



# Surface preparation of silicon carbide for improved adhesive bond strength in armour applications

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## Abstract

Surface treatments of silicon carbide have been investigated with the aim of improving the strength of the bond between the ceramic and an epoxy adhesive. Three surface conditions have been characterised; as-fired, air re-fired and KrF laser processed. A number of characterisation techniques have been used to determine the morphological and chemical changes that have occurred to the surface. Scanning electron microscopy of the re-fired and laser processed samples showed surfaces that appeared glassy, with the laser processed surface showing a different morphology. X-ray photoelectron spectroscopy indicated both treatments had oxidised the surface and the laser processed surface also had a greater concentration of hydroxyl groups. The wettability of both surfaces had improved and the laser processed surface was found to be highly hydrophilic. Mechanical testing of joints prepared with this technique showed them to have the highest strength in tension, with the locus of failure being cohesive.

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## 1. Introduction

Ceramic based armour systems feature increasingly on modern armoured vehicles. The main benefit of these systems is that they combine a high resistance to penetration with a low density. These features are ideal for armour. However, a major disadvantage of these systems is the reduced multi-hit performance compared with metallic based armour.

Ceramic armour typically comprises a ceramic front strike face, which is adhesively bonded to a composite or metal backing. A ballistic impact leads to a compressive stress wave being transmitted through the ceramic to the back face of the ceramic. On reaching the free surface, the wave is reflected, leading to a tensile stress in the ceramic, which is the main cause of the failure of the ceramic by fracture. The intensity of the reflected

stress wave is dependent on the amount of energy that can be transmitted to the adhesive layer,<sup>1</sup> which in turn depends on the acoustic impedance of the adhesive.<sup>1</sup>

The two main adhesive systems used with ceramic armour systems are polyurethane and epoxy. The impedance mismatch between polyurethane and ceramic is greater than for epoxy and ceramic.<sup>1</sup> Using epoxy results in a 13-fold increase in the amount of energy transmitted from the ceramic to the adhesive and hence the ceramic is less likely to fail.<sup>1</sup> However, the ability of the adhesive to absorb energy is only of practical benefit if the ceramic remains bonded to the backing; the adhesive must not fail and hence polyurethane is preferred over epoxy currently as it is less likely to fail. If the bonding between ceramic and epoxy could be improved then not only would the ceramic be more likely to survive a ballistic impact because of the reduced intensity of the reflected stress wave, but also a stiff adhesive such as epoxy would reduce the bending of the ceramic during the impact. A further consequence of reducing the effect of a single impact might be a move towards an armour that is capable of withstanding multiple hits. Thus, there are many attractions to developing a technique to improve the bond strength between a ceramic and an epoxy adhesive.

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Previous research on alumina showed that preparing the surfaces to be bonded by using a laser treatment led to an increase in the number of hydroxyl groups on the ceramic surface and an increase in the adhesive bond strength.<sup>2</sup> Thus, it is hypothesised that increasing the number of hydroxyl groups on the surface of silicon carbide would also lead to an improvement in the strength of the bond between the ceramic and an epoxy adhesive. In this investigation this hypothesis is tested by using two methods to change the surface chemistry of silicon carbide and then investigating the effects of those treatments on the strength of tensile and shear joints made using an epoxy adhesive.

## 2. Experimental methods

### 2.1. Silicon carbide samples

Solid state sintered silicon carbide (Sicadur F) tiles were supplied by Ceramtec ETEC GmbH. The as-received tiles were used as control samples with no additional processing other than to clean the surface using a solvent wipe prior to material characterisation and adhesive bonding experiments.

In an attempt to increase the native surface oxide, samples of silicon carbide were refired in air at 1100 °C for 1.5 h.<sup>3</sup> All samples were cleaned prior to adhesive bonding. In order to measure the surface contamination caused by this technique a pre-cleaned sample was characterised using X-ray photoelectron spectroscopy.

Laser ablation was performed on a third set of samples using a 248 nm krypton fluoride ultra violet excimer laser. The laser was traversed across the surface. To obtain an even coverage each raster overlapped the previous by half the width of the laser spot. The intent of this technique is to oxidise<sup>4</sup> and possibly introduce hydroxyl groups<sup>2</sup> to the surface.

### 2.2. Characterisation of ceramic surfaces

A Hitachi 3200 N scanning electron microscope was used with a secondary electron detector and a backscattered electron detector at an acceleration voltage of 25 kV. All samples were coated with ~3 nm of sputtered gold prior to characterisation.

X-ray photoelectron spectroscopy was performed using a VG ESCALAB mk II-XPS using a non-monochromated Al K $\alpha$  source. Using the Al K $\alpha$  source there was a depth of analysis of 5–6 nm. At least two measurements were taken in separate locations on each of the surfaces that were analysed. The data were referenced to carbon at 285 eV. The data were then peak fitted to determine the silicon carbide and oxide atomic concentration using the silicon peak. The oxygen peak was also peaked fitted to determine the atomic concentration of the hydroxyl groups.

The sessile drop technique was used to measure the surface wettability and energy. A computer controlled syringe with a camera perpendicular to the surface was used to determine the contact angle of the liquid on the surface. Distilled water and glycerol were used to determine the surface energy using the Owens and Wendt method.<sup>5</sup>

### 2.3. Mechanical testing of joints

Epoxy – silicon carbide joints were prepared to measure the tensile and shear strength of the bond. The epoxy, which comprised two resin components and one hardener, was provided by Resiblend PLC. The product is referred to as ESK T + ESK LV2 + ESK LVH2.

The control sample required only cleaning prior to bonding. Cleaning was carried out using a solvent wipe of methanol and then isopropyl alcohol to remove any residue. The refired sample was also cleaned using the same method after refiring. For the laser processed sample only the face that was in contact with the epoxy was processed. The whole sample was cleaned prior to laser processing.

The butt joint for measuring tensile strength required two pieces of silicon carbide with a 0.5 mm epoxy layer bonding them together. The joints were visually inspected prior to mechanical testing to determine that the adhesive had covered the entire joint face. A schematic diagram of this joint is shown in Fig. 1. The experiments followed ASTM standard D2094-00 for the preparation of bar and rod specimens for adhesion tests. The joints were tested at a rate of 1.0 mm per minute. At least 6 samples of each surface type were prepared for mechanical testing.

Joints were also prepared for measuring the strength in shear. The experiments followed ASTM standard D3528-96, the standard test method for determining the strength of double lap shear adhesive joints under applied tensile loads. The set-up for this joint is shown in Fig. 2.

All joint samples were mechanically tested to failure using an Instron 8800 testing machine with a 50 kN load cell. The load measurement uncertainty had been confirmed by certification to be 0.22% for loads 20–100% (10–50 kN) of the load cell range. At least 6 samples of each surface type were prepared for mechanical testing.

After testing, some fracture surfaces from both tensile and shear testing were observed using SEM, with a view to identifying the failure locus of the joints.

## 3. Results and discussion

### 3.1. Observations

The as-received silicon carbide samples were a dark glossy grey colour, Fig. 3(a). Following refiring in air the appearance changed to a glossy blue colour, Fig. 3(b). Laser processing produced a surface that had silver and black stripes, Fig. 3(c).

During laser processing of the sample it was noticed that a plasma was created. This suggests that the energy supplied to the surface was sufficient to cause decomposition. Silicon carbide has been assumed to decompose at temperatures greater than 2750 °C.<sup>6</sup>

### 3.2. Scanning electron microscopy

Three samples of silicon carbide were analysed using scanning electron microscopy; control, refired and laser processed.

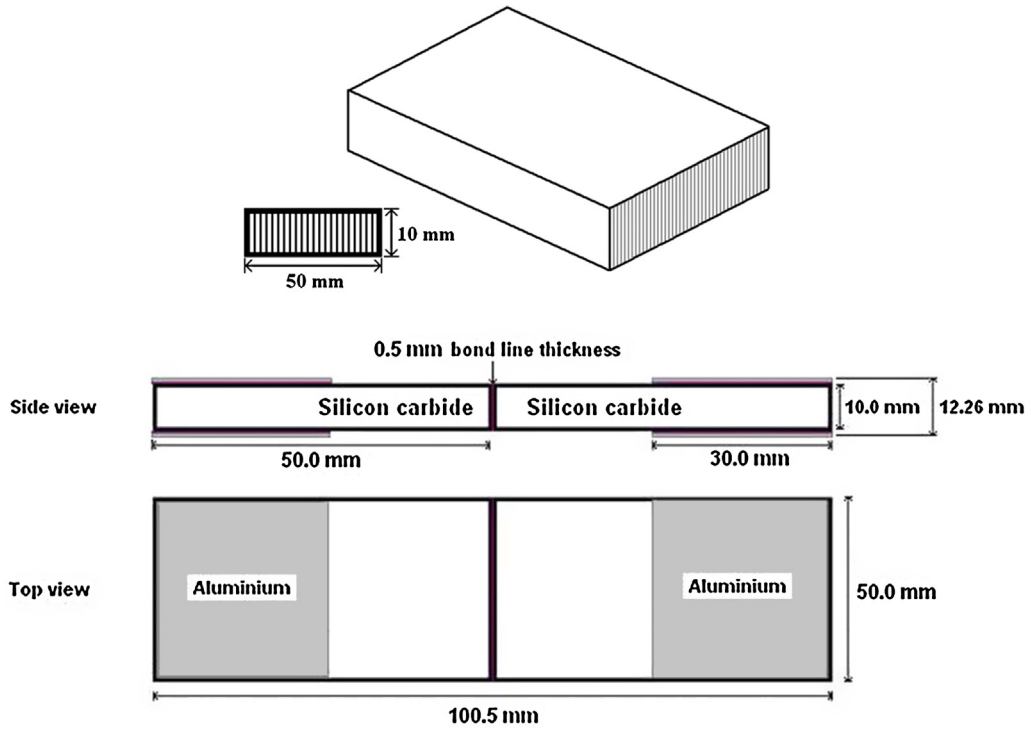


Fig. 1. A schematic diagram of the bonded butt joint including bonded aluminium tabs that will aid the gripping in the mechanical testing machine.

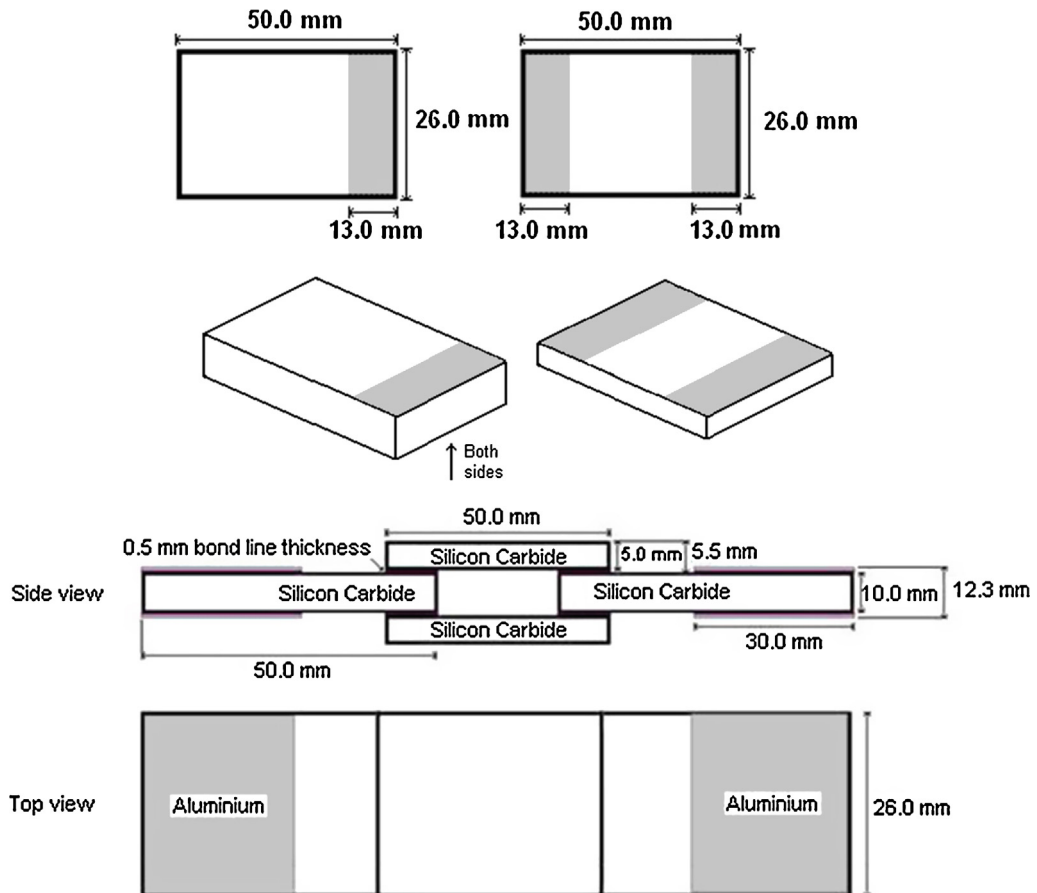


Fig. 2. A schematic diagram of the double lap shear joint including bonded aluminium tabs.

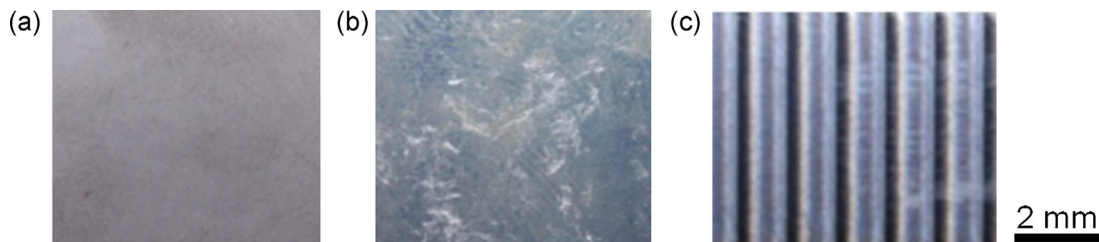


Fig. 3. Photographs of (a) control, (b) refired and (c) laser processed silicon carbide surface.

The control sample was as-fired and no further processing was carried out. A micrograph of the surface is shown in Fig. 4(a). As well as grains of silicon carbide there are regions of increased porosity which are consistent with the formation of agglomerates in the initial powder that have not broken down completely in subsequent processing.

A refired sample was produced using the control silicon carbide and refiring at 1100 °C for 1.5 h in air. A micrograph of the sample surface is shown in Fig. 4(b). Refiring the samples caused a change to the microstructure. As expected, the surface appears to have formed a glassy layer resulting in less pronounced grains. A micrograph of the refired surface is shown in Fig. 4(b).

Initial characterisation of the effect of laser processing concentrated on a single line pass with the laser. As the laser traversed along the sample it appeared to melt the surface then displace material forwards and out to the side. This results in long strands of material on the surface that terminate at the edge of the laser spot. There is also an area outside of the laser spot that shows a distinct difference from the rest of the un-exposed surface (a heat affected zone (HAZ)). The effect of laser processing on the surface is shown in Fig. 5.

As the supplied energy across the laser spot reduces towards the edges (due to a Gaussian energy distribution) it is necessary to overlap each pass of the laser in order to process an entire surface. The effect of this on the surface is shown in the micrographs in Fig. 6. It was observed with the single pass that the surface had been molten and that material had been displaced. By traversing the laser first one way then back in the opposite direction with an overlap with the first pass, the displacement of the surface is changed with the long strands of material being replaced by

protruding mounds (Fig. 6) and the surface morphology appears uniform across the laser treated area.

### 3.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was carried out on the control, refired and laser processed samples, with a focus on the silicon and oxygen content of the surfaces. Following acquisition, peak fitting allowed the oxide (Fig. 7(a)) and hydroxyl group concentration (Fig. 7(b)) to be quantified. The peak fitted results from the XPS are shown in Fig. 7.

The control surface shows that silicon and a small amount of oxygen are present in the surface (Fig. 7(a)). A very small peak consistent with the presence of hydroxyl groups was also found (Fig. 7(b)). Analysis of the refired sample showed a large silicon peak and also a large oxygen peak. This is consistent with the oxidation of silicon; note that the silicon peak has also shifted to a higher binding energy (when compared with the control) which is a characteristic of a change in bonding.

Analysis of the laser processed surface found a number of peaks for both silicon and oxygen. The silicon peak is consistent with only an oxide, and no carbide, being present in the surface. The oxygen peak was large and shows components that can be attributed to the presence of oxide, hydroxyl and a small amount of H<sub>2</sub>O. It is suggested that the surface energy of the sample may be elevated.

The atomic concentrations measured from XPS analysis are shown in Table 1. The results show the atomic percentage measured for the control, refired and laser processed samples taken from the silicon and oxygen peaks. The control sample was found to be silicon carbide with a small amount of oxide

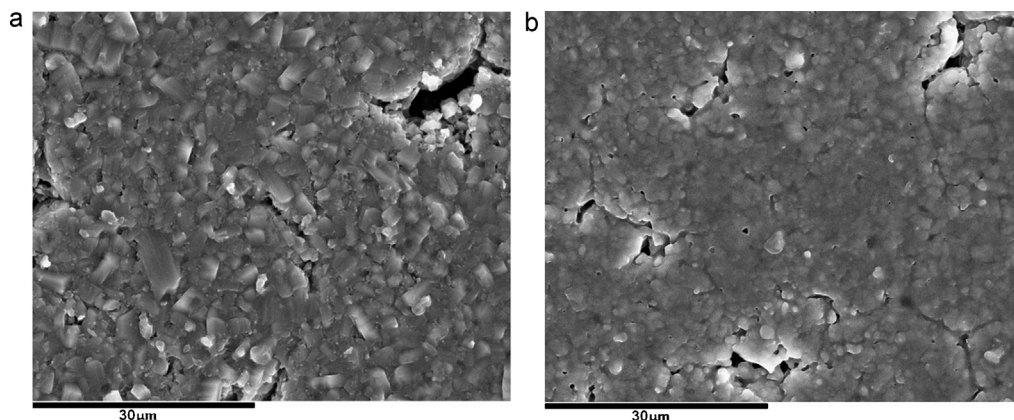


Fig. 4. Micrographs of the control silicon carbide surface (a) control and (b) refired in air at 1100 °C for 1.5 h.

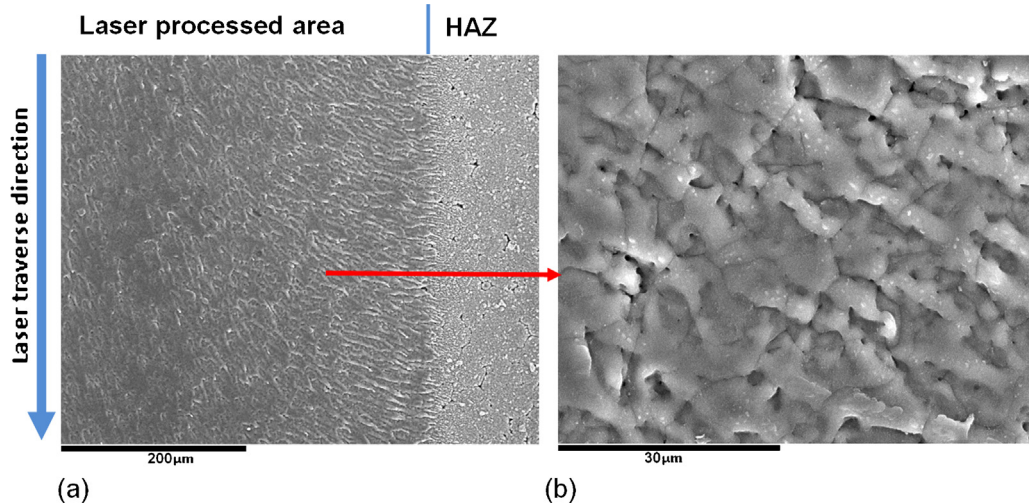


Fig. 5. Micrographs of the laser processed silicon carbide after a single pass with the laser.

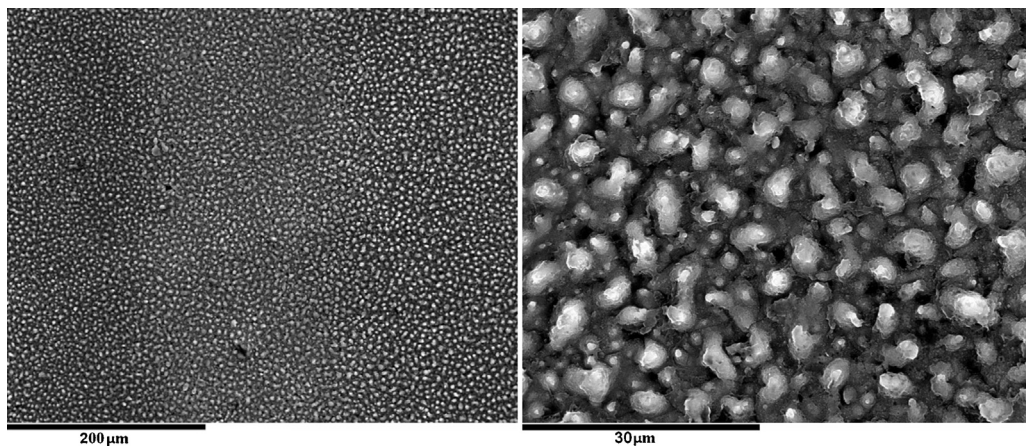


Fig. 6. Micrographs showing the laser processed silicon carbide surface after overlapping passes.

detected. The refired and laser processed sample showed no silicon carbide present, instead the surface was found to be oxidised. The hydroxyl groups were also quantified and were greatest for the laser processed sample. This shows that the laser process causes a distinct chemical difference to the surface in comparison with simply refiring the sample. To determine the effect of these chemical changes to the wettability of the surface the sessile drop technique was used. The most distinctive change in the chemistry was observed on the laser processed sample surface. The hydroxyl groups suggest an increase in the surface energy and this may lead to an improvement in the adhesive bond strength. The surface energy has been broken down into polar (acid-base) and dispersive (Van der Waals forces)

components using Owens and Wendt's method.<sup>5</sup> The results are shown in Table 2. It was found that refiring and laser processing increased the wettability and surface energy of the surface. The laser processed sample demonstrated the greatest improvement in wettability. In many instances a contact angle could not be measured for the sample indicating that it was below the limit of the apparatus ( $7^\circ$ ), so the stated value of  $10^\circ$  is an over-estimate, as it is an average of the values that could be recorded and ignores part of the data set. Despite these uncertainties it can be concluded that this sample had a high surface energy with the major contribution coming from the polar component. If the silicon carbide behaves in the same way

Table 1  
The carbide, oxide and hydroxyl concentration for each processed sample surface.

	Silicon carbide (at.%)	Oxidised silicon (at.%)	Hydroxyl (at.%)
Control	29.9	2.5	1.0
Refired	0.0	32.0	0.0
Laser	0.0	35.8	50.1

Table 2  
Contact angle and surface energy for each surface preparation technique.

Sample	Contact angle ( $^\circ$ )		Surface energy ( $\text{mJ m}^{-2}$ )		
	Water	Glycerol	Polar	Dispersive	Total
Control	$84 \pm 1$	$67 \pm 1$	3	38	41
Refired	$41 \pm 2$	$41 \pm 1$	47	10	57
Laser	$10 \pm 1$	$24 \pm 1$	71	7	78

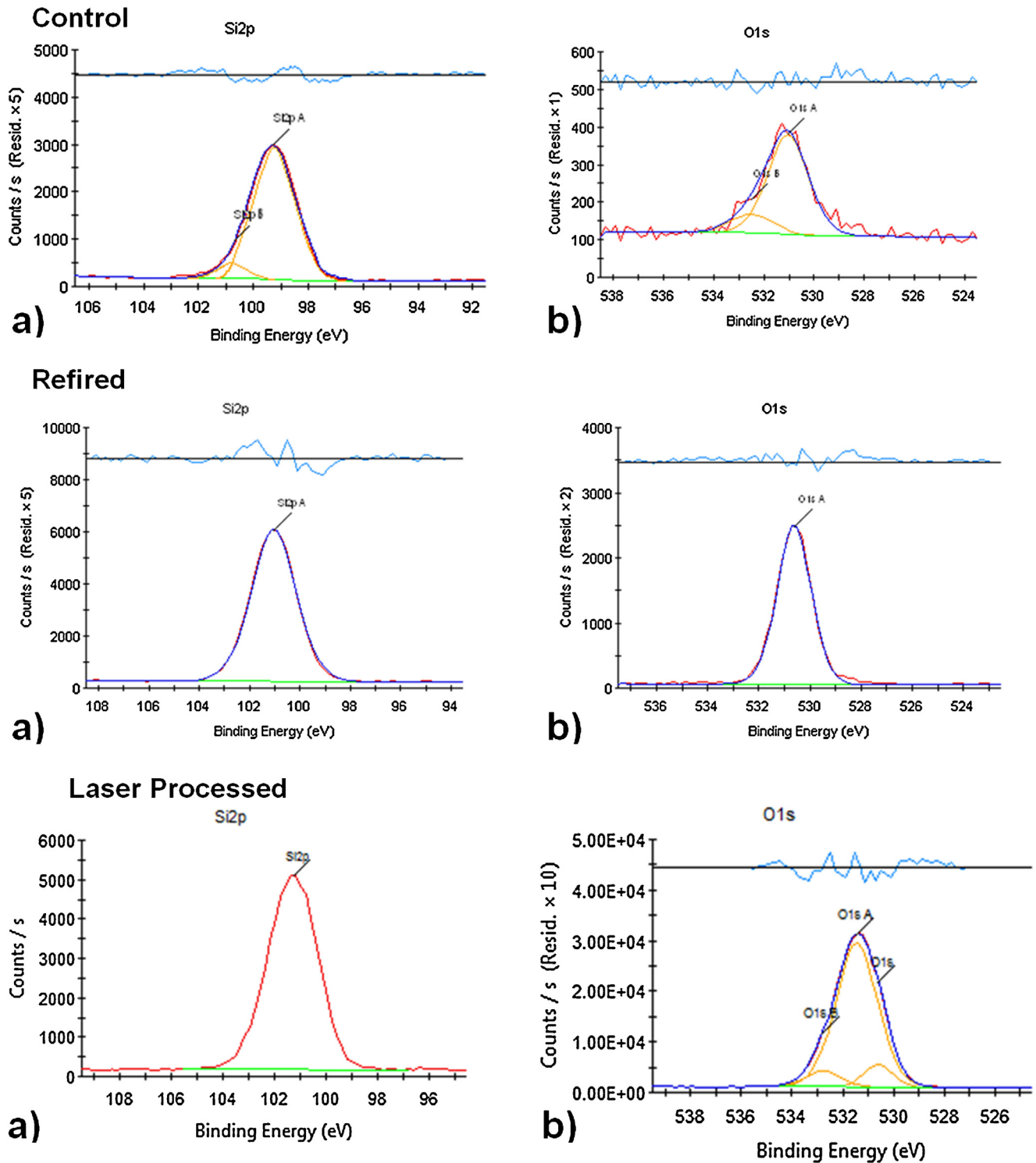


Fig. 7. Peak fitted XPS spectra showing the (a) silicon and (b) oxygen analysis for each surface preparation.

as alumina then it is predicted that the laser processed surface is expected to demonstrate the greatest improvement in adhesive bond strength.<sup>2</sup> The refired sample also demonstrated an increased wettability and hence surface energy over the control, which indicates this may also have an improved adhesive bond strength.<sup>7</sup>

#### 3.4. Quasi-static mechanical testing of joints

Mechanical testing was carried out in tension and shear. The results are shown in Table 3. In tension, the control surface has poor adhesive bond strength and the refired sample had an improved strength (18% higher). Laser processing improved the

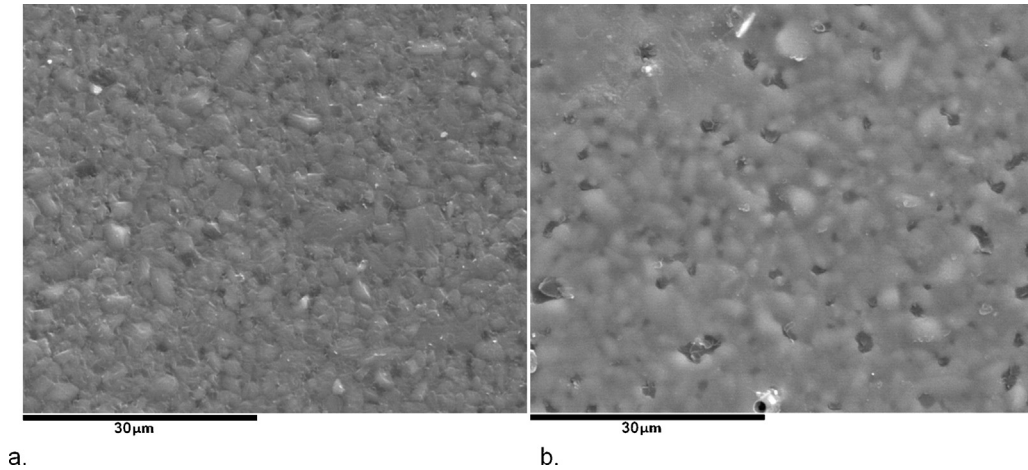


Fig. 8. A micrograph of the failed (a) control and (b) refired samples tested in tension.

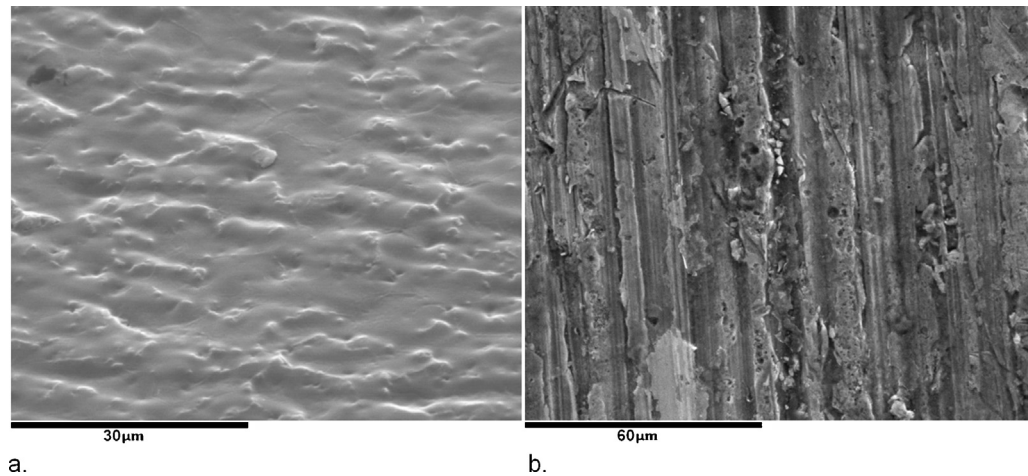


Fig. 9. Two micrographs showing the alternating crack surface of the failed laser processed tensile joint, (a) a thin layer of adhesive, (b) a thick layer of adhesive.

strength by 109%. In shear, the refired and laser processed samples demonstrated high bond strength. The failure of the joint was from failure within the ceramic and not from failure of the adhesive layer. Observation of the failed tensile joints using the control and refired surfaces with scanning electron microscopy confirmed a lack of adhesive bonded to the surface, Fig. 8. Therefore the failure was concluded to be at the interface between the adherend surface and the adhesive.

It was found that the failed tensile laser processed joint surface was entirely covered by adhesive but some areas were

thinner than others. During scanning electron microscopy the adhesive layer was thin enough to allow electrons to pass through it and some of the features of the ceramic surface were partially visible, Fig. 9(a). Other areas of the surface had a thick layer of adhesive, Fig. 9(b). The failure was confirmed to be cohesive.

Examining the failed shear control joint surface with scanning electron microscopy (Fig. 10) it was found similarly that the grains were exposed and no evidence of the adhesive layer was found. This confirms the failure was located at the interface between the adhesive and the silicon carbide surface.

The failed shear joints for both the refired and laser processed surfaces failed cohesively in the ceramic. A small area of the laser processed surface was left behind after the failure. This was analysed using scanning electron microscopy. It was found that this area had a thin layer of adhesive. This reduces the pronounced features of the laser processed surface and also shows some cracks in the thin adhesive layer, Fig. 11.

Table 3  
Mechanical testing results for each surface preparation.

Sample	Tensile strength (MPa)	Shear strength (MPa)
Control	11 ± 1	6 ± 1
Refired	13 ± 2	31 ± 2
Laser	23 ± 2	28 ± 1

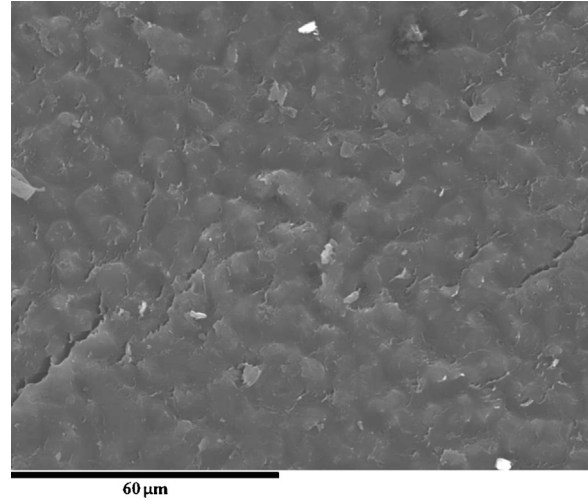
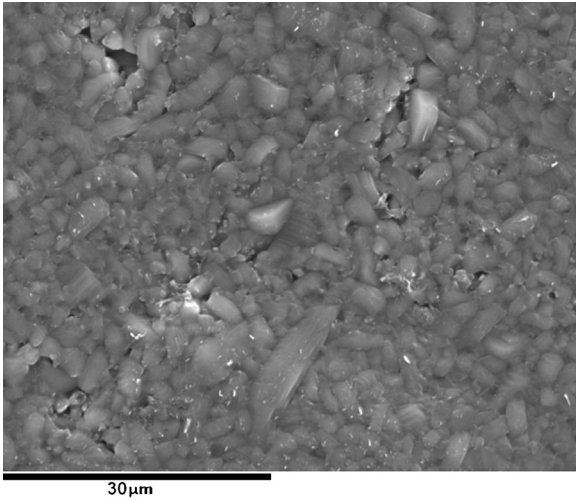


Fig. 10. A micrograph of the silicon carbide surface from the failed control double lap shear joint.

Fig. 11. A micrograph showing a thin layer of failed adhesive on top of a laser processed silicon carbide surface.

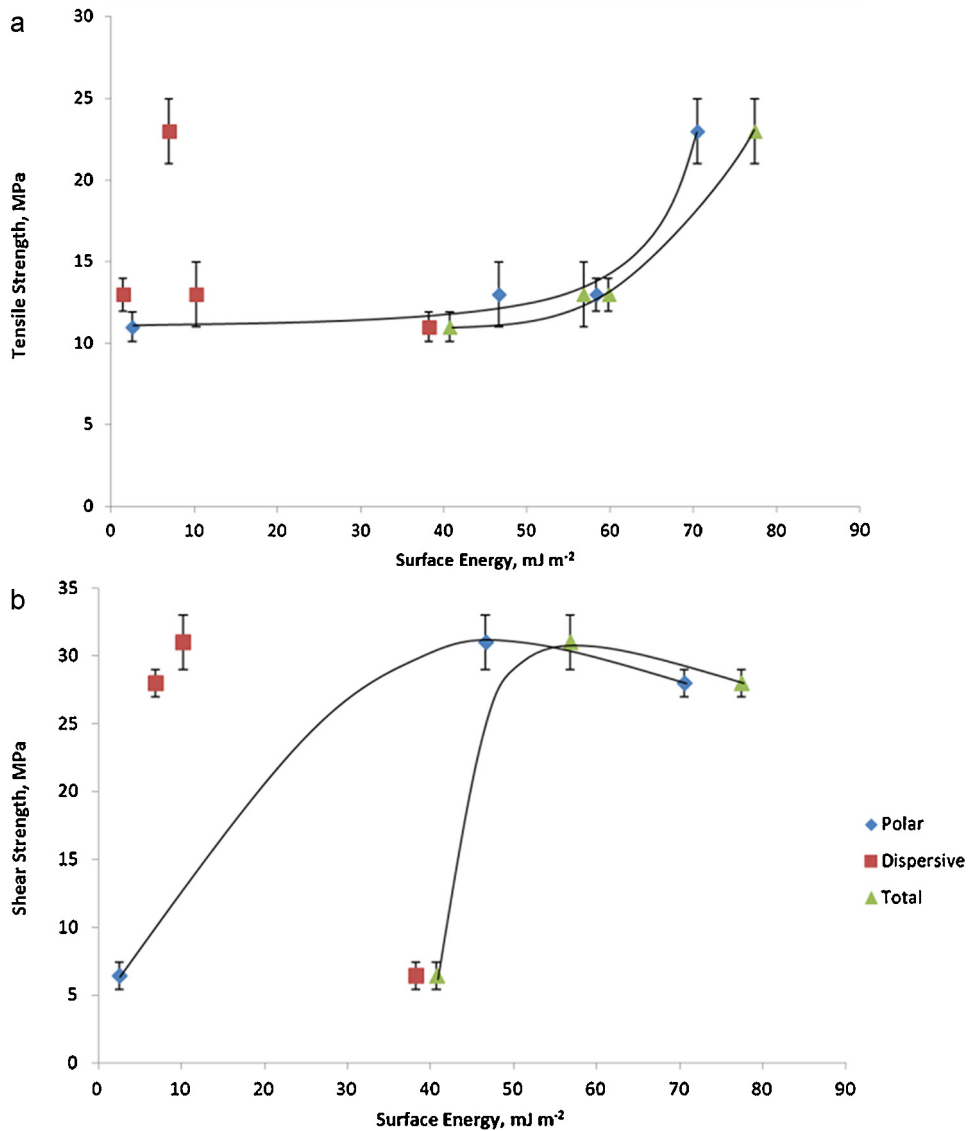


Fig. 12. Polar, dispersive and total surface energy for each sample shown with the corresponding tensile strength.



The failure of the double-lap joint within the ceramic material will be promoted by the stress concentration associated with this test geometry. This limits the achievable shear stress in the adhesive at joint failure, in contrast to the butt joint test where the test gives a better measure of the adhesive/interface strength. The use of a different shear geometry, such as the asymmetric 4 point bending test defined in ASTM C1469-10, has been proposed in other research.<sup>8</sup> The reduced stress concentration and more uniform adhesive shear stress in this geometry might enable the performance of the refired and laser processed surfaces to be distinguished. Despite the limitations of the double-lap shear joint, the results still show that the refired and laser treated surfaces perform significantly better within a joint than the control.

It was found that the adhesive bond strength increased with contact angle and surface energy, see Fig. 12. For the samples tested in shear the failure loci of the refired and laser processed joints was found to be in the ceramic and so the results appear to plateau as the strength of the ceramic is exceeded. In particular the polar component of the surface energy shows a correlation with the bond strength. These data support the hypothesis from previous work<sup>2</sup> in which it is postulated that the surface is more likely to undergo hydrogen bonding with the adhesive when the surface has a greater polar surface energy. More specifically, there is a greater opportunity to bond with the epoxy when there are more hydroxyl groups on the surface.<sup>9</sup>

#### 4. Concluding remarks

Silicon carbide was processed by refiring in air and laser processing. Both techniques caused morphological and chemical changes to the surface. The effect of these changes on the adhesive bond strength to epoxy was investigated.

Refiring silicon carbide in air at 1100 °C for 1.5 h resulted in an oxidised, glassy surface. It was also found that these changes improved the wettability through increased surface energy. The polar component of the surface energy was increased significantly and this is attributed to the oxidation of the surface. Mechanical testing showed that the adhesive bond strength was improved in both tension and shear over that found for the control samples.

Laser processing of the silicon carbide resulted in a roughened and oxidised surface. The hydroxyl group concentration was found to be much greater than for the other samples. This resulted in the greatest increase in the wettability and surface energy. The adhesive bond strength in tension demonstrated a cohesive failure of the adhesive layer which shows the maximum bond strength was achieved. In shear the strength was significantly improved for both refired and laser processed samples. The resulting failures were cohesive, but this time in the ceramic.

The observed differences between the loci of failure in the butt joints and shear joints, for both the refired and laser treated samples, indicate that the butt joint provides a more useful measure

of adhesive/interface strength. The (tensile) data from the butt joints show that the laser processed samples are stronger than both the control and the refired samples. Although the refired and laser treated samples exhibited a significant improvement in shear strength when compared to the control sample, the premature failure of the ceramic adherend meant that it was not possible to distinguish between the two treatments in this test.

In conclusion, an increased adhesive bond strength had been attributed to a chemical change and in particular the increase in the number of hydroxyl groups that resulted from laser processing. It is hypothesised that the increase in the concentration of the hydroxyl groups has allowed more hydrogen bonds to form between the adhesive and the ceramic surface, which has in turn lead to an improvement in the strength of the joint such that it is limited by the strength of the ceramic or epoxy but not the interface. A similar finding was hypothesised with previous work using a similar processing technique for alumina. The experimental results showed that the hydroxyl concentration had led to an increase in the surface energy which had caused an increase in the strength of the adhesive joints. To further this research ballistic testing is needed to establish that the benefits seen in quasi-static mechanical testing are realised in practice.

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#### References

- 1 Zaera R, Sánchez-Sáez S, Pérez-Castellanos JL, Navarro C. Modelling of adhesive layer in mixed ceramic/metal armours subjects to impact. *Compos A Appl Sci Manuf* 2000;31:823–33.
- 2 Harris AJ, Vaughan B, Yeomans JA, Smith PA, Burnage ST. Surface preparation of alumina for improved adhesive bond strength in armor applications. *Adv Ceram Armor VIII Ceram Eng Sci Proc* 2012;33(5): 149–60.
- 3 Yamamoto T, Hijikata Y, Yaguchi H, Yoshida S. Oxide growth rate enhancement of silicon carbide (0001) Si-faces in thin oxide regime. *Jpn J Appl Phys* 2008;47(10):7803–6.
- 4 Neri F, Barreca F, Sebastiano T. Excimer laser ablation of silicon carbide ceramic targets. *Diamond Relat Mater* 2002;11:273–9.
- 5 Owens DK, Wendt RC. Estimation of the surface free energy of polymers. *J Appl Polym Sci* 1969;13:1741–7.

- 6 Sciti D, Melandri C, Bellosi A. Excimer laser-induced microstructural changes of alumina and silicon carbide. *J Mater Sci* 2000;35: 3799–810.
- 7 Levallois F, Helt S, Baziard Y, Petit JA. Structural adhesive bonding of sintered silicon carbide (SSiC) subjected to thermal treatment in air atmosphere. *J Adhes Sci Technol* 1999;13(2):237–87.
- 8 Ferraris M, Ventrella A, Salvo M. Shear strength measurement of AV119 epoxy-joined SiC by different torsion tests. *Int J Appl Ceram Technol* 2013:1–8.
- 9 Leadley SR, Watts JF. The use of monochromated XPS to evaluate acid-base interactions at the PMMA/oxidised metal interface. *J Adhes Sci* 1997;60:175–96.