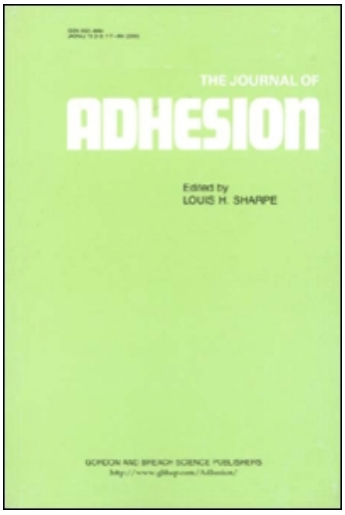

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Molecular structure of interfaces formed with plasma-polymerized silica-like primer films: Part III. Mechanical strength and environmental durability of the primer/aluminum and primer/titanium interfaces

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MOLECULAR STRUCTURE OF INTERFACES FORMED WITH PLASMA-POLYMERIZED SILICA-LIKE PRIMER FILMS: PART III. MECHANICAL STRENGTH AND ENVIRONMENTAL DURABILITY OF THE PRIMER/ALUMINUM AND PRIMER/TITANIUM INTERFACES

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In order to characterize the properties of film/metal interfaces formed between plasma-polymerized amorphous silica-like (a-SiO_2) films and metal substrates, lap joints and wedge test specimens were made from aluminum and titanium adherends that were pretreated with plasma-polymerized a-SiO_2 primer films. High breaking strengths of all the lap joints due to cohesive failures within the adhesive indicated that the adhesive/a-SiO_2 and a-SiO_2/metal interfaces were very strong. In addition, since failure was cohesive within the adhesive, the different interfacial structures at the a-SiO_2/aluminum and a-SiO_2/titanium interfaces were cohesively strong. In order to maximize the environmental stress placed upon the a-SiO_2/metal interfaces, the a-SiO_2 primer films on the metal adherends were pretreated with silane primers before adhesive bonding. This ensured that differences in environmental durability at the a-SiO_2/metal interface, if any, would be observed. However, no interfacial failures of pretreated substrates was observed, indicating that the a-SiO_2/aluminum and a-SiO_2/titanium interfaces had very high environmental durability. This correlated well with the results obtained in Parts I and II of this work, which supported the formation of strong Al-O-Si and Ti-O-Si bonds at the a-SiO_2/metal interface.

Keywords: Plasma-polymerized primers; a-SiO_2 films; Lap joints; Wedge test; Interfacial analysis; Suboxide; Aluminum/epoxy bonds; Titanium/epoxy bonds

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INTRODUCTION

In order to validate further the a-SiO_2/metal interfaces that were characterized and modeled in Parts I and II of this study, mechanical strength and durability specimens were prepared and tested. Previous data have shown that the a-SiO_2/aluminum interface has a mechanical strength superior to the cohesive strengths of the structural epoxy adhesives that were used [1]. The infrared and XPS analyses of thick a-SiO_2 films, from Parts I and II, respectively, showed no differences in the bulk chemistry or structure for thick a-SiO_2 films that were deposited on aluminum and titanium substrates. This indicated that choice of substrate, titanium or aluminum, would not affect the bonding strength of the adhesive/a-SiO_2 interface. However, no experimental data have been obtained for adhesive joints made with titanium adherends that have been plasma pretreated with a-SiO_2 primer films.

The model interfaces from Part I showed that primary bonds, Ti-O-Si and Al-O-Si, should effectively stabilize the a-SiO_2/metal interface against moisture-induced debonding. Wedge testing of adhesive joints made from aluminum adherends that were pretreated with plasma-polymerized a-SiO_2 films supported this notion, since they showed an extremely stable a-SiO_2/aluminum interface [2]. However, to date, no durability testing of the a-SiO_2/titanium interface has been carried out. It is clear that a significant amount of support for the model a-SiO_2/metal interfaces that were developed in the previous parts of this work can be obtained by testing their strength and durability when used in adhesive joints. Thermodynamically driven chemical reactions have been shown to occur to different degrees between a-SiO_2 deposited on aluminum and titanium substrates. This suggests that different mechanical properties at the a-SiO_2/metal interface may result when comparing aluminum substrates with titanium substrates. Thin film depositions of a-SiO_2 on metal substrates showed that the a-SiO_2/aluminum interface had a silicon suboxide-rich region that was two molecular layers thinner than the corresponding region at the a-SiO_2/titanium interface, which was five molecular layers thick, ca. 1.6 nm. In addition, it was concluded that both Al-O-Si and Ti-O-Si bonds were formed between the a-SiO_2 primer and oxide surface of the metal substrate.

If covalent bonding strengthened the a-SiO_2/metal interface for a-SiO_2 deposited onto aluminum and titanium substrates, then similar mechanical and durability behavior would be expected from them when used as adherends in adhesive joints. Alternatively, if a hydrogen-bonded a-SiO_2/metal interface were created, it would likely fail under environmental and mechanical stress. In order to test this

hypothesis, mechanical and durability testing of adhesive joints was carried out with a high cohesive strength adhesive. In order to make observations that were consistent with the conditions used to interpret the a-SiO_2/interface, plasma depositions were carried out using the in situ XPS plasma reactor using the same pretreatment and deposition conditions that were used previously. However, due to the size limitation of the plasma chamber, adherends that were slightly shorter in length than that of the standard wedge test specimen had to be used.

To ensure cohesion of the adhesive/a-SiO_2 interface during durability testing, an epoxy-silane adhesion promoter was applied to the aluminum and titanium substrates after plasma deposition and immediately before adhesive bonding. The wedge test configuration maximized the environmental strain at the a-SiO_2/metal interface during durability testing. Since the goal of this work was to compare the durabilities of the a-SiO_2/aluminum and a-SiO_2/titanium interfaces, the adhesive/a-SiO_2 interfaces were strengthened by the silence and a high-strength adhesive was used.

EXPERIMENTAL

Lap Joints

The lap joints were prepared in accordance with ASTM standard D-1002-72. Aluminum and titanium substrates (25 mm $\times$ 102 mm) were cut from 3.2 mm and 1.6 mm thick 2024-T3 and Ti-6Al-4V sheet, respectively. A 25 mm $\times$ 25 mm area on the end of each substrate was first rough polished with 600-grit silicon carbide polishing paper and water and then further polished to a mirror finish by using 6 μm and then 1 μm diamond particles in oil slurries. After polishing, the samples were rinsed in reagent-grade toluene several times and blown dry with a stream of nitrogen gas.

Wedge Test Specimens

The wedge test specimens were made in accordance with ASTM standard test method D-3762. Aluminum and titanium substrates (25 mm $\times$ 102 mm) were cut from 3.2 mm and 1.6 mm thick 2024-T3 and Ti-6Al-4V sheet, respectively. The adherend surfaces were grit-blasted using 50 micron alumina particles in a stream of prepurified compressed nitrogen gas.

Plasma Pretreatment

A substrate was mounted on the sample holder in the XPS plasma reactor with the polished area of the sample centered within the

chamber and facing the plasma applicator. Each substrate was plasma-etched for 10 min at 100 Watts RF power using 40 standard cm^3 per minute (SCCM) argon and 10 SCCM oxygen at 500 mTorr pressure. Plasma polymerization was then carried out for 3 min at 100 Watts RF power using 40 SCCM of argon, 10 SCCM of oxygen, and 0.5 SCCM hexamethyldisiloxane (HMDSO), at 500 mTorr pressure. As a control, some wedge test substrates were only plasma etched so that the effectiveness of the wedge-testing environment could be checked.

The plasma-pretreated surfaces of the wedge test adherends were treated with an aqueous solution of γ-glycidoxypropyltrimethoxysilane (γ-GPS) by placing the adherends into the solution for 15 min. Thesubstrates were then dried in a convection oven for 1 h at 93°C. The concentration of the γ-GPS solution was 1% by volume in water [3].

A high-strength structural epoxy adhesive, Ciba-Geigy AV-3131, was used to bond the lap joints and wedge test specimens adhesively. Figure 1 shows the lap joint and wedge test specimen geometries.

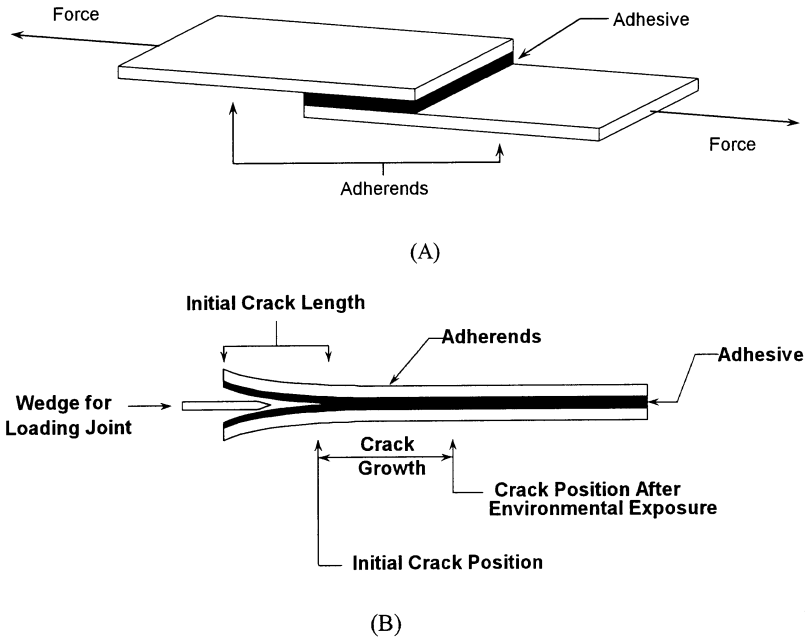

FIGURE 1 Diagrams showing (A) an adhesively bonded lap joint with the same geometry used for this study and (B) the wedge-test specimen for environmental durability testing.

Pairs of treated lap joint substrates were adhesively bonded by applying a thin layer of the adhesive to the polished areas of each adherend. For the lap joints, the polished ends of each adherend were positioned to create a 12.7 mm overlap and were held in place with binder clips. In the case of the wedge test specimens, the pretreated surfaces of the adherends were coated with adhesive and bonded together. Clean metal wires, 0.36 mm diameter, were placed between the ends of the adherends to ensure a constant bond thickness. The adhesive was then cured in a convection oven at 175°C for 30 min in accordance with the adhesive manufacturer's recommendations.

The breaking strengths of the lap joints were obtained using an Instron tensile-testing machine. The testing conditions were carried out in accordance with the ASTM standard test method D-1002-72. Three samples for each test condition were tested, and the average breaking strengths along with their standard deviations were calculated.

Wedge test conditions were carried out in accordance with ASTM standard test method D-3762. Three wedge test specimens were tested for each set of pretreatment conditions. Once the wedges were driven into the ends of the specimens, the initial cracks were measured. The joints were then placed into a heated bath of distilled and deionized water held at 60°C. Over the duration of approximately two weeks, the specimens were periodically removed from the water long enough to measure and record their crack lengths. At the conclusion of testing, the adherends of each specimen were separated in order to allow inspection of the failure surfaces.

RESULTS AND DISCUSSION

Lap Joints

The average breaking strengths along with their standard deviations are reported in Table 1. All specimens exhibited high breaking strengths, ca. 30 MPa, and failure always occurred in a purely cohesive manner within the adhesive. This indicated that the as-bonded mechanical strength of the interface created between the a-SiO_2 primer and the metal substrate was greater than the cohesive strength of the high-strength adhesive. In addition, no significant difference between the breaking strengths of lap joints prepared with aluminum substrates and those prepared with titanium substrates was observed. This meant that the thicker suboxide region that developed at the a-SiO_2/titanium interface had a very high cohesive strength and did not

TABLE 1 Breaking Strengths of Lap Joints Prepared From Polished Metal Substrates That Were Plasma Etched and Coated With Plasma-polymerized a-SiO_2 Primer Films

Polished substrate	Plasma treatment[a]	Breaking stress[b] (MPa)	Failure mode
Aluminum	10-min plasma etch	29.9 ± 0.81	100% cohesive within adhesive
Aluminum	2.4-nm a-SiO_2 primer	29.2 ± 0.59	100% cohesive within adhesive
Titanium	10-min plasma etch	29.1 ± 2.8	100% cohesive within adhesive
Titanium	2.4-nm a-SiO_2 primer	29.4 ± 3.2	100% cohesive within adhesive

[a] All substrates coated with a-SiO_2 primers were plasma etched prior to deposition.
[b] Three joints were tested for each plasma treatment.

act as a weak boundary layer. The high-breaking strengths of the lap joints supported the proposed model of the a-SiO_2/metal interface that had strong chemical bonding between the metal oxide and the initially deposited network of a-SiO_2.

Wedge Test Specimens

The crack length versus exposure time for the aluminum and titanium wedge test specimens are shown in Figures 2 and 3, respectively. The observed difference in initial crack lengths between aluminum and titanium specimens was simply due to the difference in adherend thickness. The control specimens showed extreme crack growth (ca. 2–2.5 cm) typical of moisture-induced interfacial failure, indicating that the environmental stress was significant. The overall crack growth of the specimens made with a-SiO_2 pretreated adherends was small, only 1.0 cm for aluminum adherends and 0.65 cm for titanium adherends. This indicated that, if debonding at the a-SiO_2/metal interface occurred, the difference in durability between the a-SiO_2/aluminum and a-SiO_2/titanium interfaces was small.

After durability testing, the fracture surfaces of the aluminum and titanium wedge test specimens were examined and are shown in Figures 4 and 5, respectively. As expected, interfacial failure of the adhesive/substrate interface was observed for all specimens that were not pretreated with plasma-polymerized a-SiO_2 primer films. However, for the wedge test specimens made with pretreated aluminum and titanium adherends, failure at the adhesive/a-SiO_2 or a-SiO_2/metal interfaces did not occur, and crack propagation occurred entirely within the adhesive. This indicated that the a-SiO_2/titanium interface was at least as durable as the a-SiO_2/aluminum interface.

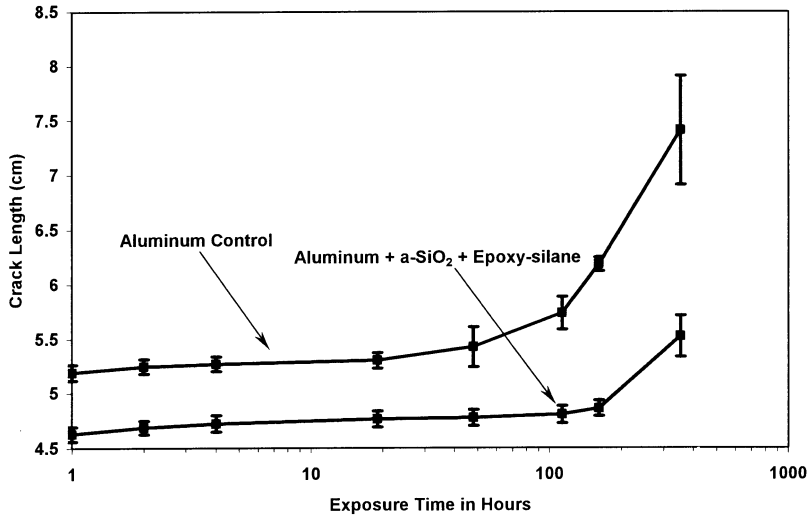

FIGURE 2 Plot showing crack growth during immersion time in water at 60°C for wedge-test specimens made from aluminum adherends bonded with Ciba-Giegy AV-3131 adhesive.

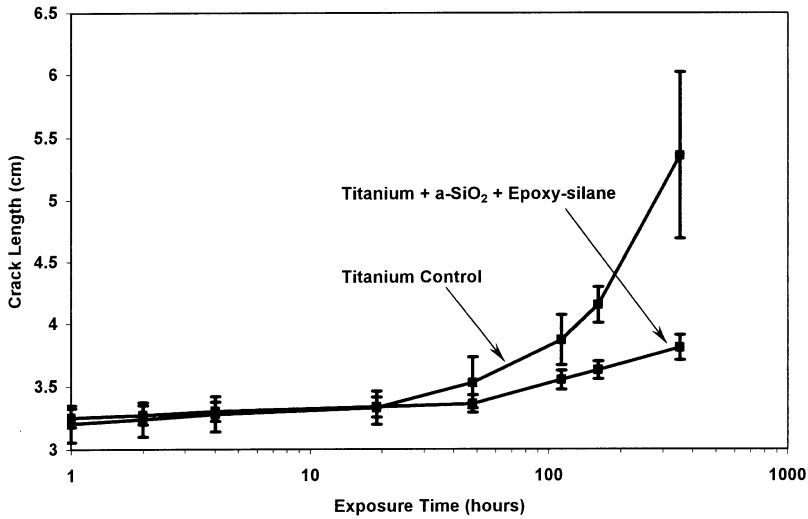

FIGURE 3 Plot showing crack growth during immersion time in water at 60°C for wedge-test specimens made from titanium adherends bonded with Ciba-Giegy AV-3131 adhesive.

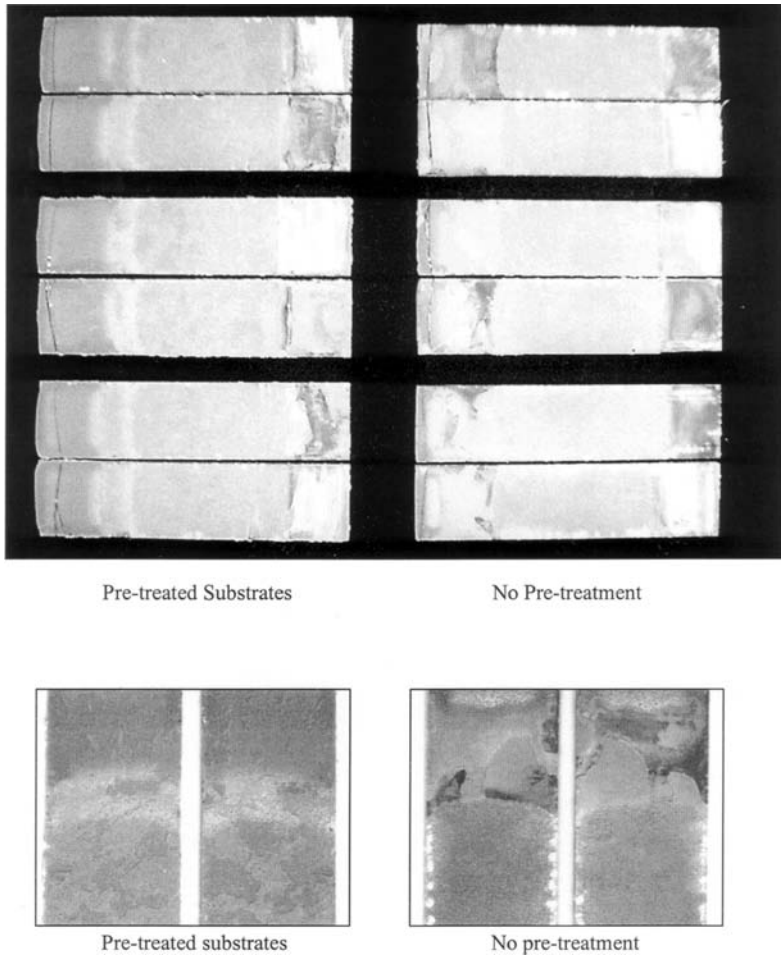

FIGURE 4 Images taken of the fracture surfaces of aluminum wedge-test specimens. The large image on top is 0.6× magnification, and the lower images are actual size.

In addition, the significant durability of the a-SiO_2/aluminum and a-SiO_2/titanium interfaces supported the conclusions of Part II, in which primary Al-O-Si and Ti-O-Si bonds were indicated to form between the a-SiO_2 film and the oxide of the metal substrates. The presence of more suboxide at the a-SiO_2/titanium interface did not have a measurable effect on the durability or cohesive strength of the a-SiO_2 primer film to the oxide on the titanium substrate.

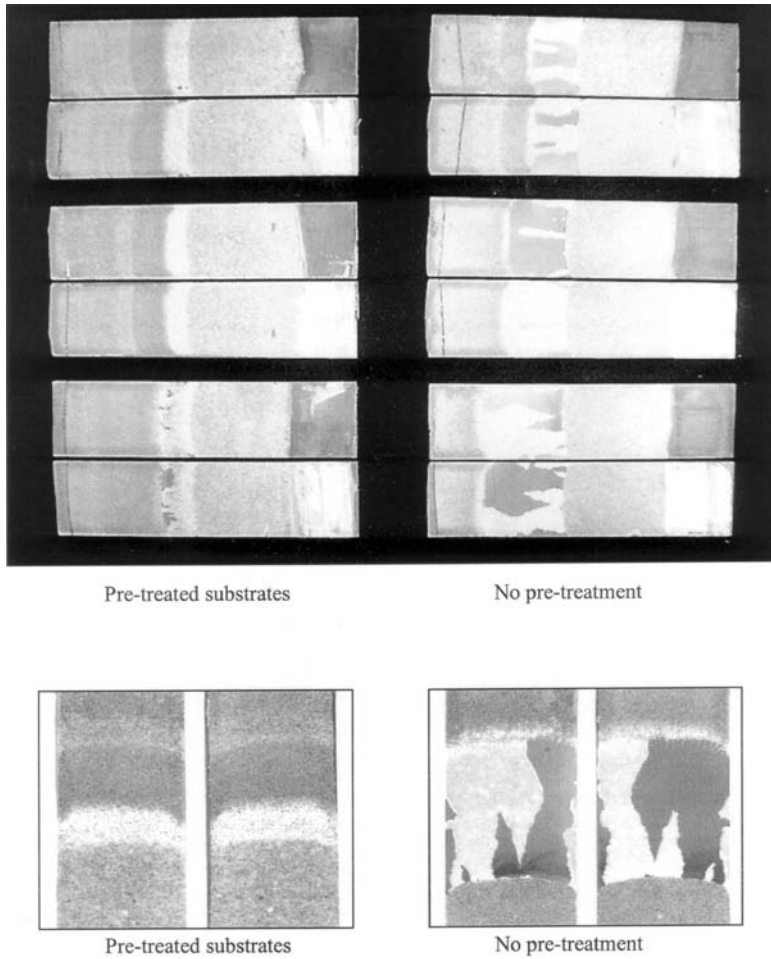

FIGURE 5 Images taken of the fracture surfaces of titanium wedge-test specimens. The large image on top is 0.6 × magnification, and the lower images are actual size.

CONCLUSIONS

The breaking strengths of lap joints made with plasma-pretreated aluminum and titanium adherends indicated that the adhesive bonding across the adhesive/a-SiO_2 interface was very strong and exceeded the cohesive strength of the adhesive, ca. 30 MPa. The adherend material, aluminum or titanium, had no measurable effect on the breaking strengths of the lap joints, and the mechanical

strength of the a-SiO_2/metal interface exceeded the cohesive strength of the adhesive, regardless of substrate. The thickness of the suboxide layer that was formed at the a-SiO_2/metal interfaces did not have any effect on the breaking strengths of the lap joints. These results supported the conclusion that Al-O-Si and Ti-O-Si bonds formed between the metal substrate and the a-SiO_2 primer film. The alternative interpretation of a hydrogen-bonded a-SiO_2/metal interface was rejected.

Durability testing of adhesive joint specimens prepared with aluminum and titanium adherends that were pretreated with plasma-polymerized a-SiO_2 primer films showed that the a-SiO_2/aluminum and a-SiO_2/titanium interfaces were very durable and could not be disrupted by moisture. In addition, the greater amount of suboxide that was detected at the a-SiO_2/titanium interface had no observable effect on durability.

These mechanical strength and durability results for the adhesive joints made from aluminum adherends pretreated with a-SiO_2 primer films were consistent with similar studies carried out previously [4]. In addition, this work showed that the technique of pretreating metal substrates with plasma-polymerized a-SiO_2 primer films for promoting durable adhesive bonding can also be applied to titanium substrates. Conventional pretreatments for titanium adherends for structural bonding are aqueous and involve hazardous materials [4]. The use of plasma techniques for pretreating titanium substrates prior to adhesive bonding would eliminate aqueous pretreatments and essentially double the technological applicability of plasma-polymerized a-SiO_2 films for structural adhesive bonding of metals.

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