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The influence of mechanical and chemical treatments on the environmental resistance of epoxy adhesive bonds to titanium

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ABSTRACT

In this investigation, the effect of mechanical and chemical treatments on titanium for bonding to a rubber toughened epoxy adhesive has been examined. Titanium alloy was roughened using either abrasion or grit-blasting techniques. An air-plasma treatment of the titanium prior to organosilane treatment also improved uniformity of the resultant thin film as determined by AFM and XPS. Grit-blasting significantly increased the titanium surface roughness and increased the alumina character of the surface layers. The fracture toughness of the epoxy-titanium bonds, as measured by the wedge test, was affected by the degree of surface roughness at short humid-exposure times. Further, the addition of a thin organosilane film to the titanium slowed degradation rates and led to higher fracture toughness at longer humid-exposure times.

1. Introduction

The surface treatment of aluminium aircraft structure prior to application of bonded repairs has successfully employed a process of grit-blasting and epoxy silane treatment for a number of years [1]. This treatment may also be employed to modify a range of metallic substrates such as titanium and steel. However, the environmental resistance of adhesive bonds prepared with the grit-blast and epoxy silane treated titanium have typically been poorer than for aluminium alloys. A number of intermediate steps are used in the grit-blast and epoxy silane process and an examination of some critical steps in the process have been undertaken in an attempt to determine how each step may affect the performance of the adhesive to titanium bonding.

Titanium represents a desirable material for the aerospace industry largely due to its high strength to weight ratio and high resistance to elevated temperatures and corrosion [2]. The preferred joining method for titanium structures is adhesive bonding, however, the key to its success relies on suitable surface treatments, which produce good bond strengths and durability. A variety of surface treatments for titanium have been described in the literature. Some initial work by Stone examined the performance grit-blasted titanium before and after treatment with epoxy and amino silanes [3]. For a range of adhesives, Stone showed that the addition of epoxy silane could significantly increase the fracture toughness of grit-blasted titanium wedge test samples. However, there was still a substantial reduction in the dry fracture toughness values for the samples exposed to a hygrothermal environment, with the toughened epoxy system cured at 120 °C showing a 15 fold reduction. Earlier work by Schrader also showed that grit-blasted and aminosilane treated titanium showed improvement in both dry and wet lap shear strength compared to grit-blasted only surfaces [4]. Boerio undertook fundamental characterisation of aminosilane films deposited on titanium and showed that the aminosilane could significantly improve the hydrothermal stability of epoxy to titanium bonded joints, with failure analysis suggesting that hydrolysis near the interface, but within the organosilane layer, was the main mechanism for bond degradation [5,6].

Reviews of titanium surface treatments for adhesive bonding applications [7,8] indicate that these treatments are divided into mechanical treatments such as grit-blasting or abrasion, as discussed above, chemical etching and chemical anodising. Typically, chemical anodising using either chromic acid or sodium hydroxide produced the strongest and most durable bonds due to the development of a micro-porous oxide layer [9]. Previous studies have shown that sodium hydroxide anodisation increases the bond strength and durability equivalent to or better than chromic acid [9–11]. However, some more recent treatments have examined plasma spray coatings [12], sol–gel film deposition [13] and plasma oxidation [14]. Plasma spray coatings of Ti–6Al–4V on titanium alloy produced wedge test results with crack extensions similar to chromic acid anodising and superior to grit-blasting [12]. It was reported that microscopic roughness contributed to the good performance of the plasma coatings [11]. Sol–gel coatings

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based on zirconium alkoxide and epoxy silane have also been shown to produce good durability on titanium with a range of adhesives, indicating very low crack growth and 100% cohesive failure when used in conjunction with grit-blasting and a chromate primer [13]. Vacuum plasma oxidation of titanium showed significant increases in lap shear strength due to increases in surface oxygen and roughness and lowering of carbon contaminant levels [14]. A recent study has shown that grit blasting followed by atmospheric plasma treatment leads to a significant increase in adhesive bond strength [15] as a result of a shift of the locus of failure from the metal polymer interface to within the adhesive.

The current work has examined the effect of mechanical and chemical treatments of titanium for bonding to a rubber toughened epoxy adhesive. Surface characterisation of the process has been undertaken and the relative effects of surface roughness, plasma and organosilane treatment have been examined using atomic force microscopy (AFM), time of flight secondary ion mass spectrometry (TOFSIMS) and X-ray photoelectron spectroscopy (XPS). Environmental resistance of the adhesive bonds formed with the titanium surfaces has been measured using the wedge test. This approach enables the chemistry and morphology of the surface modified titanium to be directly related to the strength and stability of the adhesive bonds between the titanium and epoxy.

2. Experimental

2.1. Sample preparation

Titanium Ti–6Al–4V alloy in the AMS4911 condition was used for all studies. The titanium surfaces were subjected to either chemical or mechanical modification prior to epoxy-silane treatment. Prior to epoxy-silane treatment, the titanium was exposed to a range of plasma, abrasion and grit blasting processes.

2.1.1. Mechanical treatments

Samples were either abraded with P200 silicon carbide abrasive paper (Carborundum Abrasives Products, USA) or metallographically polished to a 1 μm finish using diamond paste (Leco, Australia). A Scotchbrite 3M No. 7447 pad was used to abrade the titanium surface followed by cleaning with methyl ethyl ketone (MEK) (Sigma-Aldrich, Australia) and deionised water.

Samples were grit-blasted at 60 psi using 50 μm diameter aluminium oxide (AccuBRADE 50, S.S. White technologies, USA) abrasive using nitrogen gas as the propellant with a DirectFlo micro-abrasive blaster (Comco Inc., USA). Samples were blasted from a 50 mm distance to provide a uniform matte grey surface finish.

2.1.2. Plasma treatments

The titanium alloy was plasma treated using an Atomflo 500 atmospheric plasma unit (Surfx Technologies, USA) [16]. The unit was operated at 140 W and a scanning rate of 2.5 mm/s using 30 L/min of helium and 1.5 L/min of oxygen from a standoff distance of 2.5 mm.

2.1.3. Epoxy-silane treatment

γ-Glycidoxypropyltrimethoxy silane (Dow Corning Z-6040®, Sigma-Aldrich, Australia) was applied to the titanium alloy as a 1% aqueous solution using distilled water for 10 min. Prior to treatment of the titanium, the organosilane had been fully hydrolysed by constant stirring under ambient conditions for at least 1 h under natural pH conditions around 4.5. The silane film was dried at 110 °C for 60 min.

2.1.4. Application of primer

A 2–7 μm thick layer of BR6747-1 corrosion inhibiting primer (Cytec Industries, USA) was applied. BR6747-1 is a one part, chromate based, water based, modified epoxy primer. The primer thickness was measured using an eddy current paint thickness monitor (Elcometer Model 4562, Elcometer Instruments, USA).

2.2. Spectroscopic characterisation

The titanium alloy surfaces were characterised by XPS using a Kratos Axis Ultra spectrometer with a monochromatised Al $K\alpha_1$ (1486.6 eV) X-ray source operated at 150 W with a 160 eV pass energy. All spectra were acquired using a 90° take off angle with respect to the sample surface. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ photoelectron peak at a binding energy of 83.98 eV. The analysis area was 700 μm × 300 μm. Spectra were quantified using Kratos XPS elemental sensitivity data after Shirley background subtraction. Atomic concentration uncertainties for all fitted spectra are estimated to be ± 10% of the measured value.

ToF-SIMS analyses were performed using a TOF-SIMS IV instrument (Ion-TOF GmbH, Germany) equipped with a reflectron analyzer, a Bi cluster ion gun (25 keV) and a pulsed electron flood source for charge neutralization. The primary pulsed ion beam current for the Bi^+ ions used was 2.5 pA and the primary ion dose density was below the static SIMS limit of 10^{13} ions cm^{-2}. For spectral acquisition, positive ion mass spectra were acquired from a 100 × 00 μm^2 area using a cycle time of 100 μs with a resulting mass resolution > 7000 at $m/z=27$. The data was analysed by normalising the ion of interest to the corrected total ion intensity for each spectrum. A group of representative ion fragments was selected for each sample. The corrected counts for these were summed and then the percentage contribution for the ion of interest was calculated. Dynamic SIMS used a Kratos SIMS 800 with a gallium ion beam operating at 10 keV with a current density of 25 nA/cm^2, which was equivalent to a sputter rate of 0.13 nm/min on anodically grown aluminium oxide.

2.3. Surface roughness measurements

AFM measurements used a Dimension 3100 Scanning Probe Microscope operating in tapping mode using a Nanoscope IIIa controller with Nanoscope software Version 6 (Veeco Instruments, USA). An etched silicon probe with a 17 μm tip height and a half cone angle of 25° and tip radius less than 60 nm was used for imaging.

2.4. Bond durability and fracture analysis of epoxy-titanium joints

Wedge style double cantilever beam specimens were prepared based on ASTM D3762 [17]. This involved bonding individual pairs of titanium fingers of 25.4 mm × 150 mm × 3.0 mm dimensions that had been pre-treated. All specimens were bonded with FM300-2K, a rubber toughened epoxy based adhesive, which was cured at 120 °C for 90 min (Cytec, USA). After wedge insertion, the sample was conditioned in a laboratory environment for 24 h prior to humid exposure at 50 °C/95% R.H. Crack length measurements were performed prior to humid environment exposure and at times ranging to 1000 h. The fracture toughness values, G_I (J/m^2), were calculated using Eq. (1) [18],

$$G_I = \frac{Y^2 \times E \times h^3[3((a+0.6h)^2+h^2)]}{16[(a+0.6h)^3+a\times h^2]^2} \quad (1)$$

where Y was the crack opening displacement, h was the adherend thickness, E was Young's modulus (113.8 GPa for Ti–6Al–4V) and

a was crack-length. Analysis of the fractured wedge-test samples was performed using the XPS conditions described in Section 2.2. Samples were cut 15 mm × 25.4 mm and analysis was performed as close to the crack tip as possible.

3. Results and discussion

3.1. Surface preparation and treatment of titanium alloy

Figs. 1 and 2 show AFM images and line scans of Ti–6Al–4V after polishing, abrading and grit-blasting. The corresponding average roughness values taken over two areas of 100 μm^2 and 2500 μm^2 for these surfaces are provided in Table 1. It is evident that the polished and abraded surfaces are relatively flat as compared to the grit-blasted surfaces. The abraded surfaces have occasional gauges, which increase the relative roughness, however, the overall values are much lower than the grit-blasted surface. Similarly the grit-blast surface is the only treatment that leads to a significant increase in the relative surface area. In practical terms, the grit-blast treatment may be expected to have an influence on the mechanical properties of the adhesive bond by providing a greater contact area and higher density of asperities which may affect the stress concentrations at the loaded interface.

Table 2 shows the atomic concentrations for polished titanium alloy following a series of chemical, plasma and mechanical treatments. Fig. 3 shows typical XPS survey spectra for the treated alloy. Carbon, oxygen, titanium and aluminium are detected on all samples, as expected. The high levels of oxygen are attributed to surface metal-oxides, while the carbon is assigned to adventitious carbon-species for samples without the γ-GPS treatment. It is noted that the plasma and grit-blasted treatments both reduce the carbon concentration as compared with the solvent only treatment. The removal of surface contamination is fundamental in improving the subsequent epoxy-silane treatment by increasing the surface energy, which facilitates improved wetting and consequentially opportunities for formation of chemical bonds between the alloy and the organosilane. Akram et al. [15] showed using contact angle measurements that a combination of grit blasting and plasma treatments of titanium increased the surface energy which resulted in an improvement in adhesive bond strength.

The grit-blasted surface has an aluminium atomic concentration of 11.5 at% which is considerably higher than for the solvent cleaned, plasma and abraded samples. This result suggests that some of the alumina grit may have been transferred onto the titanium alloy surface. A dynamic SIMS spectrum and depth profile (Fig. 4) of the grit-blasted surface supports the XPS results. In Fig. 4b, the positive ion species Al^+, Na^+, Ti^+ and TiO^+ are monitored as a function of etch time. There is an initial rapid decrease in the Na^+, Ti^+ and TiO^+ signals associated with the removal of surface oxides, whereas the Al^+ signal exhibits a gradual decline. Typically, the secondary ion signal is sensitive to oxygen levels present at the surface and the slow decline in the aluminium signal is likely to indicate an increased alumina character of the alloy surface. In contrast, the rapid decline in the titanium oxide signal is probably due to the removal of the titanium oxide surface layer. The grit-blasting of the titanium

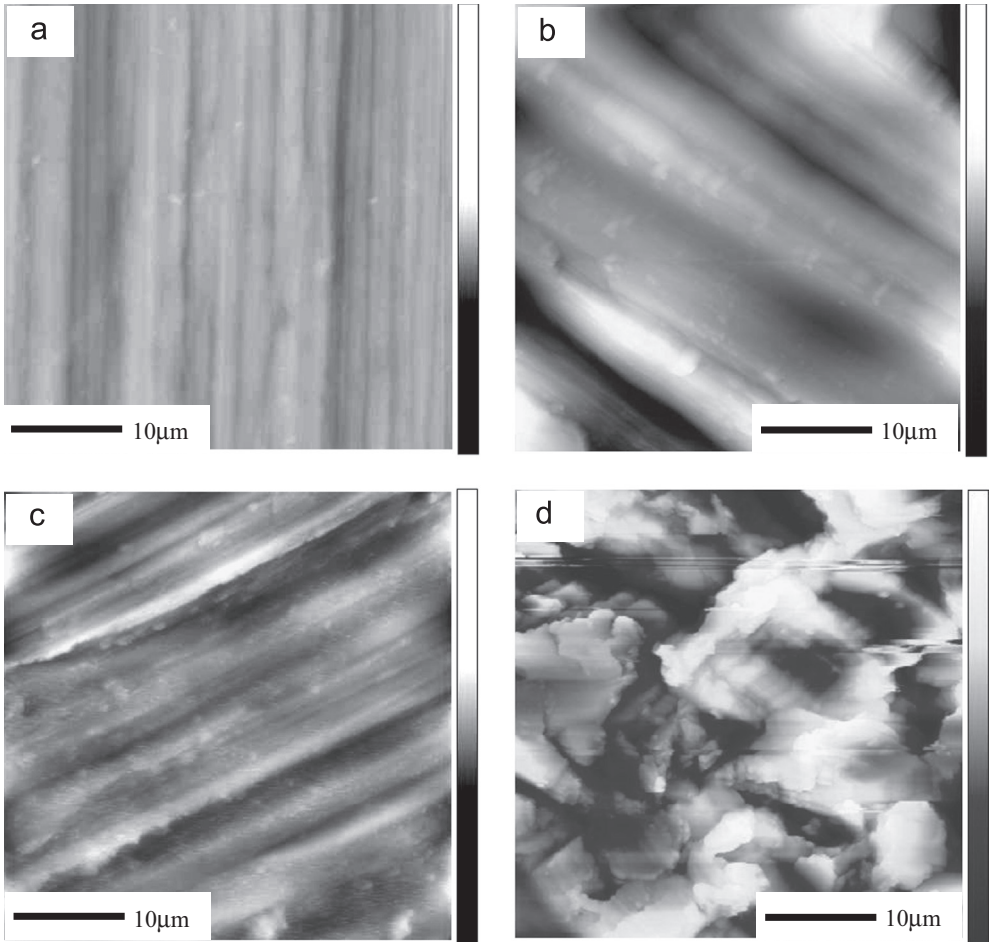

Fig. 1. AFM images of Ti–6Al–4V after (a) polishing, (b) P-200 abrasion, (c) Scotchbrite® abrasion and (d) grit-blasting with 50 μm alumina. Height scale is 0 nm (black) to 1000 nm (white).

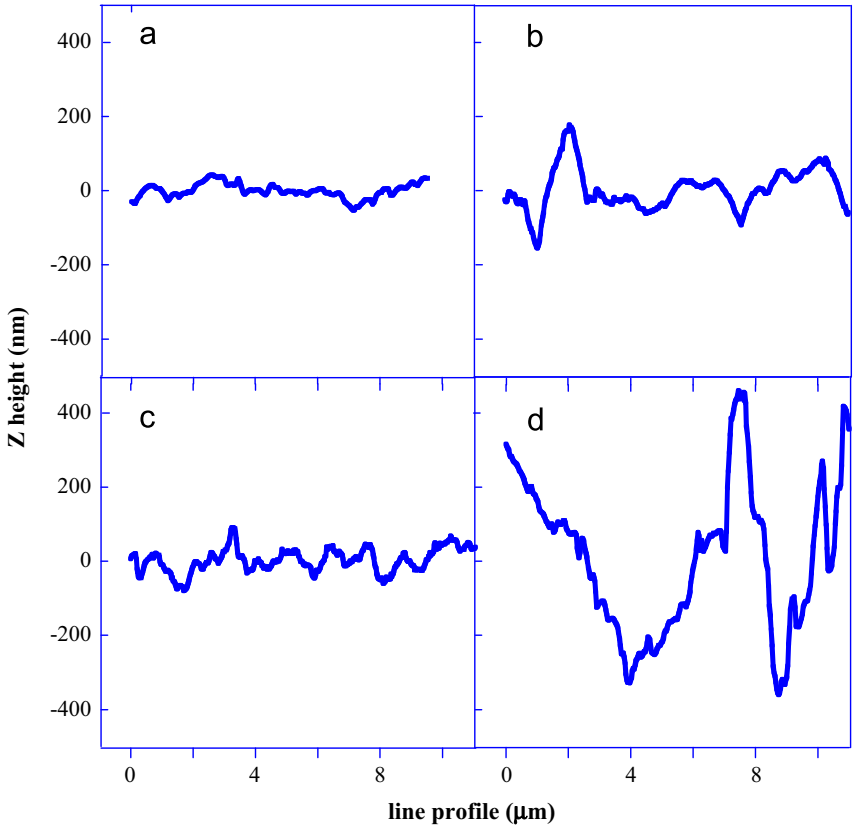

Fig. 2. Line profiles from AFM scans of (a) polished, (b) P-200 abraded, (c) Scotchbrite® abraded and (d) 50 μm alumina grit-blasted Ti–6Al–4V alloy.

Table 1
Average roughness, R_a, and relative surface area for different levels of abrasion applied to Ti–6Al–4V alloy determined by AFM.

Scan area	Surface	Polished	Scotch-brite®	P-200	Grit-blast
100 μm²	R_a	18	27.3	49	182
	Relative surface area	1.02	1.04	1.03	1.40
2500 μm²	R_a	110	148	212	493
	Relative surface area	1.01	1.07	1.07	1.30

Table 2
XPS analysis of polished Ti–6Al–4V alloy after surface treatment using a combination of abrasion, cleaning and chemical methods.

Ti–6Al–4V treatment	Atomic concentration (%)								
	O 1s	Ti 2p	C 1s	Al 2p	Si 2p	V 2p	Zn 2p	N 1s	Na 1s
MEK+water	47.1	12.8	36.5	2.5	–	0.5	0.0	0.6	–
MEK+γ-GPS	40.6	7.2	46.0	1.4	4.7	–	–	–	–
MEK+plasma	54.6	18.0	22.8	2.9	–	0.3	0.1	1.3	–
MEK+plasma+γ-GPS	33.7	0.2	56.9	–	9.2	–	–	–	–
abrade+plasma	49.1	17.2	29.0	2.6	–	0.6	0.2	1.4	–
abrade+plasma+γ-GPS	35.5	1.1	55.3	–	8.1	–	–	–	–
grit-blast	48.0	8.5	25.6	11.5	–	–	0.1	–	4.0
grit-blast+γ-GPS	36.5	1.7	51.7	3.6	6.8	–	–	–	–

surface is expected to create a surface with a mixture of alumina and titania chemistry, which may influence subsequent reaction with the organosilane.

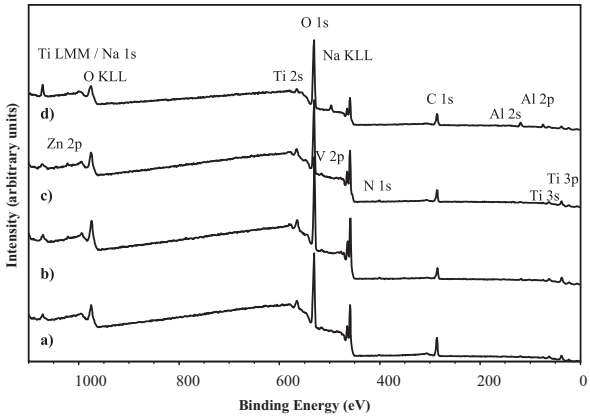

Fig. 3. Typical XPS survey spectra of treated Ti–6Al–4V alloy, (a) MEK+water, (b) abrade+plasma, (c) abrade and plasma and (d) grit-blast.

3.2. Epoxy-silane treatment of titanium alloy

XPS results of the titanium alloy following epoxy-silane treatment are also shown in Table 2. Fig. 5 shows representative survey XPS spectra of the titanium alloy after γ-GPS treatment. For each of the samples, an increase in the carbon and silicon and decrease in titanium, oxygen and aluminium are observed. The silicon represents the marker element for the presence of the organosilane. It is noted that the solvent cleaned surface after plasma treatment has the highest silicon concentration followed by the abraded and plasma treated surface (8.1 at%), the grit-blasted surface (6.8 at%) and finally the solvent-cleaned surface (4.7 at%). AFM measurements on the polished titanium alloy with and without plasma treatment, following immersion in γ-GPS, are presented in Fig. 6. The results indicate that particles of organosilane form on the

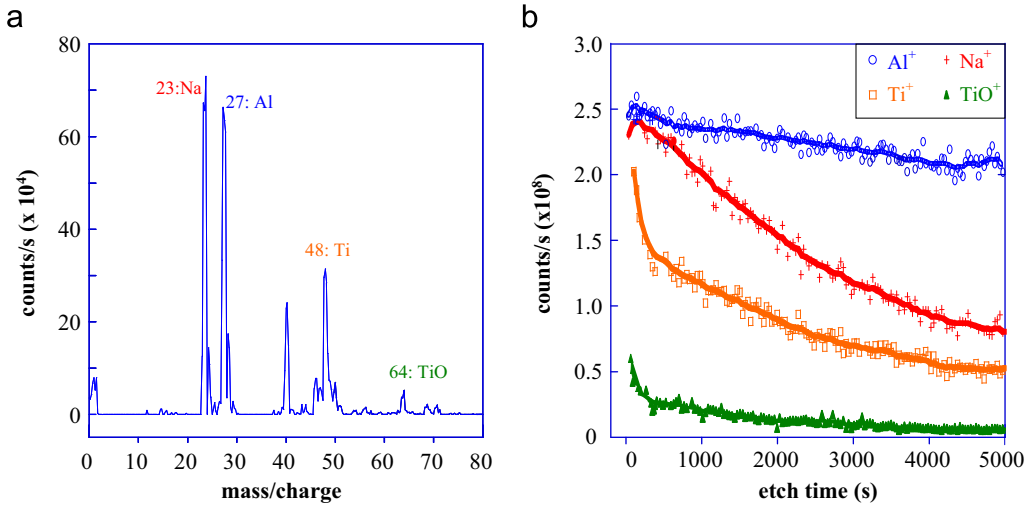

Fig. 4. Dynamic SIMS (a) spectrum and (b) depth profile of grit-blasted Ti–6Al–4V alloy indicating signal intensity for Al, Na, Ti and TiO positive ions with etch time.

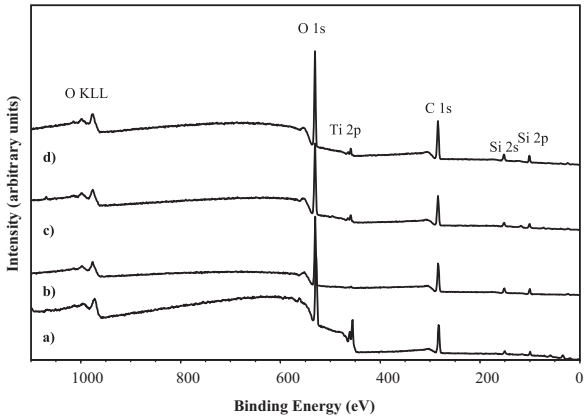

Fig. 5. Typical XPS survey spectra of treated Ti–6Al–4V alloy, (a) MEK+water+γ-GPS, (b) abrade+plasma+γ-GPS, (c) abrade and plasma+γ-GPS and (d) grit-blast+γ-GPS.

sample without plasma treatment, whereas film uniformity and coverage increased on the plasma treated surface. In addition, after plasma treatment, the organosilane film appears to have a greater density of small particles suggesting that the reaction of the organosilane is altered on the plasma treated surface. The higher organosilane coverage on the plasma treated surface is consistent with the higher silicon atomic concentration measured by XPS.

Static SIMS measurements were undertaken to characterise the molecular structure of the organosilane film deposited on the titanium alloy surface. Fig. 7 shows the percentage contribution for the prominent positive ion fragments representative of the substrate (Ti^+, Al^+) and hydrolysed organosilane (Si^+, $SiO_2H_3^+$ and $Si_2O_4H_3^+$) for the titanium alloy treated using plasma, grit-blasting and organosilane. A control sample of γ-GPS was also included by allowing a drop of organosilane solution to evaporate on the titanium surface leaving a thick film. Fig. 8 shows positive SIMS spectra for selected masses before and after γ-GPS treatment on plasma and gr-blast samples. Prior to organosilane deposition, the Al^+ and Ti^+ signal dominate the spectrum for the plasma treated sample, while the grit-blasted sample displays a strong Al^+ signal and weaker Ti^+ signal. This result is consistent with the XPS data presented above suggesting the increased alumina character of the grit-blasted surface. Following the deposition of organosilane, the Si^+ signal increases and there is evidence of silanol species ($SiO_2H_3^+$ and $Si_2O_4H_3^+$). The relative intensity of the three fragments indicative of the organosilane molecule is greater for the plasma treated surface than the grit-blasted surface, which suggests improved film coverage on the plasma treated surface. The presence of the $SiOAl^+$ and the $TiOSi^+$ fragments provides some evidence for chemical bonding of the organosilane to the titanium alloy, but interestingly the relative intensity of the $SiOAl^+$ fragment was greater on the plasma treated surface than the grit-blasted surface. This may indicate chemical interaction between the organosilane and aluminium present in the titanium alloy. These results are consistent with the work of Abel et al. [19,20] investigating the interaction of γ-GPS and oxidised aluminium. It was reported that the presence of the $AlOSi^+$ fragment demonstrated the formation of a covalent bond between the aluminium and γ-GPS.

3.3. Chemical stability of epoxy-silane treatment

Fig. 9 shows the ratio of aluminium to silicon and titanium to silicon for grit-blasted and organosilane treated titanium alloy. In a 50 °C/95% relative humidity environment (Fig. 9a), the elemental ratios remain relatively unchanged over a 500 h period, which indicates that the organosilane film remains attached to the titanium surface. This contrasts to Fig. 9b, where the relative concentration of aluminium and titanium increase significantly over a similar period of exposure, thereby suggesting the gradual removal of the organosilane film. It would appear that once a critical concentration of moisture is exceeded, the organosilane film becomes unstable. It should also be noted that potentially moisture in both humid and aqueous environments could lead to degradation of the silane to aluminium or titanium bonds which would not necessarily be detected in the current experiments. However, previous studies of γ-GPS films on aluminium have indicated that the silane film was observed to desorb in a 95% R. H. environment [21]. Notably the relative change in the ratios for both aluminium and titanium is equivalent in the two environments, which may indirectly suggest the hydrolytic stability of the organosilane bonds to the alumina and titania regions is similar. This would be consistent with the ToF-SIMS results (Fig. 7), which showed that the γ-GPS produced both Si–O–Al and Si–O–Ti fragment ions, suggesting reaction between the organosilane and alumina and titania surface regions.

3.4. Mechanical testing and failure surface analysis

Fig. 10 displays fracture energy measurements for the titanium alloy wedge tests exposed to 50 °C/95% relative humidity indicating the effect of surface roughness prior to and following the application

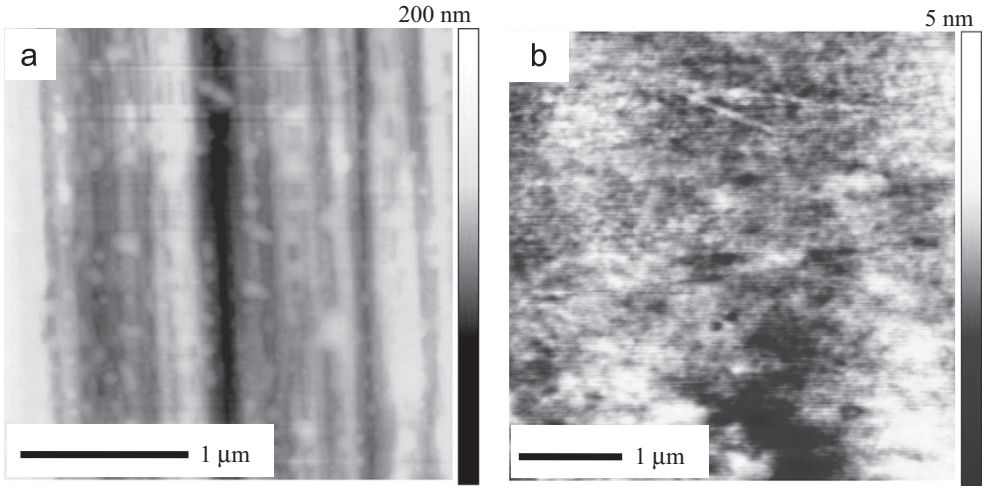

Fig. 6. AFM images taken on polished Ti–6Al–4V alloy (a) without plasma and (b) with plasma treatment, following immersion in 1% solution of γ-GPS.

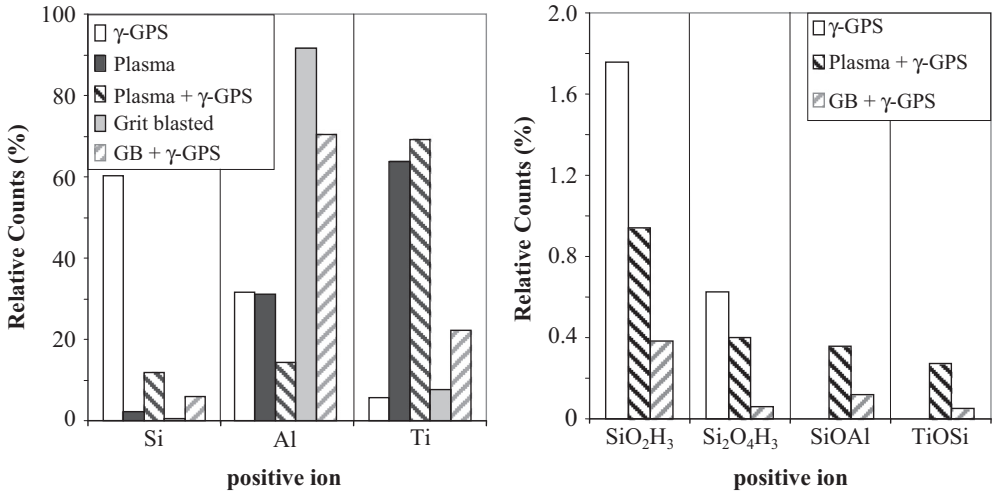

Fig. 7. Static SIMS spectra for Ti–6Al–4V alloy treated using plasma, grit-blasting and γ-GPS indicating relative positive ion counts.

of γ-GPS and BR6747-1 primer. The grit-blasting appears to lead to a higher fracture toughness for the initial humid exposure in comparison to the polished and plasma treated wedge specimens. The grit-blasted sample shows a rapid decrease in fracture toughness after only 10 h of exposure. The addition of organosilane and primer slows the rate of degradation, leading to higher fracture toughness at extended exposure times. Comparatively, the polished and plasma treated samples show a similar trend to the grit-blasted samples, but the rates of degradation are more rapid and the fracture toughness at longer exposure times is lower. This result suggests that the epoxy-silane and primer treatments both slow the adhesive bond degradation rates and that the grit-blasting facilitates a higher initial fracture toughness.

The elemental compositions of the wedge test fracture surfaces are displayed in Tables 3 and 4. The overall elemental compositions of the fracture surfaces are quite similar and indicate the fracture surface that has the appearance of the epoxy adhesive is characterized by high carbon levels with oxygen and nitrogen concentrations around 15% and 4%, respectively. The fracture surface with the metallic appearance is characterized by relatively high carbon concentrations and titanium and aluminium indicative of the alloy surface. The overall compositions suggest that the fracture occurs near the interface and is a combination of fracture within the adhesive layer and at the adhesive–titanium interface. Generally, the levels of titanium appear to decrease on the failure surfaces with metallic appearance for the samples that were grit-blasted, which would be consistent with a reduction in fracture at the epoxy-titanium interface. Notably little or no aluminium was detected on the adhesive fracture surfaces for the grit blasted treatments, which would imply that the embedded alumina from the grit blasting did not have a significant effect on the joint fracture toughness. For example the silane and silane+primer samples have very similar fracture toughness at extended exposure, yet no aluminium was detected on the adhesive fracture surface for the primer sample (Tables 3 and 4). Interestingly, the levels of silicon on the metallic fracture surfaces appear to be quite low relative to the organosilane treated titanium alloy shown in Table 2. The reduction in silicon concentration may be accounted for by the reduced area of metal exposed on the fracture surface, but may also be indicative of organosilane desorption that has either occurred prior to or post fracture. As the organosilane film deposited on the titanium alloy was shown to be stable under the environmental conditions of the wedge test (Fig. 8), this may suggest that the low levels of silicon on the fracture surfaces are associated with changes in the organosilane film stability in the presence of the epoxy adhesive. The presence of nitrogen on all fracture surfaces is associated with the adhesive cross-linking agent, which, if not fully reacted, would be capable of reacting with the moisture and producing high-pH conditions at the interface.

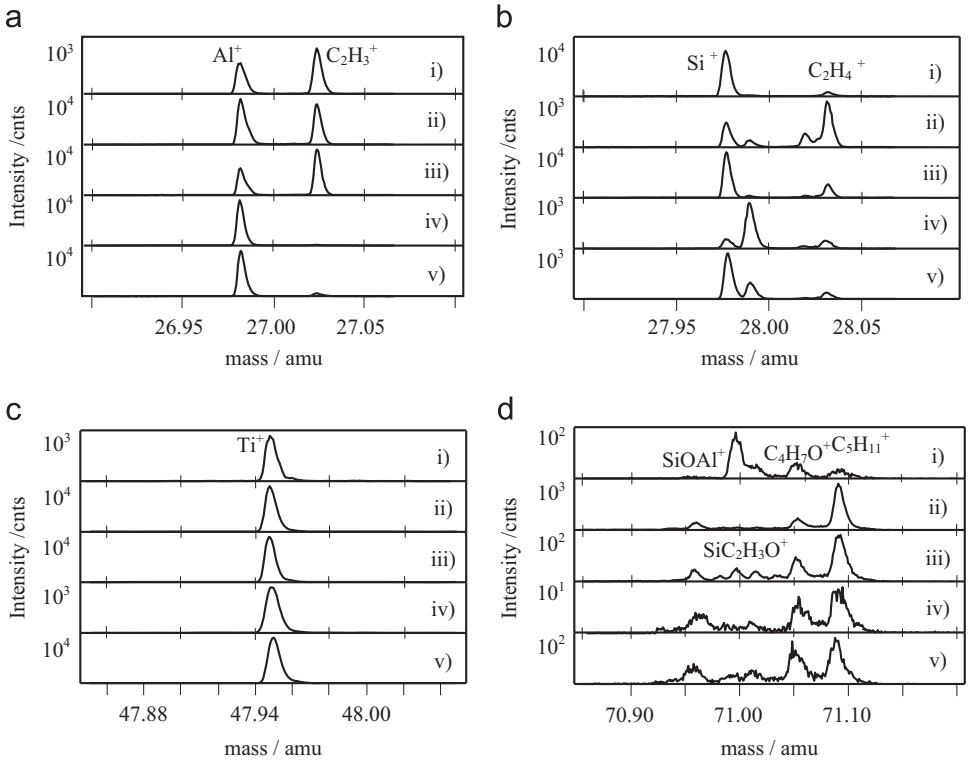

Fig. 8. Positive TOF-SIMS spectra of selected masses for the treated alloy: (i) γ-GPS drop on Ti–6Al–4V alloy, (ii) plasma treated Ti–6Al–4V alloy, (iii) plasma and γ-GPS treated Ti–6Al–4V alloy, (iv) grit-blast Ti–6Al–4V alloy and (v) grit-blast and γ-GPS treated Ti–6Al–4V alloy.

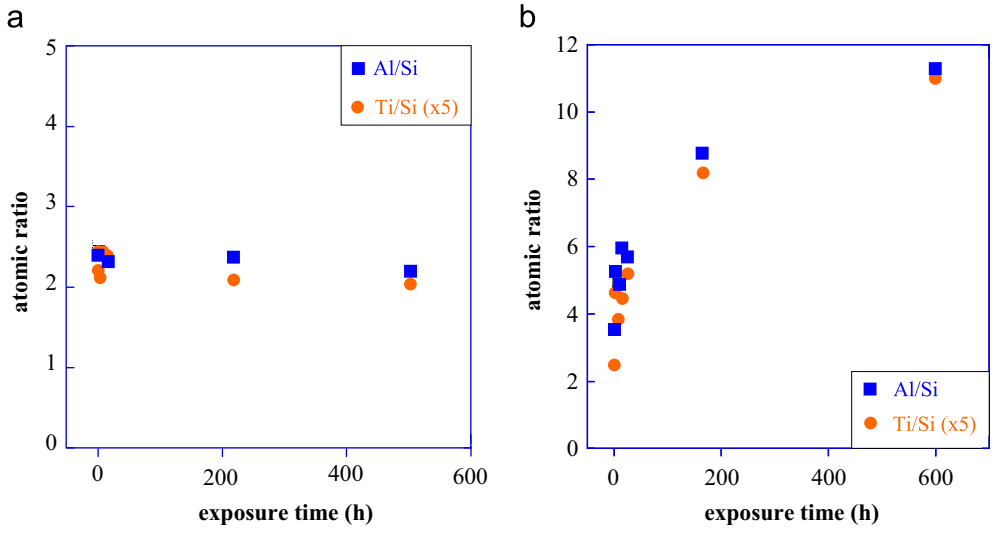

Fig. 9. The change in the Al:Si and Ti:Si ratios for grit-blasted Ti–6Al–4V alloy treated with 1% solution of γ-GPS and exposed to (a) 50 °C/95% R.H. and (b) 50 °C deionised water.

4. Conclusion

Characterization of titanium alloy surfaces after abrasion and γ-GPS treatments indicate the grit-blasting is the only process which significantly increases the surface roughness, whilst plasma processing improves surface cleanliness and the uniformity and coverage of the organosilane film. Grit-blasting modifies the titanium chemistry by increasing alumina content in the surface layers. However, the γ-GPS film deposited on the grit-blasted titanium surface appeared to be hydrolytically stable under the conditions of the wedge test, with ToF-SIMS results suggesting reaction between the organosilane and the alumina and titania surface regions. The environmental resistance of the epoxy-titanium adhesive bonds, as assessed by the wedge test, appeared to be affected by both the level of surface roughness and the γ-GPS treatment. Grit-blasting increased the adhesive bond fracture toughness at short exposure times, compared to flat surfaces, whilst the γ-GPS treatment appeared to slow the decrease of fracture toughness and lead to higher values at extended exposure times in humid environments. The fracture surfaces of all samples indicated failure propagated close to the adhesive and metal interfacial region, with evidence for some shift further into the adhesive layer for the grit-blast and organosilane treatments. The absence of high silicon

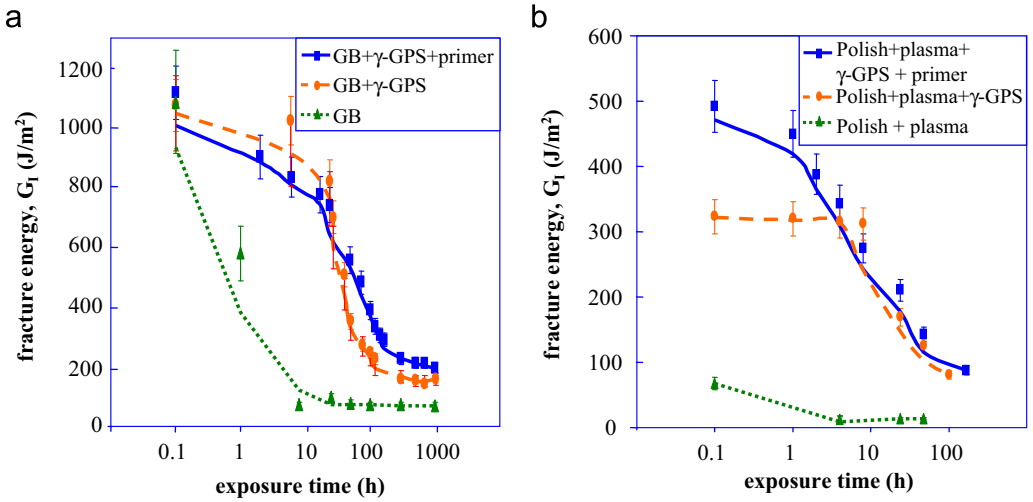

Fig. 10. Fracture energy, G_I, measured for Ti–6Al–4V wedge tests exposed to 50 °C/95% R.H. environment, indicating the effect of (a) grit-blast and (b) polishing prior to and following the application of γ-GPS silane and BR6747-1 primer.

Table 3
Elemental characterization of polished, Ti–6Al–4V, wedge-test fracture-surfaces after plasma, γ-GPS and BR6747-1 primer surface pretreatments (Note only elements indicative of the Ti–6Al–4V, γ-GPS and the BR6747-1 primer have been included).

Treatment	Failure surface	Atomic concentration (%)						
		C 1s	N 1s	Si 2p	Ti 2p	O 1s	Al 2p	Cr 2p
Plasma	Metal	52.2	2.1	1.3	7.6	35.0	0.9	0.0
	Adhesive	75.7	3.8	0.0	0.0	17.2	0.0	0.0
+γ-GPS	Metal	33.8	1.9	1.2	12.2	47.0	2.8	0.0
	Adhesive	72.9	4.6	1.3	0.0	19.0	0.0	0.0
+γ-GPS+primer	Metal	40.0	3.7	0.7	9.8	41.0	1.8	1.7
	Adhesive	74.8	3.8	1.4	0.0	18.9	0.0	0.2

Table 4
Elemental characterization of grit-blasted, Ti–6Al–4V, wedge-test fracture-surfaces after plasma, γ-GPS and BR6747-1 primer surface pretreatments (Note only elements indicative of the Ti–6Al–4V, γ-GPS and the BR6747-1 primer have been included).

Treatment	Failure surface	Atomic concentration (%)						
		C 1s	N 1s	Si 2p	Ti 2p	O 1s	Al 2p	Cr 2p
Grit-blast	Metal	39.3	4.2	0.0	3.7	39.0	9.7	0.0
	Adhesive	77.2	4.0	0.3	0.0	14.6	0.7	0.0
+γ-GPS	Metal	37.5	1.5	1.5	7.2	43.8	5.8	0.0
	Adhesive	76.5	3.4	2.1	0.0	15.1	0.8	0.0
+γ-GPS+primer	Metal	47.8	4.1	1.6	3.2	35.6	3.8	0.2
	Adhesive	81.2	3.8	0.5	0.0	12.5	0.0	0.0

levels on the metal fracture surfaces may indicate there are regions where the organosilane film has desorbed, which was not expected based on the hydrolytic stability measurements.

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