Surface characterization and compositional evaluation of a fibre laser processed silicon nitride (Si3N4) engineering ceramic

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Compositional Evaluation and Characterization of a Fibre Laser Processed Silicon Nitride Engineering Ceramic

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Abstract

Fibre laser surface treatment of a cold isostatic pressed (CIP) Si₃N₄ engineering ceramic was performed using various processing gas compositions to observe the changes on and within the surface of the engineering ceramic; in particular, surface topography, material removal, chemical composition, surface hardness and distribution of the heat affected zone (HAZ). Surface melting and distribution of the melt zone were found with all fibre laser radiated samples, as well as surface finish and the material removal varying with changes in the gas composition. Fibre laser processing of the Si₃N₄ with N₂ assist gas proved to be the most effective combination for effecting micro-structural changes as small sized elongated grains were found as a result of the faster cooling rate. Consequently, O₂, ambient air and compressed air produced considerable amount of morphological changes. This was found to be due to de-composition, material removal of the upper most surface layer and the Si₃N₄ ceramic’s interaction with the assist gas compositions and the atmosphere at elevated temperatures. Maximum material removal was found when O₂ assist gas was employed, taking in account of the O₂ generating an exothermic reaction and consequently excessive heating. The compositional analysis revealed a chemical change occurring within all fibre laser radiated surfaces of the Si₃N₄ engineering ceramic as fibre laser radiated Si₃N₄ was transformed to SiO₂.

Keywords: Fibre laser, Si₃N₄ engineering ceramic, processing gases, material removal, surface finish, chemical composition.
1. Introduction

Engineering ceramics have found wide usage in various industrial sectors. In particular, applications in the aerospace and automotive industry comprehensively use engineering ceramics because of their advantageous thermal and mechanical properties when compared to metal and alloys, as well as high wear resistance and low co-efficient of friction which are particularly ideal for high speed bearings, exhaust valves and clevis pins. Turbo charger rotors, pistons, hybrid bearings comprising of a Si$_3$N$_4$ casing and ZrO$_2$ or Si$_3$N$_4$ balls and a metallic casing are regularly used due to the ceramics extended functional life, better performance and efficiency in comparison to metallic components. Good thermal insulation and high melting points have enabled engineering ceramics to be readily used for many components within a gas turbine engines. Engineering ceramics also have high acoustic damping capacity to reduce engine noise and are operational in underwater environment due to their corrosive resistance and environmental stability [1-5]. The die electric properties of the ceramics also make them applicable for missile radomes.

Laser surface treatment in comparison to the conventional surface processing techniques offers competitive advantages. Those are; high speeds, shorter processing times, deep penetration and accuracy. Such advantages are an asset to the manufacturers and allow them to achieve better tolerances, reduced production costs, shorter lead times as well as just in times delivery. Laser surface treatments can be a superior technique for processing of engineering ceramics for a glazing application as an example which can potentially improve the surface finish as well as the aesthetics of the ceramic component/product. Another example where laser processing of ceramics can be effective is by applying the laser shock processing technique which is successfully being used for enhancing the wear rate; co-efficient of friction; hardness and to reduce component mass of metals and alloys [6-8]. This
is achieved by forming shockwaves within the metals/alloys and inducing a compressive residual stress layer. Similar effect can also be achieved with ceramics whereby the functional life of the ceramic components/products can be enhanced if the effects of the laser-ceramic interaction are further understood [9].

Several previous investigations have revealed interesting results when using industrial lasers (high powered) to surface treat refractory ceramics. Previous work by Wang et al. [10-12] were conducted using refractory ZrO$_2$ and Al$_2$O$_3$ ceramics to investigate the microstructural characteristics after melting of the ceramic substrate by using a CO$_2$ laser. Surface cracking was found in the treated area, but changes to the laser parameters led to modified surface composition and morphology. Further work was conducted by Wang et al. [13] using an Nd: YAG laser to surface treat refractory ceramics by adding nano-particles to modify the surface density and the corresponding microstructure. The laser treatment was conducted prior to and after adding the nano-particles. Results linking to their previous investigations [10-12] showed dendrites that were much finer after the addition of the nano-particles. Triantafyllidis et al. [14] performed an investigation using double laser sources: a CO$_2$ and a high powered diode laser (HPDL), to investigate the possibility of generating a crack-free surface on refractory Al$_2$O$_3$ ceramics by balancing out the thermal gradient and elongating the solidification rate. The results presented crack- and pore-free surfaces along with deeper penetration in comparison with the single laser processing technique. Further work by Triantafyllidis et al. [15] demonstrated laser cladding of thin sheets of Al$_2$O$_3$ by employing a high powered CO$_2$ laser. Substantial grain growth was found on the surface of the treated ceramics along with increase in the grain size.
Variation in employing processing gases has been the subject of several studies. The effect of laser processing of metals using various shield gases has extensively been investigated [16-20]. Minami et al. [21-22] used various processing gases assisted by a HPDL to remove ceramic tile grout. Compressed air, Ar, N$_2$, and O$_2$ were used to study their effects on the microstructure, material removal and thermal changes. The findings revealed O$_2$ to be the most effective gas as it maximized the materials removal rate. Lawrence et al. [23] used O$_2$, Ar, and He to study the influence of concrete surfaces from employing a HPDL. The results showed appearance of porosity with all of the gases used. Minimal surface cracking and porosity was found from using O$_2$ in comparison with Ar and He. Better interaction with O$_2$ was also reported in order to generate sufficient heat and fluidity within the melt pool in comparison to Ar and He. This was due to the faster cooling rate occurring with the Ar and He which resulted in trapping the gas bubble and maximized the possibility to form surface cracking and porosity in contrast with using the O$_2$ processing gas.

A number of researchers have also worked with laser surface treatment of ceramics to identify the effects of laser beam on material properties, such as the frictional wear [24] and the flexural strength of Si$_3$N$_4$ [25]. Research by Malshe et al. [25] investigated the possibility of eliminating imperfections within Si$_3$N$_4$ ceramics by applying the CO$_2$ laser which executed a square beam. The findings showed that the fracture behaviour was considerably affected by surface treating Si$_3$N$_4$. Fracture origins were reduced and bending strength was improved. A four point bending test, fractographic analysis and scanning electron microscopy (SEM) were used to analyse the materials surface integrity. The material was also reported to have undergone reflowing and rebinding process. These workers assumed that the surface integrity was improved by the secondary glassy phase changing to YSiA1ON because of the processing temperature during the CO$_2$ laser treatment was measured to be higher than the
stable equilibrium upper temperature of the secondary glassy phase. Shukla and Lawrence [26] investigated the effects of the fibre laser surface treatment on the fracture toughness of ZrO₂ engineering ceramics in their previous investigation. Results showed changes in the fracture toughness within the ZrO₂ from the fibre laser radiated surface. It was concluded that a change in the fracture toughness occurred due to softening of the fibre laser radiated zone and the possible change in the composition.

Despite the use of CO₂, Nd:YAG and HPDL to process various technical ceramics; no other investigation except the one of Shukla and Lawrence [26] has been done hitherto by employing a fibre laser to process engineering ceramics. This study focuses on the laser-material interaction occurring during the fibre laser surface treatment of a Si₃N₄ engineering ceramic in various processing gas environments: compressed air; O₂; Ar; N₂ and ambient air (no assist gas). The investigation comprised of observing the surface morphology, changes in the composition, the material removal, the topography, the surface hardness and the heat affected zone (HAZ). The fibre laser was used for the surface treatment due to several advantages despite the operating wavelength of the fibre laser being in the same regions as that of the Nd:YAG laser. Those advantages are: a better beam quality, smaller spot size, depth of field (longer focal length), depth of penetration, high brightness and better stability. The beam quality of the fibre laser is (M² = 1.2) which would execute high power density in a same spot size in comparison to the Nd:YAG laser beam, this in turn, is likely to produce produces better interaction leading to deep penetration into the ceramic. The longer focal length allows the fibre laser to operate from longer distances which is ideal to avoid backscatter and beam reflection. Lastly, the high brightness offered by the fibre laser in comparison to that of the Nd:YAG laser is the most advantageous as it induces more photon energy by executing higher power per wattage which inherently reduces the cost of the
surface treatment also and has a real potential to produce better interaction zone in comparison to that of the Nd:YAG laser.

2. Experimental Methodology

2.1. Background of test materials

The material used for the experimentation was cold isostatic pressed (CIP) Si$_3$N$_4$ with 90% Si$_3$N$_4$, 4% Yttria, 4% Al$_2$O$_3$ and 2% other, unspecified content by the manufacturer (Tensky International Company, Ltd.). Each test piece was obtained in a bulk of 10 x 10 x 50 mm$^3$ with a surface roughness of 1.56$\mu$m (as-received from the manufacturer). This was to reduce the laser beam reflection as the well polished shinier surfaces of the ceramic would reduce beam absorption. The experiments were conducted in ambient condition at a known atmospheric temperature (20°C). All surfaces of the Si$_3$N$_4$ to be treated were marked with black ink prior to the laser treatment to enhance the absorption.

2.2. Fibre laser surface treatment

A 200 W fibre laser (SP-200c-002; SPI, Ltd.) emitting a continuous wave (CW) mode beam at a wavelength of 1.075 $\mu$m was used in this work. The focal position was kept to 20 mm above the work-piece to obtain a 3 mm spot size. The processing gases used were O$_2$, N$_2$, Ar, compressed air as well as ambient air (no gas) supplied at a flow rate of 25 l min$^{-1}$. Programming of the laser was conducted using an SPI software which integrated with the laser system. A 50 mm line was programmed using numerical control (NC) programming as a potential beam path which was transferred by .dxf file. The nozzle indicated in Figure 1 was removed for all experiments. To obtain an operating window, trials were conducted at the fixed spot size of 3 mm and by varying the power between 25 and 200 W and varying the traverse speed between 25 and 500 mm min$^{-1}$. From these trials it was found that 125 W at
100 mm min\(^{-1}\) were the ideal laser parameter to use in terms of achieving minimal surface cracks.

![Figure 1 Schematic diagram of the experimental set-up for the fibre laser surface treatment of the Si\(_3\)N\(_4\) engineering ceramic.](image)

**2.3. Method of Analysis**

A Vickers diamond indenter (Vickers (HVTM); Amstrong Engineering, Ltd.) was used to indent the as-received and the fibre laser radiated surfaces of the Si\(_3\)N\(_4\) engineering ceramic in the standard manner [26-28]. The measurement was first conducted 50 times over the as-received surface plane of the Si\(_3\)N\(_4\) ceramic by using an indentation load of 30 kg. From this an average hardness of 1351 Hv was found for the as-received surface of the Si\(_3\)N\(_4\) engineering ceramic. Thereafter, changes in the surface hardness of the fibre laser radiated samples were also investigated in their own right and to determine the location of the HAZ. Indentations were made from approximately on the centre of the fibre laser radiated track outwards for 4 mm in increments of four diamond widths into the laser unaffected region of
the sample. Thereafter, the size of the indentions was measured to determine the surface hardness in the prescribed way [26–28].

The surface topography of the Si$_3$N$_4$ prior to and after the fibre laser surface treatment was investigated to determine the effect of the fibre laser beam upon the near (top) surface. This was done by using a white light interferometer (WLI) three-dimensional (3-D) surface analysis system (Infinite Focus IFM 2.15; Alicona, Ltd.). This analysis with the WLI produced 3-D surface profiles of around 2 mm (determined by the diameter of the white light beam) in length across the width of the as-received and the fibre laser radiated samples.

The as-received and the fibre laser radiated surface of the Si$_3$N$_4$ were observed at a microscopic level to examine the surface morphology using a scanning electron microscope (SEM) and the elemental composition to a depth of 1μm by means of energy dispersive X-ray (EDX) analysis (Stereoscan 360; Carl Zeiss Leo, Ltd.). Prior to the SEM and the EDX analysis, the samples were carefully washed in distilled water, and then dried in hot air (150°C) for around 30 s. After this, all the samples were Au coated to enhance the surface electrical conductivity.
3. Results and Discussion

3.1. Surface observations of the as-received surface of the Si$_3$N$_4$ engineering ceramic

Figure 2 shows the as-received surface of the Si$_3$N$_4$, with the surface appearing somewhat coarse, specifically in Figure 2(a) (with surface micro-cracks) and closely packed grains being seen in Figure 2(b). The grains were measured to be ranging between 1.5 to 2.5 µm. There was no evidence of the porosity pre-existing on the surface of the as-received Si$_3$N$_4$ ceramic from observing the SEM images. A compositional study of the as-received surface of the Si$_3$N$_4$ showed it to be comprised of 15 wt% C, 20 wt% O$_2$, 35 wt% Si, 4.5 wt% Y, and 5.5 wt% Al$_2$O$_3$. This finding has close relations to that given by the manufacturer’s specification of the ceramics chemical composition. N$_2$ content of about 20 wt% would also exist in this sample, but the EDX system used was unable to detect any N$_2$ within the chamber. This is not a problem as the un-detected N$_2$ can be found from substituting the percentage of the other elements that were present.

![SEM images of the as-received surface of the Si$_3$N$_4$, (a) at x 500 and (b) x 3000 resolution.](image)

Figure 2: SEM images of the as-received surface of the Si$_3$N$_4$, (a) at x 500 and (b) x 3000 resolution.
3.2. Investigation of the HAZ on the fibre laser surface treatment of the Si$_3$N$_4$ engineering ceramic

From measuring the surface hardness of the fibre laser radiated Si$_3$N$_4$ ceramic; it was found that the fibre laser treatment resulted in a change in the surface hardness thereof on the various zone of the Si$_3$N$_4$. The hardness changed from within the untreated zone to the HAZ and the fibre laser radiated zone. The hardness values are given in Figure 3. It was found that the fibre laser radiated zone comprised of the softest surface layer. The hardness increased as the diamond indentation was induced into the heat affected region, the interface between each zones and the untreated surface layer as presented in Figure 3. The hardness was reduced to 1054 Hv on the track and ranged between 1000 to 1200 ± 10% Hv on the outer edges of the laser treated track particularly for the Si$_3$N$_4$ surface treated by using O$_2$ assist gas. The hardness increased along the edges of the track indicating that the respective surface layer was less influenced. The untreated surface as indicated in Figure 3 on both sides of the track ranged from 1400 to 1600 Hv ± 10% Hv. Variation in the hardness value can be seen with changing indentation loads. If a lower indentation was used then the penetration of the diamond indenter would be rather low and so, would only measure the hardness on the surface rather than the sub-surface. This is why an indentation load of 30 kg was used in this investigation.
3.3. The topographical effects of the fibre laser surface treatment of the Si$_3$N$_4$ engineering ceramic using various processing gases

3.3.1. \textit{O}_2 assist gas

Figure 4 shows the surface topography of a Si$_3$N$_4$ sample fibre laser radiated using an O$_2$ assist gas. The laser treated zone, as indicated in Figure 4, is comprised of a newly formed (melted and solidified) surface layer with some degree of materials removal occurring as a result of the fibre laser surface treatment. The depth of the material removal was up to 278\,\mu m. The grey and white areas present in the laser treated zone indicate surface oxidation which was further identified from the microscopic and the compositional analysis (see section 4.4). The HAZ comprises of some degree of discoloration which is an indication of the...
distribution of heat. The surface finish in terms of Ra was measured to be 12.1μm Ra within the laser treated zone. This points to a severe change occurring in the surface morphology of the laser treated zone, as is apparent from a comparison of the surface finish for the as-received sample which was measured to be 1.58μm (Ra). The changes in the surface roughness occurred due to the formation of uneven surface layer from the Si3N4 ceramic melting and re-distributing which formed the asperities on to the surface as seen in Figure 4.

![Figure 4](image)

Figure 4 A topographical image of the surface profile of the Si3N4 treated by the fibre laser radiation using an O2 assist gas.

### 3.3.2. Compressed air assist gas

The upper surface profile of the Si3N4 sample treated with the fibre laser beam using a compressed air assist gas is given in Figure 5, which shows significantly less material removal than that of the sample treated with an O2 assist gas (see Figure 4). The depth of material removal was up to 101μm. This indicates that the laser-material interaction during the treatment was less reactive in comparison to the surface treated by the fibre laser using O2 assist gas. The surface finish within the laser treated zone was 2.12μm Ra and was much smoother than that of the sample fibre laser radiated with an O2 assist gas, signifying a less effective surface treatment. This was because of the less interaction occurring between the fibre laser-Si3N4 and with using the compressed air. However, the whitening effect on the top
surface of the track shows that oxidation took place, but not as much as the O₂/fibre laser radiated sample.

Figure 5 A topographical image of the surface profile of the Si₃N₄ engineering ceramic treated by the fibre laser radiation using compressed air assist gas.

From comparison of the compressed air/fibre laser radiated surface to the O₂/fibre laser radiated surface of the Si₃N₄ engineering ceramic (see Figure 4), shows similar effects in the near (top) surface layer. Surface oxidation is apparent as well as formation of craters where the surface has become much smoother. Although, the average of the surface finish resulted to being much coarser due to the craters comprising of gradients. This confirmed the melting and the redistribution of the melt zone. More porosity and trapped air holes are also seen in this sample.

3.3.3. N₂ assist gas

The sample treated by the N₂/fibre laser radiation shows a smaller surface track produced from the fibre laser treatment in comparison to the O₂/fibre laser radiated sample in Figure 4. This is due to N₂ being an inert gas and minimizing the effect of oxidation. The surface profile presents melting solidification and a possible vaporization of the ceramic during the laser/Si₃N₄ interface. The sample also comprised of a smoother surface finish (0.801μm)
when compared to the as-received surface and O₂/fibre laser radiated sample. This led to less material removal in comparison with the samples treated by O₂ and was 143μm which was 41μm higher than the sample in Figure 6. The laser material interaction between the fibre laser using N₂ on the Si₃N₄ ceramic may have been less in comparison to other gas types used in this study.

Figure 6 A topographical image of the surface profile of the Si₃N₄ ceramics treated by the fibre laser radiation using N₂ assist gas.

3.3.4. Ar assist gas

The surface treated by the Ar/fibre laser radiation in Figure 7 showed similar effects compared to the surface treated by the N₂/fibre laser radiation in Figure 6. This was however, predicted as Ar being an inert gas would also minimize the effect of oxidation and provides a much protective treatment from the atmosphere. The material removal in this case was 176μm, and was slightly higher than the surfaces treated by the fibre laser radiation using N₂, compressed air, and O₂ assist gasses. The surface finish found was 1.61μm (Ra) after the laser treatment which again was rougher than that of the as-received surface.
3.3.5. Ambient Air (no assist gas)

The laser alone treated surface using no assist gas produced similar result to that of the surface treated by the compressed air assist gas. This could be due to the compressed air having identical properties to the atmospheric gas properties which produced similar results during the laser alone treatment [30]. However, it can be observed from Figure 8 that there are also formations of trapped air holes on the laser treated zone. Those were not seen using other gases except compressed air and O₂ assist gasses. It can be gathered that the trapped air holes were formed as the surface melted and re-distributed leaving the trapped gas to form such a surface profile. The material removal was up to 121μm for this treatment. The surface finish was found to be 2.56μm (Ra) which in comparison with the as-received surface was much courser. This has occurred due to the melting and formation of the new surface layer.
Figure 8 A topographical image of the surface profile of the Si$_3$N$_4$ engineering ceramic treated by the fibre laser radiation with using no assist gas.

Table 1 Summary of the effects of the material removal, the surface finish and the surface topography of the surface treated with the fibre laser radiated surface of the Si$_3$N$_4$ engineering ceramic from using various assist gas compositions.
3.4. Microscopic analysis and the effect of the fibre laser radiation using the various assist gases on the chemical composition

Observation of the SEM images of the sample treated by the fibre laser radiation by using O₂ assist gas showed a significantly modified surface profile which comprised of a newly formed surface layer. This can also be seen with images from the other laser gases used but the effects are rather distinct from using O₂. The surface profile in this case was slightly different to that of the as-received surface as the fibre laser treatment had melted the top layer which then redistributed unevenly and altered the surface finish and the chemical composition as further seen in this study. The HAZ of the surface treated with fibre laser beam was also considerably broad in comparison with the samples treated by other assist gases. This was because of O₂ being a reactive gas where more chemical changes had occurred in comparison to using an inert gas. The reason for the sample treated with an O₂ assist gas producing large area of laser affected zones was due to the faster burning rate of the O₂ than the traverse speed of the laser beam as stated by Bass [29]. Bass also stated that non-metallic materials such as ceramics are more sensitive to chemical changes from using O₂. On account of this, a courser surface finish was found by using the O₂ in this investigation. If the burning rate of O₂ was slower than that of the fibre laser traverse speed, then the opposite reaction would occur where the laser treated zones would be narrow and produce a smoother surface finish. The processing temperature in this case would also be high. In general, the use of O₂ is appropriate for fibre laser processing of ceramics if deep penetration or faster processing speeds are required, but if the surface roughness and the material removal are more important then Ar or N₂ in particular is also ideal.

The content of O₂ found with the sample treated by O₂/fibre laser radiation was reasonably high for obvious reasons. Up to 38 wt % of O₂ was observed and was the highest in
comparison to the surface treated using other assist gases. In comparison to the as-received surface; the C content was reduced to 5.56 wt % and Si was 18.21 wt % as further presented in Figure 14. There was also 18.80 wt % Y found in this sample. The element Y is found in most earth-wares and is also expected to occur within the Si₃N₄. From this it can be observed that a chemical change has occurred after the O₂/fibre laser surface treatment when compared to the as-received surface.

![SEM images](image)

Figure 9 SEM images of the fibre laser radiated surface of the Si₃N₄ using O₂ assist gas in (a) x 50 resolutions (b) x 3K resolution and (c) the HAZ at x 3K resolution.

The fibre laser radiated sample with a compressed air assist gas also showed significant levels of melting. The grains are exposed in comparison to that of the as-received sample. The level of oxidation is not in evidence as much as was the case with samples fiber laser radiated with an O₂ assist gas. This was because of the O₂ content being lower in the elements found in the compressed air than that of the pure O₂. The chemical composition found when using compressed air was 24.39 wt % C, 37.82 wt % O₂, 30.43 wt % Si, and 4.21 wt % Y. The Si was decrease in comparison to the as-received surface, however, not as much as the O₂/fibre laser radiated surface. This indicated that a compositional change had also occurred when performing the fibre laser surface treatment with using compressed air as an assist gas.
The morphology of a sample fibre laser radiated with a compressed air assist gas is shown in Figure 10. It can be said that due to high temperatures produced during the laser material interaction (in the region of over 2000°C), the surface has also undergone some decomposition which in turn produced the material removal which intrinsically changed the surface morphology as the Si₃N₄ was exposed to the atmosphere at such high temperatures. The irregularity of the material removal during the decomposition of the ceramic should also be considered as this has also contributed to the change in the surface morphology and the surface finish. Furthermore, the change in the morphology also depends on the how much the grains are covered and the level of bonding between the new surface layer produced by the fibre laser radiation and the secondary phase of the Si₃N₄ ceramic. The sample treated in ambient air by using the fibre laser has some relation to the sample fibre laser radiated with an O₂ assist gas.

The laser alone (no assist gas) treated sample comprised of the highest O₂ content after the O₂ treated sample. Up to 42.60 wt % O₂ was found and is evident from the image in Figure 11(b) and (c). This was the highest and probably occurred due to the lack of processing gas being
introduced at the surface during the fibre laser-Si$_3$N$_4$ interaction and also because of the extra heat generated which characteristically formed a high O$_2$ content within the surface layer treated by the fibre laser radiation. Some areas of the treated zone also comprised of porosity that was produced from surface melting and distribution of the melted surface during the solidification stage. The C content in the laser alone treated sample was 28.67 wt %, and Si being 28.73 wt %.

![Figure 11](image.png)

Figure 11 SEM images of the fibre laser alone radiated surface of the Si$_3$N$_4$ engineering ceramic using no assist gas in (a) at x 500, (b) at 3K and (c) the HAZ at 3 K resolution.

SEM surface images of samples fibre laser radiated with N$_2$ and Ar assist gasses are shown in Figure 12 and Figure 13, respectively. As one can see, the HAZ and the fibre laser radiated area was much smaller and shaper when a N$_2$ assist gas was employed. The shape of the grains has also changed with N$_2$, as presented in Figure 12(b), where rod type grains have been formed in some areas which are not seen on other samples. There is also evidence of porosity formation in the interface between the HAZ and the laser treated area which, except for Ar, is not apparent in the surfaces treated using the other assist gases. This was because of the increase in the cooling rate which allowed the molten surface to be formed as gases were trapped from escaping, this result relates to the work of Lawrence and Li [23]. It can be said that similar effects have been achieved when using N$_2$ and Ar since they are both inert and less reactive to a chemical change in comparison to the other gases, including ambient air (no
gas). This result is in good agreement with that of the Bass [31] and the findings of Minami et al [21]. It is also believed that the processing temperatures reached during processing with N₂ and Ar assist gases were much lower to those reached when using O₂, compressed air or ambient assist gases. Yet at the same time, there was evidence of porosity found on the interface between the HAZ and the surface treated by the fibre laser radiation for both samples that were treated with N₂ and Ar assist gases, as can be seen in Figure 12 and Figure 13. The elemental analysis given in Figure 14 showed 35.47 wt % O₂, 35.45 wt % Si, 6.99 wt % C and 10 wt % Y. The O₂ content within the sample laser treated with N₂ assist gas is the lowest in comparison to the other samples but there is only a small amount of difference between the O₂ content found within each of the samples. However, the use of N₂ certainly modified the surface profile as rod like grains had began to form as shown in Figure 12 (b). The N₂/fibre laser radiated surface of the Si₃N₄ also showed enlargement of the grains in comparison to the as-received surface.
Figure 12 SEM images of the fibre laser radiated surface of the Si$_3$N$_4$ engineering ceramic using N$_2$ as the assist gas in (a), (b) and (c) the HAZ and (d) the interface between the HAZ and the fibre laser radiated zone.

The microscopic images in Figure 13(d) showed an evidence of the surface melting with using Ar assist gas. This in comparison to N$_2$ was somewhat different as the grain boundaries of the Ar/fibre laser radiated sample had began to bind into each other. The interface between the HAZ and the laser treated zone in Figure 13(c) also shows that porosity within the ceramic has been covered with the re-solidified materials. This can relate to the concept of crack healing where the fibre laser radiated surface areas were close to their melting temperatures and were solidified and covered the surface cracks and formed a new surface layer. Similar result was also reported by Malshe et al. [25] during a CO$_2$ laser processing of a Si$_3$N$_4$ ceramics. The solidified surface however, particularly in the interface between the fibre laser radiated surface and the HAZ showed evidence of splatter occurring from the melt-zone as the material was pushed to the side of the laser created track. This appears in all the fibre laser radiated samples but is more present in the samples using N$_2$ and Ar assist gases. This indicates that there is less heat produced during the interaction of the fibre laser-Si$_3$N$_4$, hence, the gas was being trapped before escaping between the HAZ and the fibre laser radiated surface. The chemical composition found on this surface was 16.36 wt % C, 35.82 wt % O$_2$, 28.43 wt % Si and 11.70 wt % Y. The chemical composition herein is similar to that of the N$_2$ expect with Ar/fibre laser radiated sample as there is more O$_2$ content present due to the Ar not coupling well with the Si$_3$N$_4$ in comparison to N$_2$ so that the surface of the Si$_3$N$_4$ is protected from an atmospheric influence.
A chemical change has been observed on all surfaces treated by the fibre laser radiation using the variety of assist gases. Evidence of surface oxidation is also found with all treated samples. However, the effects are remarkable from using reactive gases in particular O$_2$. The sample treated in ambient condition using no assist gas also showed similar results to that of the O$_2$ and compressed air assist gases. Over all, the increase in C and O$_2$ content has been seen for all laser processing gasses used (see Figure 14) which formed a new surface layer. From 5 different conditions used; C, O$_2$ and Si as elements, all appear within the treated surfaces to some extent. Owing to this; it can be said that a change in composition has taken place as the fibre laser radiated surfaces of the Si$_3$N$_4$ engineering ceramic were altered to form SiO$_2$. The formation of SiO$_2$ was also discussed by Lysenko et al. [32] who stated that the SiO$_2$ results from heating silicon at elevated temperature (1600 °C). The temperature
during fibre laser processing in this study from using any of the gas compositions was much higher than 1600 °C. This is evident from the topographical and the microscopic images where melt zones are found which indicated that the formation of the SiO₂ layer was unavoidable even by using less reactive assist gases such as Ar and N₂.

Figure 14 Chemical composition of the Si₃N₄ engineering ceramics for the as-received, the fibre laser alone and the fibre laser radiated surface by using different assist gas compositions.
4. Conclusions

Fibre laser surface treatment of the Si₃N₄ engineering ceramics was performed by using various processing gas compositions. Laser treated surfaces were induced with a diamond indenter to determine the HAZ. It was found that the laser surface treatment softened the treated zone to 1054 Hv for the Si₃N₄ and increased in hardness within the interface between 1100 to 1200 Hv and the respected untreated areas between 1430 to 1680 Hv. This ensured the location of the different zones found from the result of the fibre laser surface treatment of the Si₃N₄ engineering ceramic.

From observing the effects produced by the various assist gas compositions; it was found that O₂ produced the highest materials removal and the roughest surface finish along with a high level of oxidation and average porosity was also found. Large surface profile of the treated and the HAZ were also observed. The results were similar using the compressed air assist gas as well as the fibre laser alone surface treatments. This was because of the content of the particular compositions within these conditions were highly reactive with the Si₃N₄ and allowed porosity, oxidation, and larger surface treated and the HAZs to occur during the fibre laser treatment. This is why the material removal was high using O₂.

The use of Ar and N₂ assist gases resulted in producing the finest surface finish with a lower material removal in comparison with the sample treated using other conditions. This was because of both processing gases being inert, hence protecting the Si₃N₄ from too much atmospheric influence as well as generating lower surface temperatures in comparison to the other assist gases used. N₂ however, showed a considerably modified surface in comparison to Ar as rod like grains were found which were not seen from other results. A compositional change was yet apparent but to a lesser extent despite N₂ and Ar showed less influence of the
atmospheric effects such as oxidation. From the compositional study, it was observed that the Si$_3$N$_4$ was transformed to SiO$_2$. This was unavoidable as the fibre laser treatment was conducted in an atmospheric condition which would drive the Si to oxidize within the atmosphere at elevated temperatures and form the new SiO$_2$ layer. The fibre laser treatment would have to be performed in a vacuum condition in order to avoid this effect.

Overall, it can be concluded that the use of various processing gases would surely influence the characteristics of the Si$_3$N$_4$ engineering ceramic. Using O$_2$ assist gas can enhance the laser interaction with the surface of the Si$_3$N$_4$ in order to remove a sufficient level of material. Thus, Ar and particularly N$_2$ assist gasses could produce a better surface treatment if aspects such as porosity, oxidation, surface finish and materials removal are considered. Nevertheless, a mixture of N$_2$ and O$_2$ would also be useful to perform a balanced fibre laser surface treatment of the Si$_3$N$_4$ so that a sufficient material removal can be found and yet, would minimize the surface roughness and increase the grain size of the Si$_3$N$_4$ engineering ceramic.
5. References


7. Hackel AL, (2005), Laser peening technology has come of age, Shot Peener (Summer 2005, shaping the future), 10-12.


6.0. Notations

Hardness
Litres per minute
Metres per minute
Cold Isostatic Pressed
Oxygen
Argon
Nitrogen
Helium
Silicon Nitride
Zirconia
Alumina
Silicon dioxide
Kilogram
Micrometre
Millimetre
Degrees Centigrade
Numerical Control
Surface Finish

$H_v$
$\text{l min}^{-1}$
$m \text{ min}^{-1}$
CIP
$O_2$
$Ar$
$N_2$
$He$
$Si_3N_4$
$ZrO_2$
$Al_2O_3$
$SiO_2$
$kg$
$\mu m$
mm
$^0C$
NC
Ra