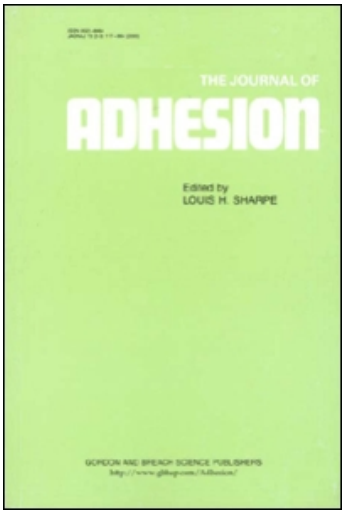

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Dillard, J. G. , Wolfe, K. L. and Holmes, B. L.(1997) 'Plasma-Sprayed Aluminum and Titanium Adherends: III', The Journal of Adhesion, 62: 1, 113 — 126
To link to this Article: DOI: 10.1080/00218469708014565
URL: http://dx.doi.org/10.1080/00218469708014565

J. Adhesion, 1997, Vol. 62, pp. 113–126
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Plasma-Sprayed Aluminum and Titanium Adherends: III

Polymeric Coatings – The Effect of Plasma-Sprayed Polymer Coatings as Primers on the Durability of Adhesively Bonded Aluminum and Titanium

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(Received 29 February 1996; In final form 14 November 1996)

The durability of aluminum and titanium adherends, plasma-sprayed with polymeric coatings, and bonded with an epoxy and a polyimide adhesive has been investigated. Organic-polymeric coatings were plasma-sprayed using epoxy, polyester, polyimide, and cyanate ester components. Durability was investigated using a wedge-type specimen by exposing the specimens to an environmental cycle that included low temperature, high relative humidity at elevated temperature, high temperature at atmospheric pressure in air, high temperature in a vacuum, and room temperature. The systems exhibiting durability comparable with that for adherends treated using standard solution methods, included aluminum or titanium coated with a bis-maleimide/cyanate ester (B-CE) or a bis-maleimide-LaRC TPI-1500® (B-TPI) mixture and bonded with an epoxy or a polyimide adhesive. For these B-CE- and B-TPI-coated specimens, failure during exposure to the environmental cycle occurred in the adhesive, indicating a favorable adherend/plasma-sprayed coating interaction.

Keywords: Plasma-sprayed adherends; aluminum; titanium; polymeric coatings; adhesive bond durability; environmental cycling

INTRODUCTION

Surface treatment is an important aspect of preparing adherends for adhesive bonding. Further, surface preparation may greatly influence

durability. Surface preparations that promote durable adhesive bonds have included solution chemical treatments and electrochemical processing of metal adherends [1,2]. Recently, the development of "environmentally friendly" surface treatments has been of interest, and efforts have focused on plasma-sprayed coatings [1–8]. Kinloch [1] reported that the durability of plasma-sprayed aluminum or steel specimens bonded with an epoxy adhesive was no better than that for specimens prepared *via* degreasing and grit blasting. Clearfield and coworkers [4] investigated the durability of specimens prepared by plasma-spraying Ti-6Al-4V alloy on titanium-6Al-4V. Samples were subsequently bonded with an epoxy adhesive (FM-300) [4]. Pike and coworkers [5] investigated plasma-sprayed alumina (Al_2O_3) coatings for adhesive bonding of composites, aluminum, and titanium and reported favorable durability. The durability performance of plasma-sprayed adherends was comparable with that for PAA (phosphoric acid anodized) aluminum and Pasa-Jell 107®-treated titanium adherends [5]. Davis and associates [6] recently compared the durability of solution treated-aluminum and titanium with specimens that had been plasma-sprayed with a variety of inorganic compounds, inorganic/polymer mixtures, and polymers. A general finding was that a coating prepared by plasma-spraying an aluminum-silicon alloy mixed with a polyester onto aluminum exhibited good dry and hot-wet durability [6]. The durability of plasma-sprayed aluminum and titanium exposed to an environmental cycle has also been studied by Wolfe *et al.* [7]. In the study [7] several inorganic compounds were plasma-sprayed on adherends and the specimens were bonded using a polyimide adhesive. Upon exposure in an environmental cycle, the plasma-sprayed systems; alumina/Al, silica/Al, $AlPO_4$/Al, MgO/Al, titania/Ti, silica/Ti, and $TiSi_2$/Ti exhibited bond durability equivalent to that for specimens prepared using standard solution surface pretreatments.

Although inorganic materials have been plasma-sprayed in adhesive bonding studies [1–7], plasma-sprayed polymeric materials have not been thoroughly investigated. Davis and coworkers [6] reported on dry and hot-wet durability of aluminum that had been plasma-sprayed with a polyester, PEEK, and mixtures of aluminum and polymers and bonded with epoxy adhesives. Some of the coated/bonded aluminum samples exhibited performance and failure modes under dry

conditions equivalent to that for solution-prepared surfaces. On the other hand, under hot-wet conditions the polymer-coated specimens failed in the coating, at the coating-substrate interface, or at the coating-adhesive interface.

The purpose of the current investigation was to plasma-spray aluminum and titanium adherends using a selection of polymeric materials to obtain a variety of surface chemistries. A principal goal was to obtain plasma-sprayed polymeric materials that might be effective as surface treatments for high performance adhesive bonding. The polymeric coating could provide modulus or stress relief between the adherend and the polymer adhesive. Ultimately, plasma-sprayed coatings could provide a method of applying adhesive to adherends for subsequent adhesive bonding. Thus, a selection of polymeric materials and mixtures of polymeric materials has been plasma-sprayed on aluminum and titanium. Plasma-sprayed specimens were bonded with an epoxy or a polyimide adhesive. Durability of the bonded samples was investigated using wedge specimens by measuring crack growth as a function of time for exposure in an environmental cycle. The selection of the environmental exposure conditions was prompted by the desire to examine bond performance under conditions that might be encountered by high performance aircraft. Failure modes were determined visually (optical microscopy) or *via* surface sensitive analytical measurements (XPS and SEM).

EXPERIMENTAL SECTION

Materials

Aluminum 6061 and titanium-6Al-4V alloys were used as adherends. Aluminum 6061 plates were purchased from McMaster-Carr Supply Co., New Brunswick, NJ, USA. Titanium-6Al-4V specimens were obtained from President Titanium, Hanover, MA, USA. 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 on each specimen was 2.5 cm × 7.6 cm (1″ × 3″).

Plasma spraying of polymers was carried out at Applied Polymer Systems (APS), Tampa, FL, USA. Before plasma spraying, the metal

adherends were grit-blasted with alumina (#80 grit) at 60 psi, and were then wiped with methyl ethyl ketone (MEK). No evaluation of the roughness of the grit-blasted surface was carried out. Pure argon was used in the plasma torch. Powders were introduced into the plasma torch using a fluidized bed or a rotary hopper. The spraying was carried out to obtain a coating thickness in the range of 75 μm to 125 μm (0.003″ to 0.005″).

Powedered polymeric materials, epoxy, polyester, cyanate ester, bismaleimide, and LaRC-TPI-1500®, were obtained from commercial suppliers [8]. The epoxy (E) and polyester (PE) powders were plasma-sprayed onto aluminum and titanium without decomposition. Under normal spraying conditions the cyanate ester and LaRC-TPI powders decomposed in the plasma. To alleviate the decomposition problem, specimens were sprayed with a 2:3 (w:w) physical mixture of BMI and CE(B-CE). LaRC-TPI was plasma-sprayed, as a 1:1 (w:w) physical mixture of BMI and LaRC-TPI (B-TPI).

The solution pretreatment procedures were described earlier [7]. Aluminum was anodized in 15% (w/w) phosphoric acid for 20 minutes at a current density of 129 amps/m^2 (12 amps/ft^2). Titanium was treated in Turco 5578® solution (37.6 g/1000 mL of H_2O) 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 solution, 360 g/1000 mL of H_2O, 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. The treatment of specimens using the solution procedures and the bonding of such specimens was carried out at least two times. The durability results were comparable and reproducible for the sets of specimens prepared.

Plasma-sprayed and solution-treated adherends were bonded in a wedge configuration [9] using a 3M AF-191 epoxy film adhesive or an American Cyanamid (Cytec) polyimide adhesive (FM-36). The bond-line thickness for all samples was 0.25 mm (10 mil). Specimens were bonded according to procedures outlined by the manufacturers. *AF-191*: Primer solution (Scotchweld® EC-3917) was applied to solution-treated adherends using a paint brush. The coating was allowed to cure at room temperature for 30 min. The specimen was then heated in a forced air oven at 120°C (248°F) for 30 min. The primer solution was only applied to PAA and Turco 5578 specimens when

bonding with the epoxy adhesive. No primer was used in bonding the plasma-sprayed adherends. Epoxy adhesive film (AF-191) was positioned between the adherends and the specimen was placed on the press platen which had been heated to 93°C (200°F). A pressure of 0.28 MPa (40 psi) was applied and the specimen was heated at a rate of 17°C/min (30°F/min.) to 177° C (350°F). After reaching 177° C (350°F), the samples were held at this temperature for 60 min. The specimens were then cooled at a rate of 6°C/min (10°F/min) to 93°C (200°F) before removing the pressure. Bonded samples were removed from the press and placed in a desiccator until initiating the environmental durability tests.

FM-36: Polyimide adhesive film was positioned between the adherends and the specimen was placed on the press platen that had been heated to 93°C (200°F). A pressure of 0.28 MPa (40 psi) was applied and the specimen was heated to 177°C (350°F) and was held at this temperature for 60 min. The samples were then cooled to 93°C (200°F) before removing the pressure. The specimens were then postcured by placing them in an oven at 260°C (500°F) for 3 hrs. Bonded samples were removed from the press and placed in a desiccator until starting the environmental durability tests.

In the durability evaluation, wedge specimens were exposed to an environmental cycle. A wedge, measuring 28 mm × 25 mm × 3 mm, (1.1″ × 1″ × 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°C	2 hrs.	24 hrs.
air, 70% RH; 66°C	2 hrs.	24 hrs.
dry air; 160°C	2 hrs.	24 hrs.
vacuum, 130 torr; 160°C	2 hrs.	24 hrs.
room temp.; 23°C	16 hrs.	24 hrs.

Crack growth was measured after each step in the exposure cycle. The crack length measurements were accurate to within ± 2 mm, and the reproducibility of the initial crack lengths among specimens with the same coating was ± 10 mm for aluminum and ± 5 mm for titanium.

The results presented in the figures represent average growth data for at least three specimens of each treatment and adherend.

Surface analysis measurements for plasma-sprayed adherends and for failed specimen surfaces were carried out *via* XPS and SEM. XPS spectra were measured using a PHI Perkin-Elmer Model 5400 photoelectron spectrometer. Photoelectrons were generated using Mg K_α radiation ($h\nu = 1253.6$ eV) [8,10–12]. The binding energy scale was calibrated in reference to the carbon 1s peak for background carbon; C 1s binding energy, 284.6 eV [8,12].

SEM photomicrographs were obtained using an ISI Model SX-40 scanning electron microscope. Samples were sputter-coated with a thin gold film (~ 200 Å) to reduce charging.

RESULTS AND DISCUSSION

The results of the durability experiments are summarized in Figures 1 and 2. In Figure 1 the crack growth data for aluminum and titanium specimens bonded with the epoxy adhesive are given. In Figure 2 the corresponding crack growth results for specimens bonded with the polyimide adhesive are illustrated. Although the results in Figures 1 and 2 are for up to 172 hrs, the exposure experiments were carried out for 3500 hrs. No change in crack length was found during the time period 172 to 3500 hrs. The initial (init.) and final, arrest (fin.) crack lengths, and mode of failure produced during environmental exposure are summarized in Table I.

Epoxy Adhesive

The findings presented in Figure 1 for specimens bonded with the epoxy adhesive reveal that the respective final crack lengths are similar for aluminum or titanium coated with plasma-sprayed epoxy, polyester, and bismaleimide-TPI. The arrest crack lengths for the comparable pairs of samples are: epoxy/Al and epoxy/Ti, 6.7 and 7.2 cm, respectively; polyester/Al and polyester/Ti, 4.7 and 4.5 cm, respectively; and B-TPI/Al and B-TPI/Ti, 3.2 and 3.1 cm, respectively. Furthermore, when comparing different coatings among the same adherends, the final crack lengths vary in the manner: epoxy > polyester > bis-

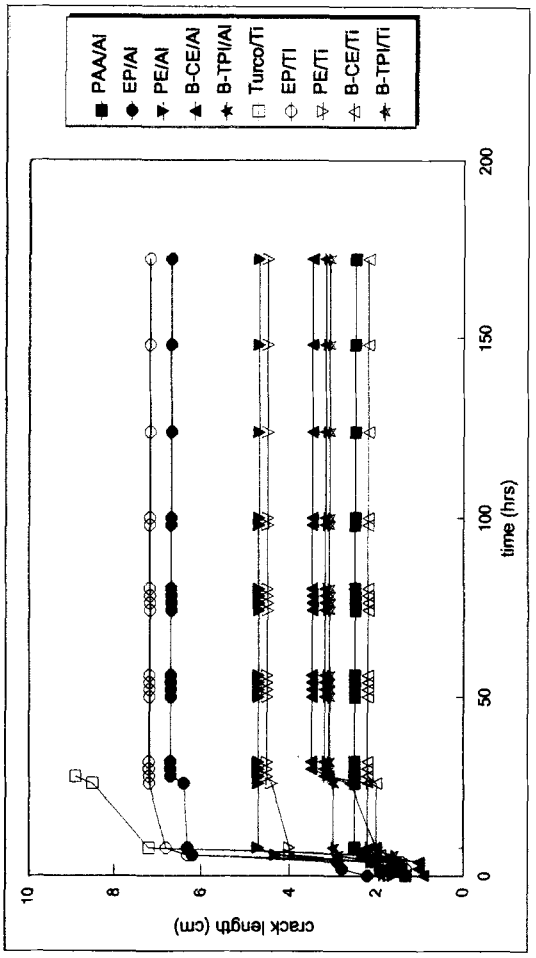

FIGURE 1 Wedge Specimen Durability: Crack length *vs.* time of environmental exposure for plasma-sprayed aluminum and titanium bonded with an epoxy adhesive (AF-191).

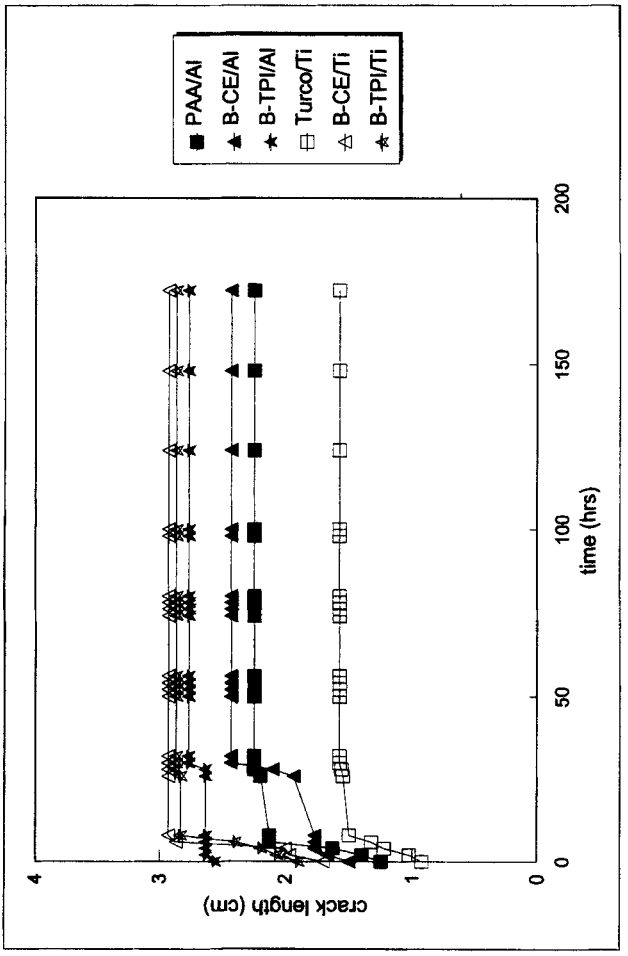

FIGURE 2 Wedge Specimen Durability: Crack length *vs.* time of environmental exposure for plasma-sprayed aluminum and titanium bonded with a polyimide adhesive (FM-36).

TABLE I Initial and Arrest Crack Length Values and Failure Modes for Plasma-Sprayed Aluminum and Titanium-6Al-4V Adherends. (Crack lengths in cm)

coating[1]	*epoxy*			*Aluminum* *mode*	*polyimide*			*mode*
	init.	*fin.*	Δ^2		*init.*	*fin.*	Δ	
E	2.2	6.7	4.5	mixed[3]	None[5]			
PE	1.6	4.7	3.1	mixed	None			
B-CE	0.9	3.5	2.4	mixed	1.5	2.4	0.9	cohes.
B-TPI	1.9	3.2	1.3	cohes.[4]	2.5	2.8	0.3	cohes.
PAA	1.3	2.5	1.2	cohes.	1.3	2.3	1.0	cohes.
coating[1]	*epoxy*			*Titanium-6Al-4V* *mode*	*polyimide*			*mode*
	init.	*fin.*	Δ^2		*init.*	*fin.*	Δ	
E	1.3	7.2	5.9	mixed[3]	None[5]			
PE	1.7	4.5	2.8	mixed	None			
B-CE	1.4	2.2	0.8	cohes.[4]	1.7	2.9	1.2	cohes.
B-TPI	1.4	3.1	1.7	cohes.	1.9	2.9	1.0	cohes.
Turco	1.3	7.3	6.0	mixed	0.9	1.6	0.7	cohes.

1. *coating*: E = epoxy; PE = polyester; B-CE = bismaleimide-cyanate ester; B-TPI = bismaleimide LaRC TPI-1500; PAA, phosphoric acid anodized; Turco, Turco 5578 treatment.
2. Δ: crack extension; final crack length minus initial crack length (cm).
3. *mixed*: failure at the adhesive-coating and the coating-adherend interface.
4. *cohes.*: cohesive failure; at the scrim cloth–adhesive interface, or within the adhesive.
5. *None*: No samples prepared.

maleimide-TPI. The respective final crack lengths for the bismaleimide-cyanate ester-coated aluminum and titanium are not equivalent; the crack length for B-CE/Al is greater than that for B-CE/Ti. When the performance of the plasma-sprayed aluminum samples is compared with that for PAA prepared aluminum, the specimens prepared with B-CE and B-TPI coatings exhibited comparable durability. Comparable durability is recognized when the respective crack lengths are equivalent to within 1 cm [8]. The durabilities of polyester- and epoxy-coated aluminum are regarded as less than that for PAA-Al due to the greater extent of crack growth; PAA/Al, 2.5 cm; PE/Al, 4.7 cm, and E/Al, 6.7 cm. It is also noteworthy that the failure mode correlates with the extent of crack growth for the PAA/Al, PE/Al, and E/Al specimens. Cohesive failure was noted for PAA/Al samples whereas mixed mode failure was found for PE/Al and E/Al adherends. Based on crack growth, the performance of B-CE/Al is similar to that for PAA/Al. However, it is argued that the performance of B-CE/Al

should be regarded as inferior when compared with PAA/Al due to the fact that mixed mode failure was observed for B-CE/Al. Alternatively, one could consider crack extension, Δ, the difference in final and initial crack lengths; a comparison is made where similar initial crack lengths were noted. From a qualitative comparison, crack growth extension results suggest that the performance for B-TPI/Al is similar to that for PAA/Al. Considering crack change variations and failure behavior, it is reasoned that the durability of B-TPI/Al is equivalent to that for PAA/Al while that for B-CE/Al is less favorable. On the other hand, the performance for epoxy- and polyester-coated aluminum specimens is regarded as inferior.

The durability performance for coated titanium bonded with epoxy reveals a situation similar to that for aluminum. Although the Turco-treated specimens failed completely, the B-CE/Ti and B-TPI/Ti specimens exhibited excellent performance. The arrest crack lengths and the extent of crack growth are low and similar to the values recorded for aluminum adherends. The failure modes for B-CE/Ti and B-TPI/Ti were cohesive. Cohesive failure was easily identified because supporting scrim cloth was visible on all failure surfaces and surface analysis results confirmed that debonding occurred at the scrim cloth-adhesive interface. The crack lengths and the extent of crack growth for the PE/Ti and E/Ti specimens were significantly greater than for the B-CE/Ti and B-TPI/Ti samples. In addition, the PE/Ti and E/Ti specimens failed *via* a mixed-mode process. Thus, for titanium bonded with epoxy adhesive, the cyanate ester- and the TPI-coated samples exhibited reasonable durability performance.

Although the focus of this study was on the performance of bonded, plasma-sprayed adherends, the significant failure for Turco-treated titanium deserves comment. Filbey and Wightman [13] investigated the durability of Turco-treated titanium bonded with an epoxy adhesive (FM-300U). In their study [13], the crack length for wedge-type specimens immersed in water at 95°C varied in the manner P/F > Turco > CAA (P/F, phosphate fluoride; CAA, chromic acid anodization). The experimental difference in the present study is that the specimens were exposed to elevated temperature and relative humidity conditions as well as to low (−20°C) and high (177°C) temperatures in the environmental cycle. For the Turco-treated titanium samples, mixed mode failure was noted in the present work, whereas in the

study by Filbey and Wightman [13] failure occurred at the epoxy/Ti-6Al-4V oxide interface. It is suggested that the combination of conditions in the environmental exposure tests leads to degradation of the adhesive as well as to changes in the Turco-produced oxide coating. Based on the limited data for the Turco system in the present study it is not possible to speculate further on the reasons for the observed behavior. That similar failure does not occur for the plasma-sprayed systems bonded with epoxy must indicate a unique interaction of epoxy with the plasma-sprayed polymer coatings. The nature of such interactions was not investigated in this study, but is the topic of further study.

Polyimide Adhesive

Aluminum and titanium, plasma-sprayed with bismaleimide-cyanate ester and bismaleimide-TPI mixtures, were studied. Specimens were not prepared with epoxy or polyester coatings for bonding with the polyimide adhesive. The results in Table I and in Figure 2 indicate that the crack lengths are approximately the same as for comparably prepared specimens that were bonded with the epoxy adhesive. All specimens bonded with the polyimide adhesive failed cohesively. As was the case for epoxy-bonded samples, scrim cloth was evident on all failure surfaces, indicating cohesive failure. One could argue that if adhesive and the plasma-sprayed polymer intermix during the curing process, a more accurate statement would be that failure occurred in the adhesive-plasma-sprayed coating region. Because of the difficulty of interpreting surface analysis data for these failure surfaces, it is not possible to determine unequivocally whether adhesive-coating mixing occurred. On the other hand, it is likely that such mixing could have occurred when it is recognized that the topographical features of the plasma-sprayed B-TPI coating showed nodular, porous features [8] which would permit adhesive penetration into the coating. By contrast, the topography for the B-CE/Ti sample was smooth and featureless [8], so intermixing and movement of adhesive into voids in the coating would be unlikely. The important observation is that failure did not occur at the plasma-sprayed coating/adherend interface.

The performance for B-TPI on aluminum and titanium is similar, while the crack length for B-CE/Al is slightly less than that for

B-CE/Ti. In fact, the performance for B-CE/Ti and B-TPI/Ti is, within experimental error, indistinguishable. The performance for Turco-treated titanium is better than that for the polymer-coated specimens. The arrest crack length, 1.6 cm, is less than that for either B-CE/Ti or B-TPI/Ti, both 2.9 cm. Although the failure mode for all titanium specimens was cohesive, the extent of crack growth varies in the manner B-CE/Ti > B-TPI/Ti > Turco/Ti. Nevertheless, the important result of the durability tests is that failure occurs cohesively indicating that the plasma sprayed coating-adherend interaction is significant and that the coating is not degraded in the extensive environmental cycle.

In comparing the performance of the polymer coated-Al/polyimide specimens with anodized aluminum it appears that equivalent performance is observed. The crack lengths, crack extensions, and failure modes (See Tab. I) are all similar. Thus, the durability of aluminum plasma-sprayed with polymeric components is comparable with that for anodized aluminum.

Although the material systems and the environmental conditions for the durability experiments were not the same, it is of interest to compare the present results with the findings of Davis *et al.* [6] where plasma-sprayed polymeric coatings were studied. Davis and coworkers [6] investigated crack growth at 95% RH at 60°C for epoxy-bonded plasma-sprayed aluminum. The polymeric coatings included a polyester, PEEK, and mixtures of an aluminum-silicon alloy/polyester, aluminum/polyester, and aluminum/PEEK. Under dry or wet exposure conditions, failure for the 60Al-Si/40 polyester specimen occurred within the coating. Thus, the debonding results in the current study for epoxy- and polyester-coated specimens are similar to those in Davis and associates' work [6].

In evaluating the reported performance for plasma-sprayed polyester-containing specimens bonded with the FM-300 epoxy adhesive, it is noted that performance is excellent for a 50 μm coating of 60Al-Si/40 polyester on aluminum and that performance degraded as the amount of alloy in the mixture was reduced. For specimens prepared with polyester at different thicknesses (50 μm and 150 μm, Davis *et al.* [6]) the initial and final crack lengths were greater than those found in this study. In addition, failure occurred at the coating interface [6] whereas failure in the current study was mixed mode. Such differences may be the result of different application conditions, dissimilar envi-

ronmental exposure conditions, or inherent differences in coating performance. From a comparison of the two investigations, it is apparent that plasma-sprayed polymeric coatings on aluminum exhibit excellent durability performance when tested under static [6] or cyclical environmental conditions (this study). A complete understanding of the mechanism(s) or process(es) by which excellent durability is achieved requires additional study of the chemical and physical nature of plasma-sprayed coatings.

SUMMARY

In this study it has been demonstrated that the durability performance of plasma-sprayed polymeric coatings on aluminum and titanium adherends that were bonded with an epoxy or a polyimide adhesive is comparable with that achieved for aluminum or titanium surfaces prepared using conventional solution treatments. The performance was evaluated using exposure to an environmental cycle which included some of the conditions anticipated for bonded systems operating in high performance situations. A general correlation was noted; extensive crack length correlated with mixed mode failure, and small to moderate crack growth correlated with cohesive failure. The principal finding is that plasma-sprayed mixtures of bismaleimide and polymeric cyanate ester or LaRC-TPI-1500 appear to be viable alternatives to solution pretreatments for the preparation of adherends for adhesive bonding.

Acknowledgment

This project was supported by: Materials Directorate, Wright Laboratory, Air Force Materiel Command (ASC), United States Air Force: Contract Number: F33615-93-C-5321.

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