma-deposited coatings. That is, all of the plasma coated samples passed the practical criterion of $\log|Z|_{\omega=0.1}$ after 7 days of immersion and none of them failed up to 60 days of immersion testing.

3.2. XPS analysis

XPS was used to analyse selected samples in order to provide information on the chemical composition of the deposits. From the Si 2p binding energies and Si:O

ratios, it was concluded that all the films were chemically ‘silica-like’ [25].

3.3. Scanning kelvin probe

In parallel with impedance measurements, specimens were tested by SKP. The potential measured by this technique may be related to the corrosion potential of the metal, indicating the presence of anodic and cathodic areas. A test area of $3\times 3 \text{ mm}$ was chosen randomly in the test specimen’s surface.

The potential maps obtained from the plasma-coated samples indicate that there is no important differentiation of anodic and cathodic areas, i.e. the coating layer is homogeneous. A typical potential map for one of these plasma-coated specimens is presented in Fig. 8. Potential maps obtained for coated samples after being painted with the chromate-free epoxy primer also showed homogeneity and no evidence of delamination was found.

3.4. Salt spray testing

Salt spray tests were carried out on plasma-coated specimens, painted with the chromate-free epoxy primer. Alclad 2024-T3 specimens, treated by chromosulfuric etching and chromic acid anodising and painted with the same epoxy were used as control specimens. All the samples tested by salt spraying passed, with no evidence of corroded or delaminated areas found.

3.5. Wedge cleavage tests

Some results from these tests are shown below in Fig. 9. The control treatments are chromic acid anodising

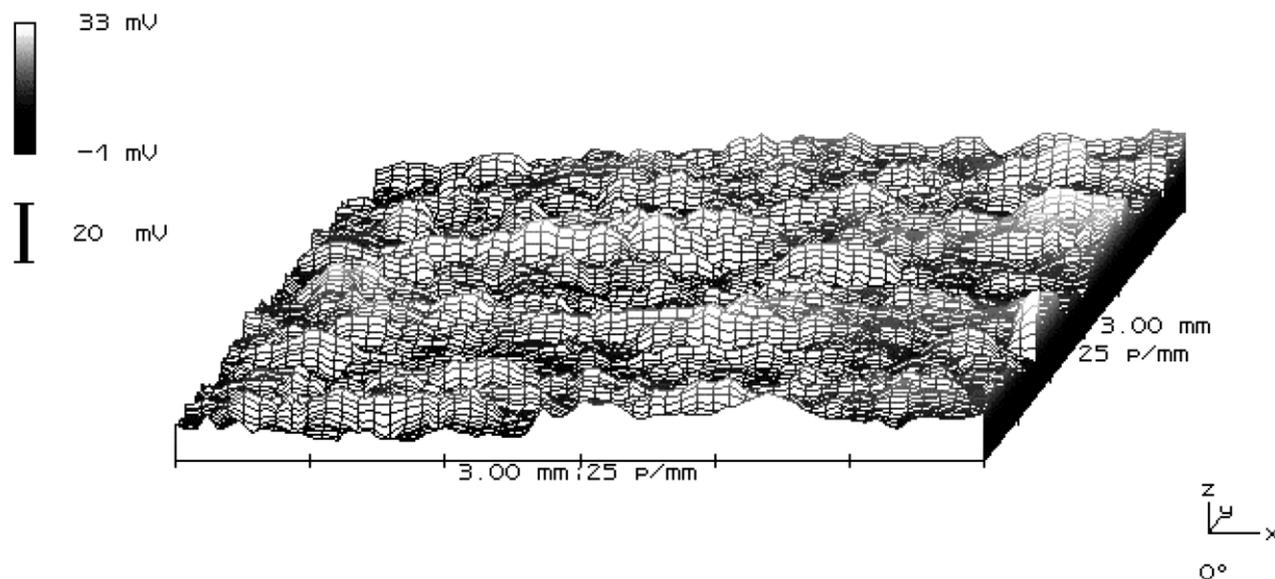


Fig. 8. Typical potential map of a polymer coated specimen.

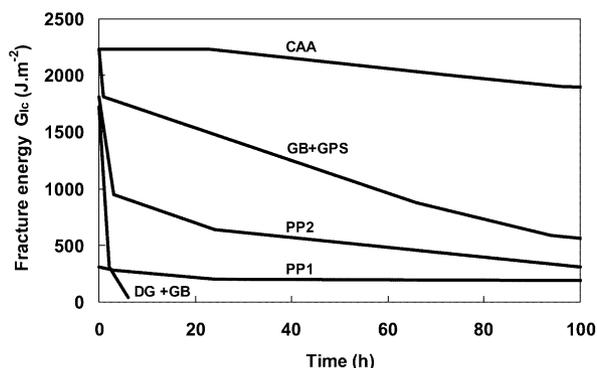


Fig. 9. Wedge cleavage test results.

(CAA), degrease and gritblasting (DG+GB) and an organosilane adhesion promoter (γ -GPS).

The CAA treatment yields the best durability in the wedge test, followed by the γ -GPS adhesion promoter (GB+GPS) but the two plasma polymerised specimens prepared from mixtures of HMDSO+H₂ (PP1, using RF bias of -500 V and PP2, using RF bias of -400 V) exhibit better performance than the specimen which was degreased and gritblasted.

4. Conclusions

Plasma coatings obtained by the plasma deposition of HMDSO improve the corrosion resistance of the Alclad 2024-T3 alloy. These coatings provide improved adhesion properties compared to grit-blasted aluminium surfaces but do not match those of chromic acid anodising.

Changes in the processing parameters do not have a strong influence on the protective properties nor on the chemical structure of the plasma coatings, although long pre-treatments and high RF bias seem to be detrimental for corrosion resistance.

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References

- [1] G. Grundmeier, M. Stratmann, *Thin Solid Films* 352 (1999) 119.
- [2] G. Grundmeier, M. Stratmann, *Werkst. Korros.* 49 (1998) 150.
- [3] T.J. Lin, J.A. Antonelli, D.J. Yang, H.K. Yasuda, F.T. Wang, *Prog. Org. Coat.* 31 (1997) 351.
- [4] H.K. Yasuda, T.F. Wang, D.L. Cho, T.J. Lin, J.A. Antonelli, *Prog. Org. Coat.* 30 (1997) 31.
- [5] T.F. Wang, T.J. Lin, D.J. Yang, J.A. Antonelli, H.K. Yasuda, *Prog. Org. Coat.* 28 (1996) 291.
- [6] H. Yasuda, B.H. Chun, D.L. Cho, T.J. Lin, D.J. Yang, J.A. Antonelli, *Corrosion* 52 (1996) 169.
- [7] C. Vautrin-UI, C. Boisse-Laporte, N. Benissad, A. Chausse, P. Leprince, R. Messina, *Prog. Org. Coat.* 38 (2000) 9.
- [8] Y. Lin, H. Yasuda, *J. Appl. Polym. Sci.* 60 (1996) 543.
- [9] J. Schwarz, M. Schmidt, A. Ohl, *Surf. Coat. Tech.* 98 (1998) 859.
- [10] Y. Iriyama, T. Ihara, M. Kiboku, *Thin Solid Films* 287 (1996) 169.
- [11] C.M. Reddy, Q.S. Yu, C.E. Moffitt, et al., *Corrosion* 56 (2000) 819.
- [12] Q.S. Yu, C.M. Reddy, C.E. Moffitt, et al., *Corrosion* 56 (2000) 887.
- [13] H. Grunwald, R. Adam, J. Bartella, et al., *Surf. Coat. Tech.* 111 (1999) 287.
- [14] A. Leng, H. Streckel, M. Stratmann, *Corros. Sci.* 41 (1999) 547.
- [15] A. Leng, H. Streckel, M. Stratmann, *ibid* 41 (1999) 579.
- [16] A. Leng, H. Streckel, M. Stratmann, *ibid* 41 (1999) 599.
- [17] R.H. Turner, I. Segall, F.J. Boerio, G.D. Davis, *J. Adhes.* 62 (1997) 1.
- [18] H-U. Poll, S. Schreiter, *Surf. Coat. Tech.* 93 (1997) 105.
- [19] J.S.C. Fernandes, M.G.S. Ferreira, Deliverable Report D701 — Brite/Euram Project NBE97-4013, IST/Lisbon (1998).
- [20] F. Mansfeld, S. Lin, S. Kim, H. Shi, *Material Science Forum* 44–45 (1989) 83.
- [21] G.S. Chen, M. Gao, R.P. Wei, *Corrosion* 52 (1996) 8.
- [22] R.G. Buchheit, R.P. Grant, P.F. Hlava, B. Mckenzie, G.L. Zender, *J. Electrochem. Soc.* 144 (1997) 2621.
- [23] C. Blanc, B. Lavelle, G. Mankowski, *Corros. Sci.* 39 (1997) 495.
- [24] P. Campestrini, E.P.M. van Westing, H.W. van Rooijen, J.H.W. de Wit, *Corros. Sci.* 42 (2000) 1853.
- [25] M.R. Alexander, R.D. Short, F.R. Jones, M. Stollenwerk, J. Zabold, W. Michaeli, *J. Mater. Sci.* 31 (1996) 1879.