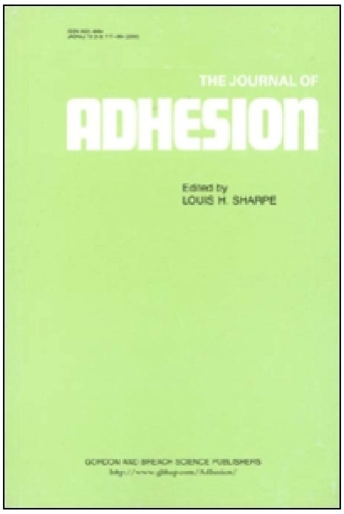

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The Durability of Adhesively-Bonded Titanium: Performance of Plasma-Sprayed Polymeric Coating Pretreatments

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The Durability of Adhesively-Bonded Titanium: Performance of Plasma-Sprayed Polymeric Coating Pretreatments

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Non-solution and electrochemical treatments in preparation for adhesive bonding of titanium have been studied. Polymeric materials, LaRC TPI-2000^{TM}, LaRC PETI-5^{TM}, and Aurum^{TM} polyimides were deposited onto titanium-6Al-4V surfaces *via* plasma spraying. The plasma-sprayed surfaces were characterized using infrared, solid state NMR, and surface-sensitive analytical methods. The chemical nature of plasma-sprayed polymers is equivalent to that for powdered materials. The durability of titanium, adhesively bonded with a polyimide adhesive, was investigated by immersing wedge-type specimens in boiling water. Crack length and the mode of failure were used to assess durability. The determination of the failure mode was accomplished using surface-sensitive analytical methods. Surface treatments using plasma-sprayed LaRC-type polyimides result in good durability as evidenced by minimal crack growth for wedge specimens and by failure in the adhesive (cohesive failure).

Keywords: Plasma-sprayed polyimide primer/coating; titanium-6Al-4V; solid state NMR; wedge-type specimen; durability; failure surface characterization; polyimide adhesive

INTRODUCTION

Environmentally acceptable surface treatments for metals are needed to attain durable adhesive bonds for high-performance applications.

The role of a surface treatment of an adherend is to promote adhesive-adherend interaction and to achieve durable adhesive bonds [1, 2]. The common surface preparations to enhance durability for adhesive bonding include grit blasting, chromic acid or sodium hydroxide anodization, and other chemical treatments for titanium [3, 4]. As interest has grown in the development of environmentally-benign surface treatments, other methods have been explored.

Plasma spraying has been used for decades to apply coatings for anticorrosion, wear resistance, and thermal barriers [5, 6]. Studies have shown that plasma-sprayed coatings adhere well to metal substrates due to interdiffusion of the coating into the metal [7]. Only a few studies have focused on plasma-sprayed coatings related to adhesive bonding [1, 8 – 11].

In a study of the durability of plasma-sprayed aluminum or steel specimens bonded with an epoxy adhesive, Kinloch [1] reported that the performance for plasma-sprayed adherends was no better than that for specimens prepared *via* degreasing and grit blasting. In the work by Clearfield *et al.* [8], titanium-6Al-4V adherends, plasma-sprayed with Ti-6Al-4V and bonded with an epoxy adhesive (FM-300), maintained their integrity when exposed to elevated temperatures. Pike and coworkers [9] plasma-sprayed alumina (Al_2O_3) on composites, aluminum, and titanium, and reported favorable durability for samples bonded with an epoxy adhesive. Davis *et al.* [10] compared the durability of solution- and plasma-spray-treated aluminum and titanium. The plasma-sprayed coatings included inorganic compounds, inorganic/polymer mixtures, and polymers. The coating prepared by plasma-spraying an aluminum-silicon alloy mixed with a polyester onto aluminum exhibited good dry and hot-wet durability [10]. The durability of plasma-sprayed aluminum and titanium bonded with a polyimide adhesive and exposed to an environmental cycle has also been studied by Wolfe *et al.* [11]. These studies [8 – 11] suggest that plasma-sprayed coatings provide bond strengths and durability equal to that found for conventional pretreatments such as chromic acid anodization.

In this work, the plasma-spraying of polymeric materials on titanium has been evaluated as a surface coating pretreatment for adhesive bonding. Polymide powders were plasma-sprayed onto grit-blasted titanium-6Al-4V. The durability of the polymers LaRC

TPI-2000, LaRC PETI-5, Aurum PD 400, and Aurum PD 450, plasma-sprayed onto titanium, has been investigated and compared with the performance for chromic acid anodized titanium. The alloy was adhesively bonded using a high-performance polyimide adhesive. The plasma-sprayed coatings were characterized using bulk and surface-sensitive analytical measurements. The durability was evaluated by immersing wedge-type specimens in boiling water and measuring the crack growth as a function of time.

EXPERIMENTAL

Titanium-6Al-4V samples (1"×4"×0.090") (2.5×10×0.23 cm) were obtained from President Titanium. LaRC TPI-2000, Aurum PD 400, and Aurum PD 450 powders were purchased from Mitsui Toatsu. The chemistry of the Aurum materials is equivalent; only the molecular weights are different. LaRC PETI-5 was obtained from Imitec. In general, the polymeric powders were used in "as received" condition in the plasma-spraying operation. Before plasma-spraying, the titanium alloy was grit blasted with alumina and cleaned to remove residual grit. Polymers were introduced into an argon-hydrogen or argon-helium plasma and the plasma conditions and spraying time were adjusted to obtain coatings of approximately 75–125 microns (0.003–0.005 in.). A comparative surface treatment was chromic acid anodization [4, 12].

The thermal properties of the plasma-sprayed and polymeric powders were measured using differential scanning calorimetry. Specimens were heated at a rate of 10°C/min. in air or in nitrogen using a TA (DuPont) Instruments, system 2100 apparatus. Glass transition temperatures, T_g, were calculated using the 1/2-delta C_p method. Lead and indium were used as standards.

Diffuse reflectance infrared spectra were obtained using a Nicolet 5DXB FT-IR spectrometer equipped with a DTGS KBr detector and external reflection accessories provided by Harrick Scientific Co. For all spectra, the sample chamber was purged with dry nitrogen gas and spectra were collected at an angle of incidence of 40° at a spectral resolution of 4 cm^{-1}. Transmission spectra were obtained using the KBr disc method. Approximately 3 percent polymer (w/w) was mixed thoroughly with KBr and ground into a fine powder from which the discs were pressed using a mini hand press.

Solid-state carbon-13 NMR spectra were recorded on a Bruker MSL 300 MHz instrument operating at 75.47 MHz. The spectra were obtained using cross polarization under magic angle spinning conditions.

The plasma-sprayed or anodized adherends were not primed and were bonded with FM-5, a supported (glass cloth) polyimide (LaRC PETI-5 based) adhesive film, provided by CYTEC. The adhesive bond line thickness was 250 microns (0.010 in.). The adhesive specimens were cured by heating to 250°C for 30 min. without pressure and then were heated to 350°C for 1 hour while a pressure of 75 psi was applied to the specimen. The sample was cooled under pressure to room temperature at a rate of approximately 10°C/min.

Durability measurements were carried out using wedge specimens [13]. The wedge specimens were immersed in boiling water and crack length was measured. At the termination of the tests, specimens were failed and the mode of failure was determined in the crack growth region that was produced during immersion in water.

Plasma-sprayed adherends and adhesively-bonded failure surfaces were characterized using XPS and SEM [14]. XPS spectra were measured using a PHI Perkin-Elmer Model 5400 photoelectron spectrometer. The analysis area was 1 mm × 3 mm. Photoelectrons were generated using Mg K_α radiation ($h\nu = 1253.6$ eV). The binding energy scale was calibrated using the background carbon 1s photopeak at 285.0 eV [14]. Photoelectron spectral peak areas were scaled 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. SEM photomicrographs were determined using an ISI Model SX-40 scanning electron microscope. Samples were sputter-coated with a thin gold film (~200 Å) [11].

RESULTS AND DISCUSSION

Characterization of Plasma-sprayed Adherends

Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy

In Figure 1 scanning electron photomicrographs of LaRC TPI-2000 powder and of a Ti-6Al-4V surface that had been plasma-sprayed with

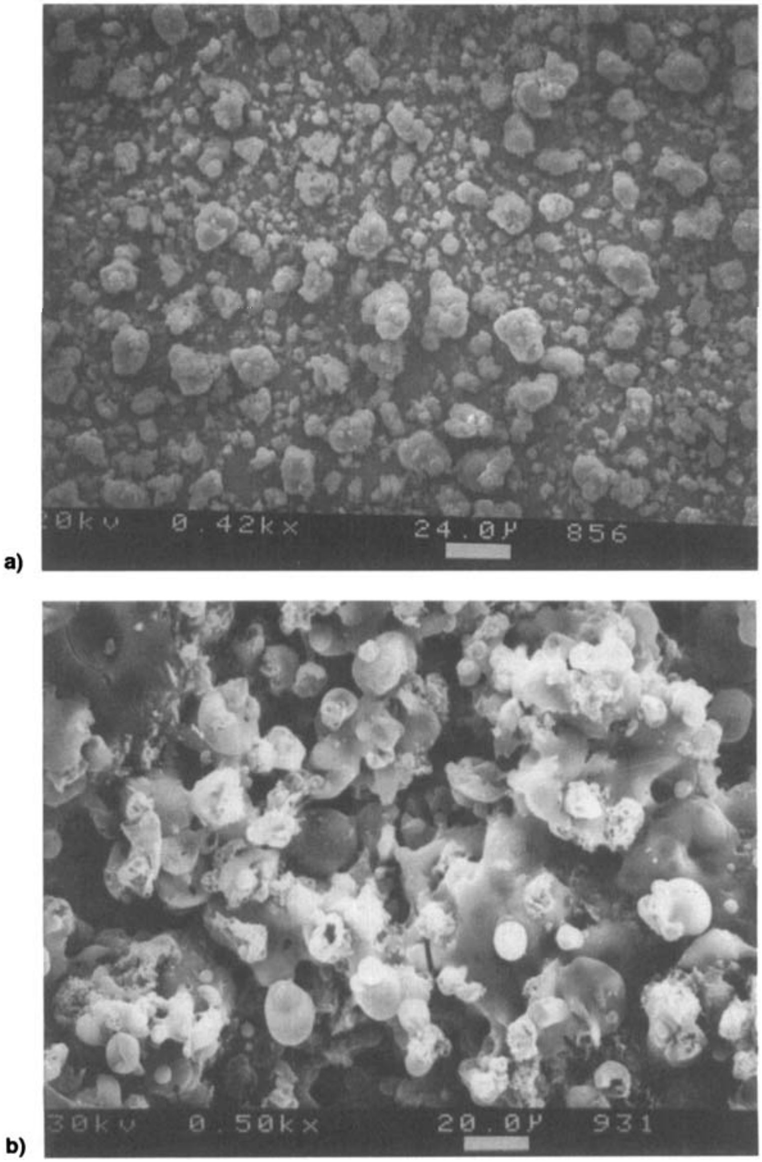

FIGURE 1 Scanning electron photomicrograph for LaRC TPI-2000 powder (top) and LaRC TPI-2000 plasma-sprayed coating on titanium (bottom).

LaRC TPI-2000 are presented. In Figure 2 similar photomicrographs are given for LaRC PETI-5 powder and PETI-5/Ti surfaces. The powders exhibited particle sizes in the range 5–40 microns. Visual or microscopic examination of the plasma-sprayed titanium specimens indicated that the surfaces appeared to be completely covered by the polymer; no voids or metallic-appearing features were observed on the coated metal surface. The plasma-sprayed surfaces are characterized by nodular deposits. From a comparison of the topographical features for the as received powder and the plasma-sprayed surface, it appears that the powder "melted" or agglomerated as a result of the plasma spraying process. Particle agglomeration is apparent on the plasma-sprayed surface as illustrated in Figures 1b and 2b where smooth surfaces and elongated-connected material features are evident. Such features are in contrast to the angular features observed for the as received powders as shown in Figures 1a and 2a. This comparison leads to the conclusion that surface melting occurred. It cannot be discerned from the micrographs whether complete melting of the whole polymer particle occurred, or if surface melting only took place. Similar surface features were noted for other plasma-sprayed polymeric materials. The nodular-like polymer deposits provide a porous surface to enhance adherend surface area and, potentially, to allow flow of adhesive into the voids of the plasma-sprayed coating.

Visual inspection of the prebonded plasma-sprayed titanium adherends indicate that coverage is uniform with no metal exposed at the surface. The XPS results confirm the uniform coverage of the titanium coupons. Neither titanium nor aluminum was detected on the surface of the prebonded adherends; the major component on the surface was the polymer. Table I lists the XPS results for the as received polymer and the prebonded plasma-sprayed titanium adherends. The principal difference between the elemental composition of the polymer powder and the plasma-sprayed polymer is a lower carbon and nitrogen and a higher oxygen content for the plasma-sprayed material. The increase in oxygen content could be due to partial oxidation of the polymer or the presence of adsorbed oxygen-containing components on the plasma-sprayed polymer surface. The increase in oxygen content is not sufficient to result in detectable changes in the carbon 1s photopeak shape when comparing the spectra for the polymer powder and the plasma-sprayed coating.

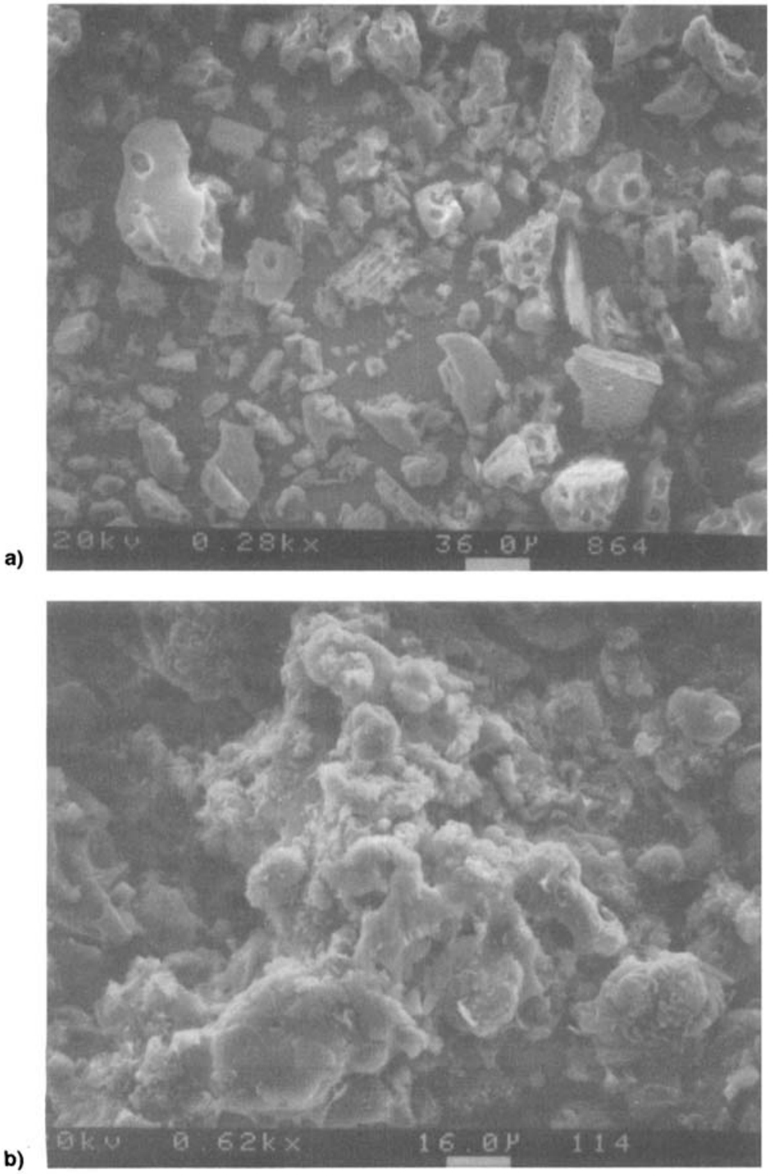

FIGURE 2 Scanning electron photomicrograph for LaRC PETI-5 powder (top) and LaRC PETI-5 plasma-sprayed coating on titanium (bottom).

TABLE I XPS surface analysis results for the as received (ar) polymer and the plasma-sprayed (ps) titanium adherends (atomic percent)

Element	*LaRC TPI-2000*		*LaRC PETI-5*		*Aurum PD 450*	
	*ar**	*ps#*	*ar*	*ps*	*ar*	*ps*
C	78.2	77.2	82.0	79.6	80.6	78.3
O	16.7	18.4	13.0	16.5	14.6	17.7
N	5.1	4.4	5.0	3.9	4.8	4.0
Ti	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Si	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

*ar: as received powder
#ps: plasma-sprayed coating

Thermal Analysis

The thermal behavior of plasma-sprayed polymers was determined to discern whether thermal decomposition took place during spraying. The T_g values for the as received and plasma-sprayed materials are summarized in Table II. The values for the first and second heats are given in the table. A comparison of the T_gs for the powder and plasma-sprayed polymer for LaRC TPI-2000 and LaRC PETI-5 materials reveals that the T_g values are little changed when comparing the results for the powder and the plasma-sprayed material. The T_g for plasma-sprayed LaRC TPI-2000 is about 8°C higher than that for the powder, a finding that could be related to removal of residual components in the powder upon spraying. The change in T_g is not likely due to changes in the polymer as will be demonstrated *via* IR and NMR results to be discussed later in this paper. For LaRC PETI-5 the T_g values for powder and plasma-sprayed material are

TABLE II Glass transition temperatures for powder and plasma-sprayed polymeric materials. (T°C/T°C-first heat/second heat)

Polymer	*As received powder*	*Plasma-sprayed powder*
LaRC TPI-2000	nd/227 (N_2)	229/235 (N_2)
LaRC PETI-5	227/229 (air)	229/228 (air)
Aurum PD 400	nd/nd	249/249 (air)
Aurum PD 450	nd/nd	251/248 (air)

nd – not determined
measure mp: indium 157.41°C — standard mp: indium 156.61°C
measure mp: lead 327.09°C — standard mp: lead 327.47°C

equivalent, indicating no significant change in properties for the plasma-sprayed material. The T_gs for the Aurum powders were not measured, although the values for the plasma-sprayed polymers are in the range expected for these polyimides [15]. The thermal measurements suggest that the polyimides are deposited on the titanium surface without degradation.

Infrared and Nuclear Magnetic Resonance Spectroscopic Analysis

Infrared spectra for LaRC TPI-2000 and for LaRC PETI-5 powders and plasma-sprayed materials are compared in Figures 3 and 4, respectively. The infrared spectral assignments for all four polyimide materials are collected in Table III. The spectral assignments were made by comparison with the spectral assignments for polyimides from the literature [16–19]. For each polyimide, the spectra are similar to those reported in the literature [16]. Imide ring vibrations and bi-

TABLE III Selected band assignments for diffuse reflectance spectra for the as received (ar) and plasma-sprayed (ps) polyimides. Assignments for the transmission spectra are given in parenthesis

band assignments		*LaRC TPI-2000*	*Aurum PD 450*	*Aurun PD 450*	*LaRC PETI-5*
imide CO in-phase	ar*	1782 (1780)	1781 (1778)	1782 (1778)	1777 (1775)
	ps#	1782 (1780)	1780 (1777)	1780 (1777)	1778 (1775)
imide CO out-of-phase	ar	1736 (1720)	1738 (1720)	1739 (1720)	1737 (1720)
	ps	1741 (1722)	1743 (1718)	1744 (1720)	1738 (1720)
imide CNC axial stretch	ar	1385 (1364)	1390 (1361)	1390 (1361)	1383 (1365)
	ps	1384 (1368)	1380 (1361)	1383 (1358)	1386 (1365)
imide CNC transverse stretching	ar	1109 (1102)	1118 (1102)	1117 (1102)	1106 (1094)
	ps	1110 (1097)	1109 (1098)	1112 (1099)	1109 (1094)
imide CNC out-of-phase bending	ar	720 (712)	722 (722)	722 (722)	741 (737)
	ps	720 (713)	722 (722)	723 (722)	743 (737)
Benzo-phenone CO stretch	ar	1664 (1664)			
	ps	1673 (1664)			
ethynyl	ar				2200 (2200)
	ps				2211 (2200)

*ar: as received powder; #ps: plasma-sprayed coating material

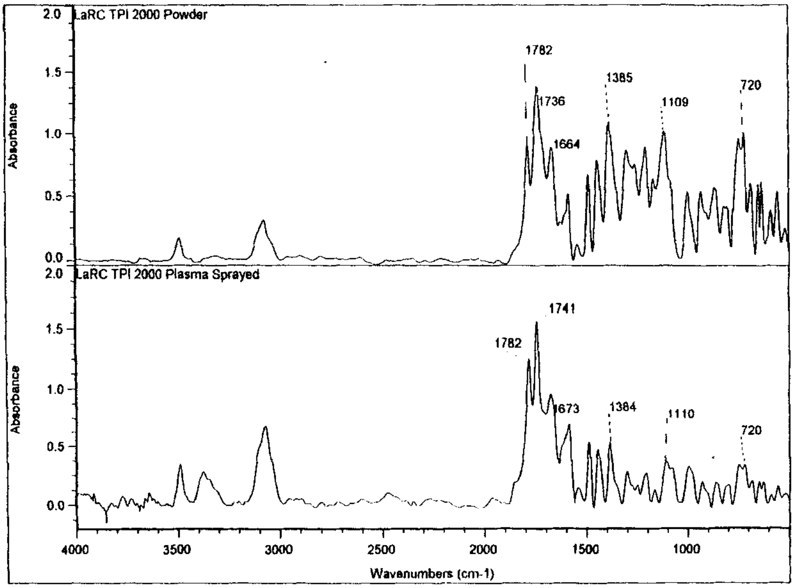

FIGURE 3 Diffuse reflectance spectrum of LaRC TPI-2000 powder (top) and LaRC TPI-2000 plasma-sprayed material (bottom).

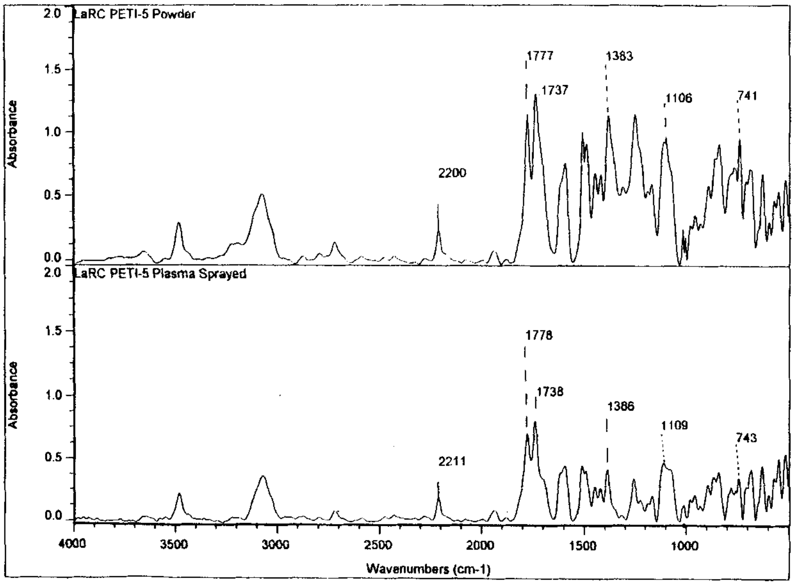

FIGURE 4 Diffuse reflectance spectrum of LaRC PETI-5 powder (top) and LaRC PETI-5 plasma-sprayed material (bottom).

and tri-substituted phenyl ring stretching frequencies agree well with earlier reports [18].

A comparative study of the spectra for the as received polyimides and the plasma-sprayed polyimides indicates that no significant chemical or physical change occurs in the poyimides when subjected to high-temperature plasma gases for microsecond periods. The minor frequency shifts that were observed can be attributed to the physical rearrangement and packing of the amorphous polymers, thus suggesting that the deposition process is principally physical and not chemical in nature.

The C-13 solid state NMR spectra for as received and plasma-sprayed LaRC TPI-2000 and LaRC PETI-5 samples are given in Figures 5 and 6, respectively. In these figures the structure for each polymer is shown and the NMR chemical shift values are given for the various carbon atoms in the polymer. The C-13 NMR chemical shift assignments were based on the spectral assignments provided by Silverstein *et al.* [17].

The principal C-13 NMR peaks for LaRC TPI-2000 occur with chemical shifts at 124.6, 132.1, 135.8, 138.9, 165.5, 190.5, and 192.8 ppm with prominent side bands appearing in the region 50 and 210, 25 and 275, and 85 and 247 ppm. The prominent peaks are assigned as follows: aromatic carbon, 124.6, 132.1, and 135.8; imide carbonyl carbon, 165.5; and benzophenone carbonyl carbons, 192.8 ppm. The unsymmetrical nature of the benzophenone carbonyl carbon peak at 192.8 ppm arises from the differing chemical nature of the benzophenone carbonyls. The shoulder on the low ppm (190.5) side of the peak is assigned to the carbonyl of the anhydride reagent, while the peak at 192.8 is attributed to the carbonyl from the amine reactant. A shoulder appearing at about 138.9 ppm on the peak in the 130 ppm region is assigned to the aromatic carbon attached to nitrogen.

The spectra for the as received and plasma-sprayed LaRC PETI-5 polyimide show C-13 signals with chemical shifts at 122.5, 131.6, 144.8, 155.9, and 165.9 ppm. Side bands are noted in the region 45 and 210, and 85 and 235 ppm. The peaks at 122.5 and 131.6 are assigned to the aromatic carbons; the signal at 144.8 ppm is attributed to the aromatic carbon attached to nitrogen; the spectral feature at 155.9 is associated with the carbon attached to oxygen of the ether moiety, and the peak at 165.9 ppm is assigned to the imide carbonyl carbon.

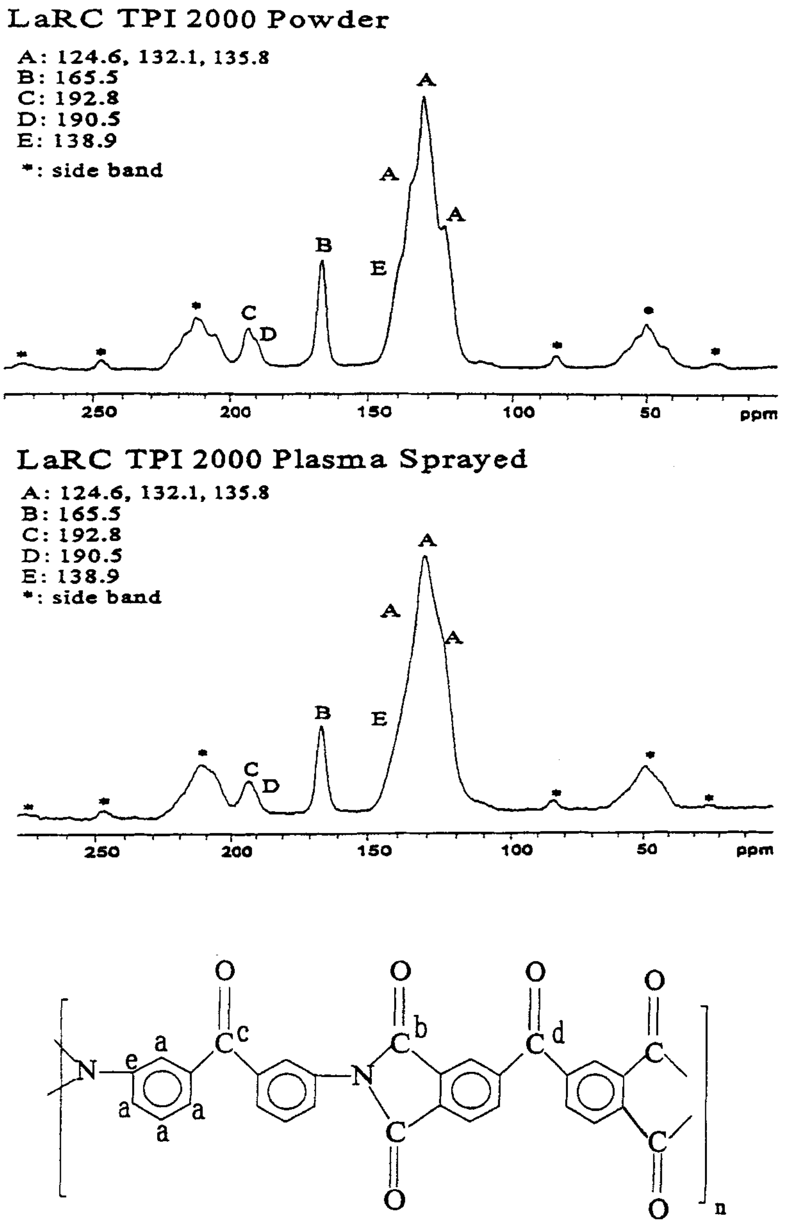

FIGURE 5 Solid state C-13 NMR spectrum of LaRC TPI-2000 powder (top) and LaRC TPI-2000 plasma-sprayed material (bottom). The chemical structure of LaRC TPI-2000 is given in the figure.

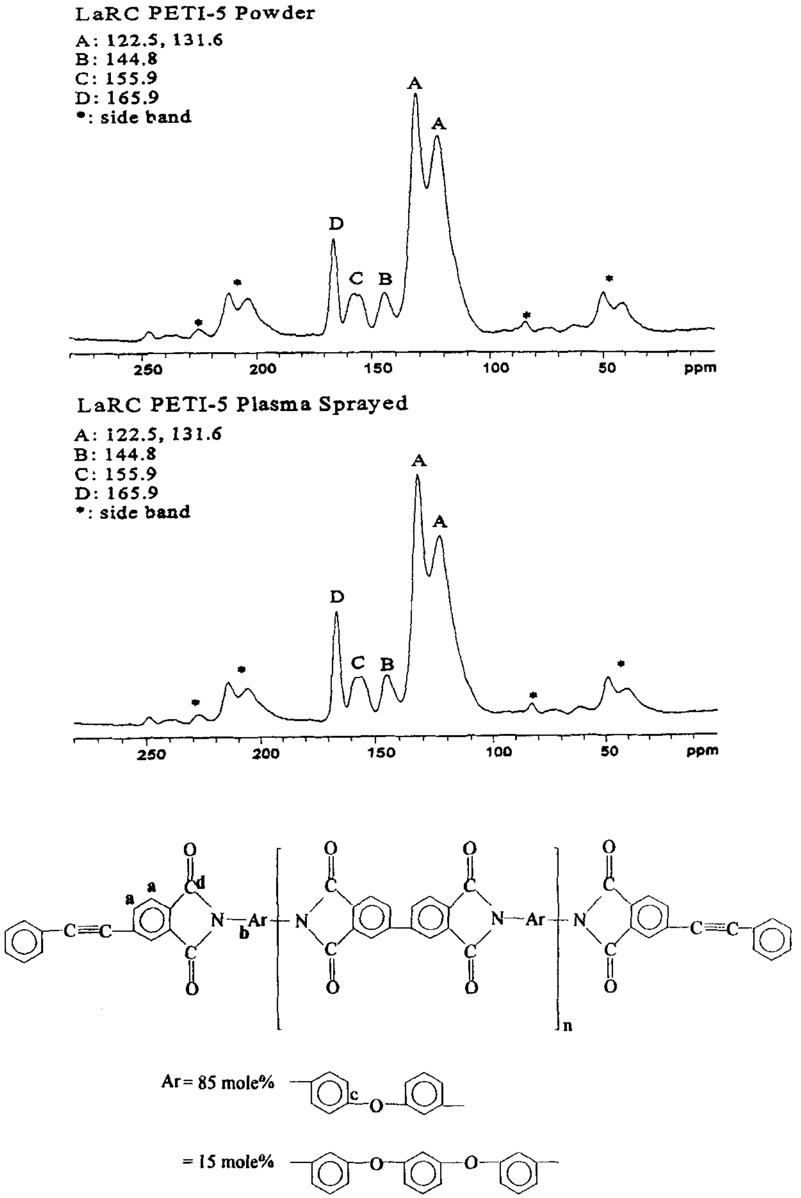

FIGURE 6 Solid state C-13 NMR spectrum of LaRC PETI-5 powder (top) and LaRC PETI-5 plasma-sprayed material (bottom). The chemical structure of LaRC PETI-5 is given in the figure.

The spectra of the as received and plasma-sprayed Aurum PD 400 and PD 450 polyimide show signals with chemical shifts at 120, 130, 150, and 160 ppm which correspond to the aromatic ring carbons (120, 130 ppm), the carbons attached to oxygen (150 ppm), and the imide ring carbonyl carbons (160 ppm).

When the respective NMR spectra of the plasma-sprayed polyimides are compared with those for the as received polymer powders, it is noted that the resolution diminishes; however, no significant differences are found in the spectra. The results support the notion that the plasma-sprayed materials are chemically equivalent to the as received powders. The comparison indicates that the polymer chemistry is not altered as a result of plasma deposition. These results agree with infrared analysis indicating that negligible degradation occurs in the polymer in the plasma-spraying process.

Adhesive Bonding and Durability

Durability, Surface Analysis and Failure Mode

The durability results for CAA-anodized titanium and the plasma-sprayed polymers are presented in Figure 7. In the figure only one set

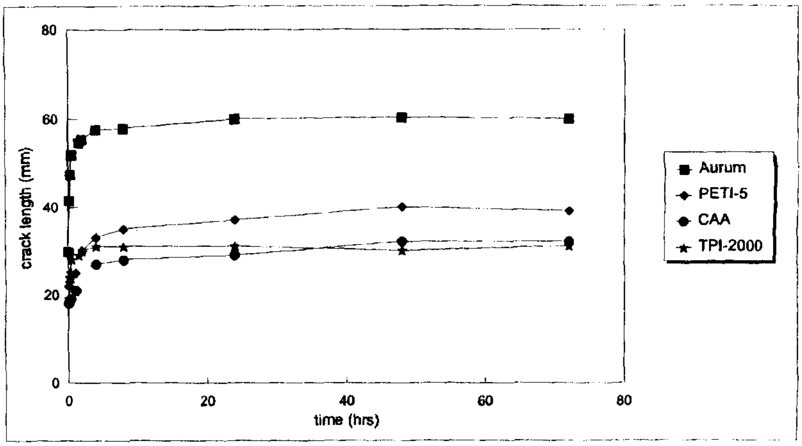

FIGURE 7 Crack growth curves for plasma-sprayed titanium wedge specimens bonded with FM-5 adhesive–immersion in boiling water.

of results is shown for Aurum-based coatings. Results for Aurum PD 450/Ti are shown. The crack length as a function of time was equivalent for specimens coated with Aurum DP 400 and Aurum PD 450. Crack growth occurs for about the first 24 hours and is arrested at longer times. The arrest crack length is approximately 30–35 mm for the CAA/Ti, LaRC TPI-2000/Ti, and LaRC PETI-5/Ti. By comparison, crack growth for the plasma-sprayed Aurum/Ti specimen is significantly greater. The smaller crack length associated with the plasma-sprayed LaRC TPI-2000 and LaRC PETI-5 polyimide-titanium specimens demonstrates comparable durability performance with CAA-titanium samples and significantly greater durability than for the plasma-sprayed Aurum polyimide coatings.

Visual inspection of all specimen failure surfaces, except the Aurum/Ti samples, suggested failure within the adhesive (cohesive failure). A scanning electron photomicrograph of one of the equivalent failure surfaces for a LaRC TPI-2000/Ti sample is shown in Figure 8. The criss-cross patterns in the micrograph are characteristic of the scrim

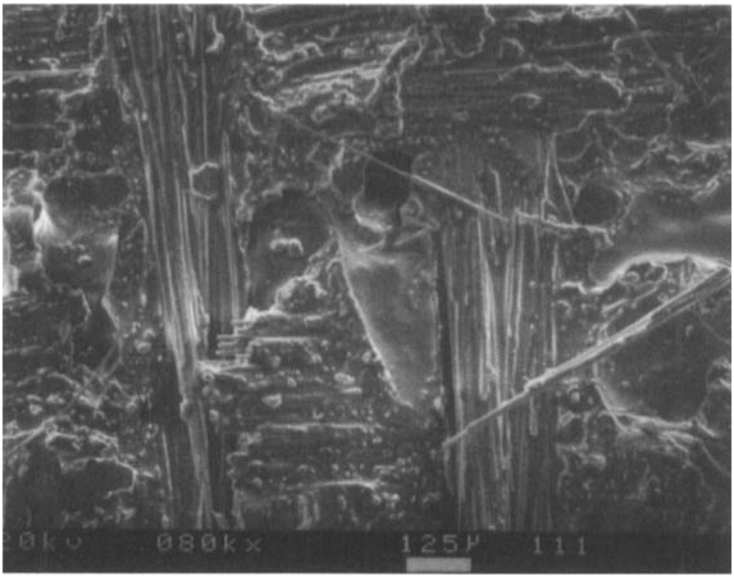

FIGURE 8 Scanning electron photomicrograph for a failure surface for a sample: plasma-sprayed LaRC TPI-2000 coated titanium–bonded with FM-5 adhesive.

cloth (glass) support, and observing this characteristic pattern suggests that failure occurs in the adhesive.

Surface analysis results are presented in Table IV for the failure surfaces for CAA/Ti, LaRC TPI-2000/Ti, LaRC PETI-5/Ti and Aurum 450/Ti samples, and for the surface of the adhesive film. An examination of the XPS data indicates differences in the failure modes among the debonded samples. The analysis results for CAA/Ti and LaRC TPI-2000/Ti failure surfaces indicate no titanium from the substrate nor aluminum from grit blasting of the plasma-sprayed LaRC TPI-2000/Ti adherend. On the other hand, elements characteristic of the adhesive, carbon, oxygen, nitrogen, and silicon (glass scrim cloth), are present on all failure surfaces for CAA/Ti and LaRC TPI-2000/Ti samples. Although the results are presented for one side of the CAA/Ti failure specimen, equivalent results were obtained for the opposite surface. That significant silicon is present on the failure surface, and that the concentration is similar for either side of the failure, indicates the failure occurs at the adhesive-scrim cloth interface. This finding and interpretation of the XPS data support the suggestion based on the SEM photomicrographs of these failure surfaces. Thus, the SEM and XPS results confirm failure in the adhesive (cohesive failure), and in particular, in the adhesive-glass cloth interface region.

Scanning electron photomicrographs for the adhesive- and metal-side failure surfaces for LaRC PETI-5/Ti failed specimens are shown in Figure 9. The presence of scrim cloth on each surface is consistent

TABLE IV XPS surface anaysis results for the failed surfaces of the plasma-sprayed titanium adherends (atomic percent)

Element	*FM-5*	*CAA*	*LaRC TPI-2000*		*LaRC PETI-5*		*Aurum PD 450*	
	film	*fs-a*	*fs-a*	*fs-b*	*afs*	*mfs*	*afs*	*mfs*
C	76.3	74.3	74.4	73.4	69.7	42.5	66.1	58.5
O	17.9	18.7	17.9	19.2	22.1	40.6	23.9	27.6
N	4.5	3.7	3.9	3.8	4.7	2.0	3.1	1.9
Ti	<0.1	<0.1	<0.1	<0.1	<0.1	1.2	0.1	1.7
Al	<0.1	<0.1	<0.1	<0.1	0.4	4.7	4.3	7.6
Si	<0.1	3.3	3.8	3.6	3.1	9.0	2.5	2.7

afs: adhesive side failure; mfs: metal side failure; fs-a: failure surface"a"; fs-b: failure surface "b", (the a and b surfaces were indistinguishable with respect to being characteristic of metal- or adhesive-like).

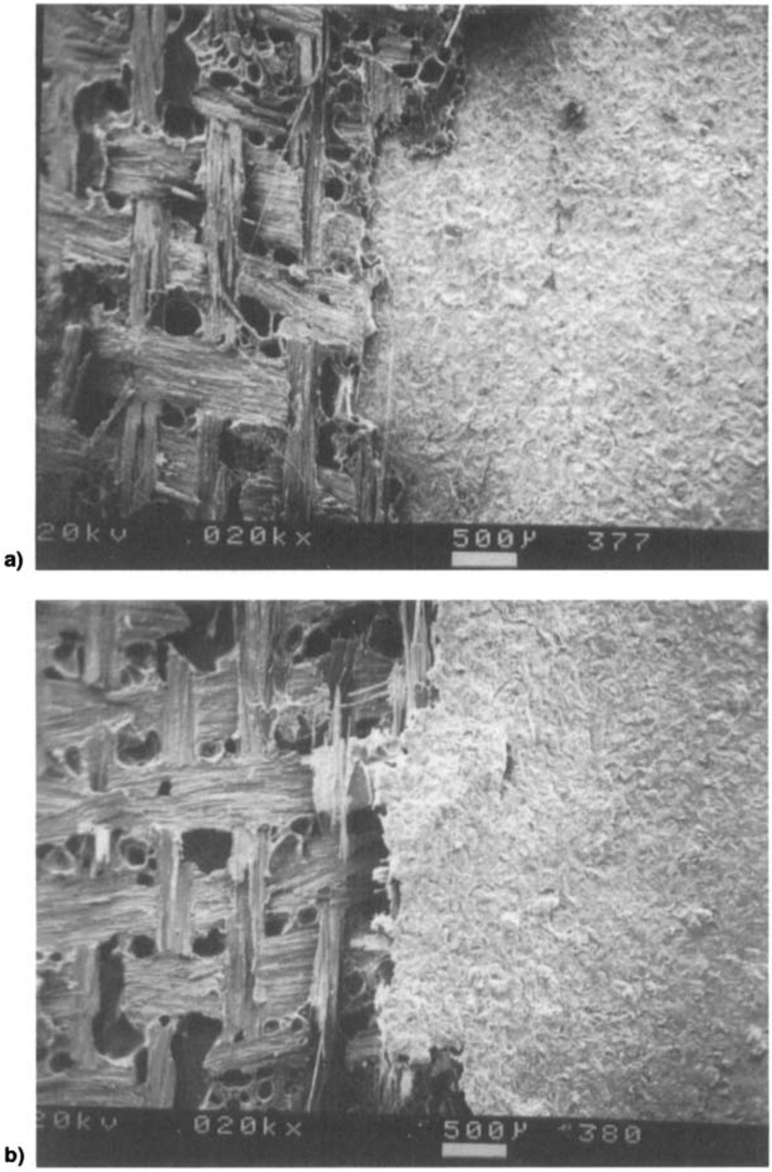

FIGURE 9 Scanning electron photomicrograph for failure surfaces for a sample: plasma-sprayed LaRC PETI-5 coated titanium–bonded with FM-5 adhesive. (top: metal-side failure surface; bottom: adhesive-side failure surface).

with failure in the adhesive. A region of adhesive (interfacial) failure is also apparent. The adhesive/polymer coating appears to have torn off one side of the specimen, exposing the rough, grit blasted metal on one surface. The corresponding polymer layer left on the other surface shows an impression of the grit blasted surface.

The XPS analysis data for the LaRC PETI-5/Ti failure surfaces (Table IV) suggest a mixed-mode failure process. The adhesive-side failure surface contains carbon, oxygen, nitrogen, and silicon at concentration levels that are similar to those associated with cohesive failure. In addition, a small amount of aluminum is found on this adhesive-side failure surface. The elements detected on the metal-side failure surface include, carbon, oxygen, nitrogen, titanium, aluminum, and silicon. The presence of titanium and of aluminum and silicon suggest that adhesive and adherend are exposed on this surface. Aluminum arises from the grit-blasted surface and silicon is attributed to the presence of glass cloth from the adhesive. To account for the presence of all of these elements, it is reasoned that failure occurs in the adherend-grit blasted-plasma sprayed interface region and also in the adhesive-glass cloth domain. Recognizing that all titanium specimens were prepared in an identical fashion for plasma spraying for all polymers and for adhesive bonding, it is apparent that some property or characteristic of the plasma-sprayed PETI-5/Ti system leads to failure in a mixed-mode fashion. Among such characteristics could be insufficient wetting of titanium by the plasma-sprayed polymer, residual stress in the plasma-sprayed coating, etc. Further investigation is needed to establish the reason for this mixed-mode failure.

The XPS results for the Aurum PD 450/Ti failure surface are included in Table IV. The XPS data for the Aurum PD 400/Ti samples are not included in the table since the elemental concentrations were similar on each failure surface and were equivalent to the results for the Aurum PD 450/Ti samples. The XPS results indicate titanium and aluminum as well as elements associated with the adhesive on both failure surfaces. The respective concentrations of the elements on the adhesive-side failure surface are similar to the concentrations detected for the LaRC PETI-5/Ti sample, with the noted exception that aluminum is present at a concentration of 4.3% on the Aurum PD 450/Ti surface. It is reasonable to suggest that aluminum is due to the exposure of grit-blasted surface. Further, the percent aluminum on the metal-side failure surface is too great to be attributed to aluminum in the alloy, and the concentrations of the adhesive elements are significantly less than those for pure adhesive. Considering the similarities and differences in the surface analysis results for the LaRC PETI-5/Ti and Aurum PD 450/Ti specimens, it is postulated that failure occurs *via* a mixed-mode process, but that the dominant failure process takes place in the grit-blasted-adherend interface region for Aurum PD 450/Ti specimens. The reasons for failure in the grit-blasted-adherend region may be similar to those discussed for the LaRC PETI-5/Ti samples; insufficient wetting of the titanium surface by plasma-sprayed polymer in the plasma-spraying process or during bonding or residual stresses in the adherend/plasma-sprayed interphase.

Having demonstrated that the debonding of LaRC TPI-2000/Ti/FM-5 specimens occurred in the adhesive (cohesive failure) and that crack growth was similar to that for CAA-prepared titanium surfaces, it was of interest to investigate the long-term durability of these samples. In Figure 10 the crack growth behavior for wedge specimens immersed in boiling water for up to about 12, 000 hr. is shown. It is

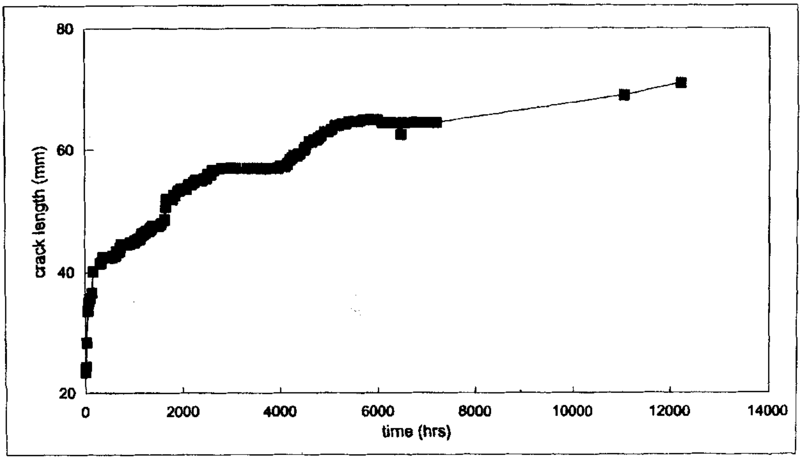

FIGURE 10 Long-term (12,000 hr.) crack growth curves for plasma-sprayed LaRC TPI-2000/Ti wedge specimens bonded with FM-5 adhesive–immersion in boiling water.

clear that crack growth increases with time, but the specimens had not completely debonded when samples were removed from the test, and were force failed (debonded) for failure characterization. Upon forced debonding of the samples, adhesive components were apprent on the surface as shown in the scanning electron micrograph in Figure 11. The appearance of fibers (scrim cloth) and the absence of features attributable to metal or to the plasma-sprayed coating support the notion that failure occurs in the adhesive. The XPS surface analysis results for the respective failure surfaces are summarized in Table V. The elemental concentrations are equivalent for the two surfaces and the concentration levels are typical of those for failed adhesive. The high concentration of silicon on the failure surfaces for the specimens immersed for 12,000 hr. (See Table V), compared with the results for specimens tested for shorter times (See Table VI), could indicate more extensive degradation at the adhesive-scrim cloth interface. For these experiments, the significant finding is that debonding occurs at the

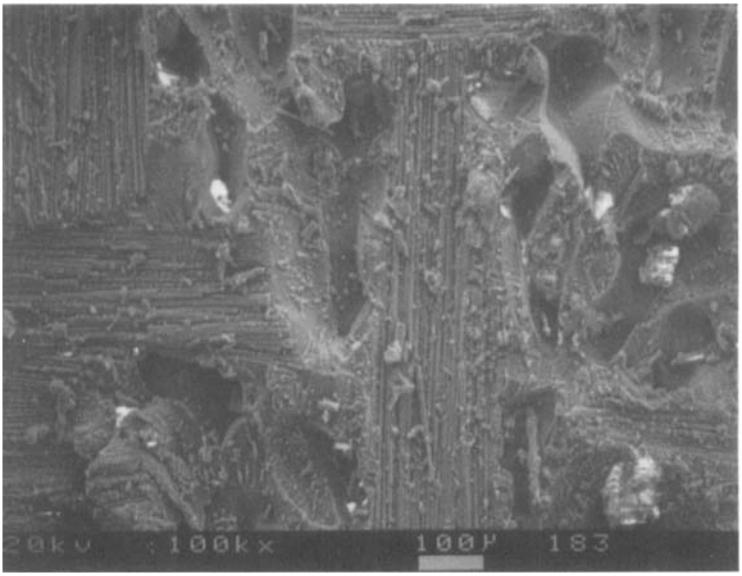

FIGURE 11 Scanning electron photomicrograph for a failure surface for a sample: plasma-sprayed LaRC TPI-2000 coated titanium – bonded with FM-5 adhesive, following immersion in boiling water for 12,000 hrs.

TABLE V XPS surface analysis results of the failed LaRC TPI-2000/Ti/FM-5 specimens 12,000 hr. boiling water immersion tests. (atomic percent)

Element	*FM-5*	*LaRC TPI-2000*	
	film	*fs-a*	*fs-b*
C	76.3	72.0	73.9
O	17.9	17.6	16.3
N	4.5	1.0	0.6
Ti	<0.1	<0.1	<0.1
Al	<0.1	0.8	0.5
Si	<0.1	8.0	7.9

afs: adhesive side failure; mfs: metal side failure; fs-a: failure surface "a"; fs-b: failure surface "b", (the a and b surface were indistinguishable with respect to being characteristic of metal- or adhesive-like).

adhesive-scrim cloth interface and that the plasma-sprayed coating – adherend interaction is not degraded in these long-term tests.

SUMMARY

These studies have described the use of plasma-sprayed polymeric coatings for adherend surface preparation. The physical features of the deposited coatings indicate that the polymer powders have melted in the plasma-spraying process. Characterization of the plasma-sprayed coating materials indicates that the polymers are deposited without detectable decomposition. Acceptable durability performance for plasma-sprayed LaRC TPI-2000 polymeric coatings has been demonstrated compared with the performance for chromic acid anodized (CAA) titanium samples. For LaRC TPI-2000 plasma-sprayed titanium, adhesively-bonded specimens failed cohesively at the support-adhesive interface upon durability testing by immersion in boiling water. Although crack propagation for bonded LaRC PETI-5/Ti samples was comparable with that for CAA-and plasma-sprayed LaRC TPI-2000-prepared titanium, failure occurred at the grit blasted-plasma-sprayed polymer interface and in the adhesive-support cloth region. The durability performance for the Aurum/Ti specimens was less favorable compared with the other treatments, since crack propagation was more extensive and failure occurred predominantly at the plasma-sprayed polymer/grit blasted interface.

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