Pulsed laser sealing of plasma-sprayed layers of 8 wt % yttria stabilized zirconia

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Results are reported of the laser surface sealing of plasma-sprayed layers of 8 wt% yttria partially stabilized zirconia (YPSZ) using pulsed treatments with powers of 0.4 and 1 kW. The structural features of the processed material were examined for a range of laser processing parameters including preheating, processing temperature and power density. By controlling the processing parameters it was possible to produce pulsed laser sealed layers of similar, or even better, quality than those produced by a continuous wave laser.

1. Introduction

The literature on the laser processing of ceramics is not very extensive and most of the work reported has been carried out with continuous wave (CW) lasers [1–6]. However, Sivakumar and Mordike [7] have studied both CW and pulsed processing using a CO_2 laser to seal plasma-sprayed layers of various ceramic coatings based on ZrO_2, Al_2O_3 and TiO_2. The ZrO_2-based ceramics were stabilized with 5 wt % CaO, 21 wt % MgO and 20 wt % Y_2O_3 and were found to be less resistant to cracking than the other ceramics. The pulsed mode was used with a high peak power density of 10^3–10^4 W mm^{-2} but with short pulse lengths varying from 0.03–0.4 ms, and a beam diameter of 0.4 mm. Laser parameters (i.e. pulse duration and pulse separation) were adjusted to give a range of depths of sealing and crack morphology.

Recently, we have used a pulsed laser to seal plasma-sprayed layers of 8 wt % yttria partially stabilized zirconia YPSZ [8]. The pulsed laser-sealed zone was shiny and of low roughness, although it had a network of cracks and shallow depressions. This work was carried out at a constant power (1 kW) and constant beam diameter (3.9 mm) but with the pulse length, and hence pulse energy, varied. The energy dependence of the various structural features, such as the depressions, was discussed. The present paper reports further results on various features including the effect of preheating of the substrate, processing temperature, and of repeated pulsing treatments.

2. Experimental procedure

Discs of mild steel substrates, 6 mm thick, were alumina blasted and then plasma sprayed, firstly with a bond layer of Co–32Cr–22Ni–8Al–0.5Y alloy (wt %) and subsequently with 8 wt % yttria partially stabilized zirconia (YPSZ) powder of ~ 80 μm average particle size. The thicknesses of the bond and ceramic layers were ~ 80 and 250 μm, respectively.

A 1 kW CO_2 laser (Ferranti MFK1 type) working at 1 and 0.4 kW was used to seal the plasma-sprayed layers. Mainly single pulses were employed without a shrouding system, although the effect of repeated pulses with a continuous movement of the sample to produce tracks, was also studied. Table I summarizes the laser parameters employed which extend over a wider range than those studied in the previous investigation [8].

In order to study the effect of preheating of the plasma-sprayed layers, samples were heated in a furnace at 1000 °C for 1 h. To prevent the oxidation of the substrate during the preheating study, a nickel-based alloy was used for the substrate instead of mild steel. After preheating, the samples were fixed on a *x–y* table and laser processed at room temperature and temperatures in the range 150–850 °C at 100 °C intervals.

The pulsed laser was used to investigate the thermal shock resistance of CW-produced sealed layers. This was achieved by pulsing a sealed layer produced by CW mode treatment (CW treatments were produced from 8.5 wt % YPSZ). In addition, the effect of multipulses (two or more) on the same site on the plasma-sprayed coating was studied.

After these laser treatments the diameters of the sealed zones and the crack spacing (crack network size) and widths (distance between faces of crack) were

TABLE I Pulsed laser parameters

Power, P	0.4 and 1 kW
Beam diameter, d	0.4–4.5 mm
Power density, P_A	25–7950 W mm^{-2}
Pulse length, t	0.1–300 ms
Energy, E	0.1–300 J
Specific energy, S	0.25–79.5 J mm^{-2}

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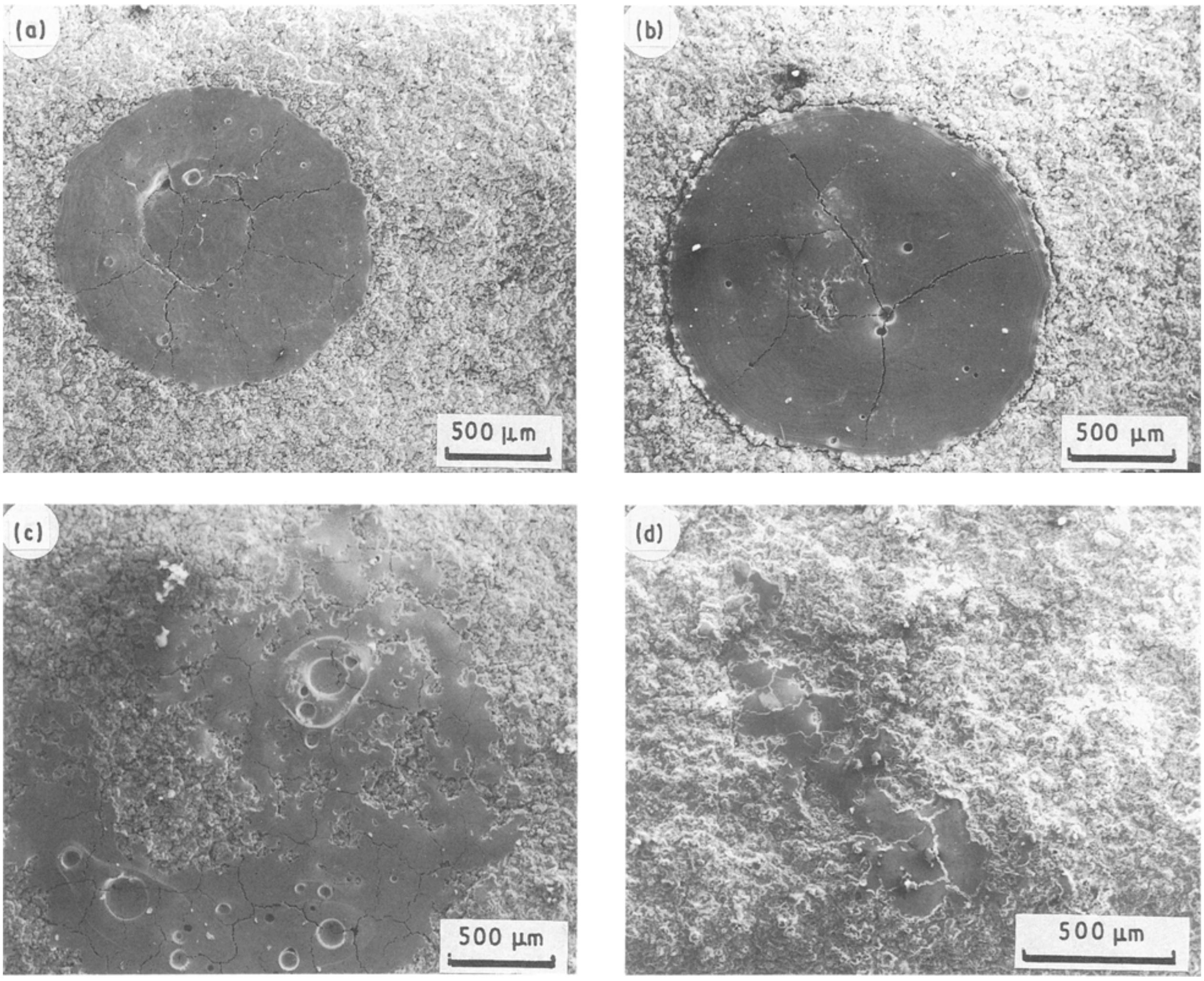


Figure 1 Scanning electron micrographs (plan view) showing the effect of power density of pulsed mode on the general appearance of the sealed region. 20 ms pulse length, 0.4 kW laser power and different beam diameters: (a) 0.4 mm, (b) 1.3 mm, (c) 3.5 mm and (d) 4.1 mm.

determined from observations of the surface using scanning electron microscopy (SEM) without any metallographical preparation. The roughness was also measured in terms of centre line average values obtained using a Talysurf. Finally, before sectioning the sample, the phases present in the sealed layer were determined by X-ray diffraction [9]. The samples were then cut transversely and ground and polished to determine the depth of sealing. Also, the compositions of the plasma-sprayed and sealed layers were determined using an energy dispersive X-ray system in association with the SEM.

3. Results and discussion

3.1. Effect of power density

Regions, pulsed sealed at 0.4 kW and different beam diameters (0.4–4.1 mm) with constant pulse length, are shown in Fig. 1. It can be seen that at the larger beam diameters (i.e. lower power densities) the laser-processed zone is not completely sealed. The minimum power density, P_A, required for effective pulse sealing to a depth of $\sim 10\,\mu m$ is deduced to be $\sim 45\,W\,mm^{-2}$ at 10 ms interaction time (i.e. $0.45\,J\,mm^{-2}$ specific energy). This value is less than those of previously reported work [8] on CW CO_2 laser sealing (e.g. 800 W power, 21 ms interaction time, $41\,W\,mm^{-2}$ power density and $0.79\,J\,mm^{-2}$ specific energy). This confirms the previous finding at 1 kW that lower specific energies (typically $< 0.5\,J\,mm^{-2}$) are needed for sealing with pulsing than with CW mode. On the other hand, the power densities are comparable for both laser modes. Furthermore, at values of power density and specific energy higher than the minimum required for sealing, the depth of sealing is greater in the pulsed mode.

CW-processed zones typically show a surface concavity, but these are of negligible depth in the pulsed mode. The formation of a concavity is attributed to evaporation loss and to elimination of porosity and it appears that for a given specific energy a higher temperature is reached in the melt pool with CW-processing conditions resulting in greater evaporation loss. The boiling point of ZrO_2 is high ($\sim 5000\,°C$) but it has been calculated that temperatures of 6000 °C can be obtained under CW processing of ZrO_2 at high specific energies [7].

Increasing the power density by decreasing the beam diameter was evidenced in the microstructure by an increase in the size of the cells. Solidification theory predicts that the cell size is larger the slower the cooling rate; therefore the results of the present and

TABLE II Comparison of the sealed cell size with that predicted from a $d^{0.8}P_A^{0.4}$ dependence on beam diameter and power density

Run	Beam diameter d (mm)	Pulse length t (ms)	Power density P_A (W mm^{-2})	Cell size (μm)	
				Measured	Predicted
1	3.9	20	83.7	1.5	[a]
2	4.1	20	30.3	1.0	1.0
3	2.5	20	81.5	1.3	1.1

[a] Run 1 used as a standard to predict the cell size of Runs 2 and 3.

TABLE III Phases present in the starting powder, plasma-sprayed layer and typical sealed layer (mol %)

Material	Monoclinic (m)	Tetragonal (t) transformable	Tetragonal (t′) non-transformable	Cubic (c)
Power	5.5	58.0	0	36.5
Plasma-sprayed layer	2.0	0	98.0	0
Laser-sealed layer	0	0	100	0

the previous work indicate that increasing power density, or increasing energy, E, by lengthening the time of pulsing, reduces the cooling rate in the melt pool. The cell size was previously shown to vary as $E^{0.4}$, which means it should also vary as $d^{0.8}$ $P_A{}^{0.4}$, where d is the beam diameter. The data from matched experiments at approximately the same power density but different beam diameters, and the converse (same diameter but different power density), confirmed this relationship (Table II).

With increasing power density of pulsing, the number of depressions per total area of sealing decreased rapidly; previously it had been found that the number decreased with increasing energy. However, the effect of P_A is more marked and it is preferable to use high power density and low interaction time to obtain good quality layers with few depressions and narrow crack width and low roughness. To obtain a required depth of sealing at a given power density, one would adjust the energy; the depth of sealing increases with increasing input energy at a given power density (Fig. 2).

The phase proportions as determined by X-ray diffraction in the precursor powder, plasma-sprayed layer and pulsed zone are presented in Table III. The

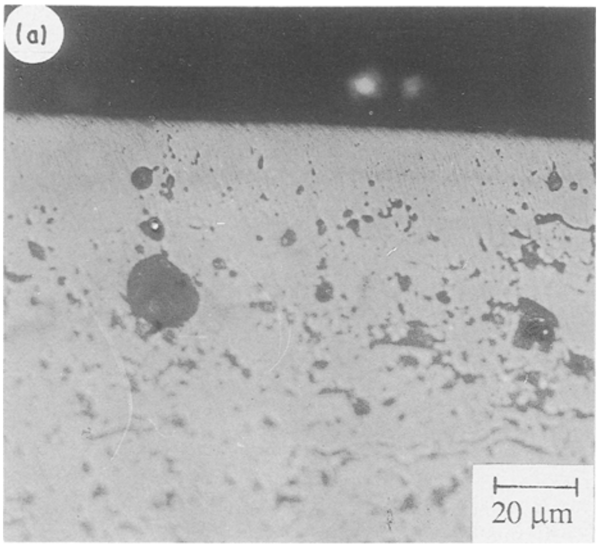
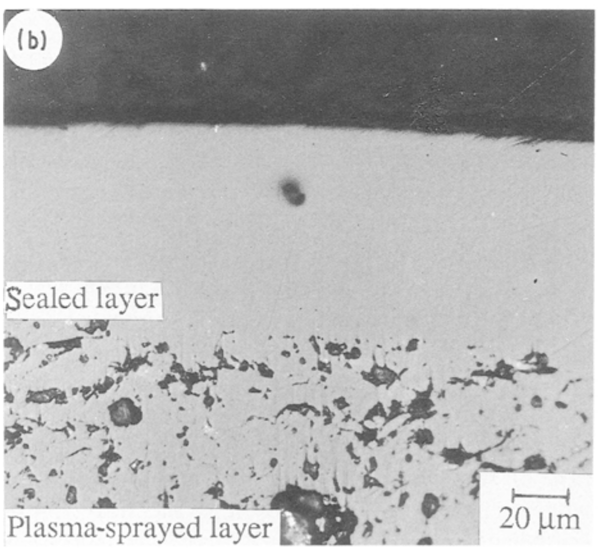
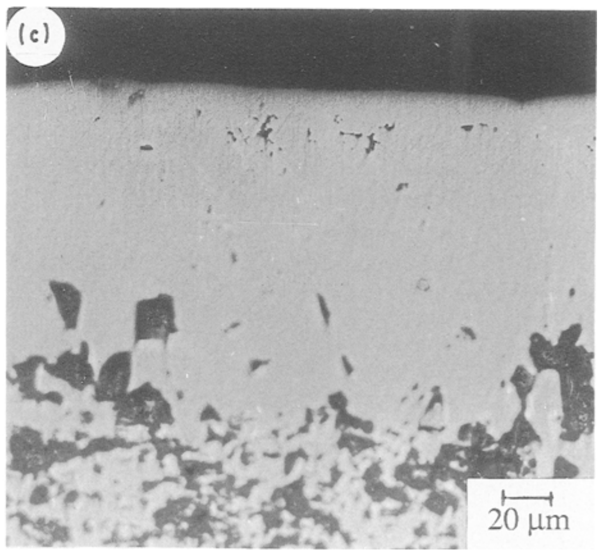


Figure 2 Transverse sections of as-sealed 8 wt % YPSZ layers showing the depth of sealing dependence on the pulse energy, 1 kW laser power, 3.9 mm beam diameter and different interaction times and energies: (a) 2 ms, 2 J, (b) 20 ms, 20 J, and (c) 40 ms, 40 J.





high t′ contents of the plasma-sprayed layer and laser-sealed zones (under all sealed conditions) are a consequence of the rapid solidification. The t′ phase has previously been found in CW-sealed layers but this is the first report of the phases present in a pulsed laser-sealed zone. The t′ phase of the pulsed laser-sealed zone exhibited the usual characteristic of not transforming during grinding or polishing.

3.2. Effect of preheating and laser-processing temperature

Preheating at 1000 °C for 1 h has been studied using a 3.9 mm beam diameter and 20 ms pulse length at 1 kW laser power and 40 ms pulse length at 0.4 kW laser power. Preheating prior to pulse laser processing markedly decreased the density of depressions. The mechanism of formation of depressions is not well understood, but it is suggested that it may be related to the release of expanding hot gases from the plasma-sprayed layer. The association of gases into bubbles, which escape upwards through the molten ceramic layer, is a probable mechanism. The preheating drives absorbed species and gases out of the plasma coating, thus reducing the availability of gas for bubble formation during laser processing. Preheating was successful in this context whether the subsequent processing temperature was room temperature or in the range 150–850 °C.

In fact, processing temperatures up to and including 850 °C had little effect on most features of the sealed regions. For example, the sealed region diameter remained at 3.5 ± 0.15 mm (Fig. 3), which was slightly less than the beam diameter, and the depth of sealing remained at 65 ± 5 μm at 1 kW and 20 ms interaction time and at 45 ± 5 μm at 0.4 kW and 40 ms interaction time. This may be attributed to the fact that the thermal conductivity of YPSZ is virtually invariant with temperature and/or to the heat content produced by processing at temperature being small compared to the energy input of the laser.

A negligible difference was found in the crack network spacing and crack width with change in processing temperature (Fig. 4). It can be shown [10] that the critical temperature change, ΔT_c, to produce microcracking due to thermal stresses associated with an infinitely fast quench is

$$\Delta T_c = \frac{\sigma_f(1 - \nu)}{E\alpha} \qquad (1)$$

where σ_f is the fracture stress, ν is Poisson's ratio, E is Young's modulus and α is the coefficient of thermal expansion. Substituting typical values (Table IV) [11, 12] for these parameters for YPSZ into this expression yields a value for ΔT_c of approximately 270 K. Thus, under an infinitely fast quench, cracking will be prevented if the temperature difference between the lowest temperature for plastic flow and the processing temperature is less than 270 K. If it is assumed that the temperature for plastic flow is approximately 60% of the melting point, i.e. 0.6 (2973) ~ 1785 K, then a processing temperature of about 1240 °C is required to prevent cracking during laser sealing. Note that the estimate of 1785 K is supported by the studies of Nieh and Wadsworth [13] which demonstrated that temperatures of 1673 K or above were necessary to prevent crack formation during hardness testing of YPSZ. Modifying the equation by the addition of some function of Biot's modulus ($\beta = ah/k$, where a is depth of sealing, h is the heat transfer coefficient and k is the thermal conductivity) to ac-

TABLE IV The properties of YPSZ used to calculate the thermal stress [11, 12]

$\sigma_f \sim 650$ MPa (fracture strength of YPSZ)
$E \sim 170$ GPa
$\alpha \sim 10^{-5}$ °C
$\nu \sim 0.29$

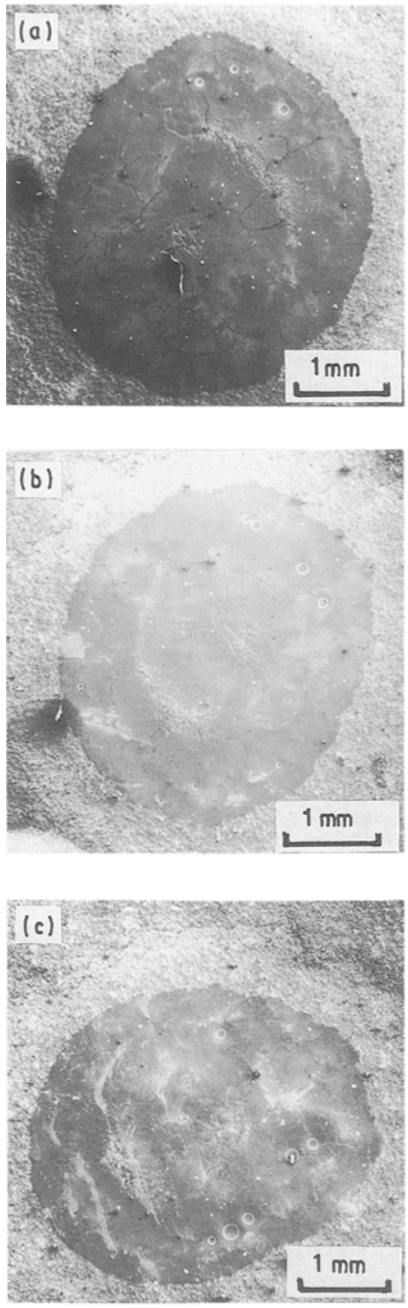


Figure 3 The general appearance of as-sealed 8 wt % YPSZ region processed at 1 kW laser power, 3.9 mm beam diameter, 20 ms pulsed length and at different processing temperatures: (a) 350 °C, (b) 650 °C and (c) 850 °C.

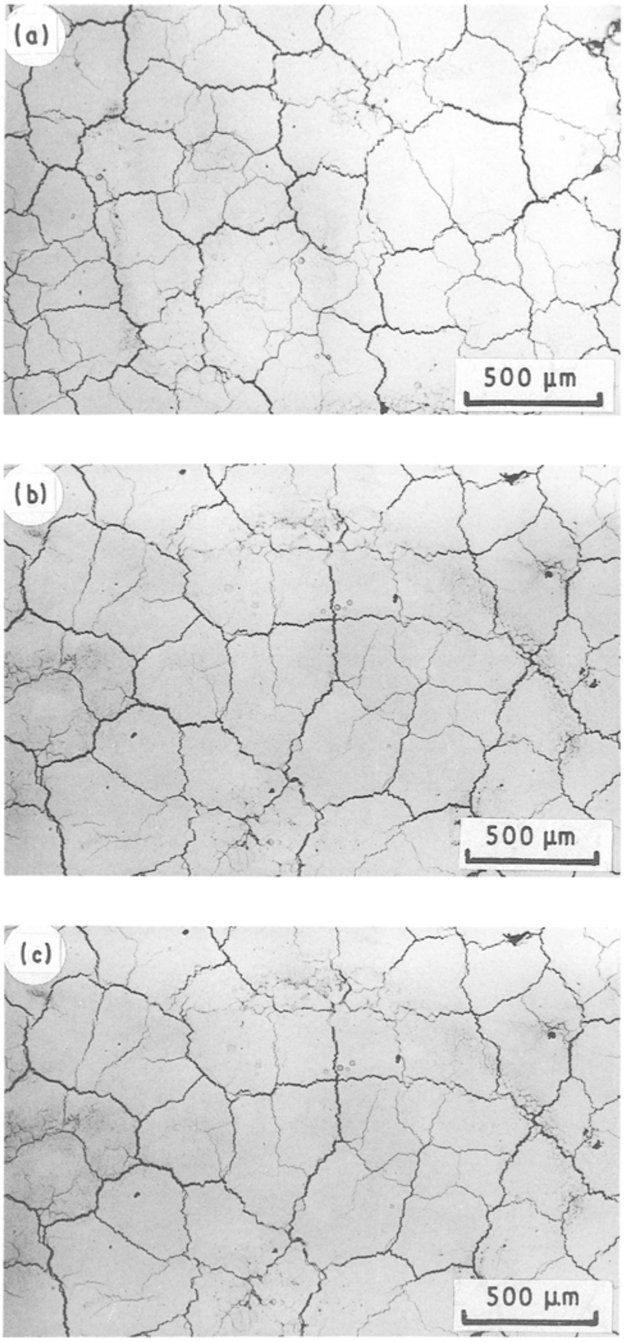


Figure 4 Plan view showing the crack width and crack spacing of as-sealed 8 wt % YPSZ layer processed at 1 kW laser power, 3.9 mm beam diameter, 20 ms pulse length and at different processing temperatures: (a) 250 °C, (b) 450 °C and (c) 550 °C.

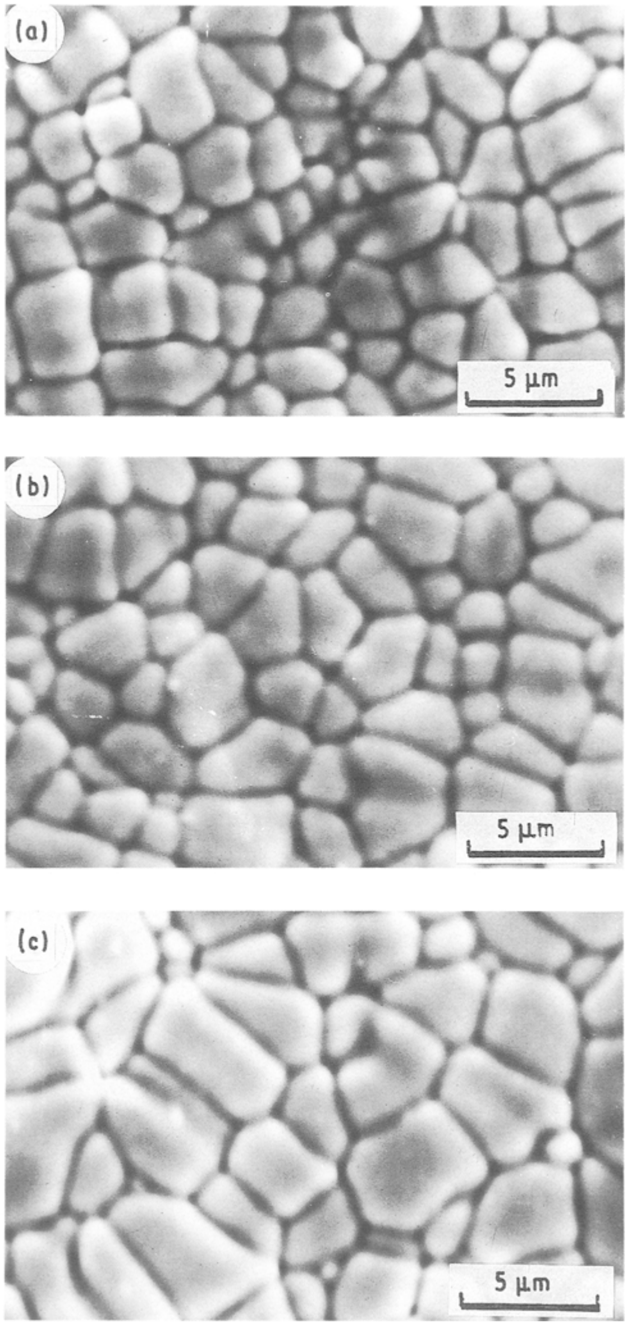


Figure 5 Scanning electron micrographs showing the cell size of as-sealed 8 wt % YPSZ region produced at 1 kW laser power, 3.9 mm beam diameter, 20 ms pulse length and at different processing temperatures: (a) 150 °C, (b) 350 °C and (c) 750 °C.

count for the quench not being infinitely fast, would increase the ΔT_c value and hence lower the predicted necessary processing temperature. Nevertheless, the simple calculation is consistent with the maximum processing temperature, 850 °C, being insufficient to prevent cracking.

The only feature of the sealed layer which was affected by the processing temperature was the cell size, which is known to be sensitive to cooling conditions from the melt. The cell size slightly increased from 1.8 µm to 2.2 µm as the processing temperature was raised from 150 °C to 850 °C, respectively and these values were greater than that obtained without preheating and processed at room temperature (~ 1.5 µm) (Fig. 5). This can be attributed to a decrease in heat transfer by conduction due to a smaller temperature difference between the melt zone and the surrounding material as the processing temperature increases; this results in a decrease in cooling rate and hence increase in cell size.

3.3. Repeated pulsing on a traversed sample

Repeated pulsing on a traversed sample with different on and off times was investigated at a power of 0.4 kW and a traverse speed of 7 mm s^{-1}. The beam diameter was 1.7 mm (i.e. under traversed conditions this corresponds to an interaction time of (d/V) of 1.7/7 = 0.243 s). The pulse lengths and pulse separations studied are shown in the Table V.

TABLE V Laser parameters for repetition pulses with sample traversed

Track no.	Traverse speed, V ($mm\,s^{-1}$)	Beam diameter, d (mm)	Interaction time d/V (ms)	Pulse length (ms)	Pulse separation (ms)	Roughness (CLA) (μm)
1	7	1.7	243	300	300	—
2	7	1.7	243	150	150	1.4
3	7	1.7	243	75	75	1
4	7	1.7	243	37.5	37.5	0.4

The width of the sealed track is expected to be a function of both the interaction time associated with the traverse speed, d/V, and also of the pulse length (time for which the laser is on) and the pulse separation (time when the laser is off); (the term frequency is used if the pulse length and pulse separation are equal and is defined as the number of pulses per second). For example for the first track, at the speed used ($7\,mm\,s^{-1}$) and beam diameter (1.7 mm), the processed region will have been melted and solidified within approximately 243 ms and the beam will cut-off for 300 ms; this means that the region of the first pulse will have solidified before the second pulse is started and the pulses do not overlap (Fig. 6a, track (i)). In contrast, in track four, the laser beam will only be on for 37.5 ms then cut-off for 37.5 ms; in this case the processed zone will receive three pulses before final solidification and hence a continuous track is produced (Fig. 6a, track (iv)).

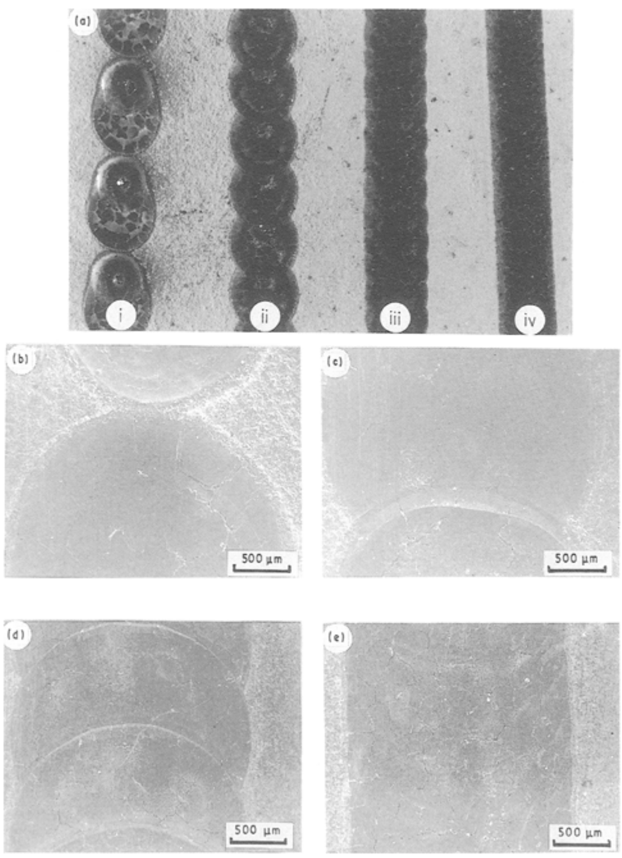


Figure 6 Plan view of 8 wt % YPSZ laser processed under repeated pulses on samples traversed relative to the beam, 0.4 kW laser power, 1.7 mm beam diameter and different pulse lengths and pulse separations: (a) general appeareance, (i) 300 ms pulse length and 300 ms pulse separation, (ii) 150 ms pulse length and 150 ms pulse separation, (iii) 75 mm pulse length and 75 ms pulse separation and (iv) 37.5 ms pulse length and 37.5 ms pulse separation; (b–e) higher magnifications of a(i)–a(iv), respectively.

The observations illustrated in Fig. 6 show that track width decreased by about 20 % on increasing the frequency from ~ 1.7 pulses per second to 13.5 pulses per second; this is due to the reduced energy per pulse and corresponding lower temperatures in the melt zone. Increasing the frequency also leads to a decrease in the crack width from ~ 11 μm at the lowest frequency to ~ 7 μm at the highest frequency. The crack network was finer (i.e. smaller spacing) the higher the frequency. The roughness improved significantly with increasing frequency; this was a consequence of the formation of a more uniform track at the higher frequencies due to overlapping of the pulses and absence of depressions (Table V). The roughness (0.4–1.4 μm) is less than in the CW mode which typically produced surface roughnesses of ~ 2.5–3 μm.

It is concluded that the depth of sealing and the roughness of the sealed layer produced with repeated pulses can be controlled by adjusting the following parameters: (i) traverse speed, (ii) beam diameter, (iii) power and (iv) frequency (off and on time) to give sealed layers of equal or better quality than those obtained in the CW mode.

3.4. Thermal shock and multipulses

Two important effects were observed in the thermal shock experiments on CW layers as illustrated in Fig. 7. Firstly, there was a high resistance to thermal shock of the sealed layers in that no crack propagation or new network cracks were observed in the surrounding CW-sealed layer. Secondly, complete removal of surface depressions, which were formed during CW laser sealing, took place during the second laser treatment. These depressions are considered to be associated with evolution of entrapped gas from the plasma-sprayed layer during sealing; little or no gas remains in the initially sealed layer to give rise to depressions during a remelting process. More than one pulse on the same site on the plasma-sprayed coating had a similar effect in removing the depressions in the processed region of the initial pulse (Fig. 8). This observation could account for the absence of depressions in traversed samples at high frequencies; under such conditions it is possible that the YPSZ has solidified and melted a number of times before final solidification.

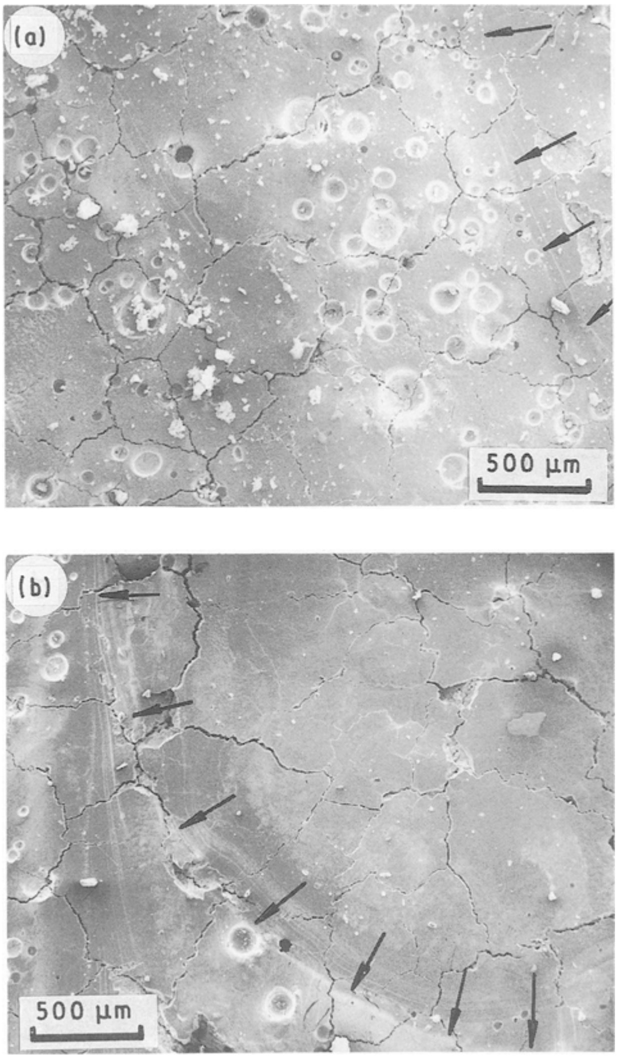


Figure 7 Scanning electron micrographs showing the effect of pulsing laser passes on the removal of depressions and thermal shock resistance of CW-sealed layer. (a) CW laser treatment (the upper right corner after CW + double pulses each of 50 J energy). CW mode conditions are 8.5 wt % YPSZ, 1 kW laser power, 5 mm beam diameter and 175 mm/s traverse speed. (b) Interface (arrows) between CW treatments and CW + pulses.

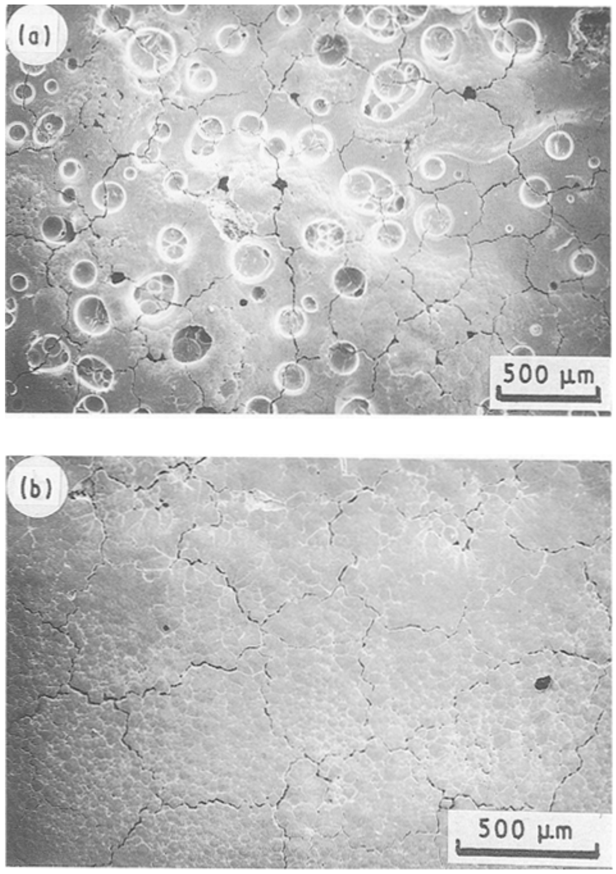


Figure 8 Scanning electron micrographs demonstrating the removal of depressions by multipulses. (a) as-sealed, single pulse, 3.9 mm beam diameter, 1 kW laser power and 10 ms pulse length (10 J energy); and (b) same as (a) with double pulses each 10 J.

4. Conclusions

The following conclusions may be drawn from this investigation of sealing of plasma sprayed ceramic layers of 8 wt % yttria-stabilized zirconia using a pulsed laser.

1. Similar features (cracking, depressions, cells, etc.) are found in both pulsed laser and CW laser-processed sealed layers but the details of these features differ, e.g. sealed layers produced by pulsing treatment contain less severe cracking than occurs as a result of CW laser processing at similar specific energies.

2. Laser parameter combinations of high power density (100–5000 W mm^{-2}) and short interaction times (0.1–20 ms) favour optimum quality of sealed zones produced by a single pulse.

3. The occurrence of surface depressions is reduced by preheating of the substrate to 1000 °C or by repeated pulsing treatments.

4. Processing temperatures up to 850 °C were not sufficient to prevent the thermally induced cracking associated with laser sealing. The only effect of processing temperature was a slight increase in cell size with increasing temperature as a result of the decrease in cooling rate.

5. The roughness of the sealed layers decreased with increasing frequency of repeated pulsing on a traversed sample and was less than that of a layer produced in the CW mode for comparable specific energies.

6. Pulsing of layers sealed by CW laser treatments or multipulse treatments on the same site produced no propagation of existing cracks or formation of new cracks, indicating good thermal shock resistance. This treatment also removed depressions as did multipulse treatments on the same site.

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