SURFACE PREPARATION OF ALUMINA FOR IMPROVED ADHESIVE BOND STRENGTH IN ARMOUR APPLICATIONS

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ABSTRACT

Surface treatments of alumina have been investigated with the aim of increasing the strength of the bond created between the alumina and a toughened epoxy adhesive. Four surface conditions have been assessed: as-fired; grit blasted; and krypton fluoride excimer laser treated under two sets of conditions. Compared with the as-fired surface, the grit blasted surface was rougher with poorer wettability, probably due to surface contamination. It was found that the laser treatments removed some of the sintering additives and caused rounding of the alumina grains, slightly increasing the surface roughness. Further, the laser treatment led to an increased surface energy and wettability, which has been linked tentatively to an observed increase in the hydroxyl groups on the surface. The adhesive bond strength was assessed by testing joints in tension and shear. It was found that the laser treated surfaces demonstrated slight improvements in bond strength, with a cohesive failure of the adhesive in tension for surfaces subjected to one of the two laser treatments, compared with failure at the interface for the as-fired, grit blasted and other laser treated samples in tension and for all samples in shear. Thus, it has been demonstrated that modifications to the surface of alumina can result in mechanical and chemical changes which affect roughness, wettability, bond strength and the locus of failure.

INTRODUCTION

Ceramic based armour systems feature on many military vehicles. The impact of a projectile on the ceramic layer initially causes a compressive stress wave to travel through the ceramic. When this reaches the back face of the ceramic it is normally reflected back as a tensile stress wave, which causes the ceramic to fracture. The intensity of this tensile stress wave depends on how much energy is reflected from the back face and how much energy is transferred to the adhesive layer, bonding the ceramic to the vehicle. The degree of mismatch in the impedance of the adhesive layer and the ceramic affects the proportions of the incident energy that are transferred and reflected¹.

With an epoxy resin there is less mismatch in mechanical impedance, than say with polyurethane, and thus more energy will be transferred into this layer¹. Additionally, the epoxy layer is stiffer and will reduce the degree of bending experienced by the ceramic layer during impact¹. As the interface between the epoxy resin and the ceramic will be subjected to stress, a surface that has not been prepared for adhesive bonding may fail prematurely.

The chemistry of the ceramic surface can influence the adhesive bond strength by controlling the type and number of bonds produced. The chemical bonds formed between an epoxy resin and alumina are termed acid – base interactions. The adhesive has a number of basic and acidic sites which can bond with the hydroxyl groups located at the surface of the alumina, either via hydrogen bonds between the hydrogen atom of the hydroxyl group and a basic site in the adhesive or between the oxygen of the hydroxyl group and an acidic site in the adhesive².

The adhesive can also join to the surface mechanically. The roughness of the surface can have positive and negative contributions to the performance. Positive factors are the consequently increased surface area for bonding, mechanical interlocking of adhesive and adherend and crack deviation from the interface during joint failure³⁻⁷. Negative factors are the reduction in wettability due to trapped air in voids and a concentration of stress due to areas of poor bond strength^{3, 4, 8}.

Surface preparation can modify the characteristics of the surface and may enhance the mechanical and chemical interaction between the adhesive and alumina. Grit blasting is a commonly used technique for roughening the surface but this can have a downside in that it may introduce contamination⁹. Laser ablation of ceramic materials has been found to cause chemical changes to the surface and when investigated these have resulted in improved wettability¹⁰⁻¹³

There is a need to improve armour systems and this work is part of a larger study aimed at optimising bond strengths between ceramics and backing systems. The objective of the current study was to investigate the effects of various surface preparations on the strength of the adhesive bond formed between alumina and epoxy resin, when tested under quasi-static loading.

MATERIALS

A 96 wt% Al_2O_3 , produced by liquid phase sintering by Anderman Ceramics Ltd. under the product name EA96, was supplied as blocks of dimensions 10.5 mm x 30.2 mm x 75.0 mm and 10.5 mm x 30.2 mm x 45.0 mm with a 1 mm 45° chamfer on the 10.5 mm long edges. The cuboids were received as-fired with the chamfer in place before the firing. The as-fired surface was used for the control experiments. For tensile testing, the 10.5 mm x 30.2 mm faces were subjected to the surface treatment and were subsequently bonded together to form a butt joint. Two smaller blocks were used with two larger blocks to form the double lap shear joints, with two surface treated and subsequently bonded areas per joint of 12.7 mm x 30.2 mm.

The joints were made using a two-part rubber toughened epoxy adhesive, supplied by Henkel under the product name EA 9309.3NA. It contained 0.130 mm diameter glass beads to control the bond line thickness. The resin was mixed with the hardener with a volume ratio of 100:22 and was cured at room temperature for 5 days prior to mechanical testing.

EXPERIMENTAL METHODS

Four different alumina surfaces were investigated: control, grit blasted, laser setting A and laser setting B. The control surface was used in the as-fired state. Grit blasting was carried out using an air powered hand held gun using alumina erodent. The gun had a 3 mm diameter orifice and traversed the area to be bonded for 30 seconds, with the erodent impacting normal to the ceramic surface. A krypton fluoride laser was used to ablate surfaces using the settings defined in Table I. The laser was rastered over the area that was to be bonded. Laser setting A overlapped the previous ablated line by half its width. A photograph of the laser ablation process is shown in Figure 1.

Table I. The settings used for the laser processing.

Laser Setting	Heat Flux	Repetition Rate	Pulse Length	Overlap
A	3.2 MW m^{-2}	100 Hz	25 ns	50%
B	6.4 MW m^{-2}	100 Hz	25 ns	None

Figure 1. A photograph of a krypton fluoride laser traversing the surface of alumina.

The prepared surfaces were characterised using a number of complementary techniques. For scanning electron microscopy (SEM) the samples were prepared by cutting to a suitable size, mounting and then coating with a thin layer of sputtered gold for imaging or carbon for chemical analysis. A Hitachi 3200N microscope operated at an accelerating voltage of 25 kV was used for secondary and backscattered imaging and for energy dispersive X-ray (EDX) analysis.

To obtain more surface-specific chemical information, X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCALAB Mk II, with a non-monochromated Al K α source, which gives an analysis depth of approximately 5 nm. This technique is also more reliable with regards to the measurement of carbon in comparison to EDX spectroscopy.

Quantitative assessments of the roughness of the surfaces were made using a Veeco Dektak 8 profilometer on an air cushioned table. A 5 μm radius diamond stylus was used. Two different types of scans were used: single line scan and map scan. A map scan is built up from a number of lines spaced 3.175 μm apart. The settings for each are shown in Table II.

Table II. The settings used for the profilometry.

	Single line scan	3D map scan
Length of scan	2000 μm	1000 μm
Duration of each scan line	30 s	10 s
Resolution across length	0.222 μm	0.333 μm
Uncertainty of height measurement	0.060 μm	0.060 μm
Stylus force	5 mg	5 mg

The wettability of the surface was measured using the sessile drop technique. A computer controlled syringe with needle was used to place a drop of liquid onto the surface. The resulting contact angle between the drop and surface was measured to determine the wettability.

Quasi-static mechanical testing was carried out on butt joints to measure the tensile strength and double lap joints to measure the shear strength. Prior to bonding the area to be bonded was wiped clean with methanol. The adhesive was applied and left to cure for a minimum of five days at room temperature. At least five samples were tested for each combination of surface treatment and joint geometry. ASTM D2094-00 was followed for the butt joint testing, using an Instron 5500R testing machine in tension with a 100 kN load cell and a cross-head displacement of 1.0 mm min⁻¹. For the double lap shear joints, five samples were tested for surface treatment and testing arrangement, ASTM D2094-00 was followed, using an Instron 8800 testing machine in compression with a 50 kN load cell and a cross-head displacement of 1.0 mm min⁻¹. The displacement data were corrected to account for the compliance of the testing machines and the alumina samples.

RESULTS AND DISCUSSION

Surface Morphologies

SEM was used to examine the surfaces of the alumina after the various treatments. Representative micrographs are shown in Figure 2. The as-received surface is reasonably uniform, with clusters of individual grains interspersed with some porosity. Grit blasting the sample has caused a lot of damage and appears to have removed a significant number of grains. Laser ablation of the surface has produced a distinct effect. Laser setting A caused the grain boundaries to recede, most probably through vaporisation of the intergranular glassy phase. Some partial merging of grains can be observed. Laser

setting B has resulted in the grains being melted and merged completely in places. Micro-cracks could be observed. These are probably due to the thermal shock caused by the rapid heating and cooling associated with laser setting B.

Figure 2. Secondary electron scanning electron micrographs showing the surface of alumina following surface preparation: a) control (as-fired), b) grit blasted, c) laser setting A and d) laser setting B.

Profilometry

The maximum (R_{max}) and mean (R_a) roughness values were obtained. The results from the line scans are shown in Table III.

Table III. The results from the profilometry.

	R_a x (μm)	R_a y (μm)	R_a y laser centre (μm)	R_{max} x (μm)	R_{max} y (μm)	R_{max} y laser centre (μm)
Control	0.6 ± 0.1	-	-	4.6 ± 0.6	-	-
Grit blasted	1.8 ± 0.2	-	-	15 ± 1	-	-
Laser setting A	1.2 ± 0.1	1.3 ± 0.2	0.9 ± 0.2	9 ± 1	9.3 ± 0.8	5.6 ± 0.2
Laser setting B	1.3 ± 0.1	1.4 ± 0.1	0.91 ± 0.08	11.8 ± 0.6	10 ± 1	8 ± 1

In agreement with the observations made by SEM, grit blasting has increased the mean and maximum roughness values. For the laser ablated surfaces, the measured roughness value depends on the direction in which the profilometry scan was made. The x direction is perpendicular to the laser traverse direction, whereas the y direction is parallel to the line of travel of the laser. In all cases, the roughness has increased, with respect to the control value, but not as much as for the grit blasted surface. Laser setting A for which the path of the laser overlaps the previous traverse by 50% produces a more uniform surface than laser setting B, for which there is no overlap, as shown in the 3D maps of the laser ablated surfaces in Figure 3.

Figure 3. 3D map built up using multiple line scans of the surface for: a) laser setting A (scanned area $\sim 700 \mu\text{m} \times 500 \mu\text{m}$) and b) laser setting B (scanned area $\sim 500 \mu\text{m} \times 200 \mu\text{m}$).

Energy Dispersive X-Ray Spectroscopy

This technique was used to estimate the composition of the ceramic and the results are presented in Table IV, with elemental compositions converted to compound compositions, assuming stoichiometry. Comparing the analyses of the as-received control sample and the fracture surface showed that the as-received surface is alumina-rich. Grit blasting appears to have removed enough of the surface to expose the bulk material.

During laser ablation a plasma was observed. This suggests some vaporisation of the sample. Micrographs of the laser treated samples also showed that the grains were more dominate, presumably due to removal of the glassy phase. EDX analysis confirms that some elements have been removed in both cases, with laser setting B, which has the higher power, removing more species.

Table IV. The results from the EDX analyses of the surfaces (all results in wt.%).

	Control	Fracture	Grit blasted	Laser setting A	Laser setting B edge	Laser setting B centre
Al_2O_3	98.9	96.7	95.9	98.6	98.8	98.9
CaO	0.1	0.2	0.3	0.2	-	-
MgO	0.3	0.4	0.8	-	0.3	-
Na_2O	0.1	0.5	0.7	-	-	-
SiO_2	0.6	2.2	2.4	1.2	0.9	1.1

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was used to obtain very surface-specific chemical information and the results are shown in Table V. The greater sensitivity of this technique, in comparison to energy dispersive x-ray spectroscopy, shows that elements have not been completely removed, although the concentrations have been reduced.

Table V. The results from the XPS analyses of the surfaces (all results in at.%)

	Control	Grit blasted	Laser setting A	Laser setting B
Aluminium	10.8	10.3	26.5	29.5
Carbon	19.1	36.3	18.5	18.4
Calcium	1.7	1.0	0.2	0.1
Magnesium	3.1	-	1.4	1.1
Sodium	5.6	1.6	2.0	1.1
Oxygen	51.4	40.8	48.1	48.8
Silicon	8.3	4.5	1.9	1.0
Other	-	5.5	-	-

The spectra from the control and two laser ablated samples were peak fitted to determine the contribution to the oxygen concentration from various sources. The results are shown in Figure 4. It is apparent that the width of the oxygen peak is much greater for the two laser ablated samples. Further, the hydroxyl group concentrations of these samples were higher than the control sample (see Table VI).

Figure 4. Peak fitted oxygen results from the x-ray photoelectron spectroscopy of alumina surfaces: a) control (as-fired), b) laser setting A and c) laser setting B.

Table VI. The contributions to the oxygen spectra from the XPS analyses of the alumina samples (all results in at.%).

	Control	Grit blasted	Laser setting A	Laser setting B
Oxygen (O ²⁻)	41.8	27.2	19.0	20.2
Oxygen (OH)	9.6	13.7	22.9	22.9
Higher order oxygen (H ₂ O)	-	-	6.3	5.6

Wettability

The sessile drop technique has been carried out to measure the wettability of the surface. Contact angles between the alumina surface and Milli-Q water or glycerol have been measured and are shown in Table VII. The contribution of surface roughness from the grit blasted data has been removed by application of the Wenzel correction⁷.

Table VII. Results from the sessile drop technique.

	Distilled Water Contact Angle, °	Change	Glycerol Contact Angle, °	Change
Control	45 ± 1	-	55 ± 1	-
Grit blasted	86 ± 1	91.1%	96 ± 1	74.5%
Grit blasted (Wenzel correction)	80 ± 1	77.8%	-	-
Grit blasted ultrasonic cleaned	82 ± 2	82.2%	-	-
Grit blasted ultrasonic cleaned (Wenzel correction)	66 ± 2	46.7%	-	-
Laser ablated setting A	14.5 ± 0.5	-67.7%	30 ± 1	-45.5%
Laser ablated setting B	31 ± 1	-31.1%	32 ± 2	-41.8%

The grit blasted surface has a larger contact angle than the control surface, meaning that the wettability has been reduced. The XPS showed a high concentration of carbon, which is indicative of contamination (despite a solvent wipe prior to analysis). Ultrasonic cleaning of the sample showed that the wettability could be improved although it was still less than for the control sample, even after correcting for surface roughness.

Laser processing of the samples has increased the wettability. In particular, the wettability of the surface prepared with laser setting A shows the greatest improvement (lowest angle) of all of the samples tested. To investigate this further, glycerol was placed on the surface of the samples and the contact angles were measured to obtain the polar and dispersive contributions to the surface energy. Laser setting A was the only surface treatment to give a greater polar surface energy than the control sample (74 compared with 62 mJ m⁻²); a higher value indicates a greater possibility of increased acid-base interactions (increased amounts of hydrogen bonding in this case) and hence might be associated with increased bond strength.

Mechanical Testing

Quasi static mechanical testing has been carried out on butt joints to measure the tensile strength and the results are shown in Table VIII. The strength of the grit blasted joint was lower than the control joint. This is probably related to the contamination and the subsequent poor wettability. The laser ablated surfaces have shown slightly greater tensile strengths than for the control sample, which might tentatively be linked to the improved wettability. Further, the laser setting A surface treatment appears to have affected the locus of failure, changing it from interfacial to a more desirable cohesive failure.

Table VIII. Results from the mechanical testing in tension.

Sample	Ultimate Tensile Strength, MPa	Change	Locus of Failure
Control	31 ± 3	-	Interfacial
Grit blasted	28 ± 2	-9.7%	Interfacial
Laser ablated setting A	36 ± 1	16.1%	Cohesive
Laser ablated setting B	33 ± 1	6.5%	Interfacial

The shear strengths of the joints are shown in Table IX. Whilst the grit blasted surface again has a reduced joint strength, there is no appreciable improvement following laser treatment. For both testing regimes, the peak values exceed the nominal values supplied by the manufacturer of the epoxy adhesive (31.0 MPa and 28.9 MPa for tension and shear, respectively).

Table IX. Results from the mechanical testing in shear.

Sample	Ultimate Shear Strength, MPa	Change	Locus of Failure
Control	30 ± 1	-	Interfacial
Grit blasted	25 ± 1	-16.7%	Interfacial
Laser ablated setting A	32 ± 1	6.7%	Interfacial
Laser ablated setting B	28.6 ± 0.3	-4.7%	Interfacial

There appears to be a correlation between the strength of the joint and the wettability of the surface (when using Milli-Q water) (see Figure 5).

Figure 5 Bond strength as a function of contact angle in the sessile drop experiment.

Further, returning to the surface energy data from the wettability results, it can be seen that the polar component is the major contributor to the total surface energy and that there is a tentative correlation between bond strength and polar surface energy (figures 6 and 7). Laser setting A produces the surface with the highest polar surface energy and this appears to result in slightly higher bond strengths and, more importantly, cohesive rather than interfacial failure in tension. Thus, further investigation of laser surface treatments, to try to find an optimum set of conditions, might be a promising line of investigation.

Figure 6. Tensile bond strength as a function of surface energy.

Figure 7. Shear bond strength as a function of surface energy.

CONCLUDING REMARKS

The mechanical and chemical changes to alumina surfaces following surface treatments, and the subsequent effect on the strength of the bond between the alumina and an epoxy resin, have been investigated. Grit blasting and laser ablation of the surface have both caused the roughness to increase, albeit through different mechanisms. Grit blasting removed material by fracture whereas laser ablation removed material through vaporisation. Further, the heating associated with the laser treatments resulted in the alumina grains being rounded and merged in places.

In terms of chemical changes to the surface, the grit blasting technique introduced contamination in the form of excessive carbon, which resulted in poor wettability and decreased the adhesive bond strength. Laser ablation resulted in the preferential removal of the glass-forming sintering aids, normally located intergranularly. XPS analysis showed that the laser treated surfaces had a greater concentration of hydroxyl groups than the as-received surface. Further, the laser treated surfaces showed an increase in wettability. Of the two laser treatments, the lower power one (setting A) resulted in a surface with a greater surface energy, and greater contribution of polar surface energy to that total, whereas the higher power setting had the same total surface energy but lower polar energy than the control surface.

Although the mechanical testing of the joints showed that the strengths were not altered significantly by the various surface treatments, there was some indication that the laser treated surfaces produced slightly stronger joints, with the laser setting that gave the highest surface energy also giving the stronger joints and the only example of cohesive, as opposed to interfacial, failure. Thus, it is suggested that surface treatments that increase the concentration of hydroxyl groups promote bonding to the epoxy resin, although the relationship between processing variables and performance needs further investigation.

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