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# Plasma-Sprayed Aluminum and Titanium Adherends: II. Durability Studies for Wedge Specimens Bonded with Polyimide Adhesive

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The durability of plasma-sprayed metals bonded with a polyimide adhesive has been studied. Metal adherend surfaces were prepared for adhesive bonding by plasma-spraying inorganic powders on aluminum and titanium. The plasma-sprayed materials included  $\text{Al}_2\text{O}_3$ ,  $\text{AlPO}_4$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  on aluminum, and  $\text{TiO}_2$ ,  $\text{TiSi}_2$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  on titanium. The coatings were sprayed at two different thicknesses. Durability studies of samples prepared in a wedge-type geometry were carried out. Bonded specimens were maintained in an environmental cycle that included exposure to the conditions; low temperature,  $-20^\circ\text{C}$ ; relative humidity at elevated temperature, 70% RH at  $66^\circ\text{C}$ ; elevated temperature ( $160^\circ\text{C}$ ) in air, high temperature ( $160^\circ\text{C}$ ) in vacuum (130 torr, 0.2 atm.), and room temperature. Crack growth rate and mode of failure were determined. The results of the durability tests indicate that thin coatings (25  $\mu\text{m}$ ) of plasma-sprayed materials perform better than thicker (150  $\mu\text{m}$ ) coatings. The crack growth rate for thin coatings (25  $\mu\text{m}$ ) of  $\text{Al}_2\text{O}_3$ ,  $\text{AlPO}_4$ ,  $\text{SiO}_2$ , and  $\text{MgO}$  plasma-sprayed on aluminum was equivalent to that for phosphoric acid anodized aluminum. Similarly, the durability performance for titanium samples prepared with a 25  $\mu\text{m}$ -thick  $\text{TiO}_2$ ,  $\text{TiSi}_2$ , and  $\text{SiO}_2$  plasma-sprayed coatings was equivalent to that for a Turco<sup>®</sup>-prepared titanium surface. Although the evaluation of durability as a function of surface chemistry was an objective of the study, it was not possible to evaluate the effect, since most failures occurred within the adhesive (cohesive failure) during the environmental tests. That failure occurred in the adhesive indicates that the coating-adherend and the coating-adhesive interactions are sufficiently robust to prevent interfacial failure under the experimental conditions investigated.

**KEY WORDS:** Plasma-sprayed adherends; anodized adherends; durability; surface characterization; polyimide adhesive; environmental exposure.

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## INTRODUCTION

The role of the surface treatment of an adherend is to promote highly stable adhesive-adherend interactions; high stability is accomplished by making the chemistry of the adherend and adhesive compatible.<sup>1-3</sup> The common surface preparations used to enhance durability for adhesive bonding of metals include aqueous chromic-sulfuric acid treatment, aqueous ferric salt-sulfuric acid treatment, phosphoric and chromic acid anodization for aluminum, as well as chromic acid or sodium hydroxide anodization for titanium.<sup>4</sup> Although these methods for surface preparation result in strong durable bonds, they require the maintenance of chemical supplies, appropriate reaction vessels, and handling and disposing of waste. Furthermore, surface pretreatments on aluminum are subject to degradation in hot moist environments<sup>5</sup> and titanium alloys experience oxide dissociation at elevated temperatures.<sup>6</sup> Also of concern is the reproducibility of surface chemistry and morphology of chemically-prepared surfaces. Small changes in preparation conditions can result in large changes in bond strength and durability.<sup>7</sup> In studies<sup>8,9</sup> of the durability of titanium using different surface treatments, it was concluded that the interfacial area between adhesive and adherend controlled durability and that alkoxide coatings on titanium increased durability relative to phosphate-fluoride treatments. Based on these studies it is reasonable to suggest that alternative surface preparations are needed to provide stability at high temperatures and to satisfy environmental regulations.

Plasma spraying has been used for decades to spray coatings for anti-corrosion, wear resistance, and thermal barriers.<sup>10-16</sup> The fundamental process that occurs during plasma spraying is that a fine powder is introduced into a gas plasma at elevated temperatures where it becomes molten and is projected onto a substrate. After the molten particle impacts the substrate, it resolidifies, having properties much different from the original powder. Studies have shown that plasma-sprayed coatings adhere well to metal substrates due to interdiffusion of the coating components into the metal.<sup>17-20</sup> This interdiffusion becomes even greater when a surface preparation such as grit blasting or gaseous plasma spraying (no powder injected) is used prior to spraying to roughen the surface and remove contaminants.<sup>6</sup>

A potential advantage of plasma spraying for the treatment of adherends for adhesive bonding is that the chemistry of the coating can be changed to be compatible with the adhesive. This can be accomplished by spraying a powder that has the desired chemistry, or in low pressure systems, reactive gases can be introduced, which can react at high temperatures with the powder being sprayed.<sup>21</sup>

Only a few studies have focused on plasma-sprayed coatings related to adhesive bonding.<sup>6,22-24</sup> Because plasma-spraying can produce coatings of different chemistry and morphology (both of which are important in adhesive bonding) the method appears to be a promising alternative to current solution pretreatment methods.<sup>6,22,24</sup> The studies performed by others using plasma-sprayed coatings suggest that plasma-sprayed coatings provide bond strengths equal to, or only slightly less than, conventional pretreatments. Previous studies also noted that adhesive bonds using plasma-sprayed coatings maintained their integrity when exposed to elevated temperatures.<sup>6</sup>

The purpose of this study was to evaluate the durability of adhesively bonded aluminum and titanium using plasma-sprayed coatings as surface pretreatments. Among the principal objectives of the study were the investigation of durability under environmental conditions that could be experienced in aircraft flight, the evaluation of durability as influenced by coating chemistry and coating thickness, and the determination the mode of failure following exposure to the selected environmental conditions. In this work, materials were selected for spraying to provide an opportunity for evaluating the durability of the specimens based on the chemical composition of the plasma-sprayed coating. Materials with different acid-base properties, such as  $\text{SiO}_2$  and  $\text{MgO}$ , were sprayed with the intention of evaluating the role of acid-base characteristics on durability. Also selected were  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  because the common practice in surface preparations is to remove native oxide and replace it with newly formed oxide. Aluminum phosphate ( $\text{AlPO}_4$ ) was also studied, recognizing that phosphate-containing components enhance durability by reducing moisture penetration at the adhesive-adherend interface.

## EXPERIMENTAL

Aluminum 6061 plates were purchased from McMaster-Carr Supply Co., New Brunswick, NJ. Titanium-6Al-4V specimens were obtained from President Titanium, Hanover, MA. The details for the preparation and characterization of the plasma-sprayed coatings were presented in a previous paper,<sup>24</sup> thus only a brief reiteration of the materials used and the thicknesses obtained will be given here. Inorganic powders were plasma-sprayed on aluminum and titanium. Specimens were grit-blasted with alumina before applying the plasma-sprayed coatings.  $\text{Al}_2\text{O}_3$ ,  $\text{AlPO}_4$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  were plasma-sprayed on aluminum adherends, and  $\text{TiO}_2$ ,  $\text{TiSi}_2$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  were deposited on titanium adherends. All coatings, except  $\text{SiO}_2$ , were sprayed at 25  $\mu\text{m}$  (0.001") and 150  $\mu\text{m}$  (0.006") thicknesses.  $\text{SiO}_2$  could not be deposited at 150  $\mu\text{m}$  (0.006") due to failure of the material to adhere to itself.  $\text{SiO}_2$  coatings were 25  $\mu\text{m}$  (0.001") and 50  $\mu\text{m}$  (0.002") thick. Aluminum and titanium adherend surfaces were also pretreated using conventional solution surface preparations. Aluminum was anodized in 15% (w/w) phosphoric acid for 20 minutes at a currently density of 129 amps/m<sup>2</sup> (12 amps/ft<sup>2</sup>). Titanium was treated in Turco 5578<sup>®</sup> solution (37.6 g/1000 mL  $\text{H}_2\text{O}$ ) at 70–80°C for 5 min. and then rinsed in DI water for 5 min. Following the initial cleaning treatment, specimens were etched in a more concentrated Turco 5578<sup>®</sup> solution, 360 gm./1000 mL  $\text{H}_2\text{O}$ , at 80°–100°C for 10 min. Titanium was then rinsed in DI water at 60–70°C. All treated samples were stored in a desiccator until bonded.

Plasma-sprayed and solution-treated adherends were bonded in a wedge configuration<sup>25</sup> using an American Cyanamid (Cytec) polyimide adhesive (FM-36). Samples were bonded following the manufacturer's suggested procedures. The bond-line thickness for all samples was 0.25 mm (10 mil). Specimens were not primed before bonding. The specimen dimensions for aluminum were 2.5 cm × 10.2 cm × 0.64 cm (1" × 4" × 0.25") and for Ti were 2.5 cm × 10.2 cm × 0.23 cm (1" × 4" × 0.090"). The

plasma-sprayed area (also the bonded area) on each specimen was 2.5 cm  $\times$  7.6 cm (1"  $\times$  3"). In the durability evaluation, wedge specimens were exposed to an environmental cycle. A wedge, measuring 28 mm  $\times$  25 mm  $\times$  (1.1"  $\times$  1"  $\times$  0.12") was inserted into the specimen. The crack was allowed to initiate and then the sample was placed in the cold environment to initiate the environmental cycle test. Samples were exposed to cycle A for 100 hrs, and then to cycle B conditions for the duration of the durability experiments (approximately 3500 hrs).

Environment	Cycle A	Cycle B
cold; $-20^{\circ}\text{C}$	2 hrs.	24 hrs.
air, 70%RH; $66^{\circ}\text{C}$	2 hrs.	24 hrs.
dry air; $160^{\circ}\text{C}$	2 hrs.	24 hrs.
vaccum, 130 torr; $160^{\circ}\text{C}$	2 hrs.	24 hrs.
room temp.; $23^{\circ}\text{C}$	16 hrs.	24 hrs.

Crack growth was measured after each step in the exposure cycle. The crack growth measurements were accurate to within  $\pm 2$  mm, and the reproducibility of the initial crack lengths among specimens with the same coating was  $\pm 10$  mm for aluminum and  $\pm 5$  mm for titanium. The results presented in the figures represent average growth data for five specimens of each treatment and adherend.

Plasma-sprayed adherends and failed adhesively-bonded samples were characterized using XPS and SEM.<sup>24,26</sup> XPS spectra were measured using a PHI Perkin-Elmer Model 5400 photoelectron spectrometer. Photoelectrons, generated using  $\text{MgK}_{\alpha}$  radiation ( $h\nu = 1253.6$  eV), were analyzed in a hemispherical analyzer, and detected using a position-sensitive detector. The binding energy scale was calibrated using the carbon 1s photopeak at 284.6 eV for background carbon.<sup>27</sup> In the presentation of the elemental results, photoelectron spectral peak areas were measured and subsequently scaled to account for ionization probability and an instrumental sensitivity factor to yield results which are indicative of surface concentration in atomic percent. The precision and accuracy for the concentration evaluations are about 10% and 15%, respectively. Multi-component carbon 1s photopeaks were curve fitted using photopeaks of Gaussian peak shape with a full-width-at-half maximum (FWHM) of  $1.6 \pm 0.1$  eV. The C 1s binding energy values were selected to correspond to carbon-carbon/hydrogen-and carbon-oxygen-containing functional groups.<sup>26</sup>

SEM photomicrographs were determined using an ISI Model SX-40 scanning electron microscope. Samples were sputter-coated with a thin gold film ( $\sim 200$  Å).<sup>24</sup>

## RESULTS AND DISCUSSION

The durability results, presented as crack length as a function of time, are presented in Figures 1–4. Figures 1 and 2 present crack length data for up to 172 hrs of exposure in the environmental cycle for aluminum and titanium samples, respectively. For exposure times of greater than 120 hours (according to cycle B), it was noted that crack length did not change in the period 172 to 3500 hrs. The final crack

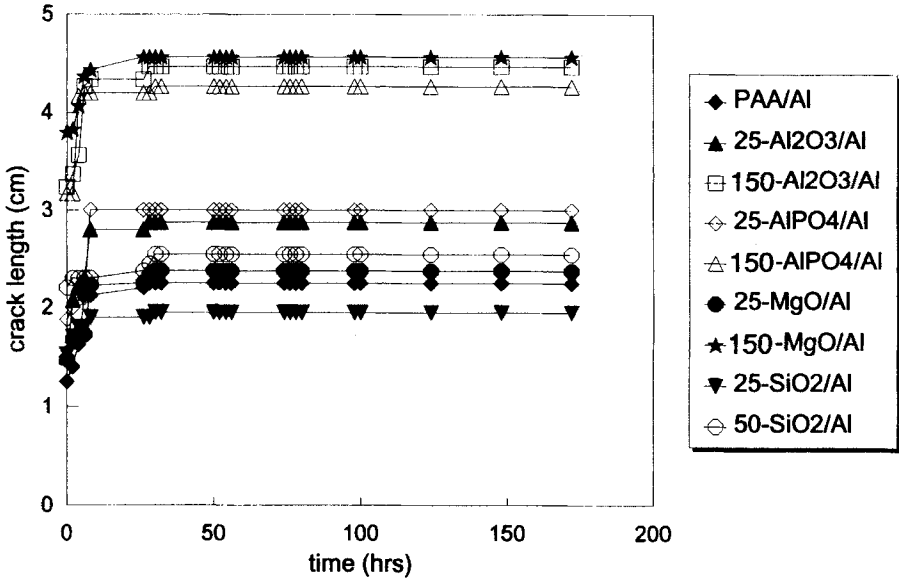


FIGURE 1 Crack length results for plasma-sprayed aluminum adherends bonded with FM-36 polyimide adhesive; Time: 0 to 172 hrs. Total environmental exposure duration 3500 hrs. Crack lengths at 172 hrs. equal to lengths at 3500 hrs.

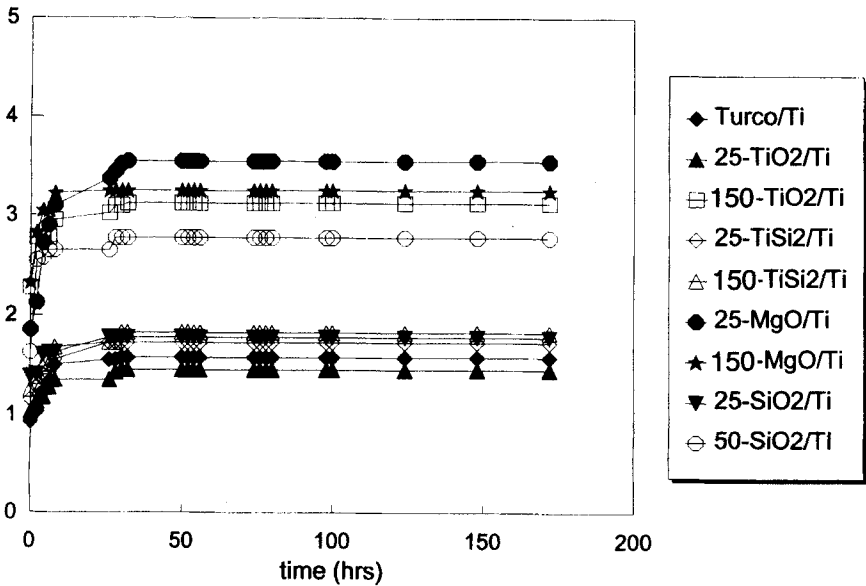


FIGURE 2 Crack length results for plasma-sprayed titanium adherends bonded with FM-36 polyimide adhesive; Time: 0 to 172 hrs. Total environmental exposure duration 3500 hrs. Crack lengths at 172 hrs. equal to lengths at 3500 hrs.

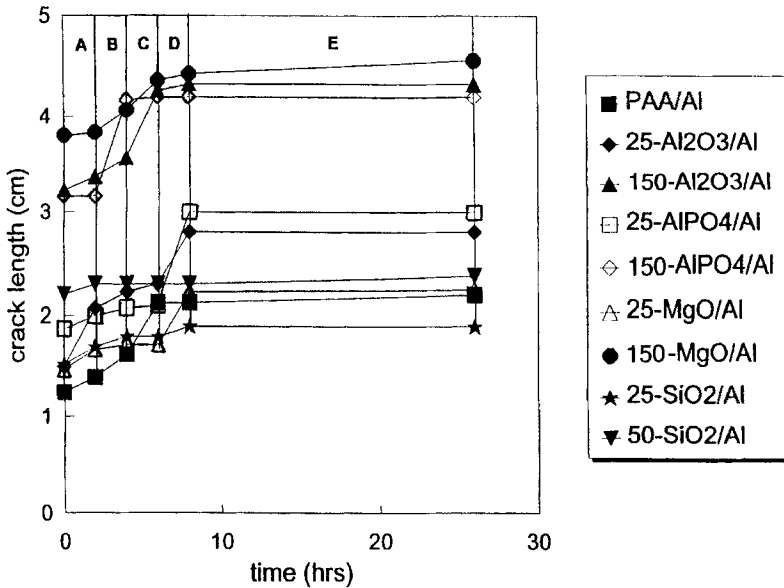


FIGURE 3 Crack length results for plasma-sprayed aluminum adherends bonded with FM-36 polyimide adhesive; Crack length during the first environmental cycle. Exposure conditions-Region A: cold, 20°C, 2 hrs.; Region B: hot/wet 66°C, 70% RH, 2 hrs.; Region C: hot atmospheric, 160°C in air, 2 hrs.; Region D: hot vacuum, 160°C, 130 torr, 2 hrs.; Region E: ambient conditions, 23°C, 16 hrs.

length data, measured at 3500 hours when the experiments were terminated, are presented in Tables I and II. It is apparent from the results in Figures 1 and 2 that crack growth ended during the second repetition of the environmental cycle, *i.e.*, after approximately 48 hours of exposure to two cycles in the environmental conditions. Crack growth occurred at different rates for samples with different surface preparations under different environmental conditions, as shown in Figures 3 and 4. Examination of the results in Figure 3 for the aluminum samples indicates that, except for the 25-Al<sub>2</sub>O<sub>3</sub>/Al specimens, crack growth in the cold portion of the cycle is small, <2 mm. Exposure to high relative humidity resulted in marked growth, >6 mm, for the 150-AlPO<sub>4</sub>/Al samples. During the exposure to elevated temperature at atmospheric pressure in air, the PAA/Al and 150-Al<sub>2</sub>O<sub>3</sub>/Al samples exhibited significant crack growth (>6 mm). In the hot-vacuum portion of the cycle crack growth of greater than 6 mm occurred for the 25-AlPO<sub>4</sub>/Al, 25-Al<sub>2</sub>O<sub>3</sub>/Al, and 25-MgO/Al specimens. For samples where significant growth was not observed, crack growth of approximately 2 mm occurred upon exposure to the various conditions of the cycle.

The changes in crack length for the titanium samples during early exposure in the cycle are given in Figure 4. The 50-SiO<sub>2</sub>/Ti, 150-MgO/Ti, and 150-TiO<sub>2</sub>/Ti samples exhibited growth greater than 6 mm during exposure at -20°C. The crack for the 25-MgO/Ti sample grew more than 6 mm in the high relative humidity portion of the test cycle. Other specimens showed incremental growth (<2-3 mm) during exposure to each of the environmental conditions.

TABLE I  
Failure Processes for Plasma-Sprayed Adherends: Aluminum Bonded  
with FM-36 Polyimide Adhesive

Thickness-coat/adherend	Arrest crack length (cm)	Failure mode (XPS) environmental exposure
PAA/Al	2.3	cohesive
25-Al <sub>2</sub> O <sub>3</sub> /Al	2.9	cohesive
150-Al <sub>2</sub> O <sub>3</sub> /Al	4.5	in the coating
25-MgO/Al	2.4	cohesive
150-MgO/Al	4.6	mixed mode (coating/ cohesive)
25-SiO <sub>2</sub> /Al	2.0	cohesive
50-SiO <sub>2</sub> /Al	2.6	cohesive
25-AlPO <sub>4</sub> /Al	3.0	mixed mode (coating/ cohesive)
150-AlPO <sub>4</sub> /Al	4.3	mixed mode (coating/ cohesive)

TABLE II  
Failure Processes for Plasma-Sprayed Adherends: Titanium Bonded  
with FM-36 Polyimide Adhesive

Thickness-coat/adherend	Arrest crack length (cm)	Failure mode (XPS) environmental exposure
Turco®/Ti	1.6	cohesive
25-TiO <sub>2</sub> /Ti	1.5	cohesive
150-TiO <sub>2</sub> /Ti	3.1	coating/metal interface
25-MgO/Ti	3.6	cohesive
150-MgO/Ti	3.3	coating/metal interface
25-SiO <sub>2</sub> /Ti	1.8	cohesive
50-SiO <sub>2</sub> /Ti	2.8	cohesive
25-TiSi <sub>2</sub> /Ti	1.7	mixed mode (coating/ cohesive)
150-TiSi <sub>2</sub> /Ti	1.8	mixed mode (coating/ cohesive)

Returning to a consideration of the general crack growth behavior (Figs. 1 and 2), it is apparent for the aluminum adherends that the ultimate crack length is dependent on the surface treatment and that at least two types of general behavior are noted. Crack length values in the range 4.3–4.6 cm are found for the 150-MgO/Al, 150-Al<sub>2</sub>O<sub>3</sub>/Al, and 150-MgO/Al samples. Crack lengths of intermediate and lesser values (<4.0 cm) were recorded for all other aluminum samples. Similarly, the crack length is small (<2.0 cm) for the 25-TiO<sub>2</sub>/Ti, Turco/Ti, 25-SiO<sub>2</sub>/Ti, 25-TiSi<sub>2</sub>/Ti, and 150-TiSi<sub>2</sub>/Ti specimens. The other titanium samples, 50-SiO<sub>2</sub>/Ti, 150-TiO<sub>2</sub>/Ti, 25-MgO/Ti, and 150-MgO/Ti exhibited crack lengths in the range 2.8–3.6 cm. It is noteworthy that the initial crack lengths for the titanium samples are less than those for the corresponding aluminum specimen. The crack length data indicate a dependence on the coating thickness, in that the specimens with thicker coatings generally showed greater crack growth. The exceptions to this general observation include the



50-SiO<sub>2</sub>/Ti and 150-TiSi<sub>2</sub>/Ti samples. The lower crack length for the 150-TiSi<sub>2</sub>/Ti specimen may be related to the fact that the chemical nature of plasma-sprayed TiSi<sub>2</sub><sup>24</sup> was found to be a titanium silicate or a mixture of TiO<sub>2</sub> and SiO<sub>2</sub>. It is possible that such a "mixed" chemistry coating could enhance adhesive bonding to the polyimide or inhibit environmental degradation of the bond, and thus improve durability. The findings regarding durability and coating thickness in this study are similar to the results of Pike *et al.*, for Al<sub>2</sub>O<sub>3</sub> plasma-sprayed on a variety of adherends.<sup>22</sup> In recent work, Davis and co-workers<sup>23</sup> reported poor performance, compared with the findings in this study, for aluminum plasma-sprayed with alumina and bonded with an epoxy adhesive. It was suggested<sup>23</sup> that primer penetration enhanced the bonding in the current study. However, since no primer was used, it is possible that the porosity of the coating in this work may have allowed penetration of polymer into the plasma-sprayed coating, thus enhancing durability. In another study by Clearfield *et al.*, who plasma-sprayed titanium-6Al-4V on titanium-6Al-4V,<sup>6</sup> it was shown that titanium with thin (50 μm) plasma-sprayed coatings exhibited crack propagation values equal to, or slightly less than, for titanium whose surfaces had been prepared by standard methods, such as chromic acid or sodium hydroxide anodization. Also in Davis' study<sup>23</sup> it was reported that titanium alloy plasma-sprayed with titanium-6Al-4V alloy and bonded with an epoxy adhesive

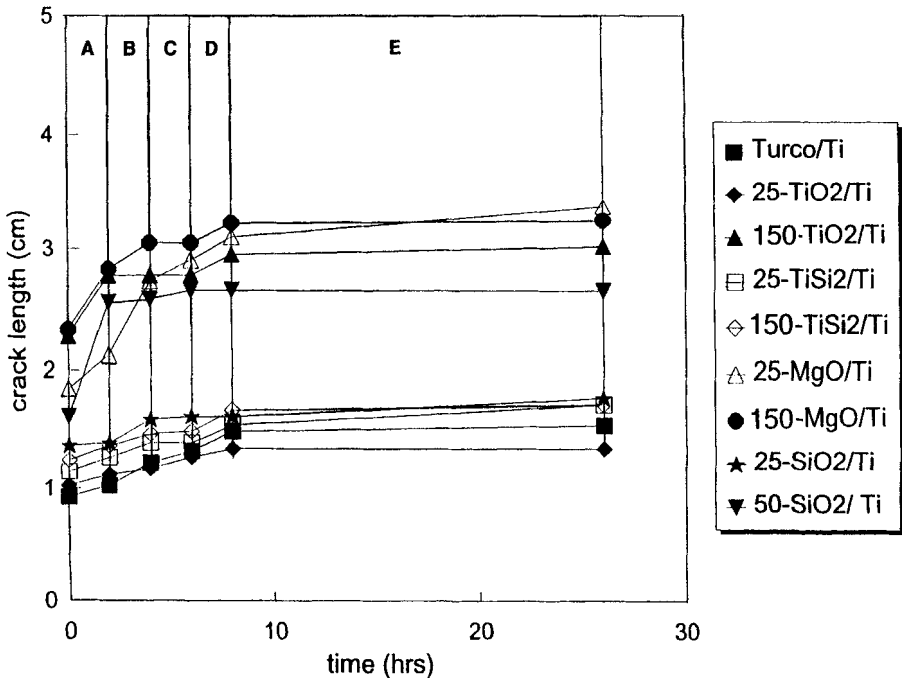


FIGURE 4 Crack length results for plasma-sprayed titanium adherends bonded with FM-36 Polyimide Adhesive; Crack length during the first environmental cycle. Exposure conditions-Region A: cold, 20°C, 2 hrs.; Region B: hot/wet, 66°C, 70% RH, 2 hrs.; Region C: hot atmospheric, 160°C in air, 2 hrs.; Region D: hot vacuum, 160°C, 130 torr, 2 hrs.; Region E: ambient conditions, 23°C, 16 hrs.

sive (FM-300M) exhibited durability performance (static exposure to 90% RH at 60°C) that was equivalent to that for chromic acid anodized-or Turco treated-titanium alloy. The findings in this study complement the results of the earlier study<sup>23</sup> in demonstrating that titanium-6Al-4V specimens, plasma-sprayed with thin (25 µm) coatings of TiO<sub>2</sub>, SiO<sub>2</sub> and TiSi<sub>2</sub>, and thick coatings (150 µm) of TiSi<sub>2</sub>, show excellent bond durability for titanium alloy bonded with a polyimide adhesive.

Exposure of adhesively-bonded, plasma-sprayed wedge specimens to an environmental cycle resulted in a variety of failure modes and durability behavior. The durability results are summarized in Tables I and II for aluminum and titanium adherends, respectively, and are presented in terms of crack length (arrest values) at the end of 3500 hrs in the environmental cycle, and the failure mode induced during environmental exposure. The failure modes were determined either visually or by XPS/SEM surface analysis. The XPS analysis results for the failure surfaces for the 25-Al<sub>2</sub>O<sub>3</sub>/Al and 150-Al<sub>2</sub>O<sub>3</sub>/Al specimens are given in Table III. The results for the two 150-Al<sub>2</sub>O<sub>3</sub>/Al failure surfaces are equivalent and suggest that failure occurs in the coating. For the 150-Al<sub>2</sub>O<sub>3</sub>/Al failure surface the carbon concentrations are in the range 15–22%, the oxygen concentrations are 50–58% and the aluminum content is approximately 25%. Nitrogen and silicon are present at low concentrations or were not detected. That failure in the coating occurred is supported by the result that the surface chemistries for the two 150-Al<sub>2</sub>O<sub>3</sub>/Al failure surfaces are the same within experimental error, and are similar to the results for a non-bonded, plasma-sprayed Al<sub>2</sub>O<sub>3</sub>/Al adherend.<sup>24</sup> The respective analysis results for the failure surfaces for the 25-Al<sub>2</sub>O<sub>3</sub>/Al specimens are also equivalent and are consistent with cohesive failure. The carbon, oxygen, and nitrogen concentrations are indicative of adhesive. The presence of silicon may arise from filler in the adhesive. The detection of aluminum on the failure surface may indicate a small contribution from a debonding process where failure occurs at the adhesive/alumina coating interface or within the coating. Nevertheless, the dominant failure mode is cohesive.

Surface analysis results for the TiO<sub>2</sub>-coated/titanium specimens indicated the same failure behavior as for the Al<sub>2</sub>O<sub>3</sub>-coated/aluminum materials. In general, the failure modes for the wedge specimens were independent of the type of adherend. The results indicate that the wedge specimens with a thin plasma-sprayed coating

TABLE III  
Surface Analysis Results for Al<sub>2</sub>O<sub>3</sub>/Al Plasma-Sprayed Specimens and Failure Surfaces

Element/specimen	Al <sub>2</sub> O <sub>3</sub> /Al	150-Al <sub>2</sub> O <sub>3</sub> /Al		25-Al <sub>2</sub> O <sub>3</sub> /Al	
	non-bonded	adh*	met*	adh	met
C	21.6	21.8	15.0	66.9	69.0
O	48.2	50.5	58.2	22.5	21.8
Al	27.3	24.8	26.3	2.4	1.8
N	<0.2	0.9	0.5	5.3	5.7
Si	<0.2	<0.2	<0.2	3.0	1.8
Na	2.9	<0.2	<0.2	<0.2	<0.2

\*adh: adhesive-side failure surface.  
met: metal-side failure surface.

(25  $\mu\text{m}$ ) failed cohesively and that samples with a thick plasma-sprayed coating (150  $\mu\text{m}$ ) failed within the coating or *via* a mixed mode process.

The extent of crack propagation (3.6 cm) and the failure mode (cohesive) for the 25-MgO/Ti specimen seem inconsistent with other results, in that the arrest crack length is comparable with that for specimens where failure occurred in the coating or in the coating/metal interface region. Visual observation and surface analysis results for the 25-MgO/Ti failure surfaces are consistent with the presence of adhesive on both failure surface. It was noted, however, that the adhesive coating on the metal-side failure surface was thin compared with the thickness of adhesive coatings on other surfaces where cohesive failure occurred. It is not possible from the available analytical data to offer an explanation for this observed result.

Failure in the  $\text{AlPO}_4/\text{Al}$  system was unique in that the surface analysis indicates a heterogeneous distribution of components on the failure surface. The XPS results for the analysis of  $\text{AlPO}_4$  powder, for the non-bonded, plasma-sprayed  $\text{AlPO}_4/\text{Al}$  surface, and for the metal-side failure surface are presented in Table IV. The XPS results for the adhesive-side failure surface were equivalent to the results for the metal-side failure surface. The analysis data for the as-received powder are consistent with the expected stoichiometry for  $\text{AlPO}_4$ . The powder also contains carbon and a small amount of sodium as impurities. The plasma-sprayed surface contains silicon at a relatively high concentration. The silicon arises from silica ( $\text{SiO}_2$ ) which was added to enhance the flow of  $\text{AlPO}_4$  in the plasma gun during plasma spraying. The changes in the concentrations of elements on the metal-side failure surface, relative to the values for the plasma-sprayed surface, reveal an increase in carbon, sodium, and nitrogen and a significant decrease in silicon. The concentrations for oxygen, aluminum, and phosphorus are little changed upon comparing the results for the plasma-sprayed and failure surfaces. That the concentrations of constituents associated with the adhesive increased while the coating component concentrations remain relatively unchanged, and that the silicon content decreased dramatically on the failure surface, suggests that failure occurred in a region where polymer and coating components were present. The presence of polymer and coating components on the failure surface indicates that adhesive has likely penetrated the porous structure of the coating and that failure is directed within this coating-adhesive region.

TABLE IV  
Surface Analysis Results for  $\text{AlPO}_4/\text{Al}$  Plasma-Sprayed Specimens and Failure Surfaces

Element/specimen	$\text{AlPO}_4$ powder	$\text{AlPO}_4/\text{Al}$ non-bonded	25- $\text{AlPO}_4/\text{Al}$ met*
C	25.3	24.4	30.0
O	47.7	49.6	47.8
Al	11.9	2.9	3.8
N	<0.2	0.7	2.2
Si	<0.2	11.1	1.4
P	11.9	9.6	7.7
Na	3.2	1.7	7.1

\*met: metal-side failure surface.

An objective of this study was to examine durability as a function of surface coating chemistry. From the failure data presented in Table I for aluminum it is apparent that the thickness of the coating (mechanical properties) appears to play a prominent role in the failure process. Among the different coatings where the acid/base nature is changed;  $\text{SiO}_2$  (acid),  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  (base), the crack length and failure modes are similar for the 25  $\mu\text{m}$ -coated specimens. Similarly, for the 150- $\text{Al}_2\text{O}_3/\text{Al}$  and 150- $\text{MgO}/\text{Al}$  samples the crack lengths are equivalent and failure occurs in the coating region. The findings for titanium adherends (Table II) are similar to the results for the aluminum samples, with the exception that both  $\text{MgO}$ -coated adherends exhibit the same crack length but the failure modes are different. The  $\text{TiSi}_2/\text{Ti}$  specimens show excellent durability as indicated by the crack length but mixed mode failure occurs. The type of mixed mode failure is of the type noted for the  $\text{AlPO}_4/\text{Al}$  specimens, in that adhesive and coating components were present on both failure surfaces. Such results suggest polymer penetration into the coating and failure in the coating-polymer domain. The durability of the  $\text{TiSi}_2/\text{Ti}$  samples may also be enhanced by the chemical nature of the coating which was characterized as a titanium silicate or a mixture of  $\text{TiO}_2$  and  $\text{SiO}_2$ .<sup>24</sup> The presence of the silicate, or titania plus silica, may inhibit moisture intrusion into the bond and/or provide a "composite-like" material (silicate plus polymer) whose mechanical properties direct crack propagation away from the adhesive or the adherend/coating interface.

## SUMMARY

The principal findings in this study are:

1. The durability of adhesively-bonded, plasma-sprayed adherends is equivalent to that for adherend surfaces prepared by standard chemical treatments when tested using cyclical environmental exposure conditions.
2. Durability performance is enhanced for thin compared with thick plasma-sprayed coatings.
3. The mechanical, rather than the chemical, properties of the coatings appear to play a significant role in determining the failure processes.

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