

# **A Two-Stage Ceramic Tile Grout Sealing Process**

## **Using A High Power Diode Laser**

### **Part I: Grout Development And Materials Characteristics**

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## ABSTRACT

Work has been conducted using a 60 W-cw high power diode laser (HPDL) in order to determine the feasibility and characteristics of sealing the void between adjoining ceramic tiles with a specially developed grout material having an impermeable enamel surface glaze. A two-stage process has been developed using a new grout material which consists of two distinct components: an amalgamated compound substrate and a glazed enamel surface; the amalgamated compound seal providing a tough, heat resistant bulk substrate, whilst the enamel provides an impervious surface. HPDL processing has resulted in crack free seals produced in normal atmospheric conditions. The basic process phenomena are investigated and the laser effects in terms of seal morphology, composition and microstructure are presented. Also, the resultant heat affects are analysed and described, as well as the effects of the shield gases, O<sub>2</sub> and Ar, during laser processing. Tiles were successfully sealed with power densities as low as 500 W/cm<sup>2</sup> and at rates up to 600 mm/min. Contact angle measurements revealed that due to the wettability characteristics of the amalgamated oxide compound grout (AOCG), laser surface treatment was necessary in order to alter the surface from a polycrystalline to a semi-amorphous structure, thus allowing the enamel to adhere. Bonding of the enamel to the AOCG and the ceramic tiles was identified as being principally due to van der Waals forces, and on a very small scale, some of the base AOCG material dissolving into the glaze.

**Keywords:** high power diode laser, ceramic tiles, grout, vitrify, enamel, glaze, wettability, adhesion

## INTRODUCTION

Ceramic tiles are considered to be one of the most cleanable surfaces available [1], and are applied to the walls and floors in a multitude of places; from hospital operating theatres to industrial clean-rooms. Currently, the tiles are applied to surfaces using either tile grouts or adhesive, with tile grout (typically epoxy based) or silicon resin being used to fill the void between adjoining tiles. A major difficulty with tiled surfaces is that contaminants can enter into, and exit a space via a tiled surface, through the tile grouts used to fill the void between adjoining tiles, or in the case of silicon resin sealants, pass around the edges of the seal because the sealant is not fully adhered to the tile surface due the presence of small voids that increase in size over time along the sealant/tile interface [1]. The problem is compounded, due to the tile grouts porosity, by water, germs and other harmful agents, which have the ability to permeate into cavities behind the tiles, corroding the bonding agent used to fix the tile to the substrate, the substrate itself or even the ceramic tile. Moreover, the predominant problem with commercially available tile grouts is that because they are very difficult to clean, over time they become contaminated, and have to be removed physically or mechanically; an arduous and costly undertaking.

This paper investigates the feasibility and characteristics of using of high power diode laser (HPDL) beams to produce a tough, inexpensive seal in the void between adjoining vitrified ceramic tiles using a newly developed amalgamated ceramic and oxide compound grout, as well as an amorphous, crack-free surface glaze on the amalgamated compound seal using an enamel powder. Thus the tiles are sealed together, preventing any further contamination activity; in effect creating a completely sealed surface that is both impermeable and relatively simple to clean and maintain since contaminants are basically arrested on the tile and glazed seal surface. Because such a seal would be an integral part of the surface as the tiles themselves, the necessity to remove old or contaminated grout from the void between the tiles would be eradicated (a 2.5-25 fold increase in wear life over conventional epoxy tile grout has been demonstrated and is described in Part II of this paper). Clearly, the economic and material benefits to be gained from the development of a more effective and efficient tile grout could be significant. At present there is no reported work concerning the sealing of tile grout using laser beams.

In previous studies the sealing of engineering ceramic surfaces using lasers has been demonstrated. The remelting of  $ZrO_2$  based protective ceramic layers using a  $CO_2$  laser [2] with power densities

ranging from 8.5-17 kW/cm<sup>2</sup> was shown to markedly decrease the level of structural defects and the lamellar microstructure. The remelting of ZrO<sub>2</sub> based protective ceramic layers plasma sprayed onto a variety of bond coats using cw and pulsed CO<sub>2</sub> lasers [3] revealed that a pulsed laser produced less cracks, whilst the use of external flowing gas, such as He or Ar, resulted in increased cracking. However, the laser treated surfaces in both studies displayed the phenomenon of delayed fracture due to unrelieved thermal stresses. The laser melting of plasma sprayed ceramic coatings based on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> by cw and pulsed CO<sub>2</sub> lasers [4] revealed that the extent of cracking was a function of the total energy input to the surface and the thermophysical properties of the ceramic coatings. Consequently it was concluded that, to avoid cracking in such materials when remelting using the CO<sub>2</sub> laser it was essential to pre-heat the workpieces to around 800<sup>0</sup>C and thus reduce the thermal gradient [4].

The firing of vitreous enamel frits onto steel substrates using CW CO<sub>2</sub> laser irradiation has proved successful [5, 6]. The fired enamels were found to be well bonded to the substrate and displayed an undulating surface morphology with minor porosities and a uniform microstructure. In both studies, however, pre-heating in a furnace of the steel substrate to 200<sup>0</sup>C was necessary in order to avoid microcracking. The firing of vitreous enamel frits onto glass substrates using CO<sub>2</sub> lasers has also been studied. Using a 4 kW-cw laser, conventional enamel frits containing PbO (to reduce the firing temperature) were fired onto flat glass sheets [7] and the resultant temperature development was analysed. Because of the localised heating nature of laser radiation, temperatures in excess of 1000<sup>0</sup>C could be achieved without causing any deformation of the substrate glass. As such, it proved possible to fire PbO-free enamel frits [8]. Furthermore, the gloss and the smoothness of the laser fired enamel were comparable to those of conventional furnace fired enamels. However, in both studies, pre- and post-heating of the enamels in a furnace to temperatures in the range of the enamel melting temperature was necessary in order to relieve thermal stresses.

Research was conducted by the authors to determine the possibility of producing a laser induced impervious surface glaze on a variety of vitrifiable substances placed in the void between adjoining vitrified ceramic tiles, thus sealing and joining together the tiles permanently. In this paper we report a new technique of producing diode laser sealed surfaces without the need of pre-heating or special atmospheric conditions. This procedure has been applied to the sealing of ceramic tile grout. The advantages of using a HPDL are numerous, namely its portability, relatively simple beam delivery and high energy efficiency. Additionally, the lasers potential for large economies of scale means that

in time, low cost laser power can be realised, thus making many HPDL application possibilities economically viable.

## **GROUT MATERIAL DEVELOPMENT**

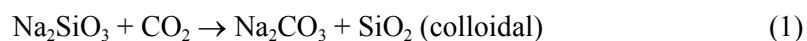
Commercially available epoxy tile grout is formulated from four main components; acrylic emulsion, limestone, dolomite and a cellulose substance. The limestone and dolomite act as fillers and the cellulose substance is added basically to thicken the grout. It is well established that glazing can only be achieved using materials containing at least some of the essential glass network forming compounds such as  $\text{SiO}_2$  and  $\text{BO}_3$ , along with some glass network modifying and intermediate compounds such as  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}$  and  $\text{MgO}$  [9]. As such, it proved impossible to directly glaze epoxy tile grouts. Also, the coating of epoxy tile grout with a vitrifiable substance was not possible since the actual bonding mechanism by which the grout adheres to surfaces to which it is applied is mechanical, or more precisely hydraulic, and is achieved as a result of the acrylic emulsion hydraulically bonding to the surface [10]. Since the grout does not bond to surfaces chemically, it is unable to withstand elevated temperatures. Indeed, at temperatures above  $200^\circ\text{C}$  the grout will actually debond from the surface it is applied to [11]; a temperature well below the softening point of commercial vitreous coating materials.

Initial experiments conducted by the authors using such materials (vitrified ceramic tile powder and pyrex glass powder) resulted in reasonable quality seals being produced. However, surface microcracks and porosities were ever-present features of the glazes, and as such, rendered them unsuitable for sealing purposes. Similarities in the results of this work are reflected by those of Shaw [12] and Fabes [13] who used laser radiation to densify sol-gel silica glass. Despite the fact that the laser densification of the sol-gel was successful, in terms of the speed of the process and the levels of densification achieved, surface blistering and microcracking always resulted. This is perhaps to be expected, since under normal glass manufacturing conditions the glass is raised to its softening temperature and held there for many hours, not just for the few seconds it takes for the laser to pass across and irradiate the glass solution or the powders. It would appear from this work that, for such materials, the laser process was too rapid, particularly in terms of the resultant high cooling rates which are typically in the order of  $10^2$ - $10^4$   $^\circ\text{s}$  [14], thus not permitting the glass network formers,  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , to fuse properly resulting in deep cracks and porosities [9]. Surface microcracking was due, in part, to the solidified material over contracting as a result of the elevated melting

temperatures caused by the relatively high SiO<sub>2</sub> content of the materials [9]. However, the formation of microcracks was principally due to excessive thermal stresses resulting from the greatly reduced heating/cooling cycle times which create a large thermal gradient between the melted region and the cooler surrounding material [15]. The resultant porosities were due to either the materials lack of fluidity when melted, preventing bubbles from escaping the surface properly [9], or the lack within the materials composition of compounds such as Fe<sub>2</sub>O<sub>3</sub> or FeS<sub>2</sub> which are known to reduce the amount of oxygen released during melting and resolidification [16].

Based on the results of these initial experiments, efforts were made to produce a glaze on the surface of unmixed, individual vitrifiable oxide materials. The results of these initial laser glazing experiments gave a clear indication that better results would be more likely from using combinations of these vitrifiable compounds in suitable ratios with other substances, and indeed with each other, in order to optimise the beneficial properties, and reduce the detrimental properties of the constituent materials. Table 1 details the amalgamated oxide compound grout (AOCG) composition that was found to give the optimum seal results and the characteristics that each compound imparts on the blend during laser irradiation.

In order to form a manageable paste the AOCG was mixed with approximately 50wt% water diluted sodium silicate solution. Sodium silicate solution, or waterglass as it is more commonly known, is a viscous colourless solution of colloidal sodium silicate. It is a silica containing aqueous solution that, when combined with other solutions such as the AOCG, forms a gel-like mass of silicate hydrate. Such a mass remains soft and malleable until it is exposed to CO<sub>2</sub> gas, either by means of a direct flow or through contact with the atmosphere, whereupon it hardens from the complete hydrolysis of the dissolved sodium silicate by the reaction [17]



Notwithstanding this, exposure of the hardened mass to water results in a reversing of the process and the mass returns to a gel-like state. However, heating of the hardened mass in effect fires the waterglass (similar to that of a ceramic material) [17], increasing its strength and enabling it to withstand water exposure. Nevertheless, despite the fact that good quality seals could be produced using the AOCG, a microscopic examination of the laser treated AOCG surface revealed the structure to be polycrystalline. Thus, such a seal would be unable to function correctly, still allowing water, germs or other harmful agents to permeate through its surface [15].

The thermal characteristics of the AOCG in terms of the compressive strength with increased temperature were investigated and are shown in Figure 1. The strength of the AOCG in terms of increasing temperature is determined primarily by the waterglass, since the strength of the individual oxide compounds varies little or not at all at relatively low temperatures ( $<500^{\circ}\text{C}$ ) [18]. As one can see, as the temperature is increased up to  $150^{\circ}\text{C}$  the compressive strength of the AOCG increases to maximum of 12.4 MPa. This is due to the extensive dehydration of the silica gel between  $100^{\circ}\text{C}$  and  $150^{\circ}\text{C}$ , resulting in a gel mass which is water-free and therefore stronger [19]. However, once the temperature exceeds  $150^{\circ}\text{C}$  the compressive strength of the AOCG decreases to 3.9 MPa from where it decreases uniformly to a minimum of 3.7 MPa at  $600^{\circ}\text{C}$ . The interim maximum in compressive strength observed at around at  $700^{\circ}\text{C}$  can be attributed to the crystallisation phenomena of the  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$  within the waterglass [19]. The maximum compressive strength of 12.4 MPa for the AOCG compares similarly with 10.5 MPa for the conventionally available waterproof ready mixed coloured tile grout. However, the general thermal resistance properties of the AOCG were found to be far superior to those of the waterproof ready mixed coloured tile grout. Even at a temperature of  $800^{\circ}\text{C}$  no breakdown of the AOCG was observed, whilst it is known that waterproof ready mixed coloured tile grout loses its integrity at temperatures above  $200^{\circ}\text{C}$  [10]. Also, at temperatures above approximately  $100^{\circ}\text{C}$  the complete irreversibility of the water glass reaction, that is, the rehydration of the water glass when exposed to water, was achieved.

As was shown earlier, without any exposure to heat the AOCG will harden simply through contact with the atmosphere according to Equation (1). However, the fact that the AOCG in this state is hydraulically bonded, as opposed to chemically bonded, combined with the retention of chemical and mechanical water (that is water that is bonded into the materials matrix and water that is added respectively) means that the hardened mass will rehydrate when exposed to water [17, 19]. Heating of the AOCG in this state is similar in effect to the firing of ceramic, in that the heating causes gradual ceramic ‘sintering’ of the materials; dehydrating the mechanical water, dehydroxylating the chemical water and generally bonding together and stabilising the substances, until at around  $100^{\circ}\text{C}$  sufficient pyrochemical changes have occurred to prevent any rehydration of the AOCG [17, 20].

To overcome the inherent problems of a polycrystalline seal, an amorphous surface layer on top of the AOCG was produced by applying an enamel glaze to the seal surface. This was achieved by applying a  $250\mu\text{m}$  layer of the enamel frit onto the laser treated AOCG surface. The composition of the enamel consisted mainly of  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , Mn, F and small quantities of Ba,  $\text{Al}_2\text{O}_3$  and Ni.

Further experiments showed (see Results and Discussion) that because of the wettability characteristics of the AOCC, it was necessary to laser treat the compound surface prior to the application of the enamel. Thus the sealing process is achieved in two-stages, and consequently the seal itself consists of two distinct components, an AOCC substrate and a glazed enamel surface; the aim being that the AOCC seal provides a tough bulk substrate which simply acts a filler for the void between adjoining tiles whilst the enamel provides an impervious surface glaze.

### **LASER PROCESSING EXPERIMENTAL PROCEDURE**

The experiments were carried out using UK standard 150 x 150 x 5mm vitrified ceramic tiles of various colours; white, navy blue, leaf green and jet black, cut into smaller pieces, 20 x 20mm, for experimental purposes and applied in pairs to an ordinary Portland cement (OPC) substrate using standard epoxy tile grout (Vallance Ltd., Leeds, UK). The spacing between the vitrified edges of each tile pair was the industry recommended 1.5mm. The fixed ceramic tile pieces were then allowed to set for the standard setting time of one day. The tiles were then sealed by means of a two stage process. A compound of mixed vitrifiable oxide powders such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub> and ZnO, etc. was produced. The oxide powders were sieved to ensure a particle size of less than 75µm, then thoroughly mixed together to ensure homogeneity, along with approximately 50wt% water diluted sodium silicate solution so as to form a manageable paste. The amalgamated oxide compound grout was then placed into the void, flush to the surface of the tiles and allowed to cure for two days. The set compound was then irradiated using the HPDL and overlaid directly with a thin layer (250µm) of enamel frit which, in order to form a manageable paste, was mixed with 20wt% white spirit. The composition of the enamel consisted mainly of the following; SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, Mn, F and small quantities of Ba, Al<sub>2</sub>O<sub>3</sub> and Ni, whilst the powder size was <75µm. The enamel frit paste was allowed to cure for one to two hours and then irradiated immediately with the defocused HPDL beam.

The laser used in the study was a surgical HPDL (Diomed Ltd.), emitting at 810nm ±20nm and operating in the CW mode with rated optical powers ranging from 0-60 W. The laser beam was delivered to the work area by means of a 4m long, 600µm core diameter optical fibre, the end of which was connected to a 2:1 focusing lens assembly mounted on the z-axis of a 3-axis CNC gantry table. The grouts were irradiated using the defocused high order mode HPDL beam with a beam spot



diameter of 1.75mm and laser powers (measured at the workpiece after fibre and optics losses using a Power Wizard power meter) of 10-45 W. Figure 2 illustrates the laser processing experimental arrangement, where the defocused laser beam was fired along the vitrifiable substances placed in the void between adjoining vitrified ceramic tiles by traversing the samples beneath the laser beam using the x- and y-axis of the CNC gantry table at speeds ranging from 1-20 mm/s. In order to study the possible effects of different process gasses, 3 l/min of coaxially blown Ar or O<sub>2</sub> assist gas was used to shield the laser optics, whilst the fumes produced were removed with an extraction system

In order to analyse the laser treated specimens, they were sectioned with a Struers cutting machine using a diamond rimmed cutting blade, and then polished using cloths and diamond suspension pastes. The sectioned samples were then examined using optical microscopy, SEM, EDX, and XRD techniques.

## RESULTS

### **Laser Effects on the Amalgamated Oxide Compound Grout**

Exposure of the AOCG to laser irradiation results in rapid heating of the surface, for most materials typically  $10^3$ - $10^5$  °C/s [14], which leads to the further densification of the AOCG surface with the removal of the pores between the starting particles of the compound, combined with growth together and strong bonding between adjacent particles [22]. A microscopic cross-sectional examination of the laser treated AOCG showed clearly an upper densified layer, with a gradual decrease in the amount of densification as the depth increased. Also, an XRD analysis revealed that the structure of the laser treated AOCG surface was of a polycrystalline nature, indicating that the densification is achieved by solid-state material transport, driven by differences in free-energy or chemical potential, rather than by the formation of a liquid glass phase, as is the case with ceramic materials [22].

The densification of the AOCG through interaction with the HPDL beam also results in a colour change; changing from beige to black. These changes are due to the resultant phase transitions and also, the presence in small concentrations of metal transition ions in various oxidation states within the AOCG composition, in particular, ferric ions in Fe<sup>3+</sup> and Fe<sup>2+</sup> oxidation state. Fe<sup>3+</sup> and Fe<sup>2+</sup> ions are known to give rise to green and blue colours respectively when subjected to intense heating [23]. However, if both phases are present within the composition, then the colour is determined by the Fe<sup>3+</sup>/Fe<sup>2+</sup> ion ratio, resulting in dark blue or black colours [23].

### **The Effects of Different Shroud Gases on the Enamel Glaze**

Figure 4 shows the typical morphology of the enamel glaze produced with (a) O<sub>2</sub> and (b) Ar shield gases. In both instances the surface is undulated and displays no porosities. However, the crack density in the Ar shield gas sample is higher than that of the O<sub>2</sub> treated sample.

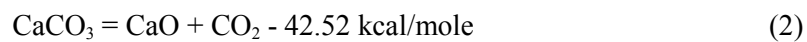
Because of its open structure, it is possible for gases to dissolve molecularly in glass, and, if the gas molecule is small enough, it can diffuse rapidly in a simple glass such as fused silica [9]. Indeed, gases such as H<sub>2</sub> and O<sub>2</sub> are known to dissolve molecularly in glass and can also react with the glass network [9]. It was noted that the quality of the enamel glazes, in terms of smoothness, porosity and microcracks, of the vitreous glazes produced was significantly influenced by the type of shield gas employed. The use of O<sub>2</sub> as the shield gas significantly reduced the number of porosities and microcracks within the vitreous glaze as well as producing a much smoother surface, indicating that a considerable amount of O<sub>2</sub> interacted with the glass network increasing the heat generation and subsequently the fluidity of the melt. In contrast, the Ar did not interact with the glass network and was consequently trapped within the more viscous melt in the form of bubbles. As such, when employing O<sub>2</sub> bubbles within the melt were much reduced and escaped from the melt more readily due to its lower viscosity, thus reducing the number of porosities.

### **Microstructures and Heat Affected Zone Characteristics**

The typical microstructure of the surface of the AOCG before and after laser irradiation is shown in Figure 4. From Figure 4(a) it can be seen clearly that before laser treatment the surface of the AOCG appears coarse, with individual crystals of the constituent components being clearly discernible. After laser treatment (Figure 4(b)) the surface appears cellular-dendritic with the crystals being semi-ordered, showing that fusion of the individual particulates has occurred. Such a solidification structure is indicative of rapidly solidified microstructures [24]. Indeed, the XRD analysis of the AOCG surface before and after laser treatment revealed that after laser treatment the AOCG surface had become more amorphous due to partial laser vitrification. On the whole, the phases present within the laser treated region were the same, however, their proportions were different. In particular, after laser treatment it was not possible to detect any SiO<sub>2</sub> whilst the Al<sub>2</sub>O<sub>3</sub> was depleted. This is probably due to the fact that these materials are glass forming elements and as such would have vitrified when laser irradiated.

The microstructure of the bond regions between the enamel seal and the laser treated AOCG and the enamel seal and the vitreous surface of the ceramic tile are shown in Figure 5. As one can see from Figure 5(b), there is no dendritic growth in any of the three bond regions which is characteristic of enamels fired onto substrates containing Fe, Si and in particular, Co [25]. However, as Figure 5(b) shows, combined with an EDX analysis of the bond region between the enamel seal and the laser treated AOCG, an interface region in which some of the base AOCG had dissolved into the enamel exists.

Figure 6 shows the heat affected zone (HAZ) produced in the AOCG as a result of the laser interaction. The HAZ is typically around 150µm thick. Because the main component of AOCG is chamotte which contains a certain amount of CaCO<sub>3</sub>, on interaction with the laser beam the rapid localised surface heating results in the decomposition of the CaCO<sub>3</sub> at temperatures between 825°C and 950°C in accordance with the recognised chemical reaction [26].



As one can see, the breakdown results in unslaked lime (CaO) and CO<sub>2</sub> gas. The CO<sub>2</sub> gas simply enters into the atmosphere, whilst the CaO either rests below the semi-amorphous irradiated zone producing a mark. Indeed, by using a phenolphthalein indicator followed by water misting, it was possible to clearly discern the HAZ around the laser treated zone on the AOCG, since phenolphthalein is an indicator which is colourless in CaO, turning violet-red in the presence of Ca(OH)<sub>2</sub> due to the change in pH.

## DISCUSSION

When a drop of liquid is placed on a solid surface it may remain as a spherical drop, or spread to cover (wet) the solid surface [27]. The angle which the liquid subtends with the solid is known as the contact angle. In practice, for wetting to occur the contact angle  $\theta < 90^\circ$ . If  $\theta > 90^\circ$  then the liquid does not wet the solid and no adhesion occurs [27]. From wetting experiments conducted (using the sessile drop technique) with the molten enamel frit and the AOCG before and after laser irradiation, the contact angle was measured

Once irradiated by the HPDL beam the enamel powder melts, transforming to a liquid phase. As such, the process of the bonding of the enamel to the AOCG substrate is determined by the

wettability of the seal. The term wetting in its most general sense is used to denote the displacement of air from a liquid or solid surface by water or an aqueous solution [27]. When a drop of liquid is in free space it is drawn into a spherical shape by the tensile forces of its surface tension. When such a drop of liquid is brought into contact with a flat solid surface, the final shape taken by the drop, and thus whether it will wet the surface or not, depends upon the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between the liquid and the solid (adhesive) [27]. The index of this effect is the contact angle  $\theta$ , which the liquid subtends with the solid.  $\theta$  is related to the solid and liquid surface energies,  $\gamma_{sv}$  and  $\gamma_{lv}$ , and the solid-liquid interfacial energy  $\gamma_{sl}$ , through the principal of virtual work expressed by the rearranged Young's equation:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (3)$$

Thus, when  $\theta < 90^\circ$  wetting will occur, whilst when  $\theta > 90^\circ$  non-wetting will result. Clearly, to achieve wetting,  $\gamma_{sv}$  should be large, while  $\gamma_{sl}$  and  $\gamma_{lv}$  should be small. Hence liquids of a lower surface tension will always spread over a solid surface of higher surface tension in order to reduce the total free-energy of the system [28]. This is due to fact that the molecular adhesion between solid and liquid is greater than the cohesion between the molecules of the liquid [27].

The adhesion intensity of a liquid to a solid surface is known as the work of adhesion. Based on the nature of the attractive forces existing across the liquid-solid interface, wetting can be classified into the two broad categories of physical wetting and chemical wetting. In physical wetting the attractive energy required to wet a surface is provided by the reversible physical forces, such as the van der Waals and dispersion forces. In chemical wetting adhesion is achieved as a result of reactions occurring between the mating surfaces, giving rise to chemical bonds [29].

In practice, complex combinations of the various bonding mechanisms actually occur, varying according to the types of materials used [29]. For the AOCG and the enamel, the mechanisms involved in ceramic-glass bonding are reasonably applicable. These principally include physical bonding (van der Waals forces), chemical bonding (oxide transformation and  $O_2$  bridging) and on a very small scale, electrochemical reactions such as the electrolytic effect due to the presence of ferric oxides within the AOCG reacting with other oxides in the enamel [29]. However, in the case of the AOCG and the enamel, the bonding mechanism is chiefly due to physical forces, since adhesion between many materials is assured by electron transfer and is thus related to bandgap energy [30].

Thus, for non-conducting materials, such as the AOCG, with large bandgaps, there will be practically no free charges inside the ceramic crystals, even at elevated temperatures. In this case the electron transfer at the interface will not take place since the electron transfer depends exclusively on the concentration of free charges in the ceramic crystal [30]. As a result, the chemical contribution to the work of adhesion is negligible [30]. Notwithstanding this, the bonding mechanism between the laser treated AOCG and the enamel is not entirely due to physical forces. As Figure 7(a) shows, slight microstructural changes at the interface between the AOCG and the enamel have occurred. Indeed, enamel glazes on ceramic materials, such as the AOCG, typically are bonded as a result of some of the base material dissolving into the glaze [29], with wetting characteristics often being achieved or enhanced by a reaction at the interface at an elevated temperature [27]. Furthermore, when the samples were pulled apart in this region debris from both components was to be found on each of the two pieces, again indicating some form of chemical bond.

Prior to laser irradiation it was not possible to fire the enamel onto the surface of the AOCG. As has already been seen, the contact angle was measured as  $118^\circ$ , and as such would prevent the enamel from wetting the AOCG surface. Indeed, laser interaction with the enamel when placed on the untreated AOCG surface simply resulted in the ‘balling’ of the enamel; the formation of small spheres approximately the diameter of the laser beam itself [31]. There are perhaps two possible reasons for the fact that laser treatment of the AOCG is essential in order that the enamel completely wets the surface of the AOCG. Firstly, HPDL irradiation of the surface resulted in the fusion of the individual crystals (Figure 5(b)), altering the structure from polycrystalline to semi-amorphous, creating a much more consolidated surface. It is well established that complete wetting of a surface will only occur if the liquid surface energy is less than the solid surface energy [37, 38]. But, this partial vitrification may have given rise to an decrease in the surface tension of the AOCG, therefore allowing the enamel to adhere to the AOCG surface since low surface energy liquids, such as the molten enamel, do not strongly adhere to high surface energy solids, such as the AOC. Secondly, wetting may have been influenced, to a lesser extent, by the increase in the number of oxides present in the AOCG surface as a result of the laser treatment, which is known to increase the likelihood of wetting [32]. Additionally, the presence of  $\text{Fe}^{3+}$  ions in the laser treated AOCG surface, as indicated by the colour change, may also have contributed to wetting, since it is known that  $\text{Fe}^{3+}$  ions effectively reduce the contact angle [33]. However, as Figure 6(a) shows, sound adhesion was ensured as a result of the enamel penetrating into the irregularities in the laser treated AOCG surface.

The glazes produced with the enamel fired using the HPDL displayed no porosities and, depending upon the shield gas used, few to no microcracks. The major reason for the reduction, and even eradication of microcracks is the reduction in the thermal gradient  $\Delta T$ , during laser irradiation. This is due partly to the fact that the softening point of the enamel powder is around 500°C, much lower than many of the other materials tested. Therefore, the tensile stresses that result from the unrelieved elastic stresses that occur due to the contraction of the material between the softening point (500°C) and ambient temperature (20°C) are much reduced to a value below that of the fracture strength. The thermal stress  $\sigma$ , induced by a thermal gradient can be calculated using the Kingery equation:

$$\sigma = \frac{E\alpha\Delta T}{1 - \nu} \quad (4)$$

where,  $E$  = Young's Modulus (N/m<sup>2</sup>)  
 $\Delta T$  = Thermal Gradient (K)  
 $\alpha$  = Coefficient of thermal expansion (K<sup>-1</sup>)  
 $\nu$  = Poisson's ratio

$\Delta T$  is the difference between the critical temperature (below which stresses can no longer be relieved) and ambient temperature. For pyrex glass this is the difference between the softening point, 780°C and ambient temperature 20°C. Since the softening point of pyrex glass is 780°C [9], that is pyrex glass can be plastically deformed at temperatures above 780°C, thermal stresses arising during cooling from above 780°C are relieved by plastic deformation. However, unrelieved elastic stresses result due to contraction occurring between 780°C and ambient temperature 20°C. Thus for pyrex glass  $\Delta T=760^\circ\text{C}$ . So, by using the following values for pyrex glass;  $E=6.42 \times 10^4 \text{ MN/m}^2$ ,  $\alpha=33 \times 10^{-7} \text{ K}^{-1}$ ,  $\Delta T=760^\circ\text{C}$  and  $\nu=0.176$ , when the pyrex glass powder was irradiated by the laser beam the thermal stress produced according to Equation (4) is 185 MN/m<sup>2</sup>. Since this is in excess of the fracture strength of pyrex glass, 120 MN/m<sup>2</sup> [9], cracking will occur, and can only be avoided by severe distortion or through the reduction of  $\Delta T$  by pre-heating. For the enamel, however, the softening temperature is 500°C, therefore  $\Delta T$  is only 480°C. Also,  $E=6.25 \times 10^4 \text{ MN/m}^2$ ,  $\alpha=33 \times 10^{-7} \text{ K}^{-1}$  and  $\nu=0.162$  [18]. Again, using Equation (5) the thermal stress induced in the enamel during HPDL irradiation is calculated to be 118 MN/m<sup>2</sup>, which is below the fracture strength of the enamel, 135 MN/m<sup>2</sup> [18]. As such, cracking will not occur, making any pre-heating completely unnecessary.

Also, because the output beam from the HPDL is inherently non-Gaussian in nature, a temperature profile that peaks in the centre of the irradiated region and tapers off to room temperature at the circumference [4] is avoided. Thus, during cooling the contraction of any part is not opposed by the neighbouring elements, which are at different temperatures when a Gaussian beam is used. As such the resultant high radial, tangential and axial stresses are greatly reduced.

## **CONCLUSION**

Vitrified ceramic tiles have been successfully sealed using a 60 W-cw high power diode laser (HPDL) with power densities as low as 500 W/cm<sup>2</sup> and at rates as high as 600 mm/min. A two-stage process has been developed using a new grout material which consists of two distinct components: an amalgamated compound substrate and a glazed enamel surface; the amalgamated compound seal provides a tough bulk substrate which simply acts a filler for the void between adjoining tiles, whilst the enamel provides an impervious surface. The temperature resistance of the AOCG proved to far superior to that of conventional tile grout, with complete integrity at 500°C, whilst the tile grout fails at temperatures in excess of 200°C.

Contact angle measurements revealed that because of the wettability characteristics of the amalgamated oxide compound grout (AOCG), laser surface treatment was necessary in order to alter the surface from a polycrystalline to a semi-amorphous structure, thus allowing the enamel to adhere. The surface of the tiles proved to accommodate complete wetting with the enamel. Bonding of the enamel to the AOCG and the ceramic tiles was identified as being principally due to van der Waals forces (dispersion forces), and on a very small scale, slight microstructural changes occurring at the interface between the AOCG and the enamel resulting in some of the base AOCG material dissolving into the glaze.

The mechanical testing and an analysis of the corrosion properties of the AOCG with and without the enamel top seal, as well as the seal's life characteristics, are presented in Part II of this paper.

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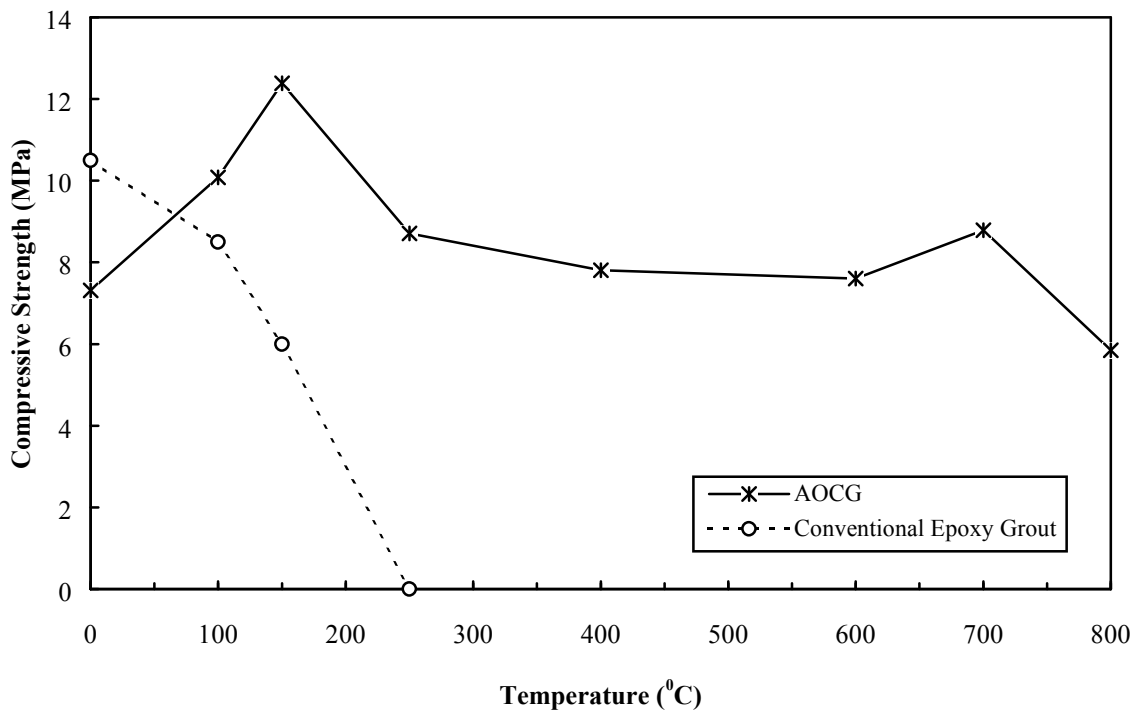
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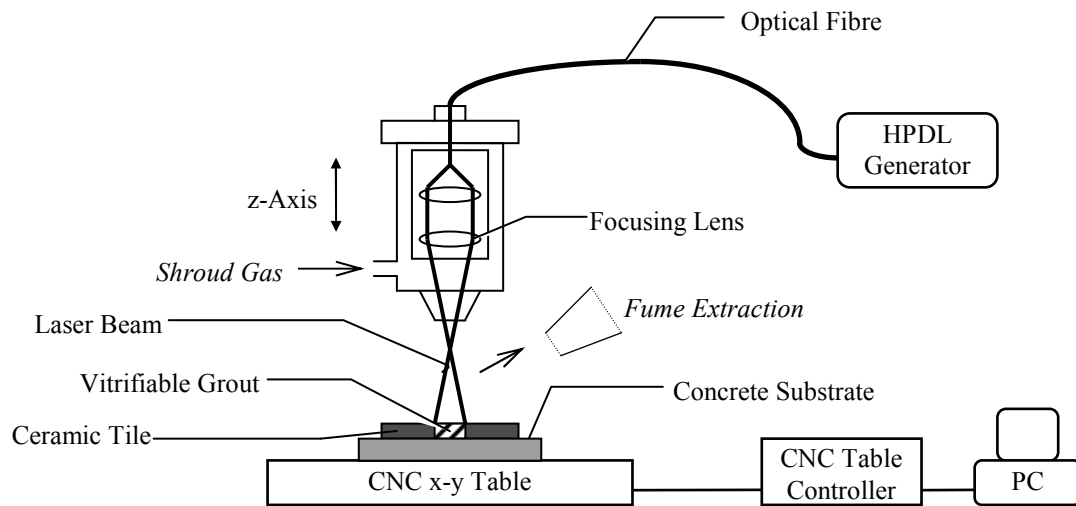
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**Figure 1**



**Figure 2**



**Figure 3**

(a)

(b)

**Figure 4**

(a)

(b)

**Figure 5**

(a)

(b)

**Figure 6**



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Table 1 : Composition and basic functions of the optimum ceramic AOCG mixture.

**Table 1**

<b>Composition</b>	<b>Characteristics</b>
Iron Oxide	Reduces amount of oxygen released during reaction and therefore reduces surface blistering and small porosities.
Silica	Glass network former. The most essential element in glass forming. Increases thermal shock and acid resistance.
Aluminium Oxide	Glass network intermediate element. Increases viscosity and improves stability towards devitrification, as well as the glasses durability
Magnesia	Glass network modifier. Lowers softening temperature. Reduces number of network bonds and therefore reduces viscosity. Has a beneficial stabilising effect.
Zinc Oxide	Imparts fluidity (reduces the viscosity) and ease of melting without effecting thermal expansion. Also increases resistance to thermal shock.