Adhesion of Spray Primers to Plasma Polymer Coatings

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ABSTRACT: The adhesion failure of a primer on a plasma-polymer-deposited substrate surface could occur at the interface of the substrate/plasma polymer or at the interface of the plasma polymer/primer. We examined the adhesion of spray (solventborne or waterborne) primers on plasma polymer coated substrate with the substrate/plasma polymer systems in which the adhesion of the plasma polymer of trimethylsilane (TMS) to the substrate was good. Waterborne primers adhered well to quite hydrophobic plasma polymer surfaces, except the untreated surface of TMS. The plasma polymer of TMS appeared to contain a significant amount of oligomers, which were not in the three-dimensional network of the plasma polymer coating and caused poor adhesion of primers. The plasma treatment of the deposited plasma polymer of TMS increased the adhesion characteristics of the primers dramatically. The oxygen-plasma treatment, however, made the interface water sensitive and made the wet adhesion poor. The argon-plasma treatment of the plasma polymer of TMS was found to be a viable process that yielded excellent adhesion of spray primers. The plasma polymer of TMS deposited by a closed system, without further plasma treatment, yielded an excellent foundation for the application of spray primers. Waterborne, nonchromated primers adhered exceedingly well and survived 8 h of boiling in water (with a scribed surface) and became virtually nonstrippable by conventional stripping agents. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1443–1457, 2002

Key words: adhesion; coatings; ESCA/XPS; ESR/EPR; plasma polymerization

INTRODUCTION

The results of the corrosion testing of coating systems employing various plasma polymer interface layers have shown that some of these systems are quite superior to standard chromate conversion coating control samples.[1–7] An ultrathin layer (~50 nm) of the plasma polymer of trimethylsilane (TMS) was applied onto an aluminum alloy, which was appropriately surface treated prior to the plasma coating. The plasma polymer layer acts as an adhesion promoter for a primer that will be applied on the surface. In such an approach, no corrosion inhibitor, in any form such as chromate conversion coating or chromates incorporated in a primer, is involved. The total elimination of environmentally hazardous and health-hazardous components from the corrosion protecting system is the objective of such an effort. The water-insensitive tenacious adhesion of an excellent barrier is the key factor in the system approach interface engineering (SAIE), which provides an alternative approach to corrosion pro-

tection without a corrosion inhibitor in the system.[8]

The most noteworthy finding among many interesting and significant results obtained in these SAIE approaches was the phenomenal adhesion obtained by the combination of the plasma polymerization of TMS followed by plasma treatment with hexafluoroethane (HFE). A cathodic E-coat (electrolytic deposition of a paint) was applied on aluminum alloys prepared by the TMS/HFE treatment, and then the E-coat, after the normal curing processes, became unstrippable by any chemical means. Commercially available stripping solution could not remove the paint. The immersion in a hydraulic fluid known as a notoriously strong stripping agent for several days did not affect the paint.

Although this TMS/HFE system was eventually abandoned due to the potentially damaging wall-contamination effect, which could change the superadhesion to an extreme case of no adhesion,[9] and to the difficulty of keeping such a wall contamination under absolute control, the system provided enough incentive to investigate how such an extraordinary adhesion could be obtained.

Postdeposition treatments may fully suffice to provide the additional interface stability to allow for their use in the development of long-life corrosion protection systems. This article focuses on how the postdeposition plasma treatment of the formed film modifies the outermost layer, allowing more flexibility in the tailoring of film surfaces with chemistries that have shown desirable properties. The effects were investigated with spray primers.

EXPERIMENTAL

All experimental procedures, except the following, were presented in the preceding article on adhesion of plasma polymers to aluminum alloys.[10]

Plasma Deposition in a Closed Reactor

To conduct plasma deposition in a closed reactor system, the anode assembly was removed, and the grounded reactor wall was used as the anode during operation. The reactor chamber was first pumped down to less than 1 mtorr. We then isolated the reactor chamber from the pump system by closing the main valve to the pumping system.

TMS gas, controlled by an MKS mass flow meter (model 247C) (MKS Instrument, Burlington, MA), was then fed into the reactor. After the system pressure reached the preset point, TMS gas feeding was stopped, and direct current power was then applied to initiate the glow discharge to start cathodic polymerization.

Application of Primers

The chromated spray primers employed in this study were waterborne Deft 44-GN-36 (A) and 44-GN-72 (A1) (Deft Corporation, Irvine, CA) and solventborne Courtauld 519X303 (G; Courtauld Aerospace, Glendale, CA). The nonchromated spray primers were waterborne Dexter 10-PW-22-2 (X; Dexter Corporation, Waukegan, IL) and waterborne Spraylat EWAE118 (D; Spraylat Corporation, Chicago, IL).

Primers were sprayed onto the substrates with an airbrush. After painting, primer-coated samples were cured according to the stipulations provided by the primer suppliers. After curing, the thickness of primer coatings was measured with an Elcometer 355 (Elcometer Inc., Rochester Hill, MI). The thicknesses of the primer coatings were controlled to be around 1.0 mill (25.4 μm). Table I summarizes the samples investigated and the codes used to describe them.

Adhesion Tests

Adhesion performance was first evaluated via the tape test according to ASTM D 3359-93B.[11] This testing method provides semiquantitative results given in grades of 0–5. Poor adhesion can be easily detected by this simple test. When the test result reaches the grade of 5, this simple test cannot distinguish between results. However, if samples are exposed to some adhesion-damaging environment before the tape test, it is possible to further distinguish the level or nature of adhesion.

The boiling water test is such a modification of the tape test.[12] In this process, the test specimens are prepared according to the standard procedure described previously. Instead of direct application of the tape test, the specimens are placed in boiling water for a predetermined period of time. In this study, times of 1, 4, and 8 h were used. Samples initially immersed in boiling water (with prescribed marks) were subjected to the tape test. Because the interface between the coating and the substrate metal was exposed to boiling water,

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

Identification Code	Meaning and Conditions
[2A]	Alclad 2024-T3
[7A]	Alclad 7075-T6
[2B]	AA 2024-T3
[7B]	AA 7075-T6
(Ace)	CH_3COCH_3 wiping with Kimwipes® tissue
(Alk)	Alkaline cleaning (65°C, 25 min)
(Dox)	Deoxidization (room temperature, 10 min, always preceded by alkaline cleaning)
(O)	O_2 plasma pretreatment (on A1 surface: 1 sccm O_2, 100 mtorr, 40 W, 2 min; on TMS polymer surface: 1 sccm O_2, 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)
Tfs	TMS plasma polymerization without anode assembly in a flow reactor (1 sccm TMS, 50 mtorr, 5 W, 1 min)
Tcs	TMS plasma polymerization without anode assembly in a closed reactor (25 mtorr TMS, 1000 V, 2 min)
A	Deft spray primer 44-GN-36 (chromated, waterborne)
A1	Deft spray primer 44-GN-72 (chromated, waterborne)
G	Courtauld spray primer 519X303 (chromated, solventborne)
X	Dexter spray primer 10-PW-22-2 (nonchromated, waterborne)
D	Spraylat spray primer EWAE118 (nonchromated, water borne)
/	Process separation mark

Codes used in parentheses indicate the surface treatment process; codes used without parentheses indicate the coating process.

the water sensitivity of the adhesion could easily be detected by this test.

RESULTS AND DISCUSSION

X-Ray Photoelectron Spectroscopy (XPS) Analysis of the Plasma Polymer Surface

TMS/HFE System

Saturated C_1- and C_2-perfluorocarbons are etching gases for silicon used in the microelectronics industry and do not polymerize well in a plasma environment. HFE does not polymerize in the absence of hydrogen.[13] However, if hydrogen atoms are available in the molecule of the substrate, HFE polymerizes by abstracting hydrogen from the polymer of TMS. After the plasma polymer of HFE covers the surface, the polymerization ceases in all practical senses.

When HFE plasma is used as the second gas plasma treatment following the plasma deposition of TMS, the two major reactions mentioned previously could occur simultaneously and in a competitive manner, namely, the etching of some of Si from the plasma polymer of TMS and the deposition of the plasma polymer of HFE by the utilization of hydrogen atoms existing in the plasma polymer of TMS. If there existed Si-based deposits (oligomers) that were not well established in the top surface region of plasma polymer of TMS, they would be the prime target of the etching by HFE.

Figure 1 depicts XPS analysis of the HFE polymer formed on the plasma polymer of TMS, which clearly indicates that the plasma polymer of HFE was formed on the surface of the plasma polymer of TMS. The thickness of such a film was anticipated to be very small because not much hydrogen is available on the surface of the plasma polymer of TMS (compared to a conventional polymer surface).

Figure 2 shows combined spectra from the depth profile of the flow-system TMS film on polished AA 2024 T3 treated with HFE plasma after deposition. Figure 3 depicts the same sets of profiles for TMS alone. The results shown in Figure 2 indicate the following three important aspects, which seem to be related to how the superadhe-
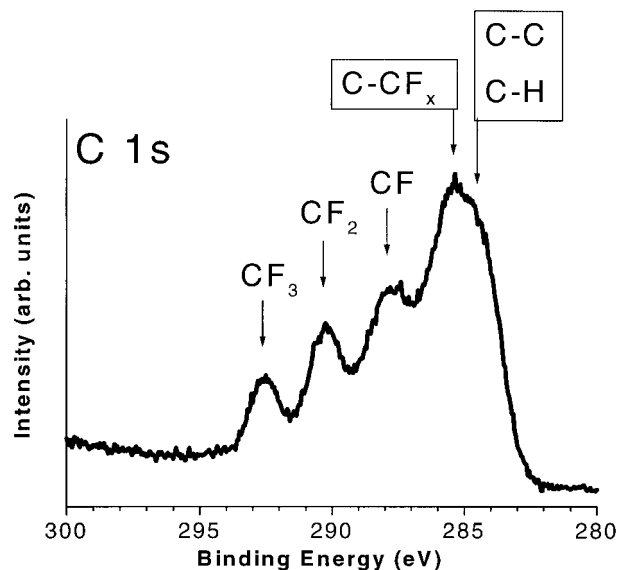
Figure 1 Monochromatic, 20-eV pass energy; C1s spectrum from the HFE plasma polymer on TMS plasma-polymer-coated 2024 panel.

sion could be achieved by this particular combination of plasma processes.

The first is that an extremely thin layer (estimated as less than a few nanometers) of the plasma polymer of HFE was formed on the plasma polymer of TMS. The second is that the oxygen content at the top surface was significantly lower. The third is that the Si content at the surface detectable by XPS was also significantly lower than the respective value for the plasma polymer of TMS (shown in Fig. 3).

TMS/Ar and TMS/O$_2$ Systems

The first and the third aspect indicate the concurrent processes of plasma polymer formation and plasma etching of Si respectively. The second aspect (small oxygen content) seems to be related to the decay characteristics of free radicals formed on polymeric substrate by plasma exposure, which is discussed in a later section. Figures 4 and 5 depict the same XPS combined profile for the Ar-plasma-treated surface and O$_2$-plasma-treated surface, respectively.

One of the postdeposition plasma treatments, characterized here, moved the surface from a carbon-rich state to one rich in silicon–oxide bonds. Another reached an intermediary position with some silicon–oxygen enrichment but in a distinctly different silicon structure, somewhat in-termediary between the bulk of the flow-film level and true silicon oxide.

TMS Deposited in a Closed System

The direction followed in the scaling of these plasma processes up to a practical level, through application within the primary existing ion vapor deposition of aluminum framework, required the investigation of operation in a nonflow environment. The parameters for good film deposition change in a closed system due to the potential depletion of particular species from the plasma. Closed-system film deposition, followed by plasma treatment, appears to be a remarkably viable technique for modifying alloy surfaces in a nonflow environment while maintaining control of the plasma film surface chemistry.

Figure 6 shows some summary surface information from three closed-system TMS films with different surface treatments. These films were deposited on Alclad 7075, which was cleaned with acetone and then treated with O$_2$ plasma prior to film deposition. The Ar-treated film also had a distinct layer on the surface, but this was composed of the intermediary bonding and was thought to be some silicon–oxycarbide bond or Si$_2$O bonding[14–16] due to the concentration variations. Other designations may be quite possible because plasma processing can leave various, frozen-in, nonequilibrium states. A unique feature of the O$_2$-treated sample was the structure in the valence band, which was highly uncharacteristic of the multitude of films investigated thus far.

The O$_2$-plasma-treated film exhibited the distinct silicon–oxide bonding, similar to the flow film that was treated with O$_2$ plasma, but had the fairly unique valence band that indicated a very different electronic structure. The surface ratio of oxygen to silicon was again nearly 2 for this film, further qualifying the silicon–oxide classification. This was the only one of the three closed-system films that had a level of silicon on the surface that was higher than the bulk level, indicating that the O$_2$ plasma had the effect of removing carbon from the film as a volatile compound and restructuring the surface into a silicon–oxide rich layer. This also manifested itself as a higher Si/C ratio than the bulk value, which was, again, unique to this film. The angular measurements showed that the top layer of the O$_2$-plasma-treated surface was thicker than the layer on the Ar- surface.
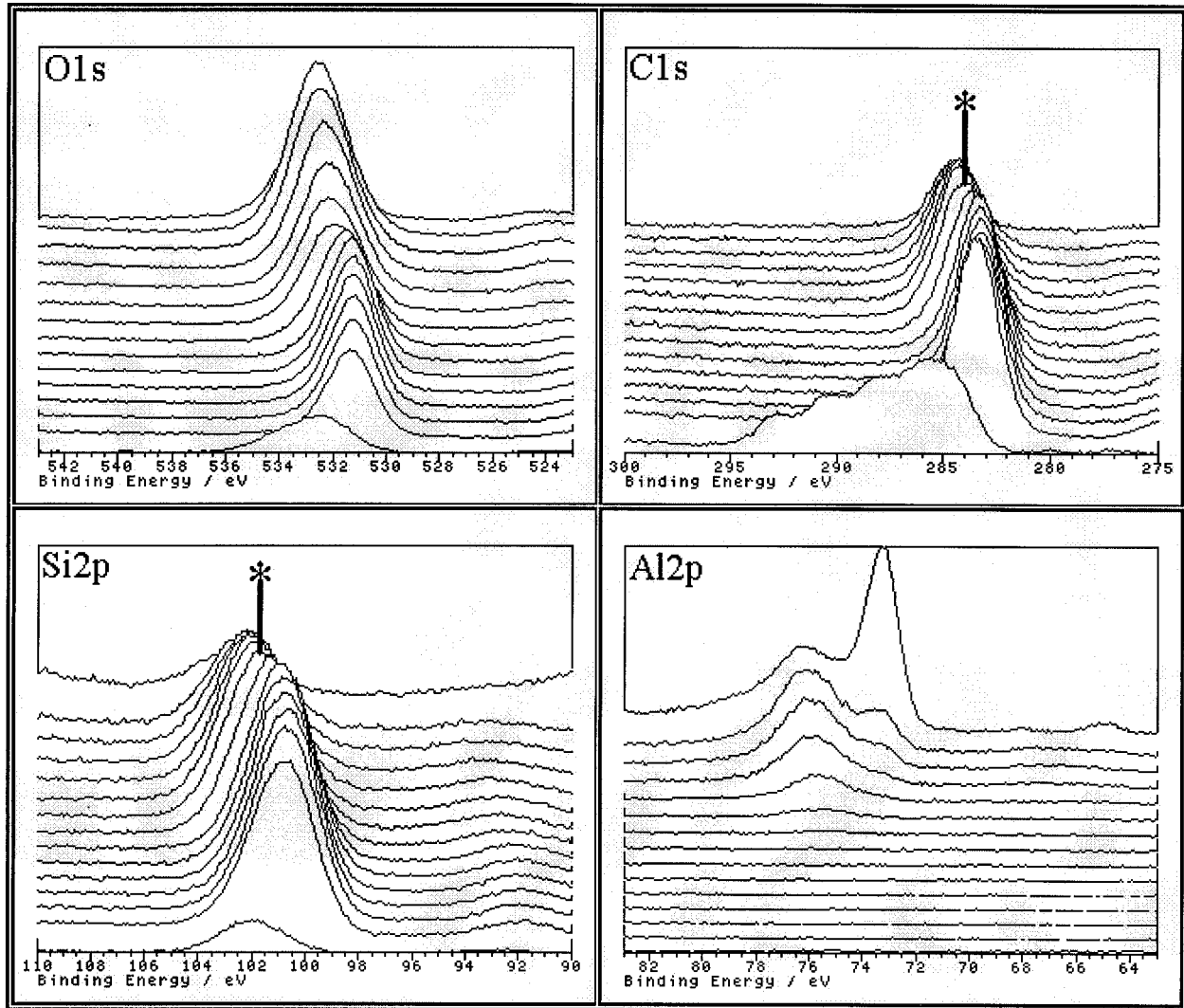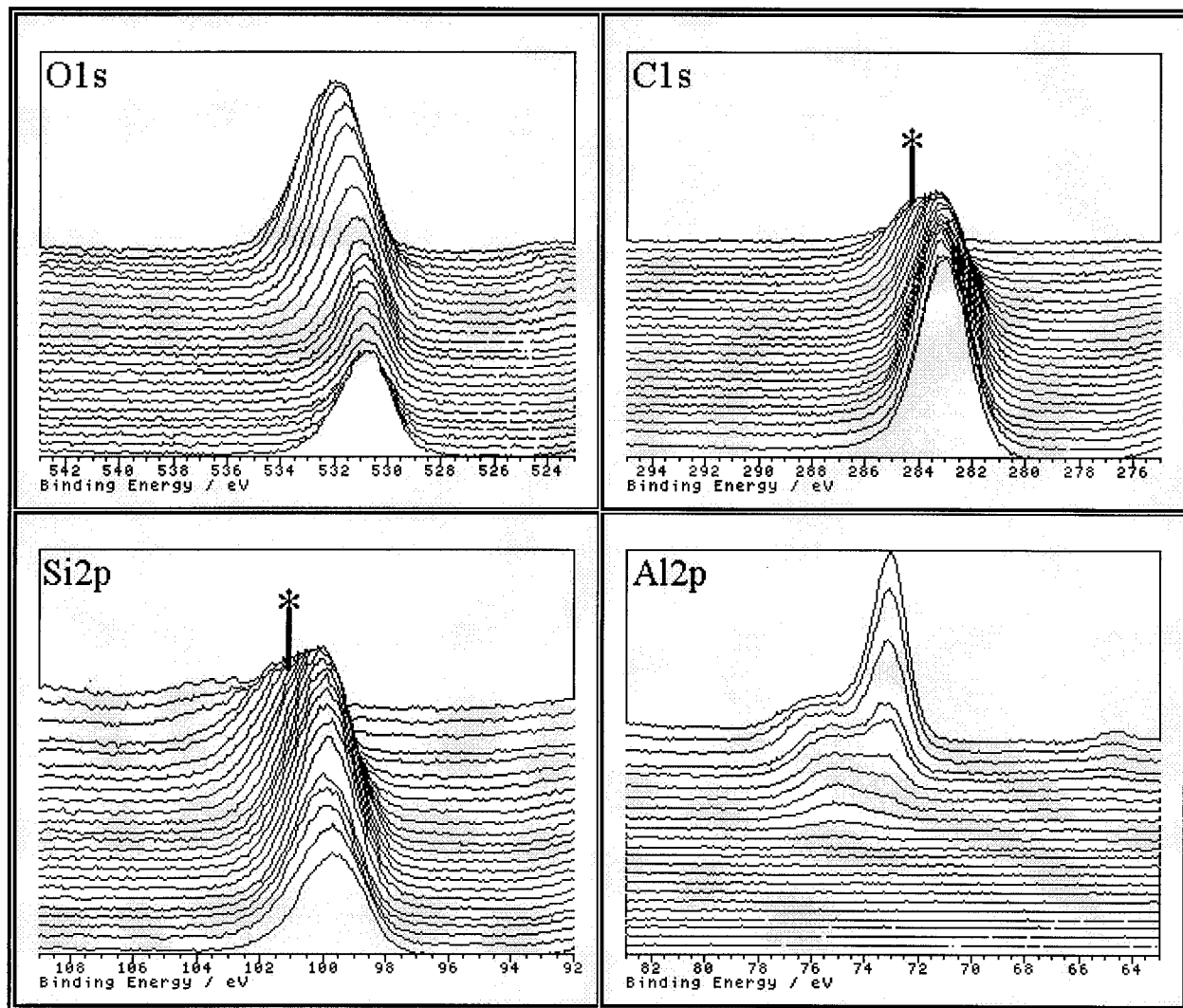
Figure 2 Combined spectra from the depth profile of the flow-system TMS film on polished 2024 treated with HFE plasma after deposition. The asterisk-marked line indicates the alloy interface region.

Adhesion of Primers

Adhesion of Waterborne Primers to Plasma Polymer Films Prepared in a Flow System

The adhesion test results of primers to plasma T/F as a function of time after the plasma treatment before the application of prime is summarized in Table II. The time kept in ambient conditions before the application of primer did not influence the adhesion of primers up to 6 days. Even waterborne primers (Primer A) survived 8 h of boiling the prescribed surface in water, and Turco stripping solution could not remove paints in 24 h. (The test was terminated after 24 h.)

The modification of TMS film was limited to the top surface region, but the structural changes, whatever was the true nature of changes, altered the adhesion characteristics of primers applied on the surface, as depicted in Table III. As shown in Table III, those two spray primers (waterborne Primer A and solventborne Primer G) did not adhere to the TMS surface. When a film came off from the alloy, the alloy surface retained the characteristic blue color of TMS, indicating the bulk of the plasma polymer film was attaching to the alloy surface. The adhesion of TMS films to pretreated alloy surfaces was good. Therefore, the reasons why the primers did note adhere to TMS
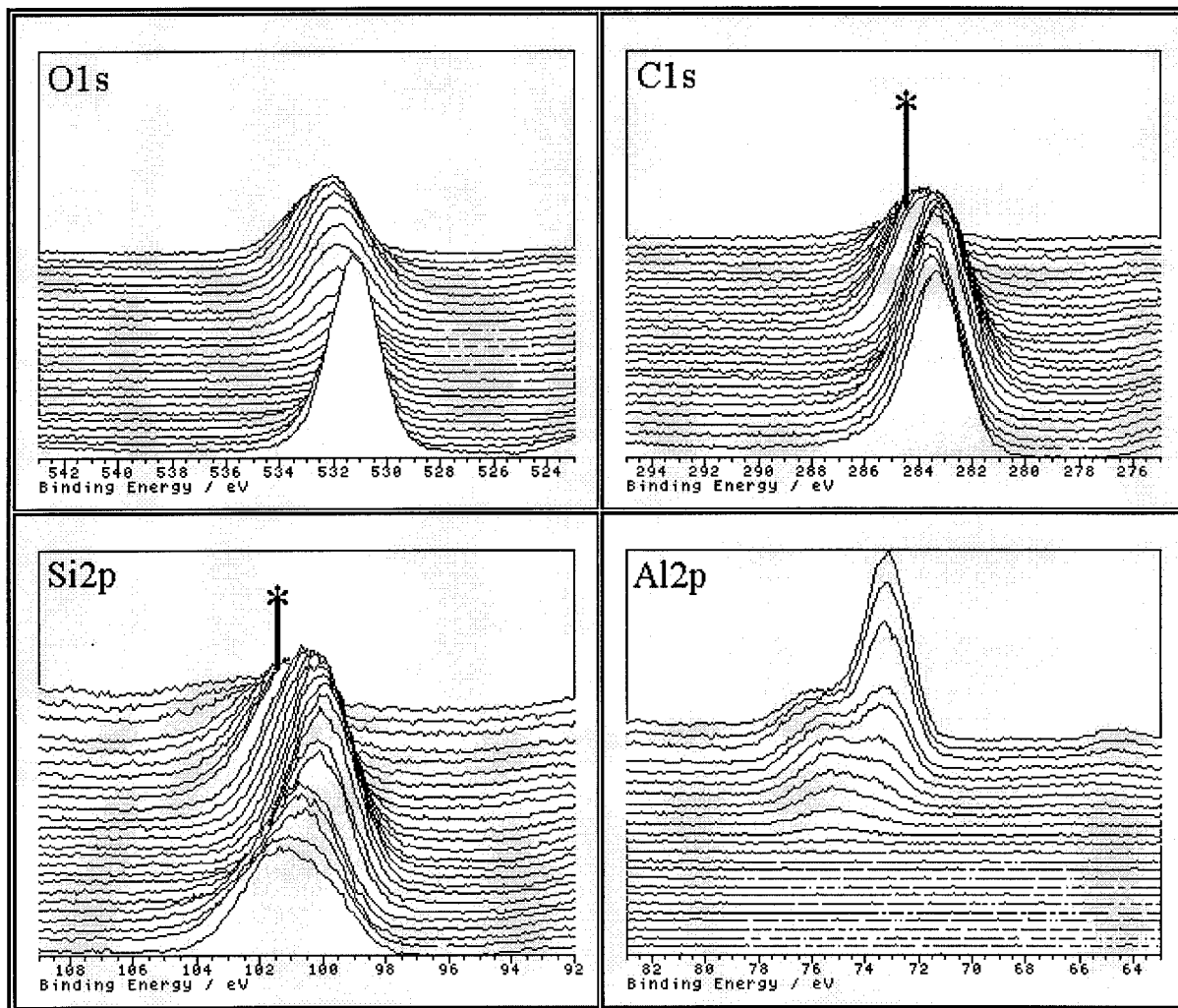
Figure 3 Combined spectra from the depth profile of the closed-system TMS film. The asterisk-marked line indicates the interface region.

surface could be speculated as (1) the wetting problem and (2) the structural weakness of the top region of TMS films.

The data presented in Table IV indicate that the low surface energy of TMS film did not seem to be the major reason because the surface of TMS/HFE was also very hydrophobic. There was no correlation between the contact angle of water and the adhesion among the samples shown in Table IV. Then, the modification of the structure of the top region of TMS by HFE plasma, for which a partial etching of loosely held oligomers of TMS might have played an important role, stands out as the major mechanism for the superadhesion.

Plasma polymerization does not occur by a chain-growth mechanism. Too many free radials

are formed within a give time, and the recombination of free radicals predominates. This situation was illustrated by the rapid step growth mechanisms, which are essentially oligomerization processes.[17] To obtain a tight network, cycles or reactions should be repeated many times, which becomes difficult when the characteristic deposition rate is high or when conditions for a quick deposition are employed. The characteristic polymerization rate of Si-containing organic compounds are nearly seven times faster than hydrocarbons.[18] It was, therefore, anticipated that the top surface of the plasma polymer of TMS should contain a significant amount of oligomers. The overshooting effect observed in the second cycle of the Whilhelmy balance force measurement
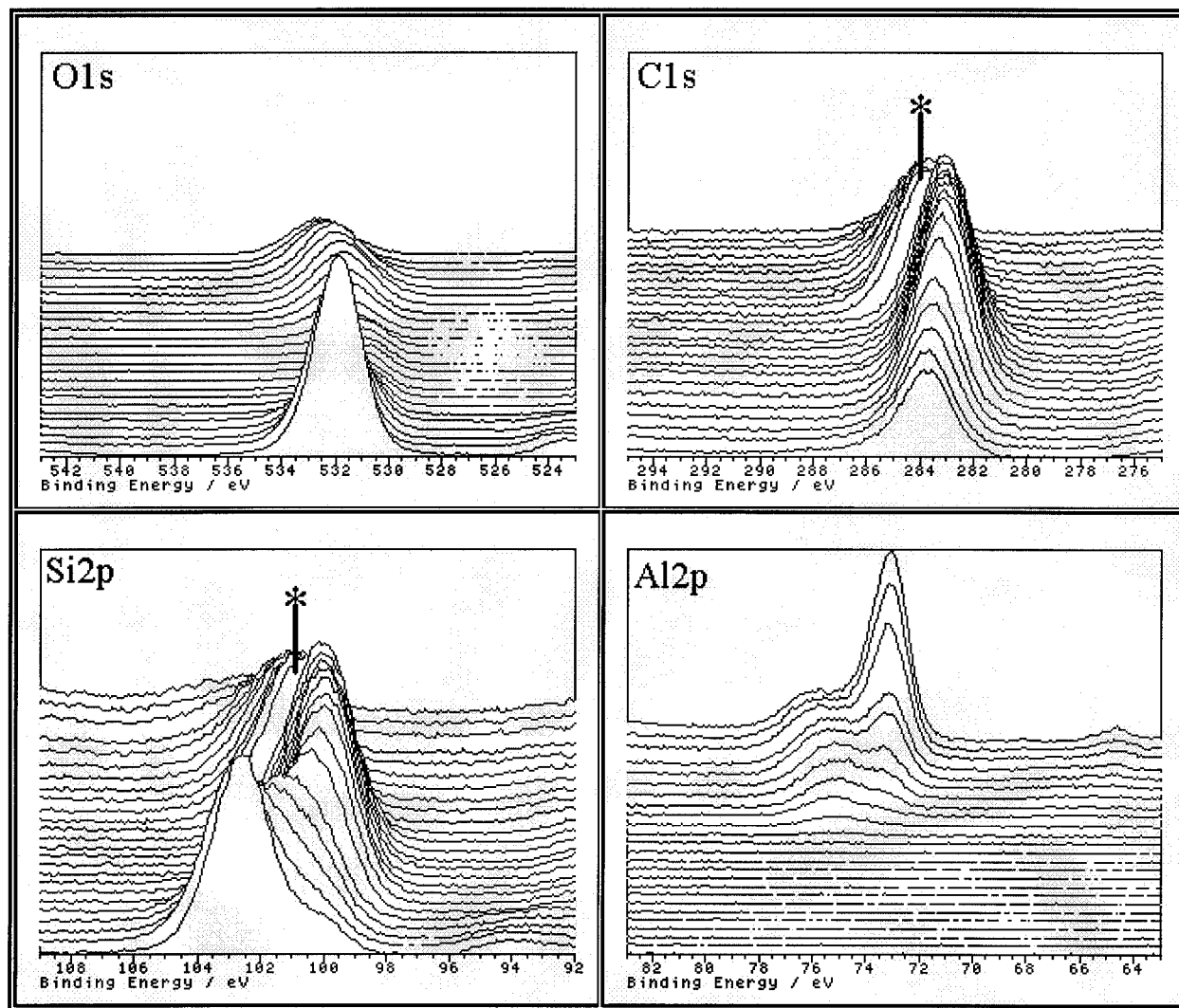
Figure 4 Combined spectra from the depth profile of the closed-system TMS film treated with Ar plasma after deposition. The asterisk-marked line indicates the interface region.

strongly suggests the presence of oligomers in the top surface region of the plasma polymer of TMS.[19]

According to this working hypothesis based on the presence of oligomers on the top surface region of the plasma polymer of TMS, the second plasma treatments of TMS film by gases other than HFE were carried out in this study. Table V depicts the effect of the second plasma treatment on the adhesion of the two selected waterborne primers. Figure 7 shows the change in the contact angle of water by the second treatments. All these data could be best explained by the conversion of a weak boundary, presumably of oligomers in nature, to a more stable and stronger network system.

Adhesion of Waterborne Primers to Plasma Polymer Films Prepared in a Closed System

As shown by XPS data, the cathodic polymerization of TMS in a closed system yielded a significantly different films structure from that prepared in a flow system. The film had a graded elemental composition structure, going from Si-rich at the alloy interface to C-rich at the top surface region. This was due to the difference in the characteristic deposition rates of C and Si.[20] Consequently, the plasma phase started to change to C-rich and Si-depleted as soon as the plasma state was created. In a flow system, the plasma phase established a new dynamic equilibrium coping with this change in the composition.

Figure 5 Combined spectra from the depth profile of the closed-system TMS film treated with O_2 plasma after deposition. The asterisk-marked line indicates the interface region.

In a closed system, no new monomer was supplied, and the plasma phase continuously changed until everything depositable left the plasma phase. The deposition rate in the closed system employed in this study reached a plateau value in approximately 2 min. Thus, the second plasma treatment by a gas plasma was built in to the closed-system polymerization of TMS. Because of this change in film structure, the adhesion of the waterborne primers to the TMS surface was very good, whereas that to TMS film prepared in a flow system was extremely poor.

Table VI summarizes the adhesion of chromated waterborne primers to the TMS film pre-

pared by a closed reactor and to the same film modified by a second plasma treatment. Table VII depicts the same for nonchromated waterborne primers. The contact angle of water on TMS films, as a function of the treatment time, prepared in a flow system and in a closed system are compared in Figure 8. The contact angle of water on the TMS film prepared in a closed system was significantly lower than that of the TMS film prepared in a flow system. However, after the second plasma treatments, the contact angle seemed to converge to more or less the same level, depending on the type of plasma treatment. In the case of the flow system, the second plasma treatment yielded

Closed System on 7A,

Top Surface Spectra (No Sputtering)

0-degree Take off angle
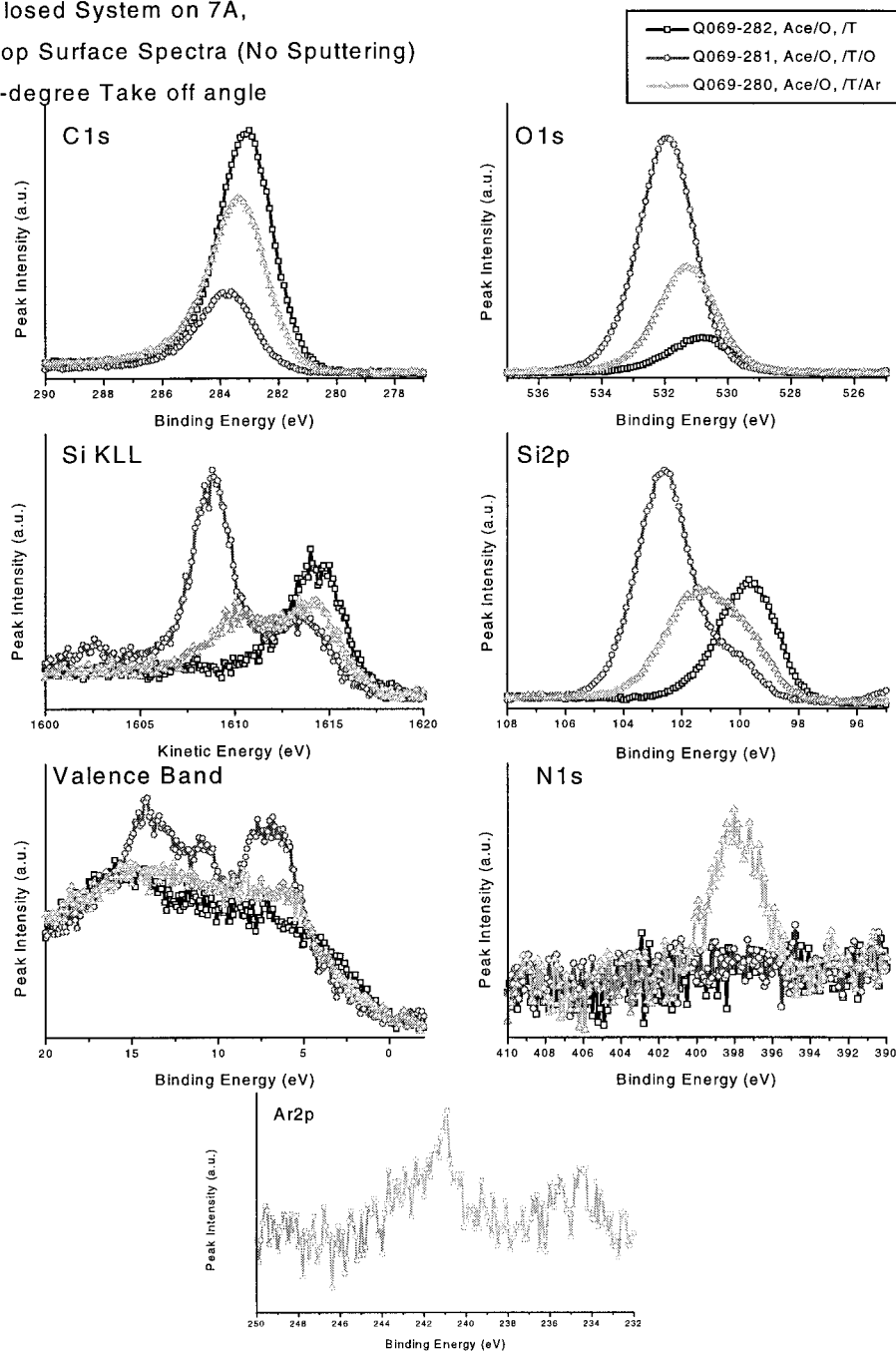
Figure 6 Plots showing a comparison of the top surface spectra from three TMS plasma polymers with different postdeposition plasma treatments. This comparison is of the normal incidence collection.

more or less the same hydrophilicity regardless of the type of gas used, except in the case of oxygen.

The second plasma treatment had an advantageous effect on the adhesion. Oxygen-plasma treatment, however, made the primer/plasma polymer interface vulnerable to water interaction and made the wet adhesion very poor. The TMS/Ar system would be sufficient to replace TMS/HFE with a great gain in the elimination of F-containing contamination.

Table II Adhesion Test Results of Primers to Plasma T/F (DC-Plasma-Polymerized TMS Followed by HFE) Coated 7075-T6 Panels (After Alk/Dox)

Primers	Air Exposure Time of T/F Before Primer Coating	Tape Test		Turco Strip-Off Time (h)
		Dry	H_2O Boiled for 1, 2, 4, 6, 8 h	
Primer A	~ 10 min	5	5, 5, 5, 5, 5	> 24
	24 h	5	5, 5, 5, 5, 5	> 24
Primer D	~ 10 min	4	4, 4, 4, 4, 4	> 24
	24 h	4	4, 4, 4, 4, 3	> 24
	48 h	4	4, 4, 4, 4, 4	> 24
	76 h	4	4, 4, 4, 4, 4	> 24
	6 days	4	4, 4, 4, 4, 4	≥ 24[a]
Primer G	~ 10 min	5	5, 5, 5, 5, 5	> 24
	24 h	5	5, 5, 5, 5, 5	> 24
	48 h	5	5, 5, 5, 5, 5	> 24
	76 h	5	5, 5, 5, 5, 5	> 24
	6 days	5	5, 5, 5, 5, 5	≥ 24[a]

Primer A is a waterborne, chromated deft primer; D is a waterborne, nonchromate spraylat primer; and G is a solventborne, chromate primer.

[a] A few blisters started to develop after 24 h of the Turco stripping test.

Although it has been well documented that argon-plasma treatment on an organic surface could produce a more cohesive skin to enhance primer adhesion through crosslinking effects on the top surface,[21] the mechanisms for the adhesion improvement of the plasma polymer of TMS were quite different from the crosslinking of conventional linear polymers as seen in the XPS analysis, the change of surface energy, and the covalent bond formation discussed later.

Potential Role of Free Radicals in the Plasma Polymer of TMS for the Adhesion of the Primer

Separate electron spin resonance (ESR) studies on the free radicals in the plasma polymers, including that of TMS by cathodic polymerization as used in this study, have been carried out recently.[22,23] Based on the results of these studies, the potential role of free radicals for the adhesion of primers placed on the surface of the plasma

Table III Adhesion Test Results of Chromated Spray Primers (Waterborne Primer A and Solventborne Primer G) to A1 Alloys Prepared with Chemical Cleanings and Plasma Surface Treatments

Substrate	Surface Preparation	Primer A			Primer G		
		Tape Test	Boiling (1, 4, 8 h)	Turco Time	Tape Test	Boiling (1, 4, 8 h)	Turco Time
[2B]	(Alk)	5	3, 3, 3	~ 5 min	5	5, 5, 5	~ 30 min
	(Alk)/T	0	—	—	0	—	—
	(Alk)/T/F	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h
[7B]	(Dox)	4	4, 4, 4	~ 30 min	5	4, 4, 4	~ 30 min
	(Dox)/T	0	—	—	0	—	—
	(Dox)/T/F	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h
[2A]	(Ace)	3	—	~ 5 min	5	4, 4, 4	~ 5 min
	(Ace/O)/T	0	—	—	0	—	—
	(Ace/O)/T/F	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h
[7A]	(Ace)	3	—	~ 5 min	5	4, 4, 4	~ 5 min
	(Ace/O)/T/F	0	—	—	0	—	—
	(Ace/O)/T/F	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h

Table IV Second Plasma Treatment Effect of TMS Plasma Coatings on the Adhesion of Waterborne Primers [Deft 44-GN-36 (A) and 44-GN-72 (A1)] to Alclad 7075-T6 Alloy {[7A] (Ace/O)}

First Layer	Second Layer	Water Contact Angle (°)	Dry Tape Test	
			Primer A	Primer A1
TMS	—	120	0	0
	HFE	103	5	5
	HFE + H_2 (1 : 1)	97	1	0
	CF_4	98	0	0
	C_3F_6	108	0	0
	CH_4	80	5	5
	CH_4 + Ar (1 : 1)	77	2	0

polymer of TMS is briefly examined here. The ESR signal of the plasma polymer of TMS is a broad signal without any hyperstructure that is assigned as the free spins on Si. To distinguish such a signal from free radicals with hyperstructures created on polymers by plasma, the term *Si dangling bond* is used in this discussion.

The Si dangling bond did not decay in a vacuum but showed fast decay as soon as the sample was exposed to ambient air. The initial stage of the decay followed first-order decay kinetics but started to deviate from first-order decay in 0.5–2 h. Slower decay followed second-order decay if a certain amount of nondecaying concentration of

Table V Surface Treatment Effect of TMS on the Adhesion of Waterborne Spray Primers [Deft 44-GN-36 (A) and 44-GN-72 (A1)] to Alclad 7075-T6 Alloy {[7A](ACE/O)}

Second Plasmas and Plasma Conditions		Primer A			Primer A1		
		Tape Test Rating			Tape Test Rating		
		Dry	Boiled for 8 h	Turco Time	Dry	Boiled for 8 h	Turco Time
—	—	0	—	—	0	—	—
HFE	5 W, 1 min	5	4	> 24 h	5	4	> 24 h
O_2	2 W, 1 min	4	2	~ 10 min	3	2	~ 8 h
	5 W, 30 s	5	3	~ 15 min	5	3	> 24 h
	5 W, 1 min	5	3	~ 10 min	4	3	> 24 h
	5 W, 2 min	5	3	~ 15 min	5	3	> 24 h
	10 W, 1 min	5	3	~ 10 min	4	3	> 24 h
Ar	2 W, 1 min	5	3	~ 20 min	5	3	~ 1 h
	5 W, 30 s	5	3	~ 10 min	5	3	~ 10 h
	5 W, 1 min	5	3	~ 20 min	5	3	~ 1.5 h
	5 W, 2 min	5	3	~ 15 min	5	3	~ 12 h
	5 W, 3 min	5	3	~ 15 min	5	3	~ 8 h
	10 W, 1 min	5	3	~ 20 min	5	3	> 24 h
	20 W, 1 min	5	4	~ 10 min	5	3	> 24 h
H_2	2 W, 1 min	5	3	~ 10 min	5	3	~ 2.5 h
	5 W, 1 min	5	3	~ 15 min	5	3	> 24 h
	10 W, 1 min	5	2	~ 20 min	5	3	> 24 h
	20 W, 1 min	5	3	~ 10 min	4	3	~ 2.5 h
He	2 W, 1 min	4	3	~ 10 min	4	2	~ 40 min
	5 W, 1 min	4	3	~ 10 min	4	2	~ 1.0 h
	5 W, 2 min	4	3	~ 20 min	4	2	~ 3 h
	10 W, 1 min	5	3	~ 1.3 h	4	3	> 24 h
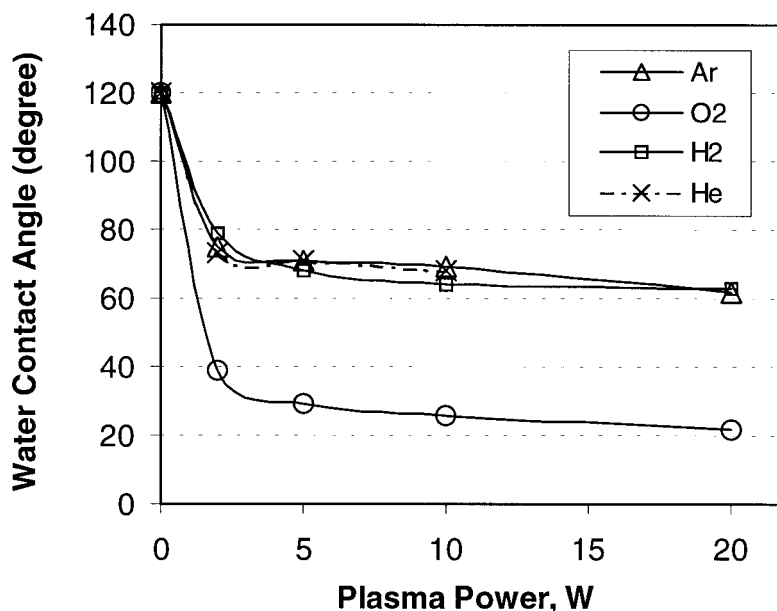
Figure 7 Water contact angle changes of TMS coatings (prepared by a flow-system reactor) with power input of second plasma treatments.

the dangling bonds was subtracted. These decay characteristics strongly indicate that there were a certain amount of dangling bonds that did not decay. The decay rate in the second stage seemed to be related to the mobility of moieties involved in the network of plasma polymers. The ramification was that the tighter network showed the slower decay.

The second plasma treatments, with HFE, Ar, and O_2, all showed common aspects, which were (1) a decrease in the initial dangling bond concen-

tration and (2) a significantly slower (close to zero in the case of HFE) rate in the second-stage decay. The decrease in initial dangling bonds could be interpreted as the result of the ablation of loosely attached oligomeric dangling bonds (particularly in the case of HFE, which is a good etching gas for Si) or the conversion of oligomeric dangling bonds to a more stable network of the plasma polymer via reactions of dangling bonds under the influence of the second plasma. Under either scheme, the adhesion of primers would be

Table VI   Surface Treatment Effect of TMS by No-Anode Assembly Plasmas on the Adhesion of Deft (Chromated, Waterborne) Primers to 7A(Ace/O)/T

| TMS Coating	Second Plasma (1 min)	Deft 44-GN-36 (A)			Deft 44-GN-72 (A1)		
		Dry Tape Test	Boiling (1, 4, 8 h)	Turco Time	Dry Tape Test	Boiling (1, 4, 8 h)	Turco Time
Closed, 25 mtorr, 1000 V 2 min	—	5	4, 3, 3	∼ 5 min	5	3, 3, 3	∼ 10 min
	Ar, 2 W	5	4, 3, 3	∼ 20 min	5	5, 4, 4	> 24 h
	Ar, 5 W	5	4, 3, 3	∼ 20 min	5	5, 4, 4	> 24 h
	Ar, 10 W	5	4, 3, 2	∼ 20 min	5	5, 4, 4	> 24 h
	Ar, 20 W	5	4, 4, 4	∼ 20 min	5	4, 4, 3	∼ 12 h
	O_2, 2 W	5	0, —	∼ 5 min	4	0, —	∼ 5 min
	O_2, 5 W	5	0, —	∼ 5 min	4	1, 0, —	∼ 8 min
	O_2, 10 W	5	0, —	∼ 5 min	4	1, 0, —	∼ 15 min
	O_2, 20 W	5	4, 0, 0	∼ 5 min	4	3, 2, 2	∼ 15 min

Table VII Adhesion Test Results of Nonchromated, Waterborne Primers [Spraylat EWDY048 (Primer D) and Dexter 10-PW-22-2 (Primer X)] to TMS Plasma Polymers

TMS Coating	Second Plasma (1 min)	Primer D			Primer X		
		Dry Tape Test	Boiling (1, 4, 8 h)	Turco Time	Dry Tape Test	Boiling (1, 4, 8 h)	Turco Time
Flow, 50 mtorr, 5 W, 1 min	—	0	—	—	3	0, —	~ 10 min
	O_2, 10 W	5	0, —	~ 2 min	5	5, 5, 5	~ 30 min
	Ar, 10 W	5	3, 3, 2	~ 2 min	5	5, 5, 5	~ 13 h
Closed, 25 mtorr, 1000 V, 2 min	—	5	5, 5, 5	> 24 h	5	5, 5, 5	~ 30 min
	O_2, 10 W	5	0, —	~ 2 min	5	5, 5, 5	~ 20 min
	Ar, 10 W	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h
Closed, TMS + Ar (25 mtorr + 25 mtorr)	—	5	5, 5, 5	> 24 h	5	5, 5, 5	> 24 h

improved because the weak boundary on the surface of the plasma polymer would be either removed or converted to the stronger structure.

The interpretation of the decrease of the decay rate needs the understanding of the decay process. The decay process of polymer free radicals created by the action of plasma was extensively investigated by Kuzuya and Kondo, and their interpretation[24] certainly helps to understand the meaning of the slower decay rate. The decay of polymer free radicals starts with the reaction of free radicals with oxygen because oxygen is the best scavenger of free radicals under a normal or practical environment. The reaction of a free rad-
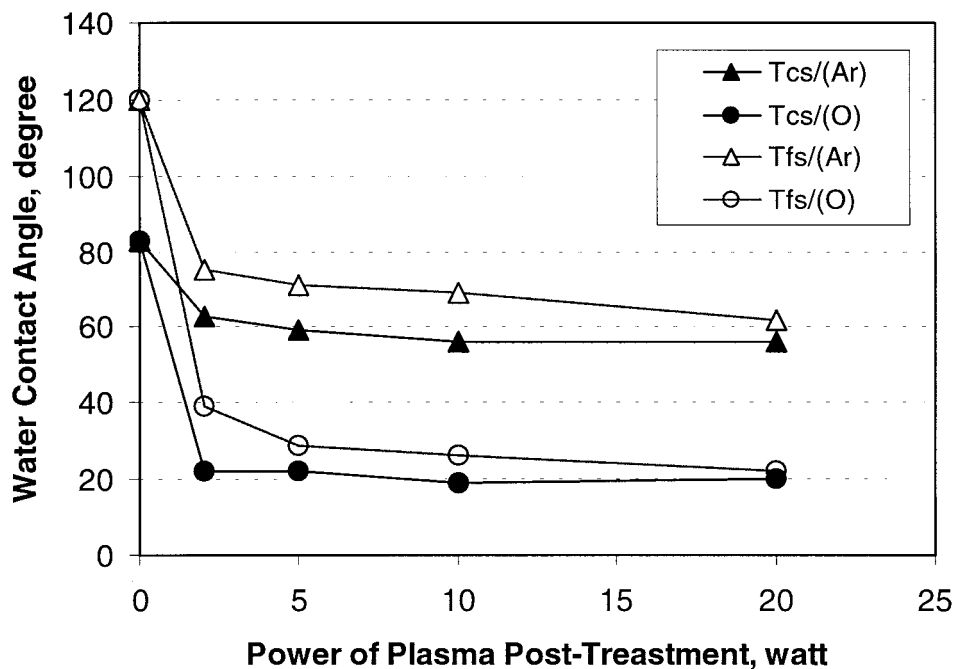
Figure 8 Water contact angle change of closed-system and flow-system TMS polymer surfaces with the power input of argon and oxygen-plasma posttreatment. Tfs = TMS deposited by a flow-system reactor; Tcs = TMS deposited by a closed-system reactor.

ical with an oxygen molecule converts a free radical to a peroxy free radical. The main route for the further reaction of the peroxy free radical is the hydrogen abstraction from the neighboring moieties. Of course, the original free radical and also the peroxy free radical can react with another free radical, but the fact that polymer free radicals created by plasma do not decay in a vacuum means that there are no two free radicals within the short distance where the recombination can occur.

The absence of this first step (hydrogen abstraction) in polymer free radicals created on polyterafluoroethylene (PTFE) explains why the PTFE free radical simply changes the shape of spin but does not decay. The exact reactions and sequences that a peroxy free radical follows are dependent on the structure of the host polymer molecules, but they are more or less a subject of speculation. A polymer free radical could end up with any of the following moieties: double bond, hydroxy peroxide, peroxide,—OH, carbonyl, carboxylic acid, and so on. Similarly, the dangling bonds in a plasma polymer would yield the same chemical moieties, although the reactions are much more restricted by the lack of mobility of the dangling bonds. Because of reactions of dangling bonds in plasma polymers with ambient oxygen when they are taken out of the vacuum reactor, nearly all plasma polymers derived from hydrocarbons, which do not contain oxygen atoms, show roughly 20 atomic percent of oxygen on XPS analysis.[17]

Thus, the slow decay of the dangling bonds could be interpreted that the system became more tight and there was no hydrogen in the vicinity of the dangling bonds. In the case of the HFE-plasma-treated TMS plasma polymer, the very slow decay could be explained by the same mechanism for the PTFE polymer free radicals. The more important question, so far as the adhesion of primer is concerned, is what will happen when a primer is applied on a surface that contains residual dangling bonds, peroxy free radicals, and possibly peroxides.

Another question from the other end is whether it is possible to create such a strong adhesion that survives 8 h of boiling with an exposed interface and that the coating cannot be stripped off by conventional stripping agents without creating covalent bonds between the primer layer and the plasma polymer layer on which the primer is applied.

There is no direct evidence to answer these questions in a definitive manner; however, the results reported in this article, together with data on corrosion resistance presented in the references cited, strongly suggest that the dangling bonds contribute to create covalent bonds between the primer layer and the plasma polymer of TMS deposited on aluminum alloys according to the principle of SAIE.

All primers used in this study were commercially available ones, and the study on the exact chemistry, which took place at the interface, was beyond the scope of this study and a series of studies along the line of SAIE. No attempt to explore such chemical reactions in a paint formulation was made so far. However, it has been observed that the plasma polymer of TMS deposited on the surface of zylconium oxide (the radio opaque pigment used in bone cement) did initiate the polymerization of methyl methacrylate by the action of a redox accelerator at room temperature.[25] Therefore, the scheme of covalent bond formation via peroxide and residual free radicals is not a far-fetched speculation.

CONCLUSIONS

The plasma treatment of the plasma polymer of TMS film prepared by cathodic polymerization significantly improved the adhesion characteristics of the spray primers investigated in this study. Among the second plasma treatments investigated, Ar-plasma treatment stood out as the most effective treatment, which was supported by ESCA data that indicated significantly different chemical bonds. Oxygen-plasma treatment increased the dry adhesion but yielded very poor wet adhesion due to a hydrophilic interface that was vulnerable for the action of water.

The closed-system polymerization of TMS yielded a graded elemental composition and achieved the second plasma treatment in the latter part of polymerization. The adhesion characteristics were excellent without further plasma treatment.

A separate ESR study indicated that the second plasma treatments, including HFE plasma, reduced the concentration of free radicals based on Si (Si dangling bonds) and also reduced the rate of decay, indicating that the second plasma treatments yielded more stable and probably stronger structures in the top region of the sur-

face. This assessment agreed with the ESCA data presented in this article.

The full ramification of these new surface chemistries has not yet been fully grasped, but the information gleaned so far has clearly aided in the understanding of the process and may serve to guide further explorations of interface engineering. As more and more of the large volume of collected data is taken into account, things that once appeared as uncorrelated or even inconsistent are now forming a much clearer picture of the rich chemistries being explored in this study. Ensuing discussions regarding the adhesion performance of these modified films will further serve to correlate and clarify the larger picture of how interface engineering can be used to build benign corrosion protection and long-life coatings systems.

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