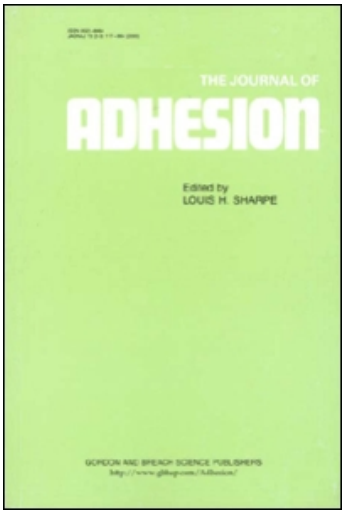

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Plasma Polymer Films as Adhesion Promoting Primers for Aluminum. Part II: Strength and Durability of Lap Joints

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Plasma-polymerized hexamethyldisiloxane (HMDSO) films (~ 800 Å in thickness) were deposited onto 6111-T4 aluminum substrates in radio frequency and microwave powered reactors and used as primers for structural adhesive bonding. Processing variables such as substrate pre-treatment, carrier gas and film post-treatment were adjusted to produce films that had different structures and properties. Films deposited using argon as the carrier gas were siloxane-like and were not wetted by typical structural adhesives. These films performed poorly as primers. When siloxane-like films were post-treated with an oxygen plasma, a silica-like surface layer was produced which was wetted by structural adhesives. However, these films were mechanically weak and were not useful primers. Silica-like films were deposited using oxygen as the carrier gas. These films had good cohesive strength, adhered well to the substrates, were easily wetted by epoxide adhesives, and were outstanding primers for structural adhesive bonding of aluminum. The initial strength of aluminum/epoxy lap joints prepared from substrates coated with silica-like primers was determined by loading joints to failure. Durability was determined by applying a static load to lap joints, exposing them to a cyclically-changing, corrosive atmosphere, and measuring the time to failure. Pre-treatment of the substrates before deposition of the primers was required in order to obtain high initial strengths and outstanding durability. The best results were obtained

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when the substrates were etched in chronic/sulfuric acid to remove the thick magnesium-rich oxide typically found on 6111-T4 aluminum and then etched in an argon plasma before deposition of the primer. The argon plasma pre-treatment removed adsorbed water from the surface of the aluminum before primer deposition, creating a more stable oxide surface to which the silica-like primer could bond.

Keywords: Plasma-polymerized primers; plasma etching; silica-like films; stressed durability; lap joints; aluminum/epoxy bonds

I. INTRODUCTION

The goal of this research was to develop a process consisting of plasma etching followed by plasma polymerization to clean aluminum substrates and coat them with corrosion-inhibiting primer films prior to structural adhesive bonding. As discussed in Part I, etching was carried out using argon and argon/hydrogen plasmas. Plasma polymerization was accomplished using hexamethyldisiloxane (HMDSO) as the monomer and argon or oxygen as the carrier gas, resulting in films that were siloxane-like or silica-like, respectively. In some cases, plasma-polymerized siloxane-like films were post-treated with either an oxygen or an argon plasma to produce primers that had siloxane-like bulk properties but silica-like surface properties. Characterization of these films was discussed in the pervious paper. In this paper, we describe the initial strength and durability of lap joints prepared from substrates that were plasma etched and then coated with plasma-polymerized primer films.

II. EXPERIMENTAL

A. Substrate Preparation

6111-T4 Aluminum substrates having the dimensions $25.4 \times 76.2 \times 2.0$ mm were degreased by wiping with Kimwipes soaked in acetone, cleaned ultrasonically in acetone for 15 minutes, rinsed with fresh acetone, and blown dry with nitrogen. Some substrates were subsequently etched in a solution of 18.4 g of chromium trioxide and 86.4 ml of sulfuric acid in 500 g of distilled deionized water at 80°C for 15

minutes. They were then removed from the solution, rinsed with distilled deionized water for 15 minutes, and blown dry with nitrogen.

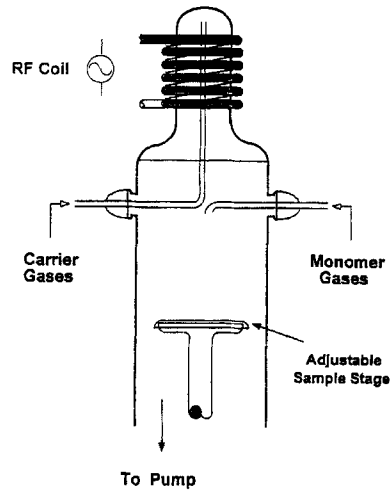
B. Plasma Pre-treatment, Deposition and Post-treatment

An inductively-coupled RF reactor (see Fig. 1A) was used in a configuration in which aluminum substrates to be treated were placed downstream from the plasma itself. This reactor has been discussed in detail elsewhere [1]. Several operating parameters, such as power, pressure and gas flow rates were varied to deposit insoluble films that were approximately 800 Å thick. Table I lists processing parameters used for each experiment. All substrates prepared in the RF reactor were pre-treated in an Ar plasma before film deposition. Siloxane-like films were deposited using HMDSO as the monomer and Ar as the carrier gas. In some experiments, siloxane-like films were post-treated with an oxygen plasma to produce a silica-like surface. Silica-like films were deposited using HMDSO as the monomer and oxygen as the carrier gas.

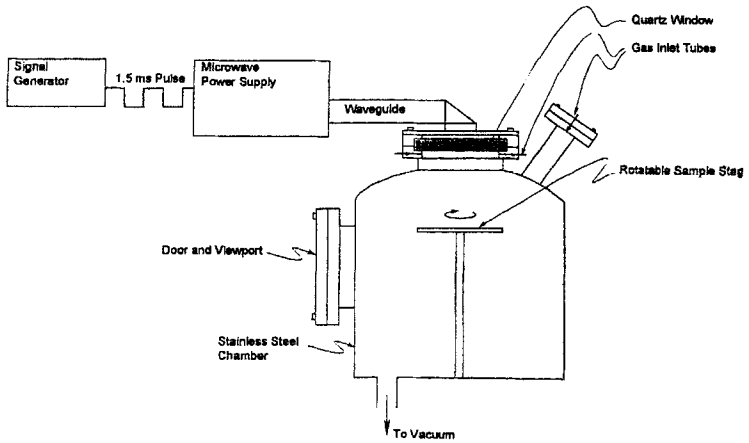
As shown in Figure 1B, the MW reactor was also operated in a downstream configuration. Monomer and carrier or post-treatment gases were introduced into the chamber above the rotating sample stage. Silica-like films with a thickness of approximately 800 Å were deposited using oxygen as a carrier gas. However, a small amount of argon was needed to ignite the plasma. Reactor parameters for deposition and etching in the MW reactor are also shown in Table I. Argon plasmas were used to pre-treat the aluminum substrates and, in a few cases, to post-treat the plasma-polymerized silica-like films. Argon/hydrogen plasmas were also used as a pre-treatment for aluminum.

C. Initial Strength Mechanical Testing

Lap joints were prepared using a modified ASTM standard D1002-72 by bonding together pairs of primed aluminum substrates using epoxy adhesives. The lap joints were then pulled on an Instron to determine their initial strength. The initial strength of joints prepared from substrates primed in the RF reactor was determined using both a



(A)



(B)

FIGURE 1 Schematic drawings of the (A)-RF and (B)-MW reactors.

two-part polyamide/amine-cured epoxy adhesive and a proprietary, commercial, one-part, toughened, dicyandiamide-cured epoxy adhesive, whereas the initial strength of joints prepared from substrates

TABLE I Processing variables for plasma etching and plasma polymerization in the RF and MW reactors

Reactor	*Process*	*Gas Flow Rates(sccm)*	*Pressure (Torr)*	*Power (Watts)*	*Time (Min.)*
RF	Ar Etch	Ar:20	1	20	10
RF	Siloxane Deposition	Ar:150 HMDSO:0.5	1	20	10
RF	O_2 Etch	O_2:25	0.5	100	10
RF	Silica-like Deposition	O_2:20 HMDSO:0.5	0.5	50	10
MW	Ar Etch	Ar:20	0.5	200	10
MW	Silica-like Deposition	Ar:5 O_2:45 HMDSO:0.2	0.5	200	10
MW	Ar + H_2 Etch	Ar:5 H_2:20	0.5	200	10

primed in the MW reactor was done using only the one-part, toughened adhesive. The two-part polyamide/amine epoxy was prepared by combining an epoxy resin (Epon 828, Shell Chemical Co.) with a polyamide/amine curing agent (V-40, Shell Chemical Co.) in the stoichiometric amounts. This adhesive was cured at room temperature for 18 hours and then in an oven at 50°C for five hours. The one-part adhesive was cured at 180°C for 30 minutes.

D. Durability Testing

The durability of the aluminum/epoxy lap joints was determined using a "stressed durability test" in which joints were stressed to 7 MPa using specially-constructed jigs and exposed to a cyclically-varying, corrosive environment [2, 3]. Each cycle consisted of immersion for 15 minutes in a 5% aqueous solution of NaCl, drying for 1 hour and 45 minutes at room temperature, and exposure to 90% relative humidity and 50°C for 22 hours. One cycle of stressed durability was completed each weekday. On weekends, the lap joints were simply maintained at 90% relative humidity and 50°C. The durability was determined as the number of cycles required to produce failure. All durability testing was conducted on joints prepared using the toughened epoxy adhesive.

E. XPS Analysis of Failure Surfaces

XPS was used to characterize the failure surfaces of lap joints that were tested for initial strength or durability. Samples were prepared for XPS analysis as follows. An aluminum substrate was placed into the finger of a polyethylene glove to protect the surface from contamination during cutting operations. A metal shear was then used to cut a 12.7 mm × 19.1 mm section containing the area of interest from the substrate. The section was then removed from the glove and placed on a sample stub for XPS analysis.

XPS spectra were obtained using a Perkin-Elmer 5300 X-ray photoelectron spectrometer. Mg Kα X-rays at a power of 300 Watts were used to excite the spectra. Most spectra were obtained at a take-off angle of 45°. High resolution (multiplex) spectra were corrected for charging by referencing the C(1s) peak for saturated hydrocarbons to a binding energy of 284.6 eV. Curve fitting of the high-resolution spectra was accomplished using software provided by Perkin-Elmer. The atomic composition of the failure surfaces was determined from the area under the peaks in the high-resolution spectra using sensitivity factors included in the instrument software.

III. RESULTS AND DISCUSSION

A. Initial Strength of Joints Prepared from Aluminum Substrates Primed in the RF Reactor

Lap joints prepared from the polyamide/amine-cured epoxy adhesive and aluminum substrates primed with plasma-polymerized films deposited in the RF reactor were pulled to determine their initial strengths (see Tab. II). The average breaking strengths of joints prepared from substrates that were cleaned in acetone, etched in an argon plasma, and then coated with siloxane-like films, siloxane-like films that were post treated with an O_2 plasma, or silica-like films in the RF reactor were $0.48 \pm 0.06, 3.10 \pm 1.17$ and 5.86 ± 0.51 MPa, respectively. These pretreatments will be referred to in subsequent discussion as RF-1, RF-2 and RF-3, respectively. Joints made from substrates that were etched in a solution of chromic and sulfuric acid,

TABLE II Initial strength and durability of lap joints prepared from aluminum substrates pre-treated in the RF reactor

Pre-treatment Number	*Chemical Pre-treatment*	*Plasma Pre-treatment*	*Plasma Primer*	*Breaking Stress (MPa)*	*Durability (Cycles)*
RF-1	acetone	10 min Ar	siloxane-like	0.48 ± 0.06[b]	Not measured
RF-2	acetone	10 min Ar	siloxane-like[a]	3.10 ± 1.17[b]	Not measured
RF-3	acetone	10 min Ar	silica-like	5.86 ± 0.51[b]	Not measured
RF-4	chromic/sulfuric acid	10 min Ar	silica-like	8.28 ± 0.43[b]	Not measured
RF-5	chromic/sulfuric acid	none	none	7.94 ± 1.16[b]	Not measured
RF-6	acetone	10 min Ar	silica-like	18.52 ± 0.35[c]	3
RF-7	chromic/sulfuric acid	10 min Ar	silica-like	22.0 ± 0.91[c]	115 ± 47[d]

[a] Plasma polymerized primer was given an O_2 plasma post-treatment.
[b] These tests were performed using a polyamide/amine-cured epoxy adhesive.
[c] These tests were performed using a proprietary toughened epoxy adhesive.
[d] The adhesive bonds in these specimens did not fail. Instead, the substrates failed due to galvanic corrosion around the bolts used to hold the joints in tension.

etched in an argon plasma, and then primed with silica-like films (pretreatment RF-4) had breaking strengths of about 8.28 ± 0.43 MPa. Joints prepared from aluminum substrates that were acid-etched but not plasma etched or coated (pretreatment RF-5) had strengths of about 7.94 ± 1.16 MPa. Thus, lap joints prepared from aluminum substrates that were acid etched, etched in an argon plasma, and primed with silica-like plasma polymerized primers (pretreatment RF-4) had breaking strengths similar to those of lap joints prepared from substrates that were acid-etched but not plasma etched or coated (pretreatment RF-5).

Lap joints prepared from aluminum substrates that were cleaned with acetone, etched in an argon plasma, and primed with silica-like films (pretreatment RF-6) and then bonded with the toughened epoxy adhesive had average strengths of 18.52 ± 0.35 MPa, while joints prepared from acid-etched aluminum substrates that were etched with an argon plasma and primed with silica-like films (pretreatment RF-7) had an average initial strength of 22.0 ± 0.91 MPa. The use of the toughened epoxy adhesive resulted in joints that failed at significantly higher loads than joints prepared with the polyamide/amine-cured epoxy. Acid etching the aluminum substrates before deposition of the primer also resulted in lap joints that had higher initial strengths.

The XPS spectra of the fracture surfaces of the lap joints prepared with the polyamide/amine-cured epoxy revealed the modes of failure. In the survey spectra of the fracture surfaces of joints prepared from aluminum substrates with pretreatment RF-1, peaks characteristic of Si were seen near 102 and 150 eV on the substrate fracture surface but not on the adhesive fracture surface. Peaks characteristic of nitrogen (400 eV) and carbon (285 eV) were seen on both surfaces. Because the adhesive failure surface contained no silicon whereas the substrate failure surface contained approximately 19%, it was concluded that failure had occurred near the primer/adhesive interface and that the adhesive did not wet the siloxane-like primer. This result confirmed contact angle measurements of water on plasma-polymerized siloxane-like films in which it was found that the siloxane-like films had low surface energy and were, therefore, not likely to be wetted by an epoxy adhesive [1].

When XPS survey spectra were obtained from fracture surfaces of lap joints made from aluminum substrates with pretreatment RF-2 and bonded with the polyamide/amine-cured epoxy, peaks characteristic of silicon (102 and 150 eV) from the primer were observed on both the adhesive and substrate failure surfaces. It was concluded that the interface between the plasma-polymerized primer and the epoxy was adhesively strong but the siloxane-like primer was mechanically weak. Failure occurred cohesively within the plasma-polymerized siloxane-like film [4, 5]. Once again this result was consistent with results from contact angle measurements [1]. The contact angle of water on plasma-polymerized siloxane-like films that were post-treated in an O_2 plasma was very low, indicating that the film had a relatively high surface energy and should be readily wetted by an epoxy adhesive.

Silicon from the primer and nitrogen characteristic of the adhesive were seen in XPS spectra of both failure surfaces of lap joints prepared from substrates with pretreatment RF-3 and bonded with the polyamide/amine-cured epoxy. Peaks due to aluminum (74 eV) and magnesium (90 eV) were also seen on the substrate failure surface. Mixed failure occurred near the aluminum/primer interface, partly within the primer and partly in the adhesive. The adhesive readily wetted the surface of the primer and the primers were cohesively strong, resulting in high joint strengths.

In order to improve adhesion between the primer and the substrate, the aluminum was etched in a solution of chromic and sulfuric acid.

Failure surfaces of lap joints prepared from aluminum substrates having pretreatment RF-4 were examined with XPS. Peaks due to silicon from the primer were seen near 102 and 150 eV in the spectrum of the substrate failure surface but not in the spectrum of the adhesive failure surface. Nitrogen and carbon characteristic of the adhesive were seen on both failure surfaces. It was concluded that failure occurred near the primer/epoxy interface, but mostly within the adhesive.

B. Initial Strength of Joints Prepared from Aluminum Substrates Primed in the MW Reactor

The initial strengths of lap joints prepared from aluminum substrates that were acid-etched, plasma-etched and primed with plasma-polymerized silica-like films in the MW reactor, and bonded with the toughened epoxy are shown in Table III. In these investigations, the effect of plasma etching before deposition of the primer was considered. Lap joints prepared from aluminum substrates that were etched in an argon plasma, primed with silica-like films (pretreatment MW-1), and bonded with the toughened adhesive had initial strengths of 21.2 ± 4.03 MPa. Very similar results were obtained from joints prepared from substrates that were pre-treated similarly but in the RF reactor (see Tab. II). Joints prepared from adherends

TABLE III Initial strength and durability of lap joints prepared from aluminum substrates that were etched in chromic/sulfuric acid and then etched and coated with a silica-like primer in the MW reactor

Pre-treatment Number	*Plasma Etching*[a]	*Plasma Primer*	*Breaking Stress (MPa)*	*Durability (Cycles)*
MW-1	10 min Ar	silica-like	21.2 ± 4.03	193 ± 23
MW-2	none	silica-like	9.83 ± 2.42	70 ± 39
MW-3	1.5 min Ar	silica-like	18.3 ± 6.15	Not measured
MW-4	5 min Ar	silica-like	22.6 ± 0.43	Not measured
MW-5	10 min Ar	silica-like	21.7 ± 1.09	Not measured
MW-6	10 min Ar/H_2	silica-like	23.8 ± 0.47	221 ± 100
MW-7	10 min Ar	silica-like[b]	22.4 ± 1.39	124 ± 23

[a] All aluminum substrates were etched in chromic/sulfuric acid *before* plasma etching and deposition of plasma-polymerized primers.
[b] Plasma polymerized primer was etched in an Ar plasma *after* deposition.

that were not plasma etched before deposition of a silica-like film (pretreatment MW-2), had breaking strengths of about 9.83 ± 2.42 MPa. When the substrates were etched with an Ar plasma for 1.5 minutes before deposition of the silica-like primer (pretreatment MW-3), the breaking strength increased to 18.3 ± 6.15 MPa. When the length of the plasma etch was increased to 5 and 10 minutes (pretreatments MW-4 and MW-5, respectively), the strengths were 22.6 ± 0.43 and 21.7 ± 1.09 MPa, respectively. Note that MW-5 was a repeat of MW-1 as far as initial strength is concerned. When the etch time was fixed at 10 minutes but the etch gas was changed from Ar to Ar/H_2 (pretreatment MW-6), a small increase in joint strength was observed, from 21.7 ± 1.09 to 23.8 ± 0.47 MPa, respectively. Lap joints prepared from aluminum substrates that were etched for 10 minutes in an Ar plasma, primed with a silica-like film, and post-treated for 10 minutes with an Ar plasma (pretreatment MW-7) failed at an average strength of 22.4 ± 1.39 MPa. It was concluded that etching in an Ar plasma for at least 5 minutes before deposition of the primer was necessary to obtain lap joints with the greatest initial strengths. However, etching gas (argon or Ar/H_2) and post-deposition etching of the primer films in an O_2 plasma did not have a significant effect on initial strength.

XPS was also used to examine the failure surfaces of lap joints prepared from aluminum substrates that were etched and primed in the MW reactor and bonded with the toughened adhesive. Peaks due to carbon and oxygen were seen near 285 and 531 eV in the survey spectra of both the adhesive and the metal failure surfaces of lap joints prepared from aluminum substrates with pretreatment MW-2 (see Fig. 2). 11% and 1% silicon (seen as peaks near 103 eV) were found on the adhesive and metal failure surfaces, respectively. In addition, 5% aluminum was found on the adhesive failure surface and 15% on the metal failure surface. The high resolution Al(2p) spectrum of the adhesive failure surface is shown in Figure 3. A peak due to aluminum oxide was seen but no peak due to metallic aluminum was observed. However, in the spectrum of the substrate failure surface, a small peak due to metallic aluminum was also seen. Therefore, failure appeared to be somewhat mixed, but mainly near the interface between the silica-like primer and the aluminum substrate.

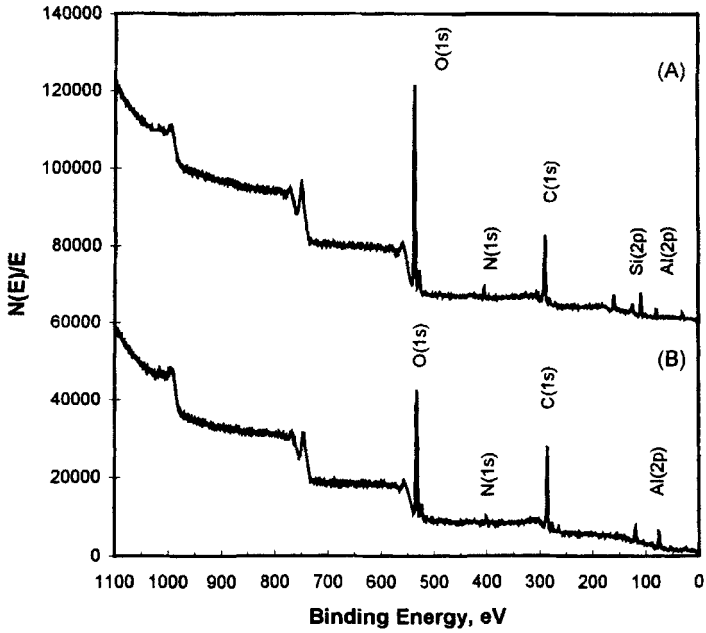


FIGURE 2 XPS survey spectra of the (A)-adhesive and (B)-metal failure surfaces of lap joints prepared from acid-etched aluminum adherends that were not Ar plasma pre-treated, but were primed with silica-like films in the MW reactor.

Lap joints made from aluminum having pretreatment MW-2 and from aluminum having pretreatment MW-1 were compared. As in the XPS spectra of the specimens discussed above, the survey spectra of both failure surfaces of joints prepared from aluminum having pretreatment MW-2 contained carbon, oxygen and aluminum (Fig. 4). 10% and 12% aluminum was seen on the adhesive and metal failure surfaces, respectively. Little silicon was observed on either failure surface. The high resolution Al(2p) spectrum of the adhesive and substrate failure surfaces of the same joints are shown in Figure 5. A peak due to aluminum oxide was seen in the high resolution Al(2p) spectrum of the adhesive and substrate failure surfaces. However, a large peak due to metallic aluminum was also observed in the spectrum of the substrate failure surface. This indicated that failure was at least partially within the metal oxide. Lap joints prepared from aluminum pre-treated with an Ar plasma

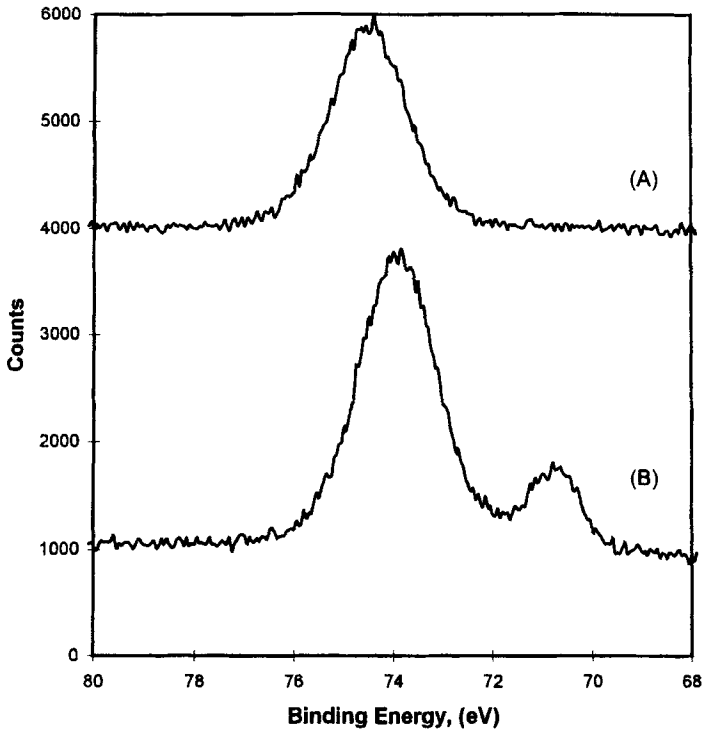


FIGURE 3 XPS high-resolution spectra of Al(2p) region of the (A)-adhesive and (B)-metal failure surfaces of lap joints prepared from acid-etched aluminum substrates that were not etched in an Ar plasma, but were primed with silica-like films in the MW reactor.

and primed with a silica-like film (pretreatment MW-1) had higher initial strengths than joints prepared from aluminum with no plasma pre-treatment and a silica-like primer (pretreatment MW-2). When plasma pre-treatment was used, failure appeared to move into the aluminum oxide, indicating better adhesion between the metal oxide and the plasma primer.

Failure analysis was carried out for all other samples that were prepared in the MW reactor and tested for initial strength. For lap joints prepared from aluminum that received some MW plasma pre-treatment and were primed with a silica-like film, failure appeared to occur in a similar position, within the aluminum oxide. Post-treatment of the silica-like primer with an Ar plasma had no effect on the failure

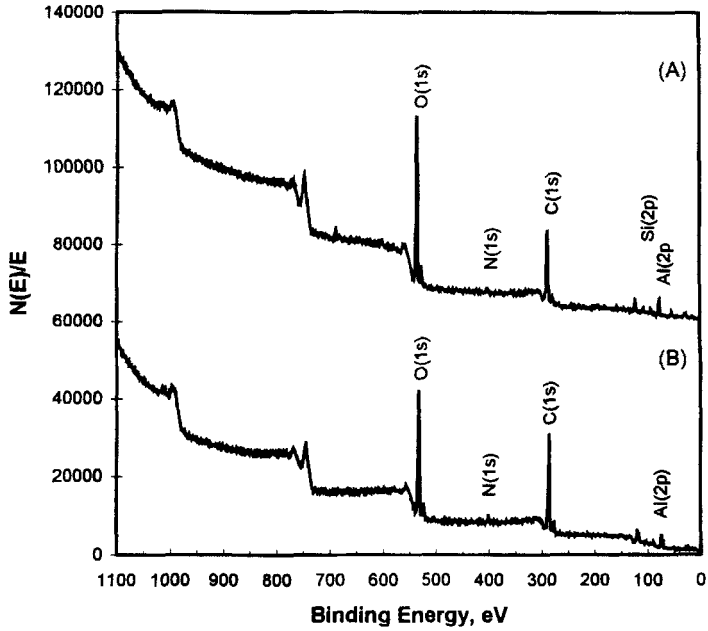


FIGURE 4 XPS survey spectra of the (A)-adhesive and (B)-metal failure surfaces of lap joints prepared from acid-etched aluminum substrates that were pre-treated with an Ar plasma and primed with silica-like films in the MW reactor.

mode of lap joints. The weak link in the joints remained the aluminum oxide.

C. Durability of Joints Prepared from Aluminum Substrates Primed in the RF Reactor

Stressed durability was determined for lap joints prepared using the toughened adhesive and aluminum substrates primed with plasma polymers deposited in the RF reactor. The results, expressed as corrosion cycles survived, are shown in Table II. As shown in Table II, adhesive joints made from substrates having pretreatment RF-6 failed after only 2 or 3 cycles.

XPS analysis was used to determine the locus of failure of lap joints prepared from aluminum substrates having pretreatment RF-6.

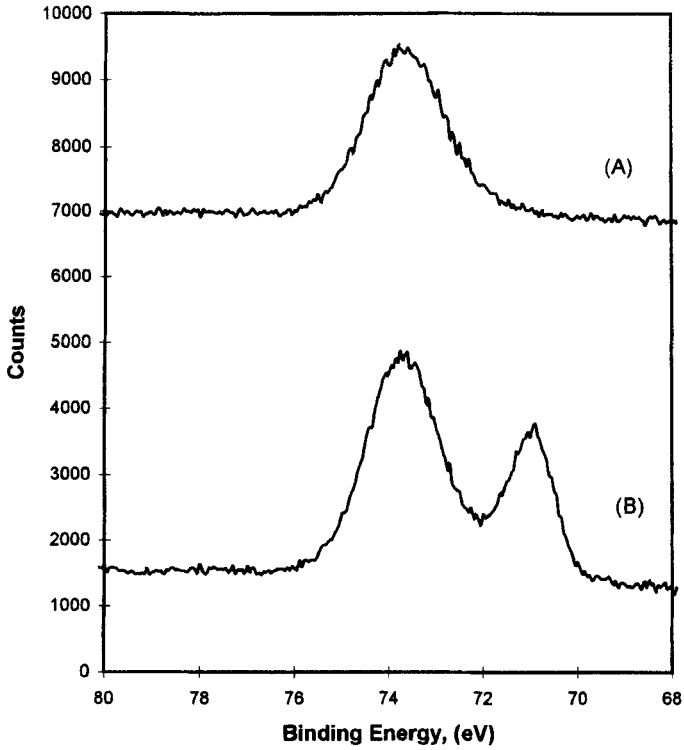


FIGURE 5 XPS high-resolution spectra of the Al(2p) region of (A)-adhesive and (B)-metal failure surfaces of lap joints prepared from acid-etched aluminum adherends that were pre-treated with an Ar plasma and primed with silica-like films in the MW reactor.

Unfortunately, the analysis was hampered by large amounts of sodium and chloride from the salt water bath that were present on the failure surfaces. However, since aluminum and magnesium were seen on at least one failure surface of each joint, it was concluded that the interface between the primer and the aluminum substrate was weak and unstable in corrosive environments. Magnesium oxide is known to form preferentially at the surface of aluminum alloys with a high content of magnesium. Magnesium oxide has also been shown to be detrimental to the durability of oxide/aluminum interfaces and to adhesive joint durability [6, 7].

Excellent stressed durability test results were obtained from joints prepared from aluminum substrates having pretreatment RF-7. For

these specimens, the adhesive bonds never actually failed. Instead, testing of the joints was stopped after an average of 115 ± 47 cycles when galvanic corrosion around the bolts that held the joints in tension caused the metal substrates to fail. Therefore, it can be said that the durability of lap joints prepared from aluminum with pretreatment RF-7 was greater than an average of 115 ± 47 cycles.

D. Durability of Joints Prepared from Aluminum Substrates Primed in the MW Reactor

Durability, expressed as corrosion cycles survived, is shown in Table III for lap joints that were prepared from the toughened adhesive and aluminum substrates that were etched in chromic/sulfuric acid and then etched and primed in the MW reactor. Lap joints prepared from substrates with pretreatment MW-1 survived an average of 193 ± 23 corrosion cycles. These joints performed as well as similar specimens prepared with primers deposited in the RF reactor. Lap joints prepared from substrates having pretreatment MW-2 failed after an average of 70 ± 39 cycles. At least some etching in an argon plasma was required to produce durable lap joints.

Adhesive joints made from substrates with pretreatment MW-6 survived an average of 221 ± 100 cycles of stressed durability testing. When the standard deviation was considered, the difference in durability between adhesive joints made from substrates having pretreatment MW-6 and joints prepared from substrates having pretreatment MW-1 was not significant. However, the large standard deviation for lap joints prepared from substrates with pretreatment MW-6 could indicate two different failure mechanisms.

The effect on durability of etching a silica-like primer film in an argon plasma was also investigated. Lap joints prepared from aluminum substrates having pretreatment MW-7 survived an average of 124 ± 23 corrosion cycles. The effect of the Ar plasma post-treatment was, therefore, to reduce the durability of the lap joints.

These results indicated that Ar or Ar/H_2 plasma pre-treatment and the deposition of a silica-like primer was the most effective treatment for lap joints prepared from acid-etched aluminum. Lap joints prepared from aluminum substrates that were not plasma pre-treated

but were primed with silica-like films had poor durability. The Ar/H_2 pre-treatment before deposition of a silica-like film produced lap joints that had more widely varying durability. Post-treatment of silica-like, plasma-polymerized primers with an Ar plasma also resulted in a reduction in durability of lap joints.

XPS analysis of the failure surfaces was used to determine the locus of failure of lap joints prepared from acid-etched aluminum that was also etched and primed in the MW reactor. Atomic concentrations calculated from representative XPS high-resolution spectra are shown in Table IV. Analysis of the failure surfaces was hampered by the presence of aluminum, probably due to the formation of corrosion products.

Figure 6 shows the survey spectra obtained from the adhesive and metal failure surfaces of a lap joint that was prepared from aluminum with pretreatment MW-2 and then tested in stressed durability. These lap joints survived an average of 70 stressed durability cycles. Similar amounts of carbon and oxygen were seen on both failure surfaces. However, the metal failure surface contained 16% aluminum, 2% magnesium, and 1% silicon. The adhesive failure surface contained 10% silicon, 6% aluminum, and no magnesium. This suggested that failure occurred near the primer/aluminum interface. Aluminum found on the adhesive failure surface was possibly the result of the formation of aluminum oxide corrosion products in the test environment.

Figure 7 shows the XPS survey spectra obtained from the adhesive and metal failure surfaces of a lap joint prepared from substrates having pretreatment MW-1 that failed after 170 cycles of stressed

TABLE IV Atomic concentrations calculated from XPS spectra of adhesive and metal failure surfaces of each lap joint after stressed durability testing. The substrates were acid etched and then pre-treated in the MW reactor

Pre-treatment Number	*Failure Surface*	*C*	*O*	*Si*	*Al*	*N*	*Mg*	*S*
MW-1	adhesive	38	46	1	13	1	1	0
	metal	33	49	1	15	1	1	0
MW-2	adhesive	39	42	10	6	3	0	0
	metal	38	41	0	16	2	2	1
MW-6	adhesive	45	41	2	10	1	1	0
	metal	28	52	9	9	1	1	0
MW-7	adhesive	54	34	3	6	3	0	0
	metal	19	61	1	18	1	0	0

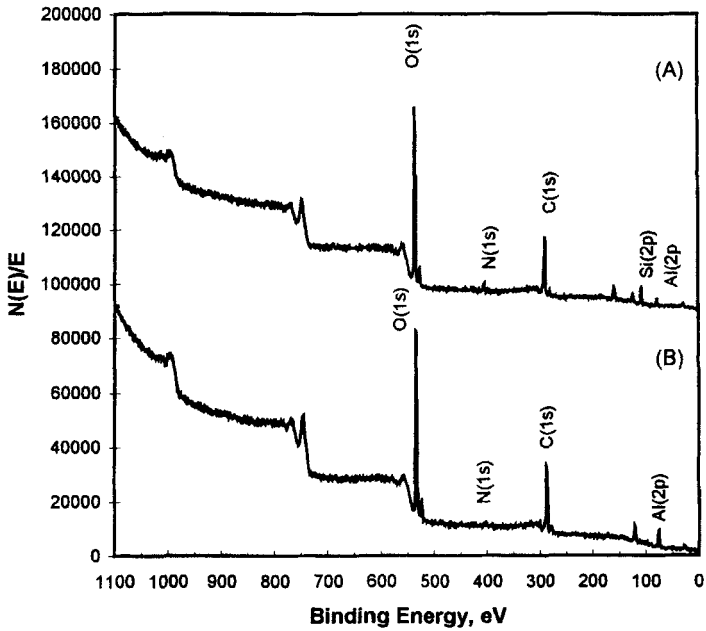


FIGURE 6 The survey spectra obtained from the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum with no plasma pretreatment and primed with a plasma-polymerized, silica-like film in the MW reactor and then tested for durability.

durability testing. Similar amounts of carbon, oxygen, and aluminum were seen on both failure surfaces. Only 1% silicon was found on the adhesive and metal failure surfaces.

The C(1s) high resolution spectra of both failure surfaces were examined for signs of adhesive (Fig. 8). As a reference, the C(1s) high resolution spectrum of the toughened epoxy adhesive is shown in Figure 9. The spectrum of the neat adhesive was broad, containing at least two overlapping peaks due to the hydrocarbon and carbon in the epoxy functional groups. In contrast, the C(1s) peaks of the adhesive and metal failure surfaces were relatively narrow and the two overlapping peaks were not visible. Since adhesive was not seen on the failure surfaces, failure in the lap joint did not occur near or within the adhesive. Some of the aluminum observed on the failure surfaces could be due to aluminum oxide corrosion products dissolved in the

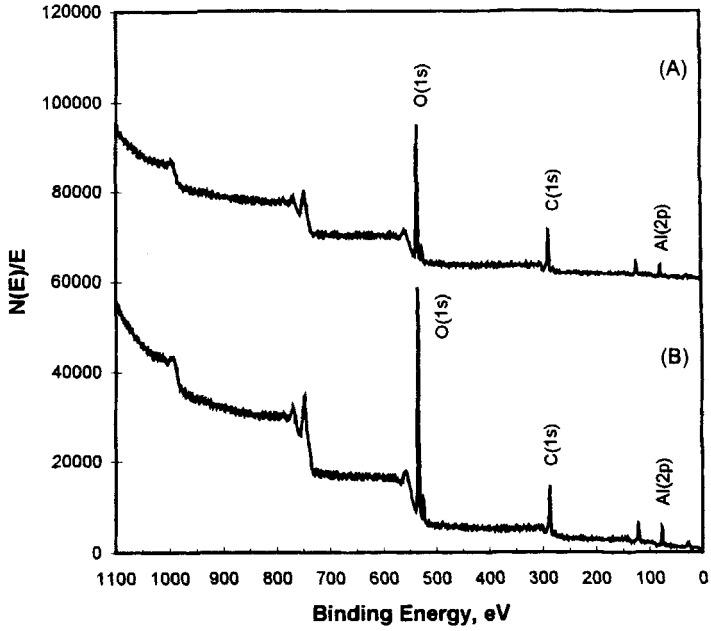


FIGURE 7 The XPS survey spectra obtained from the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum pre-treated in an Ar plasma and primed with a silica-like film in the MW reactor and then tested for durability.

wet test environments and redeposited onto exposed areas of the joint. Nevertheless, because evidence of adhesive was not seen in the C(1s) high resolution spectra and very little silicon was observed on either failure surface, failure was considered to have occurred within the aluminum oxide.

Figure 10 shows the XPS survey spectra obtained from the adhesive and metal failure surfaces of a lap joint prepared from aluminum with pretreatment MW-6. The metal failure surface contained 52% oxygen, 28% carbon, 9% aluminum and 9% silicon. The adhesive failure surface contained 41% oxygen, 45% carbon, 10%aluminum and 2% silicon. As seen with the lap joints prepared from aluminum with pretreatment MW-1, both the adhesive and metal failure surfaces were very similar. However, the peak in C(1s) high resolution spectra (Fig. 11) was very broad and asymmetric, suggesting the presence of epoxy adhesive on the failure surfaces. Since adhesive, aluminum, and

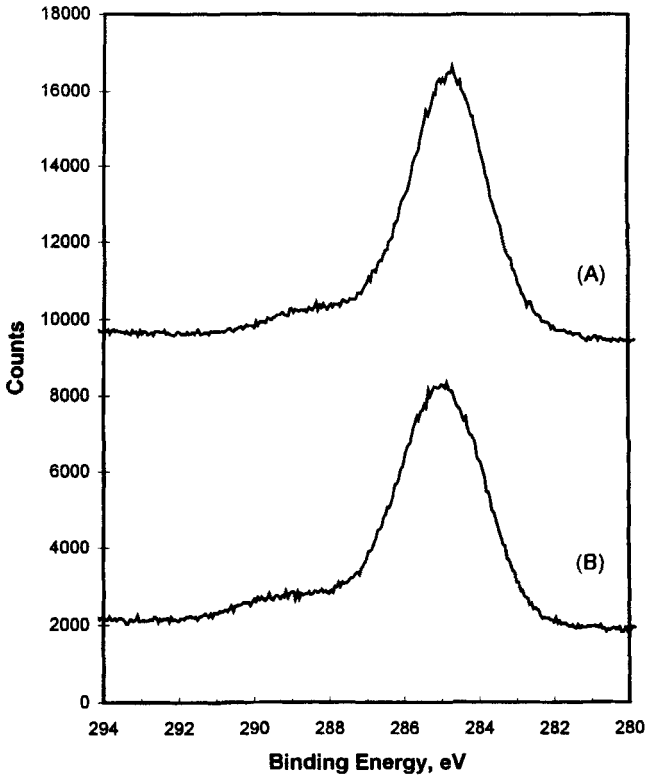


FIGURE 8 The C(1s) high-resolution spectra of both the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum pre-treated in an Ar plasma and primed with a silica-like film in the MW reactor and then tested for durability.

silicon were observed on both the adhesive and metal failure surfaces, failure was considered to be mixed, exposing adhesive, aluminum from the substrate, and silicon from the primer.

Figure 12 shows the survey spectra obtained from the adhesive and metal failure surfaces of a lap joint prepared from aluminum substrates having pretreatment MW-7. The metal failure surface appeared oxide-like, containing large amounts of aluminum and oxygen. The adhesive failure surface contained carbon and nitrogen in addition to aluminum, silicon, and oxygen. The C(1s) high resolution spectrum of the adhesive failure surface contained a strong, broad peak characteristic of the

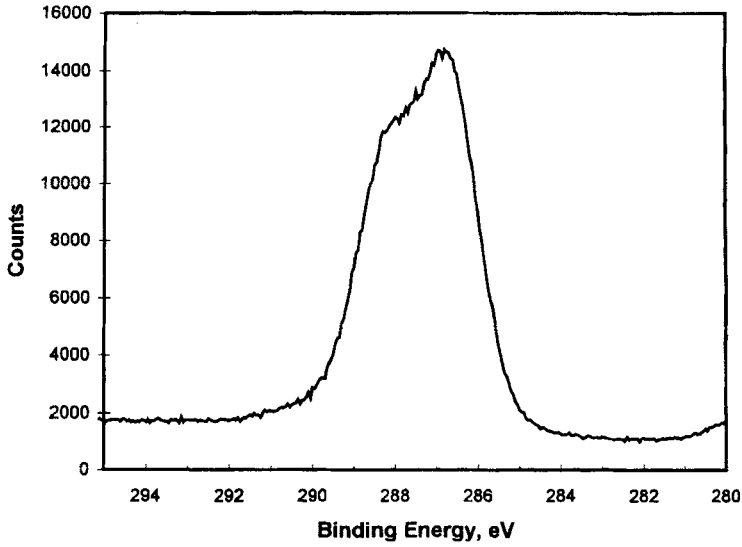


FIGURE 9 The C(1s) high-resolution spectrum of the epoxy adhesive.

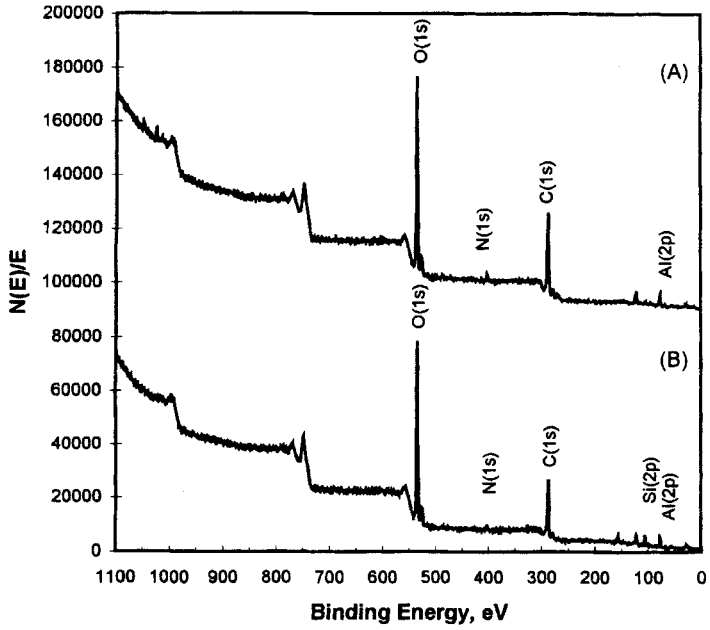


FIGURE 10 The XPS survey spectra obtained from the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum pre-treated in an Ar/H_2 plasma and primed with a silica-like film in the MW reactor and then tested for durability.

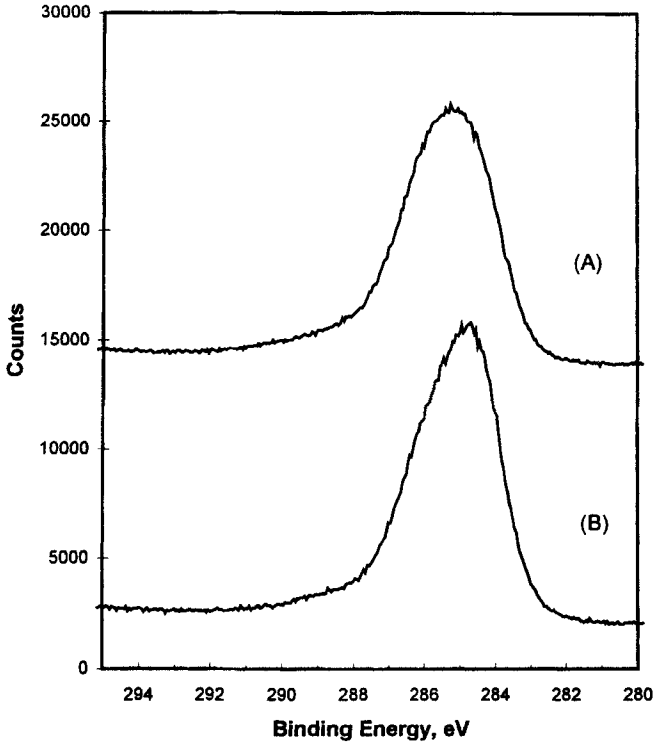


FIGURE 11 The C(1s) high-resolution spectra of both the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum pre-treated in an Ar/H_2 plasma and primed with a silica-like film in the MW reactor and then tested for durability.

adhesive. The primer was possibly obscured by aluminum oxide corrosion products. Failure appeared to be mixed, passing through the primer and aluminum oxide and exposing some adhesive.

An Ar plasma etch followed by deposition of a silica-like primer was the most effective treatment for lap joints prepared from acid-etched aluminum. It resulted in durable joints that appeared to fail within the aluminum oxide. In part I, the Ar plasma pre-treatment was found to remove adsorbed water from the surface of the aluminum substrates before deposition. This removal of surface contaminants was necessary for strong, durable adhesion between the primer and the aluminum substrate. Lap joints prepared from acid-etched aluminum that was not

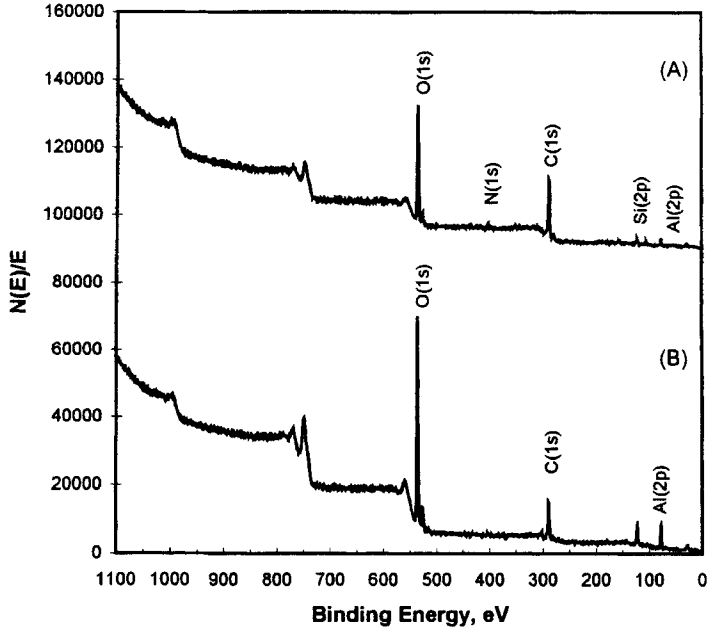


FIGURE 12 The XPS survey spectra obtained from the (A)-adhesive and (B)-metal failure surfaces of a lap joint prepared from acid-etched aluminum pre-treated in an Ar plasma, primed with a silica-like film, and post-treated with an Ar plasma in the MW reactor and then tested for durability.

plasma etched but was primed with silica-like films were not durable. In this case, failure seemed to occur near the primer/aluminum interface.

Pre-treatment in a Ar/H_2 plasma before deposition of a silica-like film also removed adsorbed water from the aluminum surface, as discussed in Part I. The durability of lap joints prepared from aluminum substrates with pretreatment MW-6 was similar to that of lap joints prepared from substrates having pretreatment MW-1, although much more variable. Since adhesive, aluminum, and silicon were observed on both the adhesive and metal failure surfaces of lap joints prepared from aluminum with pretreatment MW-6, failure was considered to be mixed, exposing adhesive, aluminum from the substrate, and silicon from the primer.

Argon post-treatment of the silica-like plasma primer deposited on aluminum also resulted in a reduction in durability of lap joints. Failure

appeared to be mixed. In Part I of this study, Ar plasma post-treatment of silica-like films was found to promote condensation of silanol groups to Si —O —Si bonds with no change in film thickness. Since the durability of joints primed with the post-treated films was reduced, hydrogen bonding of the silanol groups with the adhesive was perhaps responsible for the good durability of lap joints prepared from aluminum primed with silica-like films without the post-treatment. Ar post-treatment left sites on the silica-like films that were possibly susceptible to hydrolysis of Si —O —Si bonds. Another explanation was that Ar ion bombardment damaged the surface of the silica-like films, creating a weak boundary layer between the primer and the adhesive. However, since the initial strengths of lap joints prepared from acid-etched, Ar pre-treated aluminum primed with silica-like films that were post-treated with an Ar plasma were high, and a weak boundary layer would affect initial strength as well as durability, this theory was not considered likely.

The effect of the cure cycle on the plasma-polymerized silica-like primers was studied in Part I. The condensation reaction of silanol groups was thermally activated at the temperature of the adhesive cure. As seen in this paper, when silanol groups were not present in the primer film, the durability of lap joints prepared from aluminum primed with silica-like films was reduced. This suggested that the hydroxyl groups in the plasma-polymerized primer were important for bonding at the primer/epoxy interface. During curing of the adhesive, silanol groups in the primer may have condensed with hydroxyl groups from the adhesive, leaving the interface less susceptible to water intrusion. In the lap joints prepared from aluminum primed with an Ar post-treated silica-like film, these silanol groups were not available to interact with the adhesive.

It is important to compare the results obtained using the plasma-polymerized primer with those obtained using other pretreatment systems. Ward and co-workers have investigated the same toughened, one-component adhesive as used in the current investigations [8]. They determined the stressed durability of lap joints prepared using aluminum substrates that were pretreated using a commercial process involving chromates. They found that joints prepared using adhesive that was not exposed to high humidities before cure had a stressed durability of 195 ± 7 cycles. Since the same

adhesive was used in the current investigations without exposure to high humidites before cure, it can be concluded that pretreatment process MW-1 and MW-6 involving acid etching of aluminum substrates, etching the substrates in an argon or Ar/H_2 plasma for several minutes, and depositing a thin plasma-polymerized silica-like film in the MW reactor were as effective as the chromate-containing pretreatment process investigated by Ward [8].

IV. CONCLUSIONS

- Plasma-polymerized HMDSO films deposited in the RF reactor with argon as a carrier gas were siloxane-like and were not wetted by typical structural adhesives. These films performed poorly as primers.
- When siloxane-like films were deposited in the RF reactor and post-treated with an oxygen plasma, a silica-like surface layer was produced which was wetted by epoxide structural adhesives. However, these films were mechanically weak and were not useful as primers.
- Silica-like films deposited in the RF and MW reactors with oxygen as a carrier gas had good cohesive strength, adhered well to the aluminum substrates, were easily wetted by epoxide adhesives, and were outstanding primers for the structural adhesive bonding of aluminum.
- Lap joints prepared from acid-etched aluminum pre-treated with an Ar plasma for 10 minutes and primed with silica-like films in both the RF and MW reactors had high initial strength and exceptional durability.
- Some plasma pre-treatment of the aluminum coupons before primer deposition was necessary to produce strong, durable lap joints.
- Argon plasma pre-treatment removed adsorbed water from the surface of the aluminum before primer deposition, possibly creating a more stable oxide surface to which the silica-like primer could bond.
- Argon plasma post-treatment of the silica-like primer reduced the hydroxyl concentration in the film. Lap joints prepared from argon pre-treated, acid-etched aluminum primed with a silica-like film that

was post-treated with an argon plasma did not perform as well in durability testing as lap joints prepared from primed aluminum without the plasma post-treatment.

- Pretreatment processes MW-1 and MW-6 involving acid etching of aluminum substrates, etching the substrates in an argon or Ar/H_2 plasma for several minutes, and depositing a thin plasma-polymerized silica-like film in the MW reactor were as effective as a chromate-containing commercial pretreatment process.

Acknowledgments

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