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K. L. Wolfe^a; K. L. Kimbrough^a; J. G. Dillard^a; S. R. Harp^b; J. W. Grant^b

^a Chemistry Department, Center for Adhesive and Sealant Science, Virginia Tech, Blacksburg, VA, USA ^b Engineering Science and Mechanics Department, Center for Adhesive and Sealant Science, Virginia Tech, Blacksburg, VA, USA

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Plasma-Sprayed Aluminum and Titanium Adherends: I. Characterization of Coatings*

K. L. WOLFE, K. L. KIMBROUGH and J. G. DILLARD **

Chemistry Department and Center for Adhesive and Sealant Science, Virginia Tech, Blacksburg, VA 24061-0201, USA

S. R. HARP and J. W. GRANT

Engineering Science and Mechanics Department and Center for Adhesive and Sealant Science, Virginia Tech, Blacksburg, VA 24061-0201, USA

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The morphological and surface chemical properties of plasma-sprayed coatings on metals have been investigated using surface characterization techniques. Organic polymeric and inorganic powders were plasma-sprayed on aluminum and titanium. Organic-polymeric coatings were prepared using epoxy, polyester, polyimide, and cyanate ester components. Inorganic coatings were obtained by plasma-spraying Al_2O_3 , AlPO_4 , MgO , and SiO_2 on aluminum adherends, and TiO_2 , TiSi_2 , MgO , and SiO_2 on titanium adherends. The organic-polymeric coatings were prepared at one thickness while the inorganic coatings were sprayed to obtain two different thicknesses. SEM photographs reveal various morphological differences in the sprayed specimens. The surface morphology ranged from smooth to nodular among the plasma-sprayed specimens. Surface chemical analysis of the plasma-sprayed coatings indicated that little or no chemical degradation of the components occurred as a result of plasma-spraying. However, plasma-sprayed TiSi_2 appeared to be a mixture of silica and a titanium silicate.

KEY WORDS Plasma-spraying; titanium; aluminum; inorganic and organic-polymeric coatings; surface characterization; morphology; surface preparation; SEM; XPS; adhesive bonding.

INTRODUCTION

The principal requirement for an adhesive bond is that the bond maintain its integrity in the structure under use conditions during the lifetime of the structure. Many components contribute to the strength and durability of an adhesive bond including the adhesive, the adherend, the surface preparation, the use conditions, and the bond geometry. For high performance applications the nature of the surface preparation often plays a dominant role for specimens exposed to severe environmental conditions.

* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

** Corresponding author.

Many surface pretreatments involve the use of organic solvents and solutions containing carcinogenic transition metals. Manufacturing industries that rely on adhesive bonding, along with the EPA and other governmental and professional groups, seek surface pretreatments that are environmentally safe. Plasma spray techniques¹ may offer an appropriate alternative method to prepare adherend surfaces for adhesive bonding. Plasma-spraying also offers the possibility of obtaining surfaces of different chemistry and morphology.¹⁻³

Clearfield and coworkers² have described the use of plasma-sprayed coatings for enhanced durability of bonded titanium. Titanium-6Al-4V alloy powder was plasma-sprayed on titanium-6Al-4V alloy adherends with the goal of obtaining a surface coating that would be stable at elevated temperatures.⁴ The plasma-sprayed coatings exhibited a micro-rough morphology and the surface morphology did not change upon exposure in a vacuum at 450°C.² Surface analysis of the plasma-sprayed coating indicated principally titanium dioxide. The studies demonstrated that bond durability, as determined *via* a wedge test, was equivalent to that for surfaces anodized in sodium hydroxide or chromic acid.² The use of plasma-sprayed alumina (Al₂O₃) coatings for adhesive bonding of composites, aluminum and titanium has been reported by Pike, *et al.*³ Alumina was plasma-sprayed to obtain a thin (50 μm) and microporous coating. The durability of plasma-sprayed adherends compared favorably with that for aluminum and titanium adherends that had been pretreated, respectively, *via* phosphoric acid anodization and PasaJell 107 procedures.

The purpose of the current investigation was to plasma-spray aluminum and titanium adherends using a variety of materials to obtain different surface chemistry and to characterize the surfaces in preparation for investigation of the durability of adhesively-bonded metal adherends. A principal goal was to obtain plasma-sprayed inorganic and polymeric materials that might be effective as surface treatments for high performance adhesive bonding. Although inorganic materials have been plasma-sprayed in adhesive bonding studies,^{2,3} no investigation of plasma-sprayed polymeric materials as a surface preparation for adhesive bonding has appeared in the literature. In this paper, the focus is on characterization of the plasma-sprayed adherends to determine the morphology and chemical stoichiometry of the plasma-sprayed coatings. The coating materials include inorganic oxides that are acidic and basic and polymeric materials that contain a variety of functional groups. These materials were selected to permit an inquiry into the influence of acid-base characteristics on the durability of adhesively-bonded metals.

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 (0.4 MPa), and were then wiped with methyl ethyl ketone (MEK). 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"). Table I lists the polymers that were sprayed and the suppliers of the polymers. The epoxy and polyester powders were sprayed onto aluminum and titanium without problems. Pure LaRC-TPI polyimide flowed easily through the plasma gun, but decomposed under a number of experimental conditions. To alleviate the decomposition problem and obtain a polyimide-containing coating, a 1:1 (w:w) physical mixture of BMI and LaRC-TPI was sprayed onto aluminum and titanium. Similarly, to obtain a coating of the cyanate ester it was necessary to spray a 2:3 (w:w) mixture of BMI and CE.

Plasma spraying of adherends with inorganic coatings was carried out at Engineered Coatings, Rocky Hill, CT, USA. The selection of coatings was based on the desire to obtain different acid/base surface chemistries on the adherends. Specimens were grit blasted with silicon carbide before applying the plasma-sprayed coatings. Al_2O_3 , AlPO_4 , MgO , and SiO_2 were plasma-sprayed on aluminum adherends, and TiO_2 , TiSi_2 , MgO , and SiO_2 were deposited on titanium adherends. All inorganic coatings, except SiO_2 , were sprayed to obtain 25 μm (0.001") and 150 μm (0.006") coating thicknesses. SiO_2 could not be deposited at 150 μm (0.006") due to failure of the material to adhere to itself. SiO_2 coating thicknesses were 25 μm (0.001") and 50 μm (0.002"). In the preparation of the AlPO_4 coating it was necessary to add silica as a flow agent to the powder upon introduction into the plasma. Thus, the analytical data presented for AlPO_4 do not correspond to pure aluminum phosphate. Table II lists the powders, selected properties of the materials, and the suppliers.

TABLE I
Polymer powders and suppliers

Polymer	Supplier
Epoxy: Everclear	Fuller O'Brien
Polyester: crystal clear	Fuller O'Brien
Cyanate ester: PT 60 (CE)	Allied Signal
LaRC-TPI 1500, polyimide	Mitsui-Toatsu
Bismaleimide (BMI)	Shell Chemical

TABLE II
Inorganic powders and suppliers

Powder	Mesh size	M.P. °C	Purity (%)	Supplier
Al_2O_3	- 25 + 5	2000	98	Metco 105SF
AlPO_4	- 44 + 5	> 1500	unknown	City Chemical
SiO_2	- 44 + 10	1700	99.9	Atlantic Equipment
MgO	- 44 + 10	2850	95	Cerac; M1139
TiO_2	- 53 + 10	1830	99	Metco 102
TiSi_2	- 105 + 44	1760	99.9	Atlantic Equipment

Plasma-sprayed adherends were characterized using XPS and SEM. XPS spectra were measured using a PHI Perkin-Elmer Model 5400 photoelectron spectrometer. Photoelectrons, generated using Mg K_{α} radiation ($h\nu = 1253.6$ eV), were analyzed in a hemispherical analyzer, and detected using a position-sensitive detector.⁵⁻⁷ The binding energy scale was calibrated in reference to the carbon 1s peak for background carbon.⁵⁻⁷ 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.^{5,6} The elemental compositional data were obtained by taking the average of at least three individual measurements. The precision and accuracy for the concentration evaluations are, respectively, about 10% and 15%. 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 ± 0.1 eV. The C 1s binding energy values were selected to correspond to carbon-carbon, carbon-hydrogen, and carbon-oxygen-containing functional groups.⁵⁻⁷

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

RESULTS AND DISCUSSION

SEM Characterization

Scanning Electron Microscopy (SEM) was used to investigate the topographical features of the plasma-sprayed coatings. The SEM photomicrographs revealed significant morphological differences when comparing the organic and inorganic plasma-sprayed coatings and also when comparing the features among the inorganic coatings. An SEM photomicrograph for the polyester-sprayed coating on titanium is shown in Figure 1. The coating is smooth with few distinguishing features. The features exhibited

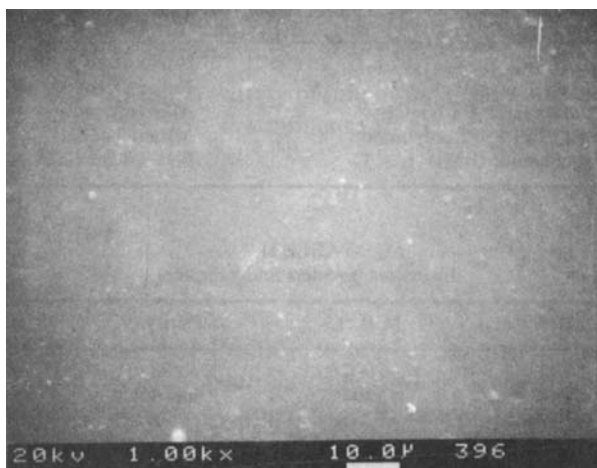


FIGURE 1 Scanning electron photomicrograph of polyester powder plasma-sprayed on titanium.

in Figure 1 were characteristic of the polyester, epoxy, and CE/BMI plasma-sprayed coatings. Among these three sprayed coatings the topographical features were indistinguishable. The surface features for the TPI/BMI plasma-sprayed coating, as revealed from the SEM photomicrograph in Figure 2, were unique compared with those for the other three polymeric coatings. The TPI/BMI coating was rough and cavernous and exhibited nodular particle-like features that were 25 to 30 μm in diameter. The surface appears to have particles stacked on top of one another. Thus, the preparation of the plasma-sprayed polymeric coatings yields smooth and rough-cavernous features. The findings suggest that the mode of coating formation may be different for the TPI/BMI specimen. No attempt was made to discover the operational parameters or application conditions that led to the differences in the features of the polymeric coatings. No significant differences were noted in coating morphology when comparing the same coatings on aluminum or titanium.

The SEM photomicrographs for the plasma-sprayed inorganic coatings are shown in Figures 3–8. Some of the inorganic coatings exhibited the splattering effect which is a common characteristic of plasma-sprayed coatings.^{1, 8} The splattering characteristics were particularly evident for the $\text{Al}_2\text{O}_3/\text{Al}$, AlPO_4/Al , and TiO_2/Ti coatings (Figures 3–5). The SEM photomicrographs for the other plasma-sprayed inorganic coatings (Fig. 6–8) MgO/Al , Ti ; SiO_2/Al , Ti ; and TiSi_2/Ti exhibited both smooth and rough features. No significant differences in coating morphology were noted when comparing the same coating, MgO or SiO_2 , on aluminum or titanium. Also there were no differences in topography when comparing specimens coated with the same material at different thicknesses.

XPS Characterization

The powders and plasma-sprayed specimens were analyzed by XPS to obtain information regarding chemical surface composition, to inquire about possible chemical

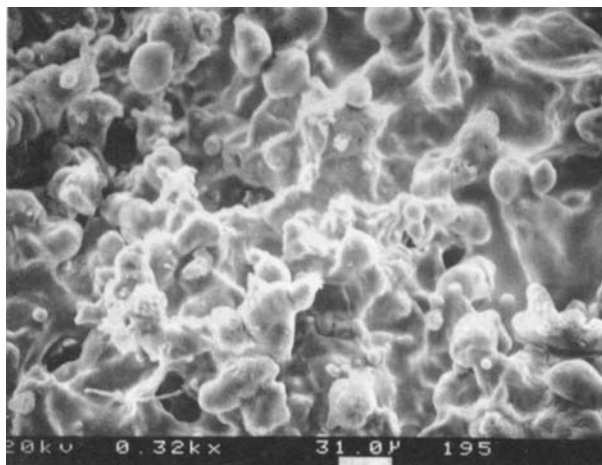


FIGURE 2 Scanning electron photomicrograph of Bismaleimide-LaRC-TPI powder mixture plasma-sprayed on titanium.

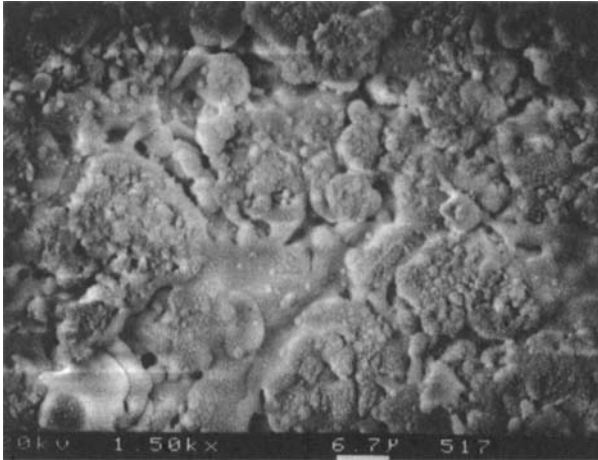


FIGURE 3 Scanning electron photomicrograph of Al₂O₃ powder plasma-sprayed on aluminum.

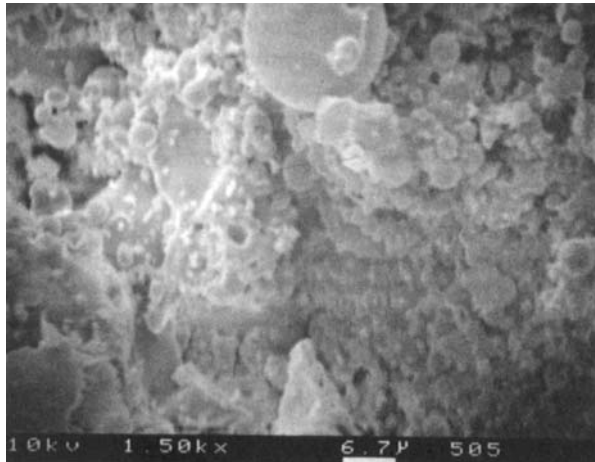


FIGURE 4 Scanning electron photomicrograph of AlPO₄ powder plasma-sprayed on aluminium.

changes resulting from the spraying process, and to obtain base-line data for use in establishing failure modes in subsequent durability experiments. Table III summarizes the XPS atomic percent composition results for the organic-polymeric powders and for the corresponding sprayed coatings. A comparison of the XPS data for the polymer powder and for the plasma-sprayed polymers (Table III) suggests that some change has taken place during plasma spraying. The change is evident by the general decrease in carbon content and the increase in the concentration of oxygen and nitrogen on the sprayed specimens compared with the results for the powders. The presence of silicon in

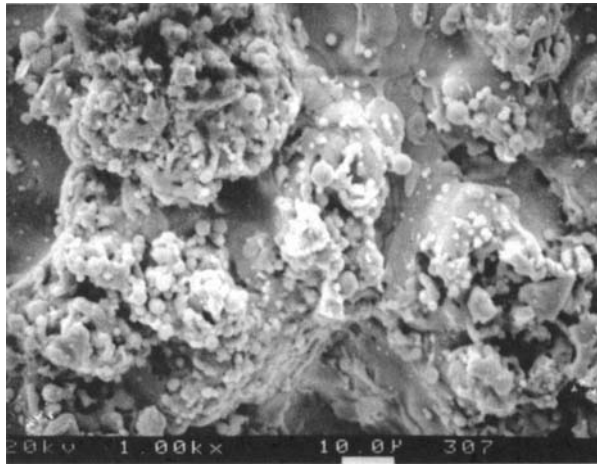


FIGURE 5 Scanning electron photomicrograph of TiO_2 powder plasma-sprayed on titanium.

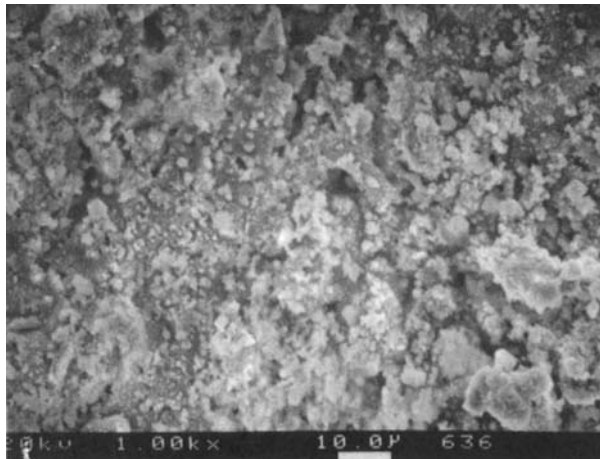


FIGURE 6 Scanning electron photomicrograph of MgO powder plasma-sprayed on aluminum.

some of the plasma-sprayed specimens is a result of the incorporation of small amounts of silica (SiO_2) contamination in the spraying chamber. The presence of silica also contributes to the increased oxygen content in the plasma-sprayed specimens. Fluorine as an organic fluoride was detected in the epoxy powder, but was removed in the spraying process and does not appear on the surface of the plasma-sprayed epoxy. The increase in nitrogen content among the sprayed epoxy and polyester samples is likely due to some reaction of the materials with nitrogen in the air outside of the plasma spraying region.

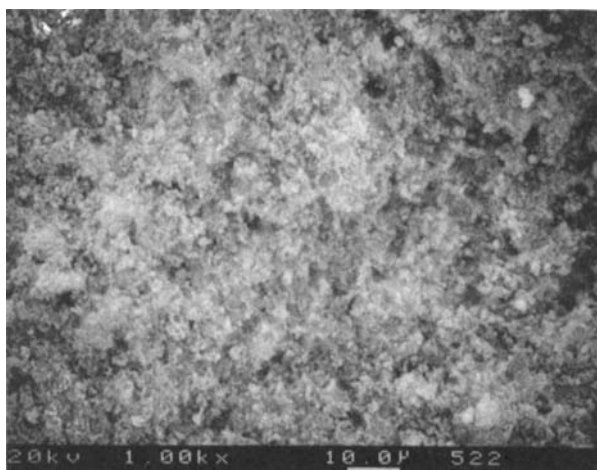


FIGURE 7 Scanning electron photomicrograph of SiO₂ powder plasma-sprayed on aluminum.

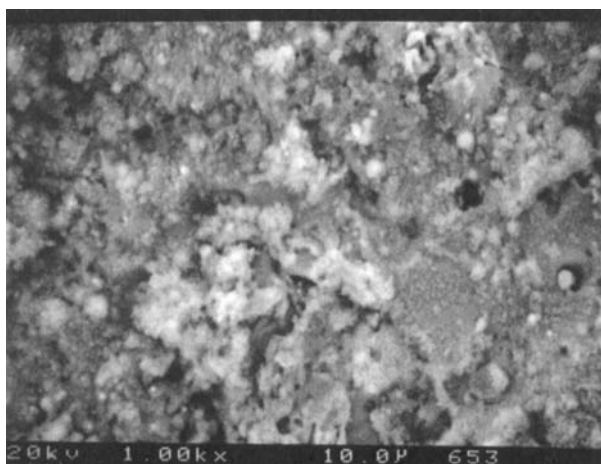


FIGURE 8 Scanning electron photomicrograph of TiSi₂ powder plasma-sprayed on titanium.

To explore possible changes in chemical functionality for epoxy and polyester plasma-sprayed specimens, carbon 1s spectra were curve fitted. Representative curve fitted C 1s spectra are presented for epoxy and polyester in Figures 9 and 10, respectively. In the figures, spectra are compared for the polymer powder and the plasma-sprayed specimen. In the fitted spectra for the plasma-sprayed epoxy material evidence is obtained for C-H/C-C, C-O, and C=O functional groups, whereas in the powder only C-H/C-C and C-O functional groups are evident. The percent composition for the oxygen-containing functional groups is only slightly greater for the plasma-

TABLE III
XPS characterization results for organic-polymer plasma-sprayed materials (atomic percent)* [P = powder; PS = plasma-sprayed coating]

Polymer	C 1s		O 1s		N 1s		Si 2p		F 1s	
	P	PS	P	PS	P	PS	P	PS	P	PS
Epoxy	78.7	70.2	16.3	20.7	1.5	4.9	nd	4.2	3.5	nd
Polyester	77.3	65.1	22.1	25.3	0.6	5.3	nd	1.3	nd	nd
CE/BMI	81.1	77.0	11.5	13.9	7.4	6.1	nd	3.0	nd	nd
TPI/BMI	77.6	70.9	18.6	22.4	3.8	6.7	nd	nd	nd	nd

nd = element not detected; atomic % < 0.2%.

* The results, labeled P, for CE/BMI and TPI/BMI are for pure powder before spraying, whereas the data, labeled PS, for CE/BMI and TPI/BMI are for the plasma-sprayed specimens which were obtained by spraying a physical mixture of the polymers.

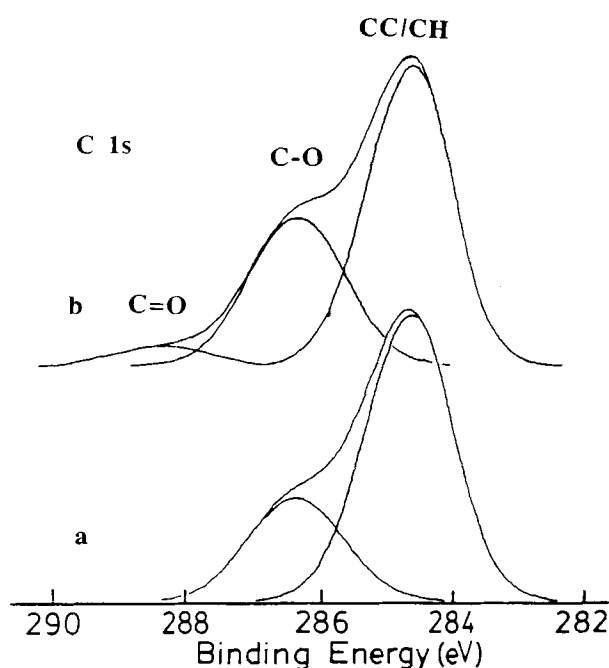


FIGURE 9 Carbon 1s x-ray photoelectron spectra for: a) epoxy polymer powder. b) epoxy polymer powder plasma-sprayed on titanium.

sprayed specimens. The appearance of the carbonyl functionality arises *via* oxidation either in the plasma or after deposition *via* reaction with air. A general result is that some oxidation of the epoxy material has occurred.

The C 1s spectra for polyester powder could be fitted by including C-H/C-C, C-O, and -O-C=O functional groups, whereas the spectra for the plasma-sprayed

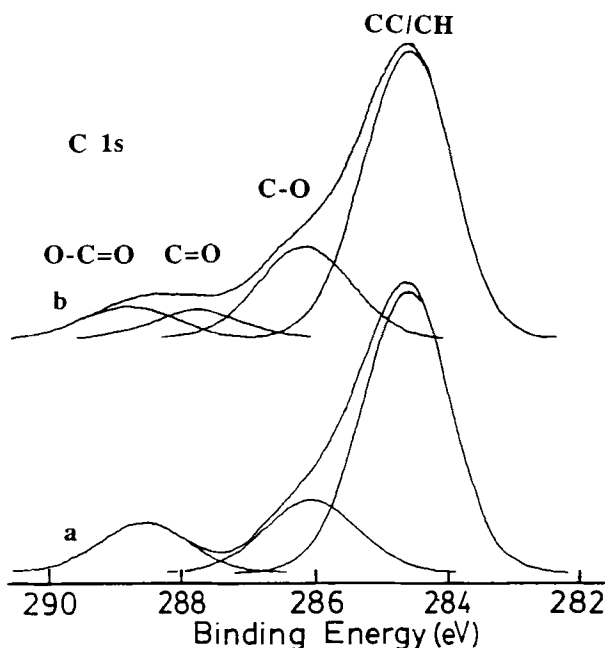


FIGURE 10 Carbon 1s x-ray photoelectron spectra for: a) polyester polymer powder. b) polyester polymer powder plasma-sprayed on titanium.

specimen could be fit using C-H/C-C, C-O, C=O, and -O-C=O functional groups. To obtain reasonable fits for the C 1s spectra for the plasma-sprayed polyester, it was necessary to increase the concentration of the C-O group and to include a contribution from a carbon doubly-bound to oxygen (carbonyl) functional group as shown in Figure 10. The functional group distribution in the polyester indicates that the carboxyl group content has decreased, leading to carbonyl-type group contribution. Alternatively, oxidation of the hydrocarbon or ether portion of the polyester could have taken place. Nevertheless, the compositional changes are small and the comparisons of functional group distributions of oxygen-containing groups for the powder and the plasma-sprayed samples indicate that little degradation of the plasma-sprayed materials has occurred. A detailed XPS functional group analysis, *via* curve fitting, for the cyanate ester- and LaRC-TPI-BMI mixtures was not carried out due to the complexity of the composition in the plasma-sprayed coating. Studies are in progress *via* other means to determine the component distribution in the sprayed coating.

The XPS surface characterization results for inorganic plasma-sprayed coatings are presented in Table IV and V. The table for plasma-sprayed specimens shows only one entry for MgO and SiO₂ although these oxides were sprayed on aluminum and on titanium. The results for MgO and SiO₂ sprayed on the two different substrates were equivalent, so only data for coatings on aluminum are presented.

The XPS data for the inorganic powders and plasma-sprayed specimens (Tables IV and V) suggest that the elemental ratios of the principal elements are not stoichio-

TABLE IV
XPS results for inorganic powders (atomic percent)

Compound	C 1s	O 1s	Na 1s	Ti 2p	Al 2p	Si 2p	P 2p*/Mg 2p#
Al ₂ O ₃	23.7	44.7	4.8	nd	21.5	5.3	nd
AlPO ₄	25.3	47.7	3.2	nd	11.9	nd	11.9*
MgO	22.0	49.8	0.5	nd	nd	3.9	23.8#
SiO ₂	15.5	54.9	0.2	nd	nd	29.4	nd
TiO ₂	19.1	58.6	nd	16.1	3.5	2.7	nd
TiSi ₂	18.2	50.2	nd	6.4	nd	25.2	nd

nd = element not detected; atomic % < 0.2%.

TABLE V
XPS results for inorganic plasma-sprayed coatings (atomic percent)

Compound	C 1s	O 1s	Na 1s	Ti 2p	Al 2p	Si 2p	P 2p*/Mg 2p#
Al ₂ O ₃	21.6	48.2	2.9	nd	27.3	nd	nd
AlPO ₄ **	24.4	49.6	1.7	nd	2.9	11.1	9.6*
MgO ₄	32.4	48.1	nd	nd	nd	1.7	17.8#
SiO ₂	10.0	64.1	nd	nd	nd	25.9	nd
TiO ₂	31.7	49.7	0.7	16.2	nd	1.7	nd
TiSi ₂	12.1	59.4	nd	1.3	nd	27.2	nd

nd = element not detected; atomic % < 0.2%.

** Nitrogen atomic % = 0.7.

metric, and that many of the sprayed specimens contain elements other than their principal elements. The principal contaminant element was carbon. To determine the chemical state of the non-principal elements, each element's contribution to the overall oxygen concentration was determined and the carbon photopeaks were curve fitted to determine the contribution of carbon-oxygen functionalities. Stoichiometric allocation and chemical speciation of oxygen in combination with other elements was also carried out. From this allocation procedure, each element's contribution to the total oxygen was determined. In some cases, the experimentally-measured oxygen content was insufficient to account for all of the oxygen-containing species (a deficiency); in other cases there was an excess of oxygen. Excess oxygen in these evaluations could be attributed to adsorbed water or to an element being bound to oxygen in ways not included in the assumptions regarding component stoichiometry and composition being used in the analysis. The results presented are reasonable within the limitations of the XPS measurements and the allocation procedure. The functional group allocation results are summarized in Table VI. No attempt was made to allocate the oxygen in plasma-sprayed aluminum phosphate since silica was added as a flow agent during aluminum phosphate deposition.

The allocation procedure yielded results that were consistent with the known stoichiometry for plasma-sprayed Al₂O₃, SiO₂, and TiO₂. The success of the allocation is likely due to the fact that there were very few contaminants in these plasma-sprayed samples. The plasma-sprayed MgO sample contained oxygenated forms of silicon and carbon. Carbonate made up 5.1% of the carbon and was assumed to be bound to

TABLE VI
Allocation of oxygen containing constituents: Plasma-sprayed coatings

Al₂O₃: Total % oxygen in sample;	48.2
Aluminum (Al ₂ O ₃)	40.9
Carbon (C–O, C = O, O–C = O [–])	12.1
Sodium (Na ₂ O)	1.5
Oxygen deficiency*	– 6.3
MgO: Total % oxygen in sample;	48.1
Silicon (silicate)	3.4
Carbon (C–O, C = O, O–C = O [–] , CO ₃ ^{2–})	25.5
Magnesium (MgO, MgCO ₃)	17.5
Excess oxygen [#]	1.7
SiO₂: Total % oxygen in sample;	64.2
Silicon (SiO ₂)	51.8
Carbon (C–O, C = O)	6.2
Excess oxygen	6.2
TiO₂: Total % oxygen in sample;	49.7
Titanium (TiO ₂)	32.4
Carbon (C–O, C = O, O–C = O [–])	8.8
Sodium (Na ₂ O)	0.4
Silicon (silicate)	3.4
Excess oxygen	4.7
TiSi₂: Total % oxygen in sample;	59.4
Titanium (titanium silicate)	7.8
Silicon (SiO ₂)	49.2
Carbon (C–O, C = O)	4.3
Oxygen deficiency	– 1.9

* Oxygen deficiency means that the total measured percent oxygen in the sample, *i.e.* 48.2% for Al₂O₃, was less than the amount attributed to the various oxygen-containing species.

[#] Excess oxygen means that the total measured percent oxygen in the sample, *i.e.* 48.1% for MgO, was greater than the amount attributed to the various oxygen-containing species.

magnesium as magnesium carbonate; the remainder of magnesium was assumed to be MgO. The small amount of unassignable oxygen (1.7%) is likely within the limits and expectations of the functionality allocation procedure.

The interpretation of the results obtained for the TiSi₂ plasma-sprayed sample presented a challenge, because the titanium concentration was 1.3% and the silicon atomic concentration was 27.2% not 2.6 atomic % as expected for the 1:2 stoichiometric ratio for TiSi₂. The chemical states of titanium and silicon for the plasma-sprayed sample are different from the corresponding chemical states for the powder. The titanium 2p region for TiSi₂ powder, shown in Figure 11, exhibited two photopeaks for titanium; the Ti 2p_{3/2} peak at 453.3 eV corresponds to titanium metal and the Ti 2p_{3/2} peak at 459.1 eV is assigned to TiSi₂. Also, the silicon 2p spectra, presented in Figure 12, indicated two chemical states in the powder sample. One Si 2p peak at 98.2 eV corresponds to silicide and the Si 2p peak at 102.5 eV is assigned to silicate. The differences in the spectra for the plasma-sprayed sample and the powder could be attributed to 1) titanium silicate and SiO₂ in the plasma-sprayed sample, 2) TiO₂ and SiO₂ in the plasma-sprayed specimen or 3) TiSi₂ and SiO₂ in the plasma-sprayed adherend. The binding energy for the Ti 2p_{3/2} photopeak (Ti 2p_{3/2}, BE = 459.7 eV) for

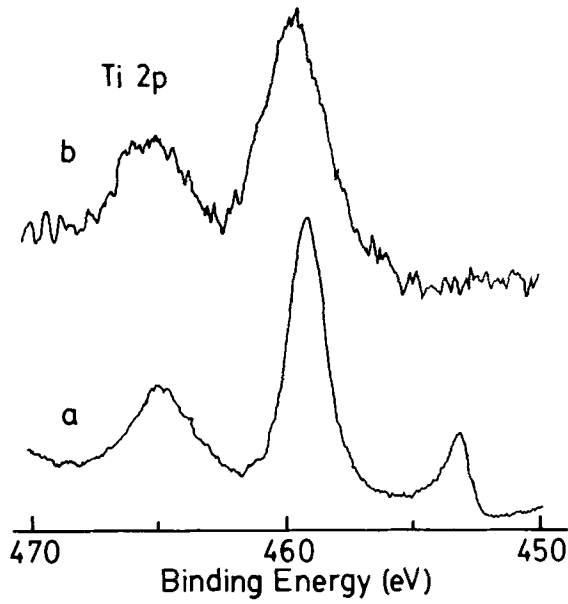


FIGURE 11 Titanium 2p x-ray photoelectron spectra for: a) TiSi_2 powder. b) TiSi_2 powder plasma-sprayed on titanium.

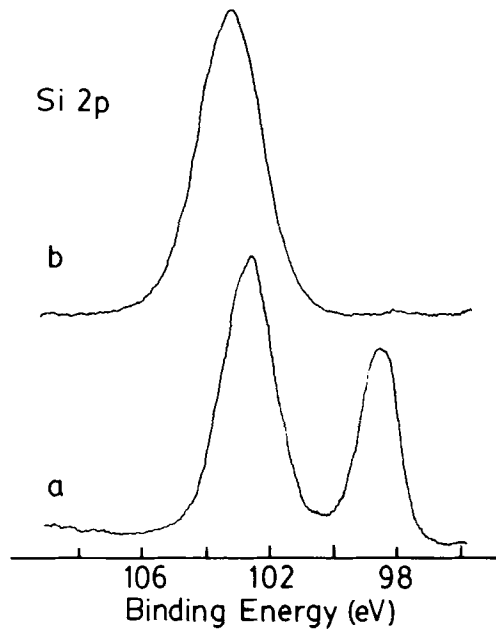


FIGURE 12 Silicon 2p x-ray photoelectron spectra for: a) TiSi_2 powder. b) TiSi_2 powder plasma-sprayed on titanium.

the plasma-sprayed sample was not equivalent to that for TiO_2 (Ti 2p_{3/2}; BE = 458.5 eV) nor for TiSi_2 (Ti 2p_{3/2}; BE = 459.3 eV). Only one silicon 2p photopeak was detected on the plasma-sprayed sample. The single silicon 2p photopeak had a binding energy of 103.2 eV, which corresponds to SiO_2 . No silicon 2p photopeak was detected in the silicide region. From these considerations it is suggested that a titanium silicate and SiO_2 were both present on the plasma-sprayed sample. Even though only one silicon 2p photopeak was detected, it is reasoned that titanium silicate and SiO_2 were present and that the two photopeaks for the two silicon-containing species overlap.

SUMMARY AND CONCLUSIONS

This characterization study has demonstrated that organic-polymeric and inorganic plasma-sprayed coatings on metal adherends retain their principal chemical characteristics. The physical state of the plasma-sprayed organic-polymeric coatings appears to be dependent on the nature of the polymer used in the plasma spraying process. The surface characterization results indicate that little or no chemical degradation of the polymer takes place under the plasma-spraying conditions used in this study.

The plasma-sprayed inorganic compounds are also little changed as a result of plasma spraying. The coatings exhibit the "splatter-type" features that are characteristic of plasma-sprayed coatings. Using a systematic approach for assigning functional group contributions, the surface chemical composition of the plasma-sprayed coatings appears to be representative of the sprayed compound. In the case of plasma-sprayed MgO, however, some carbonate formation was found as a result of the reaction of MgO with carbon dioxide from the air. For plasma-sprayed TiSi_2 it was suggested that a coating composed of silicon dioxide and a titanium silicate was most consistent with the XPS data.

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References

1. J. H. Zaat, *Ann Rev. Mater. Sci.*, **13**, 9 (1983).
2. H. M. Clearfield, D. K. Shaffer, S. L. Vandoren and J. S. Ahearn, *J. Adhesion* **29**, 81 (1989).
3. R. A. Pike, V. M. Patarini, R. Zatorski and F. P. Lamm, *Int. J. Adhesion Adhesives* **12**, 227 (1992).
4. H. M. Clearfield, D. K. Shaffer, J. S. Ahearn and J. D. Venebales, *J. Adhesion* **23**, 83 (1987).
5. D. Briggs, "Applications of XPS in polymer technology", in *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, D. Briggs and M. P. Seah, Eds. (John Wiley, New York, 1983), Chap. 9.
6. J. G. Dillard, C. Burtoff and T. Buhler, *J. Adhesion* **26**, 203 (1988).
7. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, Ed., *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1979).
8. D. Matejka and B. Benko, *Plasma Spraying of Metallic and Ceramic Materials* (John Wiley, New York, 1989).