Laser surface treatment of porous ceramic substrate for application in solid oxide fuel cells

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Abstract. Laser has offered a large number of benefits for surface treatment of ceramics due to possibility of localized heating, very high heating/cooling rates and possibility of growth of structural configurations only produced under non-equilibrium high temperature conditions. The present work investigates oxidation of porous ZrB²-SiC sintered ceramic substrates through treatment by a 1072 ± 10 nm ytterbium fiber laser. A multi-layer structure is hence produced showing successively oxygen rich distinct layers. The porous bulk beneath these layers remained unaffected as this laser-formed oxide scale and protected the substrate from oxidation. A glassy SiO₂ structure thus obtained on the surface of the substrate becomes subject of interest for further research, specifically for its utilization as solid protonic conductor in Solid Oxide Fuel Cells (SOFCs).

1. Introduction
Nowadays, laser has become an alter native tool for materials processing, in particular for surface modification of refractory ceramics. However, the laser involvement on the treatment of structural ceramics for the purpose of protonic conducting fuel cell electrodes is still in initial stage.

As known, typical physical phenomenon occurs during laser-ceramic interaction such as heating, surface melting, surface vaporization, plasma formation and ablation [1]. These phenomena provide various treatments on the samples. One of the desirable lasers for surface treatment is ytterbium fiber laser (Yb-fiber laser). According to M. N. Zervas [2], high power Yb-fiber laser has been drawing attention to the material processing and other industrial applications. This due to their attractive features such as higher energy conversion efficiency (> 30 %), which is more than yttrium aluminium garnet (YAG) or CO₂ lasers [3–5] and finally the most highlighted feature is high heat localization that lead to higher precision of customizing product.

Several studies have reported Yb-fiber laser as a major tool for various properties modification such as electrical, mechanical, chemical and thermal. Study by Boutinguiza et al. [6] has reported that pulsed Yb-fiber laser ablation can be used to synthesize titanium oxide (TiO₂) at controllable size nano particles. In addition, they have also reported that the laser can be employed for formation of nano particles in solutions with reduced contamination, high particle collection, ease of preparation, low costs of processing and eventually many kind of colloidal nano particles can be obtained [6].

Meanwhile, other researchers [3–5] have employed laser particularly for the modification of physical properties of ceramics and morphology modification. The most recent study is on
modification of electrical properties which have been conducted via Yb-fiber laser [4,5] of such ceramics such as zinc oxide (ZnO) and TiO₂. Kido et al. [3] have also conducted patterns of the thermoelectric iron silicide on alumina substrates using the Yb-fiber laser. Apart from that, the same laser type also has been employed for the fabrication of ion conductive lines on glass surface, preparation of MgB₂ superconductive phase lines, crystal growth in CuO-doped lithium disilicate glasses[7] and surface densification of porous ZrC [8].

The idea to expand the usage of laser in favour of multi-layer formation is considered to be compelling. In aiming to produce protonic conducting layer which serves as electrolyte and undisturbed sub-layer as electrode could be a solution towards lowering operating temperature of solid oxide fuel cells. In near future it is expected that the weakness of anion conducting electrolyte could be resolved.

Yb-fiber laser have shown numerous promising future prospects for material processing to be further developed therefore, the current study will focus on the surface characterizations of ZrB₂-SiC ceramic substrates that had been treated via laser specifically for protonic conduction. Additionally, it may lead to greater understanding of laser treatment.

2. Materials and experimental procedures

The substrates consist of mixed raw powders which purchased from H.C Starck, USA; zirconium diboride (ZrB₂; Grade B; 97 %+) and silicon carbide (SiC; Grade UF-25-α-SiC; 98 %+). Average particle size for ZrB₂ and SiC was 1.5 µm and 0.45 µm, respectively. The average particle size was identified by laser diffraction particle size analyzer (Horiba; LA-950V2). They were used without further treatment.

2.1. Powder mixture preparation and pelletizing

With the intention of simple mixing, both powders were immersed together in ligroin also known as petroleum ether. ZrB₂ was mixed with 30 vol.% SiC. The mixtures were stirred for approximately 5 min in a 30 kHz ultrasonic bath. Then, the slurry was left overnight for solvent evaporation and put in the oven at 80 °C to remove excess moisture for the pelletizing. The mixed powders were pelletized by uniaxial cold pressing at 40 MPa using stainless steel die 10 mm in diameter. The dimension of pellets produced from 1.15g was roughly 10 mm in diameter and 4 mm in thickness.

2.2. Sintering

Ambient sintering was conducted in the Nabertherm (VHT-08-22/GR) furnace under argon flow. The set-up temperature and holding time were 1900 °C and 2.5 hr, respectively. Both heating and cooling rate was kept at 10 °C/min.

2.3. Laser oxidation conditions

The surface oxidation was employed via ytterbium fiber laser (IPG, Oxford, MA, USA; model LCF 100). It was conducted under ambient environment. As shown in Figure 1, a round spiral laser pattern was scanned onto the ZrB₂-SiC ceramic substrates. The laser specifications were as tabulated in Table 1. The beam diameter was reduced to 1.25 mm with beam reducer (LINOS) and the pattern dimension was 8 mm × 8 mm in diameter. An optimum laser power was identified at 70 W.
Table 1. Typical specification of ytterbium fibre laser and treatment condition

| Laser Parameters                  | Condition         |
|-----------------------------------|-------------------|
| Mode of operation                 | Continuous wave   |
| Central emission wavelength       | 1072 ± 10 nm      |
| Nominal output power              | 100 W             |
| Typical beam quality              | < 1.1             |
| Laser beam diameter               | 1.25 mm           |
| Environment                       | Ambient           |

3. Characterization techniques
The surface view and fractured morphological structure of the cross section of ZrB₂-SiC ceramic composites were observed through scanning electron microscope SEM (Philips XL30) equipped with EDS (Oxford Instruments-INCA, UK). X-ray diffraction was performed using Siemens D5000 diffractometer equipped with a Cu anticathode and a back monochromator. These characterizations were conducted for as sintered and laser-treated pellets.

4. Results and discussion
4.1. Untreated ZrB₂-SiC ceramic substrates
Figure 3 represents micrograph of sintered SiC-ZrB₂ polished surface in BSE mode after pressure less sintering at 1900 °C. As can be observed, light phase indicates ZrB₂ and grey phase as SiC. Approximately 30 % remaining porosity can be seen very well in between the grains. The pores were expected due to the usage of pressure less sintering and absence of the sintering aids other than a major contribution from fine SiC powder which acts as a second phase and also helps reduce the sintering time and temperature. The SiC grains were distributed uniformly and played a positive role in sintering as can be observed in the micrograph. The microstructure obtained is consistent with the other previous studies on ZrB₂-SiC ceramic composites[9–25].

Figure 1. A round spiral laser pattern was designed for laser surface treatment[26]

Figure 2. Micrograph of laser-treated surface of ZrB₂-SiC at 70 W in secondary electrons mode (SE)[26]
4.2. Laser-treated ZrB$_2$-SiC ceramic substrates

Micrograph of laser-treated surface of ZrB$_2$-SiC substrate is presented in Figure 2. The laser treatment on the surface of the substrate has resulted in surface melting. This glassy surface layer is expected to be rich in oxide. The overlapping laser track is still visible due to high heat localization from the laser as well as the spiral pattern. If observed closely a network of fine white line scan be observed which is also known as crazing. This similar structure is discussed Mahmod et al. (2015) studies [26].

The SEM study of the cross section reveals a multilayer structure. On Figure 4 it is revealed just below the treated ZrB$_2$-SiC surface. Beneath the heat affected multi-layer structure the bulk of the substrate remained unaffected. Here, a multi-layer structure formation could be divided into four main layers, although these are not very clearly divided by a boundary but are diffused into each other. A descriptive micrograph in Figure 4 displays the predicted compounds that are present in every layer. In Figure 5, micrograph of higher magnification of silica rich layer is presented in order to highly focus on the surface layer fractured cross-section. Apparently, the silica thickness is approximately 8 µm. From our point of view, spherical particles can also be observed and identified as ZrO$_2$ particles. EDS analysis was conducted to verify the presence of each element. Figure 6 (a), (b), (c), and (d) present the composition and elemental distribution within each layer.

As seen at layer 1, EDS pattern in Figure 6(a) exhibited higher peak of Si and also Zr together with O element. These peaks give indication of silica rich layer with some presence of ZrO$_2$. However, C element could also be observed. In our opinion, it could be due to the decomposition of SiC. The following reaction could have possibly occurred:

$$\text{ZrB}_2 + \text{SiC} + 4\text{O}_2 \rightarrow \text{SiO}_2 + \text{B}_2\text{O}_3 + \text{ZrO}_2 + \text{CO} \quad (1)$$

Figure 6(b) displayed EDS analysis at layer 2, sharp peaks of Zr, Si and O elements were present and the region is depleted of B and C elements. The high peak of Zr indicates a higher concentration of ZrO$_2$ and lower peak of Si indicates that small amount of SiO$_2$ is also present. The depleted B and C elements could be assumed as a result of partial decomposition ZrB$_2$ and SiC. Figure 6(c) represents a very sharp peak of Zr and B. These peaks place in evidence that layer 3 is rich with ZrB$_2$ and apparent porous SiC. Finally, Figure 6(d) represents the unaffected region just above the bulk. The depletion of O element also confirmed the effective glassy layer which is pronounced as resistant towards the oxidation.
The use of laser surface treatment in this particular case is conducted to cover the surface of a porous mixed boride carbide ceramic composite substrate with a glassy layer. The treatment was conducted in
ambient atmosphere hence sufficient oxygen was available for oxidation of the surface layer. Such interesting results have been reported for the first time [26] whereby the laser heat is localized and the oxygen rich surface layer actually protects further oxygen penetration into the bulk of the substrate. Future investigation of the thermal and electrical conductivity of glassy layer would allow understanding and forecasting the use of such structures for protonic conductivity within solid oxide fuel cells.

5. Conclusion and outlooks
Conclusively, the present study has shown that laser surface treatment can be employed on ZrB$_2$-SiC ceramic composites. The localized heat treatment due to intense laser results in a multi-layer structure. The silica-rich glassy layer formation signifies that the oxidation has been highly localized. This formation protects the beneath layer. Furthermore, the round spiral laser pattern allowed a uniform heat distribution but it can be also customized according to various applications. Further study is required to be carried out on the performance of glassy layer as a protonic conductor. Other type of ceramic materials such as TiB$_2$ could be suggested to be employed for laser surface treatment that might offer solutions for the crazing pattern that occurred in the present study.

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