

# Adhesion of the Plasma Polymer of Trimethylsilane to Aluminum Alloys

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**ABSTRACT:** The adhesion of a plasma polymer and the corrosion protection offered to aluminum alloy substrates depends on the cleanliness of the substrate surface and the state of oxides on the aluminum alloy surface. Both factors are dependent on what type of alloy is used, and consequently, the best preparation of the substrate surface differs on the type of aluminum alloy. Oxygen plasma treatment is effective for the elimination of organic surface contamination, but plasma treatment, such as that of mixed argon and hydrogen, cannot be used to modify the surface state of oxides on these alloys. This is because oxides of aluminum are stable and thus resist plasma modification, and prolonged plasma treatment has been observed to change concentrations of alloy components at the surface due to the heating of the alloy. Chemical cleaning of the surface is necessary before the application of the plasma polymer used for corrosion protection enhancement. Once the surface was properly prepared, a plasma polymer of trimethylsilane (TMS), prepared by cathodic polymerization, adhered well to aluminum alloys investigated in this study. Major adhesive failure, however, occurred as a consequence of reactor contamination when hexafluoroethane (HFE) plasma treatment of initially formed TMS plasma polymers was employed. Plasma pretreatment of the substrate with O<sub>2</sub> or postplasma treatment of the plasma polymer of TMS with Ar (instead of HFE) was effective in eliminating the surface-contamination effect on the adhesion. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1387–1398, 2002

**Key words:** adhesion; coatings; ESCA/XPS; nanolayers; plasma polymerization

## INTRODUCTION

An ultrathin layer of the plasma polymer of trimethylsilane (TMS) has been successfully utilized for the corrosion protection of aluminum alloys by means of system approach interface engineering

(SAIE).<sup>1–7</sup> The SAIE concept emphasizes the fact that the corrosion protection of a metal depends on the overall corrosion protective behavior of an entire system including the bulk characteristics of the coatings and interfacial factors. SAIE by means of low-temperature plasmas utilizes low-temperature plasma treatment and the deposition of nanofilm by plasma polymerization. SAIE does not rely on electrochemical corrosion-protecting agents such as six-valence chromium, and hence, the process is totally environmentally benign. A nanofilm of the plasma polymer of TMS

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(typically 50 nm) is applied on an appropriately prepared surface of an aluminum alloy. Then, a corrosion protective primer coating (typically 30  $\mu\text{m}$ ) is applied onto the surface of the plasma nanofilm. The adhesion of a multilayer coating system is the prerequisite for success of the SAIE approach. Therefore, the adhesion of the first layer of the nanofilm prepared by plasma polymerization is the most crucial factor in this approach because if this layer delaminates from the substrate surface, the rest of coatings cannot function at all.

This article addresses fundamental factors involved in the surface state created by various chemical treatments of native alloy surfaces and the interface between the plasma polymer of TMS and the newly prepared substrate alloy surface. It should be emphasized, however, that the adhesion of a plasma polymer per se was not the objective of this study. The adhesion that leads to better corrosion protection by the principle of SAIE was the objective, which required the water-insensitive adhesion relevant to corrosion protection.

## EXPERIMENTAL

### Materials

Aluminum alloy panels were  $7.62 \times 15.2 \times 0.08$  cm and included AA2024-T3 ([2B]), AA7075-T6 ([7B]), Alclad 2024-T3 ([2A]), Alclad 7075-T6 ([7A]), which were procured from Q-Panel Lab Products (Cleveland, OH).

The chemicals used in the chemical cleaning of the aluminum alloy panels were Turco 4215-S, a commercial alkaline cleaner purchased from Turco Products, Inc. (Wilmington, CA); Amchem 7, a commercial deoxidizer purchased from Amchem Products, Inc. (Ambler, PA); nitric acid (65%) purchased from Fisher Scientific (St. Louis, MO).

The following chemicals were used in plasma pretreatment and in the plasma polymerization process: the diatomic gases oxygen ( $\text{O}_2$ ; 99.9%) and hydrogen ( $\text{H}_2$ ; 99%), were procured from Airgas (Radnor, PA). TMS gas of 97% minimum purity was procured from PCR, Inc. (Gainesville, FL) and Lancaster Synthesis, Inc. (Windham, NH). All the gases and monomers were used as received without any further purification.

### Surface Preparation

Acetone (Ace) wiping with Kimwipes® was first used to clean the ink marks and loose organic

matter from the surfaces of the Al alloy panels. Chemical cleaning of the aluminum alloy panels was performed by alkaline cleaning and deoxidization. The Turco 4215-S alkaline solution was prepared and used per McDonnell Douglas process specification P.S. 12030 (Boeing Co., St. Louis, MO). The Amchem 7 deoxidizer solution was combined with nitric acid and was prepared and used per McDonnell Douglas process specification P.S. 12050.1 (Boeing).

Alkaline cleaning of Al panels was performed by immersion in an alkaline bath at 65°C (150°F) for about 25 min, or until each panel became water-break-free when rinsed with deionized (DI) water; they were then thoroughly rinsed with DI water. In the case of deoxidization, the panels first went through the alkaline cleaning process and were then immersed in a deoxidization bath at room temperature for 10 min, rinsed with DI water, immersed in DI water for 5 min, and finally air dried.

Before plasma polymer deposition, plasma pretreatment by simple gas plasmas was applied to aluminum panel surfaces to remove possible contaminants and thus to promote plasma polymer adhesion. TMS was mainly used as the monomer of direct current (DC) cathodic plasma polymerization. Plasma conditions for sample preparation and the sample identification codes are summarized in Table I.

## Plasma Reactor System and Operation

### Flow System

DC cathodic polymerization of TMS was carried out in a bell-jar-type reactor. The bell jar had dimensions of 635 mm in height and 445 mm in diameter with a total volume of approximately 70 L. The DC plasma generator was an MDX-1K magnetron drive power supply (Advanced Energy Industries, Inc., Ft. Collins, CO). Two anodes consisting of stainless steel plates ( $25.4 \times 25.4 \times 0.16$  cm) with magnetron enhancement were placed 15.5 cm apart in parallel. An iron ring (17.5 cm in outside diameter, 13.8 cm in inside diameter, and 0.16 cm thick) and an iron center plate (5 cm in diameter and 0.16 cm thick) were attached coaxially on the backside of each anode plate as magnetic field distributors. Eight pieces of permanent magnet bar were equidistantly attached on the iron ring and iron plate with the south pole pointing to the center of the iron plate. The magnetic field strength of each magnet ranged from 700 to 800 Gauss. Two Al panels (forming a  $15.2 \times 15.2$

**Table I Sample Identification Codes and Associated Plasma Conditions for Sample Preparation**

Identification Code <sup>a</sup>	Meaning and Conditions
[2A]	Alclad 2024-T3
[7A]	Alclad 7075-T6
[2B]	AA 2024-T3
[7B]	AA 7075-T6
(Ace)	CH <sub>3</sub> COCH <sub>3</sub> wiping with Kimwipes® tissue
(Alk)	Alkaline cleaning (65°C, 25 min)
(Dox)	Deoxidization (room temperature, 10 min, always preceded by alkaline cleaning)
(O)	O <sub>2</sub> plasma pretreatment (on Al surface: 1 sccm O <sub>2</sub> , 100 mtorr, 40 W, 2 min; on TMS polymer surface: 1 sccm oxygen, 50 mtorr, 10 W, 1 min)
(Ar)	Ar plasma treatment (1 sccm argon, 50 mtorr, 10 W, 1 min)
T	TMS plasma polymerization with anode magnetron enhancement (1 sccm TMS, 50 mtorr, 5 W, 1 min)
F	HFE plasma polymerization (1 sccm HFE, 50 mtorr, 5 W, 1 min)
A	Deft spray primer 44-GN-36 (chromated, water borne)
A1	Deft spray primer 44-GN-72 (chromated, water borne)
G	Courtauld spray primer 519X303 (chromated, solvent borne)
X	Dexter spray primer 10-PW-22-2 (nonchromated, water borne)
D	Spraylat spray primer EWAE118 (nonchromated, water borne)
/	Process separation mark

<sup>a</sup> Code used in parentheses indicates the surface treatment process; code used without parentheses indicates coating process.

cm square) were placed in the middle of the two parallel anodes and used as the cathode of the plasma system. The detailed operation procedures of such a reactor system were described elsewhere.<sup>1</sup>

### Closed System

In the closed-system operation, there was no anode assembly arranged inside the bell jar. Two Al panels (forming a 6 × 6 in. square) were placed in the center of the bell jar and used as the cathode of the plasma system. On initiation of the glow

discharge, the stainless steel bottom skirt, on which the bell jar was placed, and the base plate functioned as the grounded anode.

The reactor chamber was first pumped down to less than 1 mtorr. The reactor chamber was then isolated from the pumping system by closure of the main valve located in between the reactor and the pumping system. TMS gas, controlled by a mass flow meter (MKS, model 247C, Orland Park, IL), was then fed into the reactor. After the system pressure reached the preset point (25 mtorr), which was measured by a pressure transducer (1 torr full scale), TMS gas feeding was stopped, and DC power was then applied to initiate the glow discharge to start cathodic polymerization.

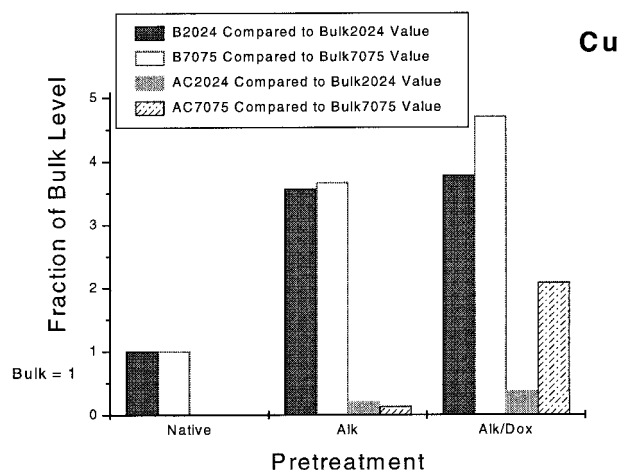
### X-Ray Photoelectron Spectroscopy (XPS) Surface Analysis

XPS, also referred to as *electron spectroscopy for chemical analysis*, data was acquired with a Kratos AXIS HS instrument (Manchester, UK), with the Mg-K $\alpha$  flood source operated at about 217 watts (15 mA, 14.5 kV). XPS data were acquired in the hybrid mode of the instrument, which combines electrostatic and magnetic lensing. The 2-mm aperture, used in the hybrid mode, limits collection to a spot size on the order of 200–300  $\mu$ m. All spectra were collected with the analyzer set at a pass energy of 80 eV, including the individual core spectra. This gave a full width at half maximum of just over 1.4 eV for the Ag 3d line. This lower resolution setting was used to minimize collection time and, thus, the exposure of the films to extended X-ray and secondary electron fluxes because these could tend to modify organic components. This also allowed for much more practical sputter-depth profiling of the films, which is not included in this discussion, and for the collection of the Si KLL Auger spectra, which have substantially smaller signal strengths, at the same resolution as the photoelectron spectra. The preferred use of the flood Mg source was based on the desire to collect Si KLL Auger spectra, which cannot be excited with an Al monochromatic source. Charge compensation was made with the manufacturer's proprietary system, at settings of: -1.5 V charge balance voltage, 1.85 A filament current and -0.5 V bias voltage.

## RESULTS AND DISCUSSION

### Pretreatment of Aluminum Alloys

The plasma sputtering was very inefficient and was unable to make significant progress in the



**Figure 1** Comparison of enriched surface copper concentrations to bulk values (B = Bare; AC = Alclad).

removal of the hydrated layer. These samples performed poorly in corrosion testing. The extended plasma sputtering caused some local heating. This heating caused the diffusion of Mg into the interface, which degraded the corrosion resistance. This is a strong contrast to the case of steel, in which plasma sputtering by Ar + H<sub>2</sub> effectively removed oxides and provided the foundation for the formation of iron silicides and carbides by the successive plasma polymerization of TMS, yielding excellent adhesion and corrosion protection.<sup>8,9</sup>

The wet chemical cleaning and the ability of the plasma deposition process to actively interact with the surface of the oxide at the beginning of the process are important for strong adhesion properties. These films appear to act as barrier films, blocking diffusion of corrosive media into the interface. The tightly adhering aspect of the films also acts as a barrier to lateral penetration of corrosive media from scribes. Without the employment of electrochemical corrosion inhibitors, the water-insensitive adhesion of a primer with good barrier characteristics was crucially important to provide better adhesion protection than that could be obtained by the electrochemical corrosion protection agents in the coating systems.<sup>10</sup>

The bar graph in Figure 1 shows a comparison of the maximum copper signal on the alloy surfaces compared to the bulk concentration of that element in the alloy after exposure to different chemical pretreatments. The values were derived from ratios of the peak areas of the copper signal at the depth of greatest concentration to the bulk value as measured in the XPS depth profiles. Thus, the ratio for the native/as-received alloy

samples was 1.0 because the native surface of the alloy was not enriched and had the largest copper concentration in the bulk.

It becomes quite apparent, on observation of the data, that the copper levels in the near-surface region were dramatically enhanced and thus could play a large role in local galvanic activity. The values for the Alclad samples were compared to the bulk values of the core material because the cladding itself had just trace amounts of copper. Due to this fact, the copper enrichment of the Alclad surface appears less dramatic in the figure, which may be slightly misleading. Any copper enrichment on the Alclad surfaces sets the stage for very strong local galvanic activity between the copper-enriched surface areas and the underlying copper-free cladding layer.

Figure 2 shows how the enrichment of surface zinc concentrations was produced by exposure to certain wet chemistries in a fashion similar to the Cu bar graph. In this case, the surface zinc concentration of the Alclad sample was compared to the bulk zinc concentration of the cladding material itself because the cladding on AC7075 did contain a significant amount of zinc.

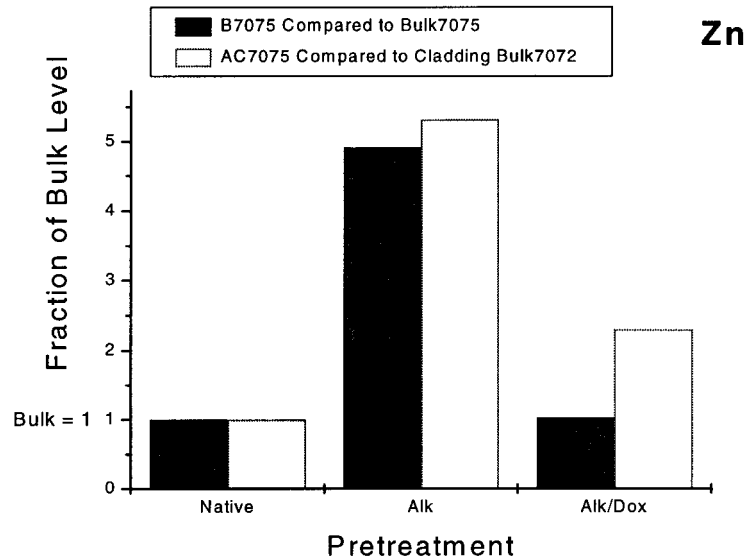
Although a copper-enriched surface has the implication of always causing accelerated electrochemical corrosion, replacing the hydrated oxide layer with a thin stable oxide layer seemed to allow the plasma films to tightly adhere to the alloy. This adhesion, coupled with the barrier properties of the films, appeared to protect this layer from penetration by corrosive agents, which would act as electrolytes in local galvanic cell formation if they were to penetrate. This could best be seen in the depth profile, which showed the thinning of the oxide layer, as well as copper (2024, 7075) and zinc (7075) enrichment.<sup>11</sup>

Two additional cleaning chemistries were investigated with XPS depth profile characterization. A pickling solution of HNO<sub>3</sub>, HF, and H<sub>2</sub>O was used by itself and was followed by the Parker-Amchem Deoxidizer 7. The enrichment of alloying elements was also observed with this chemistry.

Along the same lines of analysis, these same wet chemistries were applied to Alclad 7075 samples. Enrichment phenomena similar to that observed with AA7075-T6 were seen on the surface of this alloy and may indicate that deoxidation would be required to eliminate the enriched zinc levels at the surface.

Results from the plasma polymer coating of alloy AA7075-T6 showed a similar trend with re-





**Figure 2** Comparison of enriched surface zinc concentrations to bulk values (B = Bare; AC = Alclad).

gard to the elimination of plasma sputtering from the process step. Significantly better results were obtained with this alloy when the chemical cleaning included a deoxidizing step. This was attributed to the removal of zinc enrichments from the alloy surface. This assessment of the poorer corrosion results from alkaline-cleaned samples that were not deoxidized was based on the electrochemical interactions between the copper-enriched regions and the zinc-enriched regions. Here, galvanic couples between regions caused corrosion of the zinc region, which caused the corrosion-induced delamination of the plasma nanofilm.

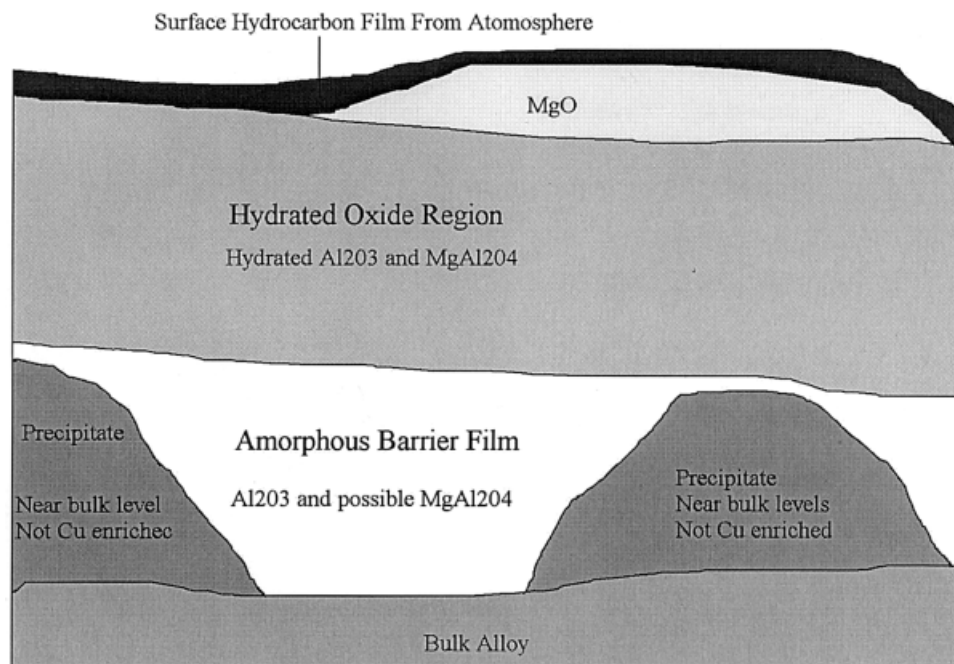
Although oxides thinner and more stable than the native hydrated oxide on Alclad 2024 were formed with alkaline cleaning and deoxidation, the surface Cu enrichment increased the galvanic attack of the AA1230 cladding. The redeposition of Cu on the surface from any exposure of the core material further accelerated the attack. The best (corrosion test) results with the plasma polymer films on Alclad 2024 were from films deposited on the native surface with no chemical cleaning.

Factors of Al alloy surfaces that influenced the adhesion of the TMS nanofilm can be schematically depicted as shown in Figures 3–5. Figure 3 depicts the surface state of the as-received Al alloys. The top surface was covered with hydrocarbon film from the atmosphere and/or intentionally applied thin film, such as the one for identification. The major factor was the relatively

thick layer of hydrated oxides, which are not stable in the context of adhesion and corrosion protection. The deposition of the TMS on either of these two top layers did not yield good adhesion. Figure 4 depicts the surface state after wet chemical treatments, and Figure 5 depicts the final surface state of TMS nanofilm coated Al alloys.

The reactive species of TMS in plasma react with the stable oxides created by the chemical pre-treatment, which is dependent on the type of alloys, and form chemical bonds between the oxides and the depositing plasma polymer. This step is evidenced by the conspicuous shift in XPS signal profiles of elements at the interface. Figures 6 and 7 depict the shift of signals at the plasma polymer–alloy interface. Attention should be focused at the plasma polymer/oxide interface, which is indicated by the asterisks.

The corrosion width observed with scribed corrosion tests seemed to indicate the extent of the corrosion-induced delamination of primer, which is a function of the corrosion of the substrate and the adhesion characteristics of the primer involved.<sup>12</sup> Although the effects of the surface pre-treatment of aluminum alloys showed a profound influence on the corrosion width, no clear-cut adhesion failure at the interfaces of the plasma polymer and the aluminum alloys was observed, except the case described in the following section. In other words, corrosion occurred as the consequence of the surface state of aluminum alloys, but it was difficult to assess the effect of the



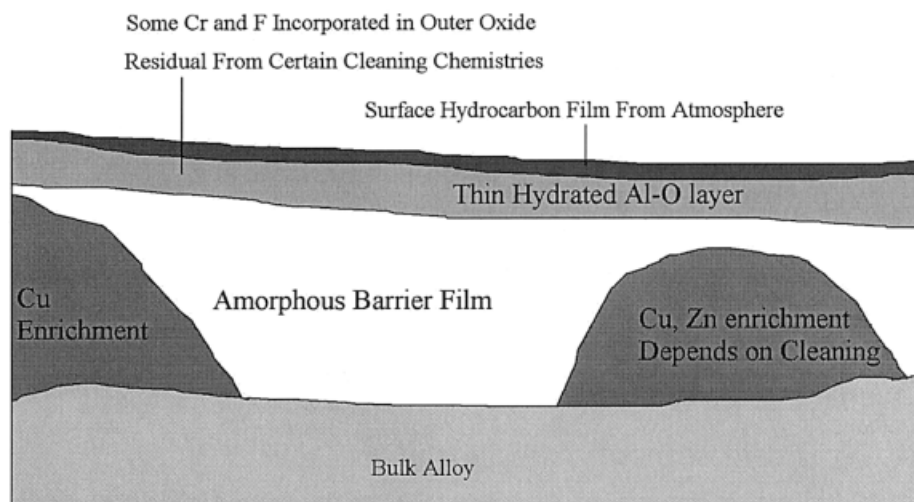
**Figure 3** Schematic drawing of native alloy surface.

adhesion of the plasma polymer to those different surface states created by different chemical pretreatments on the basis of the corrosion test results.

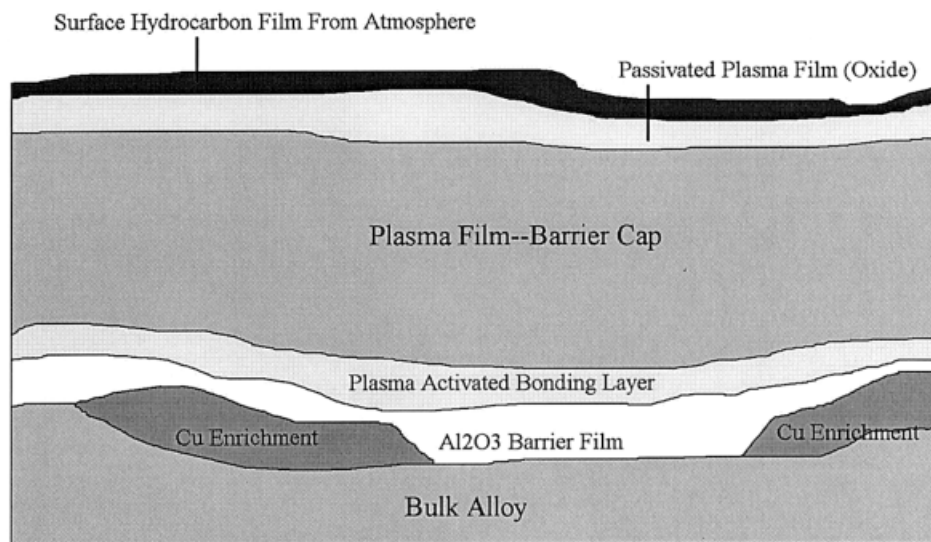
#### Adhesion Failure of the Plasma Polymer of TMS to Aluminum Alloys

One of most outstanding features of the SAIE approach was the superadhesion of primers to

aluminum alloys attained by a particular plasma polymerization system, which consisted of the plasma polymerization of TMS followed by the plasma polymerization of hexafluoroethane (HFE). Conventional primers applied on the plasma polymer became virtually unstrippable by most potent chemical stripping agents available on the market. While exploring this superadhesion, we discovered that the superadhesion abruptly changed to no ad-



**Figure 4** Schematic drawing of a chemically cleaned alloy surface (Mg removed from oxides; precipitate/deposit:  $\text{CuAl}_2 = 2024$ ,  $\text{CuAl}_2$  and Zn phases = 7075Alk).



**Figure 5** Schematic drawing of plasma film on the chemically cleaned alloy.

hesion when one step of the plasma polymerization processes was inadvertently omitted. This was the only case for clear interfacial failure at the plasma polymer and alloy. Fortunately, on the other hand, it provided us a rare opportunity to investigate the failed interface of the plasma polymer to aluminum alloy because the plasma polymer layer was found to be intact, adhering well to the primer layer. This finding provided important information relevant to the fundamental mechanisms of the initial step of plasma polymer deposition and of adhesion of the plasma polymer to the substrate and, therefore, is explained in some detail.

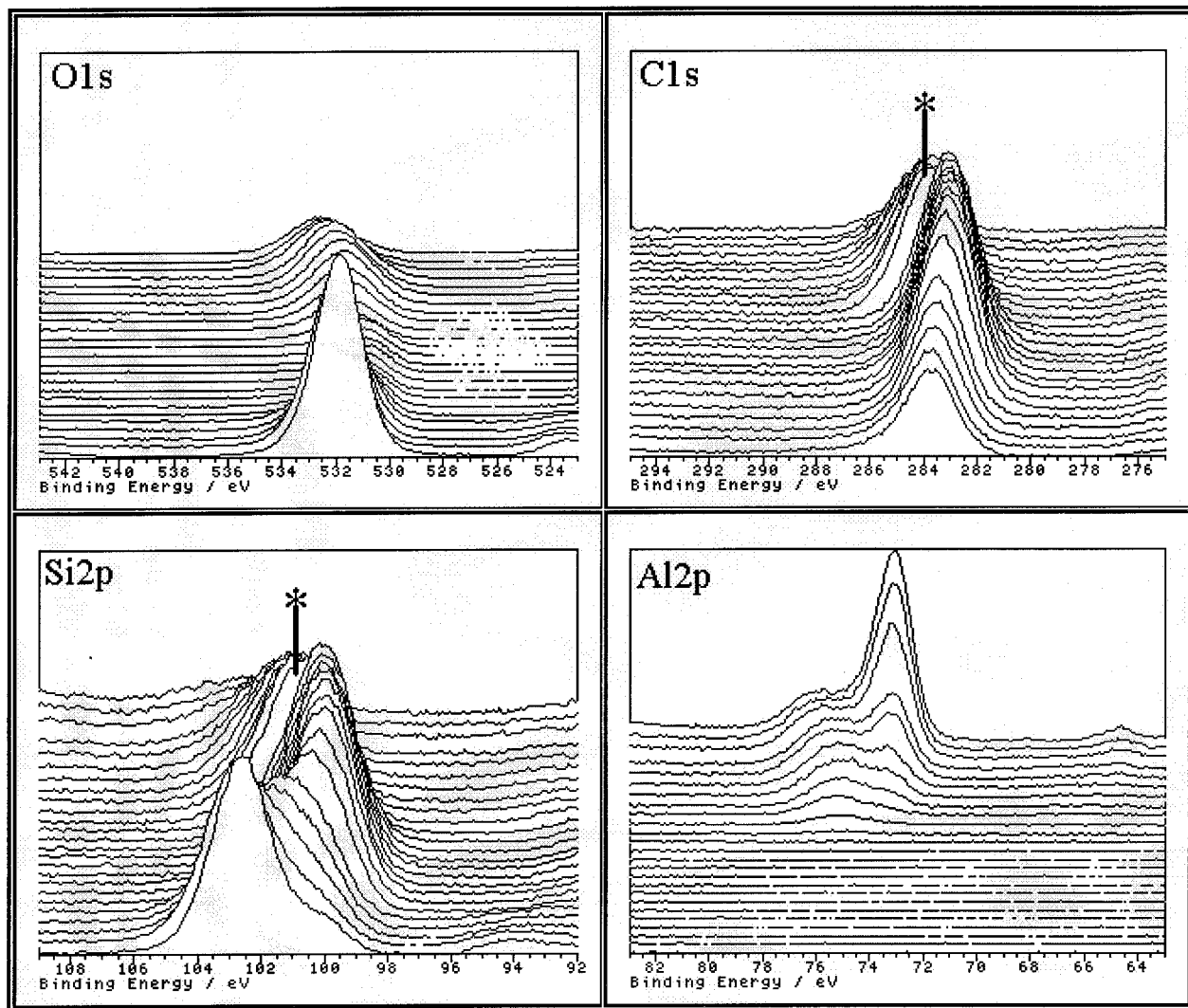
It should be emphasized here that TMS nanofilm under investigation was prepared by cathodic polymerization, which differs significantly from the conventional plasma polymerization carried out by high-frequency (kHz range), radio-frequency (typically 13.5 MHz), or microwave (typically 24.5 GHz) electrical power input. Because of high incidents of ion bombardment during the process of the deposition, the film has a much higher packing density of the depositing elements (Si and C), which reflects in the value of the refractive index. The refractive index of cathodically polymerized TMS is over 2.0, whereas that for TMS polymerized by other methods lies in the range of 1.6–1.7. The deposition rate on to the cathode is 2–30 times faster than that to the powered electrode surface in other modes of discharge. The deposition of approximately 50 nm thick film took place in 1 min, and the tempera-

ture rise due to the polymer deposition was found to be roughly 2°C. The details of cathodic polymerization were presented previously elsewhere.<sup>13,14</sup>

It should be also emphasized that HFE is not a monomer of plasma polymerization in general sense, which does not form polymer in a hydrogen-free environment<sup>15</sup> but forms polymer in presence of hydrogen atoms either provided by the addition of hydrogen gas or from hydrocarbon substrates that contact with plasma. In this particular process of plasma polymerization of HFE on the surface of the plasma polymer of TMS, plasma polymerization of HFE occurred by utilization of hydrogen atoms existing on the surface of the TMS plasma polymer. The thickness was only few nanometer and did not increase with extended treatment time because no hydrogen was available after the plasma polymer of HFE covered the surface of the TMS plasma polymer substantially.

The adhesion of an ultrathin film prepared by cathodic polymerization of TMS on aluminum alloys can be generally considered excellent, unless the initial stage of the film deposition is interfered with by some plasma factors. The reactor-wall contamination of F-containing oligomers left from the previous plasma processes caused serious adhesion problems when O<sub>2</sub> plasma pretreatment of the alloy surface was inadvertently omitted.<sup>16</sup>

The oxygen plasma treatment was initially employed to eliminate possible contamination of the cleaned surface with organic materials but not to modify the surface state of the alloy. It turned



**Figure 6** Combined spectra from the depth profile of closed-system TMS film treated with an  $O_2$  plasma after deposition. The asterisk-marked line indicates the interface region.

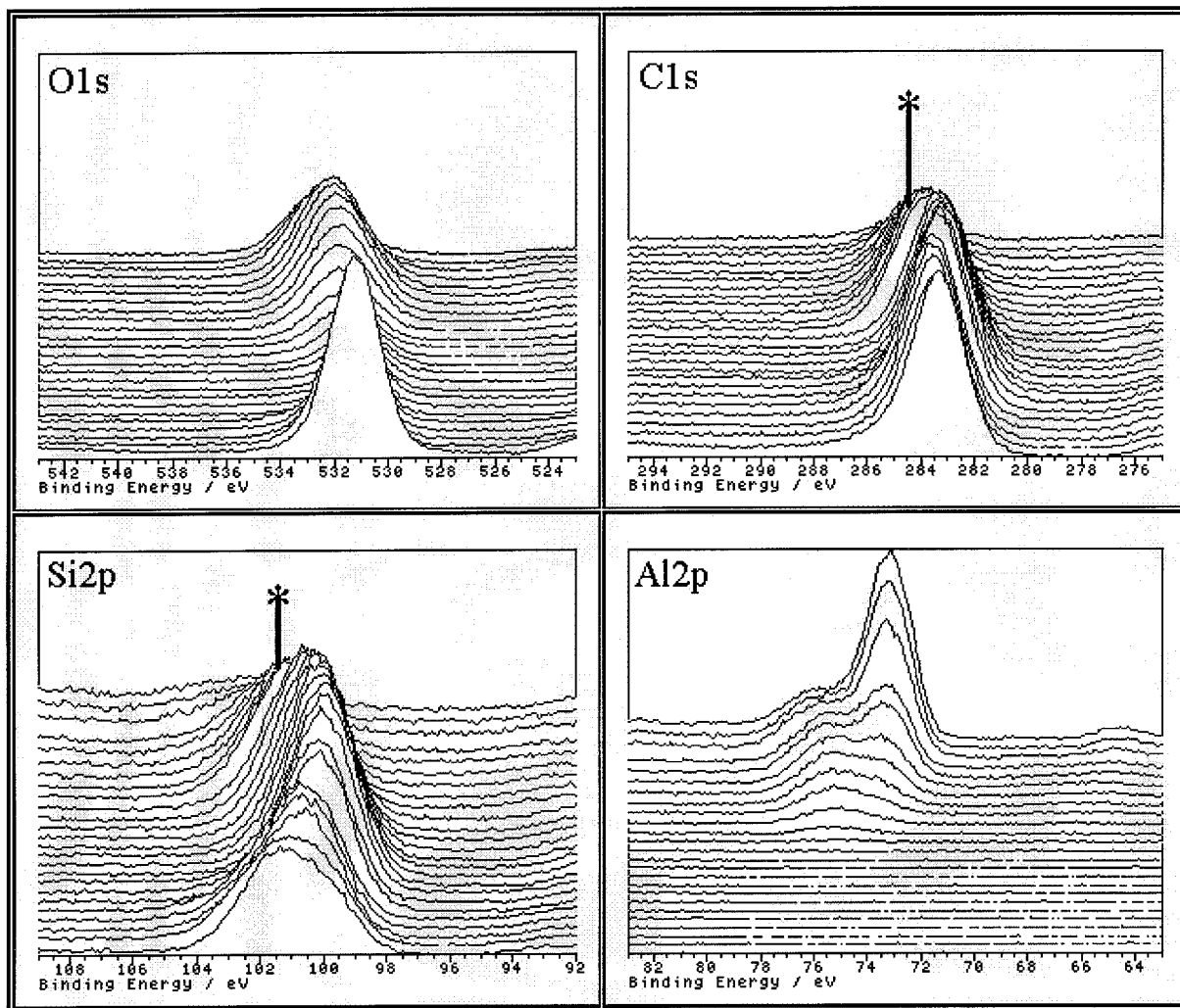
out, however, the oxygen plasma treatment played a key role in the successful operation of two consecutive plasma polymerizations of TMS and HFE. With oxygen plasma treatment, the initial sequence of plasma polymerization was always TMS/HFE. The influence of HFE plasma polymerization in the previous run was removed by the oxygen plasma treatment. In the event of inadvertent omission of oxygen plasma treatment, the initial sequence of plasma polymerization changed to HFA/TMS, although HFA plasma polymerization was performed in the previous run.

If HFE plasma polymerization did not leave any influence on the reactor (no reactor-wall con-

tamination), the change of sequence would not have influenced the plasma polymerization of TMS in the subsequent run. The effect of HFE plasma polymerization in the previous run caused extremely poor adhesion of the plasma polymer of TMS to the substrate alloy. This change could be correlated to the significantly reduced Si content at the interface, which was detected by XPS analysis of the delaminated paint film that contained an intact layer of plasma polymer. Figure 8 depicts the difference of Si/C XPS atomic ratios for the superadhesion interface and for the no-adhesion interface.

When we examined the plasma polymer coated systems, which showed adhesion problems after



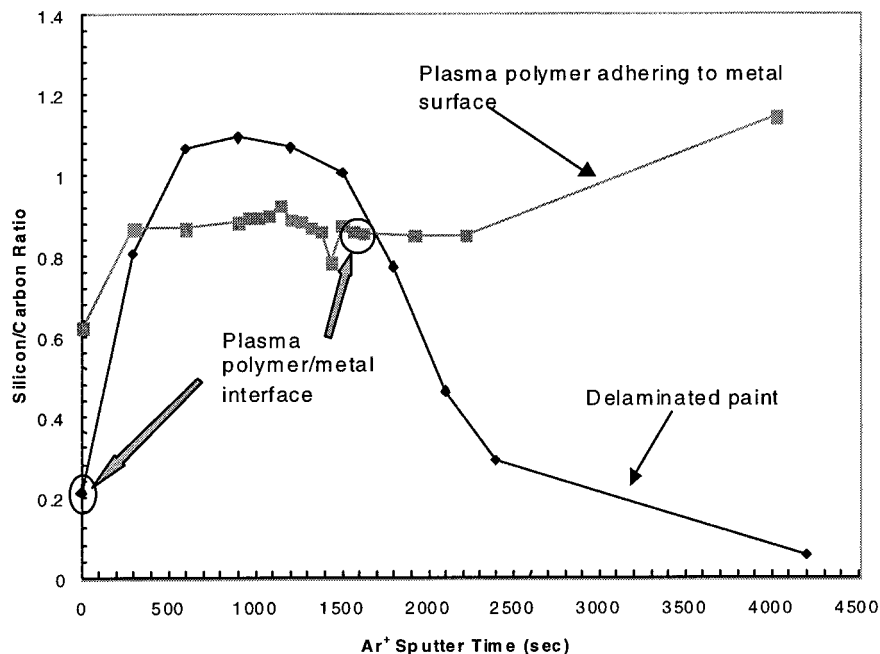


**Figure 7** Combined spectra from the depth profile of closed-system TMS film treated with an Ar plasma after deposition. The asterisk- marked line indicates the interface region.

primers were applied; we found that the adhesion of the plasma polymer was so poor that the plasma polymer layer could be wiped off with a tissue paper or a cotton swab wetted by an organic solvent or even with water. This suggests that the adhesion of the plasma polymer to a metal surface could be either excellent or extremely poor and that such a difference could be easily detected by a simple (solvent) wiping test. This principle was used to evaluate adhesion, as shown in Tables II and III. Although Ace was used in the test, the solvent effect had no influence on the test results as mentioned previously because well-prepared plasma polymers in this kind of application are insoluble and infusible. The same test could be performed with a dry cotton swab, yielding the same results.

Table II gives a comparison of the surface cleaning effects tested by a simple solvent wiping method. Preferred chemical pretreatments of aluminum alloys were used (i.e., Ace clean only for Alclad 2A and 7A, alkaline cleaning for bare 2024-T3 [2B], and deoxidizing for bare 7075-T6 [7B]), which yielded good adhesion and which were supported by excellent corrosion resistance obtained by primer coated systems.<sup>1-3</sup> The results also show the positive effect obtainable by the brief plasma treatments with O<sub>2</sub> or Ar shown by the Ace-cleaned [2B] and [7B].

The brief plasma pretreatment could be considered as added insurance to provide an appropriate surface state of the substrate, which was subjected to the subsequent plasma polymer deposition. This effect could be seen in the results



**Figure 8** XPS atomic ratio (Si/C) for the failed interface (delaminated paint) and for a good-adhering interface.

obtained with substrates, in which F-containing contamination was intentionally introduced by depositing the plasma polymer of HFE + H<sub>2</sub> for a

**Table II** Surface Cleaning Effects on the Adhesion of Plasma Polymers of TMS

Substrate	Chemical Clean	Plasma Clean	Plasma Coating	Adhesion (Ace Wiping)
[7B]	(Ace)	—	T <sup>a</sup>	Poor
		(O) <sup>b</sup>	T	Good
		(Ar) <sup>b</sup>	T	Good
[2B]	(Ace)	—	T	Poor
		(O)	T	Good
		(Ar)	T	Good
[2A]	(Ace)	—	T	Good
		(O)	T	Good
		(Ar)	T	Good
[7A]	(Ace)	—	T	Good
		(O)	T	Good
		(Ar)	T	Good

<sup>a</sup> 1 sccm TMS, 50 mtorr, DC-5 W, 1 min.

<sup>b</sup> 2 sccm O<sub>2</sub> or Ar, 100 mtorr, DC-40 W, 2 min.

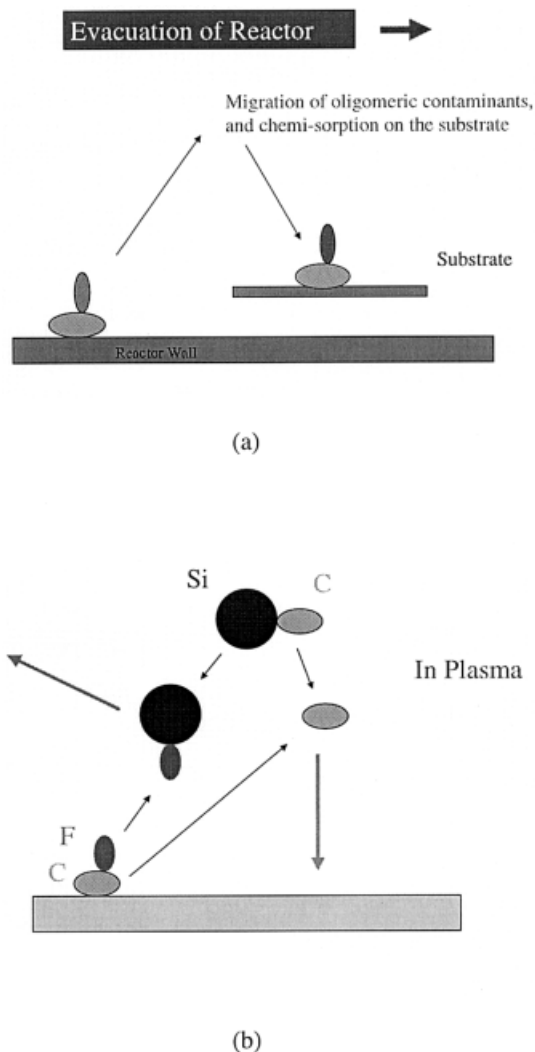
brief time (5 s), which yielded a deposition less than few nanometers thick. A thin layer of fluorocarbon plasma polymers on 7075-T6 surface behaved as contaminations on the surface, which led to poor adhesion of the subsequent TMS plasma coatings, as shown in Table III. Although the clean surface provided by deoxidized 7075-T6 substrates gave very good adhesion to TMS plasma coatings, the presence of an ultrathin layer (a few nanometers thick) completely destroyed the adhesion. When oxygen or argon plasma treatment was applied just before the plasma polymerization of TMS, the good adhesion was restored. These plasma pretreatments ap-

**Table III** Plasma Surface Cleaning Effects on the Adhesion of TMS Plasma Polymers to the Al Substrate [7A](Dox)

Surface Contamination on [7A](Dox)	Plasma Cleaning	Plasma Coating	Adhesion (Ace Wiping)
—	None	T	Good
HFE + H <sub>2</sub> (1:1) (5W, 5 s)	None	T	Poor
	(O)	T	Good
	(Ar)	T	Good

peared to remove the contaminant (F-containing plasma polymer); however, the careful investigation revealed the following mechanisms of how the good adhesion was restored.<sup>16</sup>

When a new substrate (Al alloy) was placed in the contaminated plasma reactor (with F-containing oligomers generated in the preceding run), the oligomers migrated to the surface of the substrate on the evacuation process. This process is depicted in Figure 9(a). When the plasma polymerization of TMS was attempted on the surface with the contamination, F atoms were emanated from the surface due to the exposure to plasma and reacted with Si in plasma phase, yielding stable



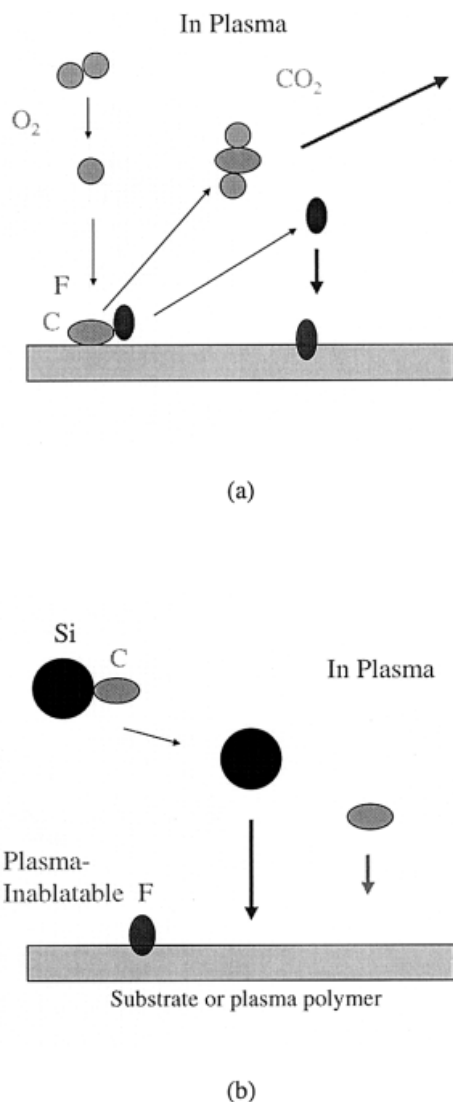
**Figure 9** Schematic representation of the mechanism of how F-containing contaminant interferes with the plasma polymerization of TMS: (a) migration of F-containing oligomers and (b) the interference in the TMS deposition by F-containing moieties.

S–F-containing moieties, which were pumped out of the system. This step is depicted in Figure 9(b). The decreased Si content and the presence of F were detected by XPS at the plasma polymer–alloy interface of poor adhesion samples. The interference of the initial stage of TMS deposition created a weak boundary and caused the poor adhesion (practically no adhesion) of TMS layer to the substrate.

When the contaminated surface was treated with O<sub>2</sub> plasma, the XPS F signal increased roughly five to six times compared to that without O<sub>2</sub> plasma treatment, indicating that the plasma treatment did not remove F-containing contaminants. However, it was found that the organic F-containing moieties changed to inorganic F-containing moieties, which changed the highly plasma-labile F to plasma nonablutable F.<sup>16</sup> This step is depicted in Figure 10(a). After F-containing (organic) oligomers were converted to inorganic F-containing oxides, the normal plasma polymerization of TMS occurred despite the increased number of F atoms on the substrate surface, as depicted in Figure 10(b). The plasma-labile F in an organic compound was converted to the plasma-nonlabile F in an inorganic compound by O<sub>2</sub> plasma treatment of the alloy surface. It is important to reiterate that O<sub>2</sub> plasma treatment actually increased the F content detected by XPS nearly five times of that without O<sub>2</sub> plasma treatment, implying that the key factor was the plasma sensitivity of F atoms but not the presence or absence of the element on the surface.

## CONCLUSIONS

Oxygen plasma treatment is effective in eliminating organic surface contamination, but plasma treatment such as that of argon plus hydrogen cannot be used to modify the surface state of oxides on these alloys. This is because oxides of aluminum are stable, thus resisting plasma modification, and prolonged plasma treatment has been observed to change concentrations of alloy components at the surface due to the heating of the alloy. It was found that chemical cleaning of the surface is necessary before the application of the plasma polymer used for corrosion protection enhancement. Once the surface was properly prepared, a plasma polymer of TMS, prepared by the cathodic polymerization, adhered well to aluminum alloys investigated in this study.



**Figure 10** Schematic representation of the mechanism of how oxygen plasma treatment prevents the interference in the plasma polymerization of TMS by F-containing oligomers: (a) oxygen plasma treatment and (b) plasma polymerization of TMS.

Major adhesive failure, however, was found as a consequence of reactor contamination when HFE plasma treatment of initially formed TMS plasma polymers was employed. A model study of surface contamination by brief (5 s) exposure of the substrate alloy to the plasma of HFE + H<sub>2</sub>

confirmed that the fluorine-containing contaminants reacted with oxides on the alloy and also substantially interfered with the initial stage of TMS deposition, yielding poor adhesion. Adhesion of the TMS plasma polymer to the Al alloy either was excellent or did not occur at all, which was determined by the absence or the presence of interference at the initial stage of TMS deposition.

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