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Surface densification of porous ZrC by a laser process

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Abstract

Thin films of 100%-dense zirconium carbide, ZrC, on top of ca. 30%-porous ZrC are obtained by using an ytterbium-doped fibre laser under argon atmosphere. It is shown experimentally and theoretically that oxidation into zirconia or oxycarbide is completely avoided at the working temperature of at least 3420 °C. This type of highly refractory materials – dense at the surface and porous in the bulk – could be used in high temperature applications where both diffusion and thermal barrier properties are needed. This process could also be used to purify from oxygen the surface of carbides obtained by thermal carboreduction of oxides.

Keywords: Zirconium carbide; Ytterbium-doped fibre laser; Dense surface; Porous core; Diffusion and thermal barrier

1. Introduction

In this report we present the first experimental results concerning the fabrication of a zirconium carbide material having a ca. 30%-porous core covered with a 100%-dense surface layer, by using an ytterbium-doped fibre laser process.

ZrC is a non-oxide ceramic with mixed ionic and metallic bonding character,[1,2] high refractory properties (melting point = 3420 °C, Vickers hardness $\simeq$ 27 GPa),[1,3,4] medium-to-good resistance to aqueous and dry corrosion, and low neutron absorption cross section.[5] It has numerous industrial applications: it is used in cutting-tool and hard-coating industry, in electric and electronic devices,[6] it is one of the candidates as coating layer for nuclear fuel in future Generation IV reactors,[7] etc. With the original morphology that we propose in the present paper, i.e., a porous bulk combined to a dense surface, the number of applications could be increased. Indeed, applications involving ZrC where both the thermal and the diffusion barrier behaviours are needed, could be imagined.

2. Experimental

Our process is the following:

(i) First, porous ZrC pellets were classically obtained by hot-press sintering from a commercial powder, under neutral atmosphere (Air Products X50S Argon). Sintering was achieved in an HP furnace (LPA, France) with a 1.5 h treatment at 1850 °C, under 40 MPa pressure. The ZrC commercial powder was from CERAC (Milwaukee, WI, USA). Its mean diameter was ca. 10 μm, its purity >99.5%. The powder was used directly, without further purification. A recent study showed that the formula of this commerical powder might be $ZrC_{0.94}$.[8]

(ii) Then, the surface of the pellets was polished (silicon carbide abrasive paper, from 600 to 4000 grits). It can be noticed here that this step of the process was of importance, the surface roughness being closely related to the laser absorbance and reflectivity by the material.

(iii) To finish, porous pre-sintered ZrC pellets were treated on their surface by ytterbium laser (IPG, Oxford, MA, USA; model LCF 100). The laser characteristics were the following: continuous wave, TEM_{00}, wavelength: 1072 ± 10 nm; output power: 100 W, beam diameter: 2.5 mm, power density: 2 kW/cm^2. A high resolution motorized X–Y table combined with an axes controller allowed to scan the

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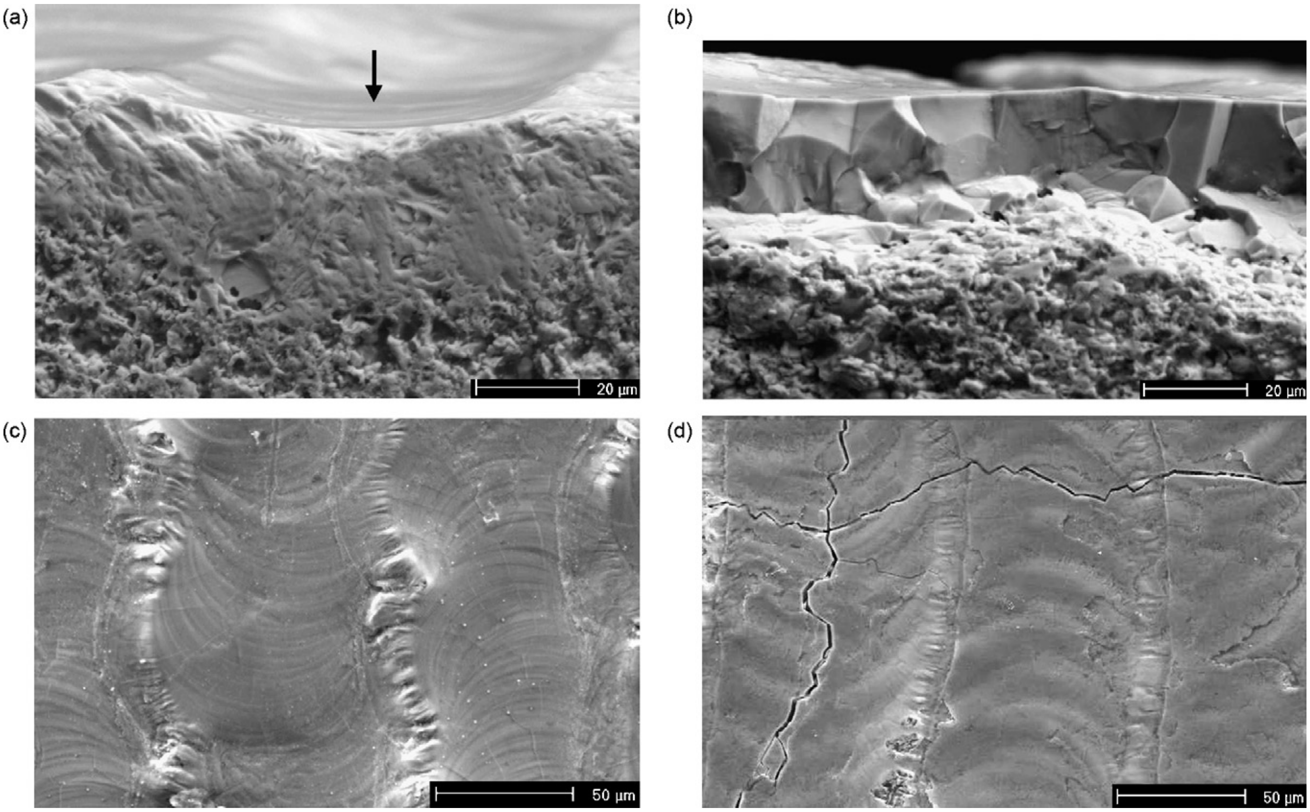

Fig. 1. SEM images (in secondary electrons detection mode) of porous ZrC after Yb-laser treatment; (a) cross section after polishing with abrasive paper; the arrow shows the center of a laser track, i.e., where Vickers hardness measurements were typically performed; (b) cross section after fracture; (c) and (d) top views as obtained after laser treatment.

surface (Newport, CA, USA; models M-ILS100CC and ESP 300). Laser treatment was performed under argon atmosphere in a homemade cell (pressure: 1 atm, flow rate: 2.8×10^{-4} m^3/s). The argon used was of the grade Alphagaz 1, from Air Liquide, France, and contained less than 2 ppm of dioxygen. In order to detect any oxidation of ZrC, samples were analyzed by X-ray diffraction at every step of the process, using a Siemens D5000 diffractometer, with copper anticathode and a back monochromator. For observations, a Philips XL 30 scanning electron microscope (SEM) was used in secondary electron mode, with in situ energy dispersive X-ray spectroscopy (EDS). For hardness measurements, a Microhardness Tester (Presi, France) was used with a load of 200 g applied for 15 s. Helium pycnometry was performed with a Quantachrome MPY-2 apparatus (Boynton Beach, FL, USA).

3. Results

3.1. Samples morphology and composition

Fig. 1 are SEM images of porous ZrC after laser treatment. Subfigure (a) is a cross section after polishing. Subfigure (b) is a similar cross section but after fracture. Subfigures (c) and (d) are top views.

Bottoms of Fig. 1(a) and (b) show that the original porous core of the sample is preserved after the laser passage. Indeed, a by-eye observation confirms a porosity of ca. 30%, as measured by helium pycnometry on pre-sintered pellets.

Tops of the same figures, and also Fig. 1(c), illustrate the high densification of the surface, especially Fig. 1(b), where a brittle fracture is displayed. Dense layers of thickness ∼25 µm with no trace of porosity can be observed.

XRD patterns of Fig. 2 compile: (a) the JCPDS-ICDD card #35-0784 for the stoichiometric compound, ZrC_1; (b) the diffractogram of the starting commercial powder; the diffractograms of the HP-sintered ZrC before (c) and after (d) laser passage. The only peaks of ZrC are visible at every step of the process, signifying that no quantitative crystallized extra phase (zirconium dioxide, etc.) is present. Moreover, no shifts on the 2θ angles were detected, i.e., the lattice parameter does not change. This proves that there is no oxygen insertion in the ZrC lattice, and hence, no formation of oxy-carbide, ZrC_xO_{1-x}.

The observations above are confirmed by the EDS analysis made on the laser-treated surface (Fig. 3). Oxygen atoms are not present at ∼0.5 keV, only the peaks of carbon and zirconium being visible. All this is an important experimental result: indeed, it shows that oxidation can be totally avoided thanks to our process.

Surface morphology is visible in Fig. 1(c) and (d). No grain boundaries are visible despite the crystallinity of the sample, as attested by Fig. 2. Picturesquely speaking, it looks like a liquid surface wrinkled by an airstream. Such a feature has already been reported for molten surfaces with intense convective flows,

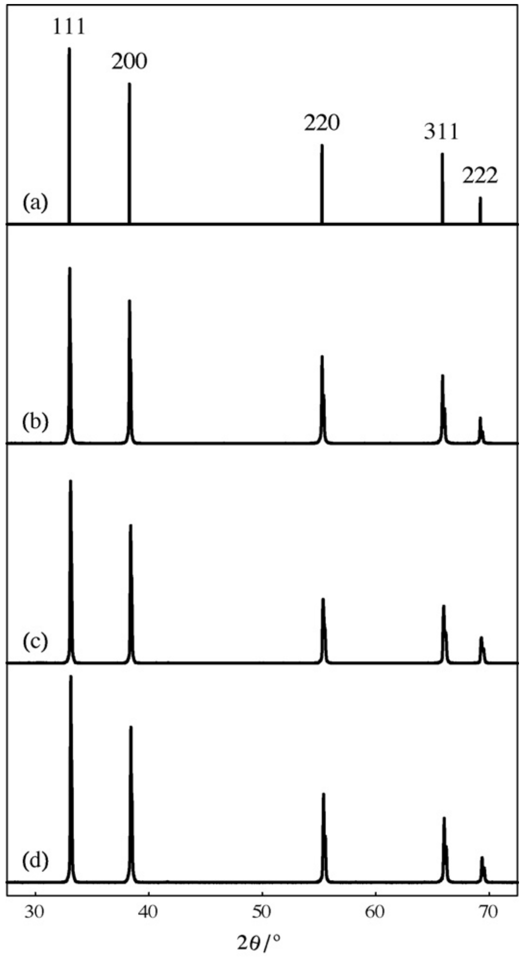

Fig. 2. X-ray diffraction patterns; (a) from ZrC's JCPDS-ICDD card #35-0784; (b) ZrC commercial powder; (c) porous ZrC obtained by hot-press sintering; (d) surface-densified ZrC obtained after Yb-laser treatment under Ar atmosphere.

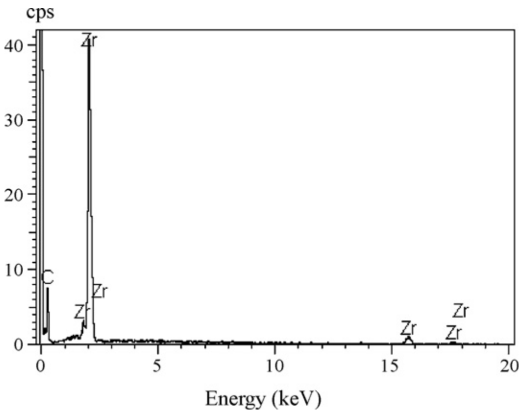

Fig. 3. EDS spectrum of the surface of laser-treated ZrC.

suddenly quenched.[9–13] This clearly indicates that the local temperature under the laser beam can reach at least 3420 °C, i.e., ZrC's melting point.

As in every high temperature surface treatment, cracks due to thermomechanical stresses appeared locally[9] on the dense layer during the rapid solidification of liquid ZrC (Fig. 1(d)). But those were few, remained superficial and did not fragilize the samples, the fracture energy being likely absorbed by the porous bulk just beneath the dense layer.

3.2. *Surface mechanics*

Vickers microhardness measurements, H_v, were performed on the surface, after laser treatment. The arrow in Fig. 1(a) shows a typical spot where these measurements were done. A hardness of $H_v = 26.3 \pm 2.7$ GPa was found (mean of 10 measurements, with a 95% confidence interval).

The angle of the Vickers diamond being normalized, i.e., $\theta = 136°$, and the diagonal of the indentation left on the surface measuring roughly 12 μm, the depth of penetration, p, can be estimated to $p = \bar{d}/(2\tan\theta/2) \simeq 2.5\ \mu\text{m}$. This latter value remains by far lower than the thickness of the laser-obtained layer, hence the present H_v measurement can be considered as representative of the surface microhardness. Note that this value of H_v is very close to that of pure and massive ZrC.[3,4]

The adhesion of the dense layer on the porous core is very good, and no pealing has been observed. This is probably due to good wettability of the liquid phase on the underlying solid which has the same composition.

3.3. *Influence of the exposure time under laser beam*

Samples were treated under laser beam for different durations. This was achieved by two different ways:

(i) by varying the scan rate between 0.1 and 1 mm/s for a fixed number of cycles (two);
(ii) by cycling 1, 2 or 3 times on the same zone at the scan rate of 1 mm/s.

Fig. 4 presents the thickness of dense carbide obtained according to the exposure conditions just given above. Thickness measurements were done on cross section micrographs, at the center of the laser spot, i.e., where the dense part is the thickest (see Fig. 1(a)).

Curve (a) in Fig. 4 shows that thickness decreases when scan rate increases. Indeed, the melted zone thickness is 53 ± 3 μm for a scan rate of 0.1 mm/s, and 42 ± 3 μm for a scan rate 10 times higher. This result is logical because samples remained for longer times under the laser beam when the scan rate was lower, and so, heat transfer was more important. This is quantified in Fig. 5, where the exposure duration at the center of the passage zone, t_{laser}, was evaluated following:

$$t_{\text{laser}} = \frac{\phi}{\text{v}}, \tag{1}$$

where ϕ is the laser beam diameter (2.5 mm), and v the scan rate. Fig. 5 shows that melting of superficial ZrC occured almost instantaneously (probably less than a second), and that the melting zone thickens slowly after having reached ca. 40 μm. No simple relation between thickness and t_{laser} could be found.

The influence of the number of cycles, given by curve (b) in Fig. 4, confirms this result: the major part of thickening is

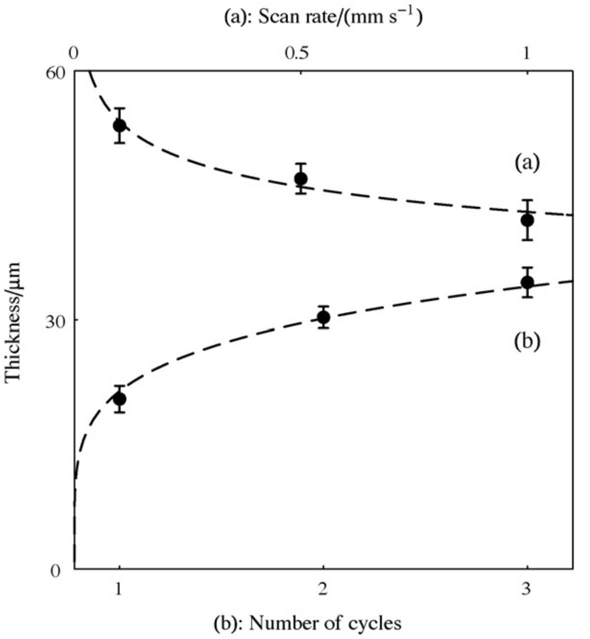

Fig. 4. Variation of the thickness of the dense surface layer with (a) the X–Y table scan rate, and (b) with the number of laser cycles. Dots are average values of 10 measurements, and error bars represent 95% confidence interval.

achieved with only one passage, with a thickness of ca. 20 μm, for only ca. 34 μm after three passages.

A slight discrepancy of roughly 5 μm, for which we have no clear explanation for the moment, can be seen for the data at 1 mm/s and two cycles. This may be due to the sintering step, or, more likely, to the polishing one (cf. Section 2).

4. Discussion

These results show that even a very short exposure under an Yb-laser beam – under the conditions precised above – is sufficient for obtaining a 20–60 μm thick dense layer of pure ZrC. This proves that energy transfer between a 1.072 μm near-infrared laser radiation and this material is important.

In fact, it appears that maintaining the samples for long durations under the laser beam do not give a thickening of the dense zone as noticeable as expected on the basis of the result obtained after short times. This is probably due to a complex heat transfer mechanism in the solid, which also may explain that no simple relation was found between exposure time and thickness of dense carbide. Indeed, heat provided to the solid by the laser radiation is evacuated by

(i) ZrC melting heat;
(ii) heat transfer inside the solid toward its bulk;
(iii) heat transfer with the surrounding gas.

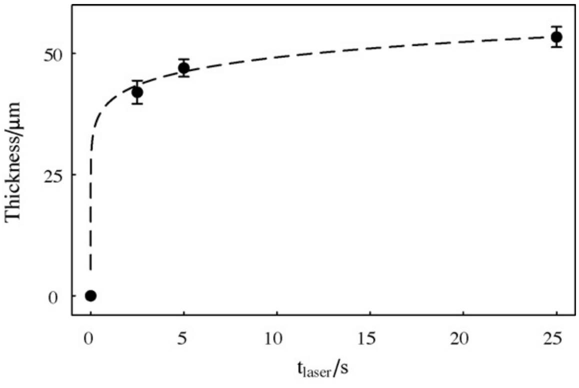

Fig. 5. Thickness vs. laser exposure time curve, obtained from Fig. 4(a), and using Eq. (1).

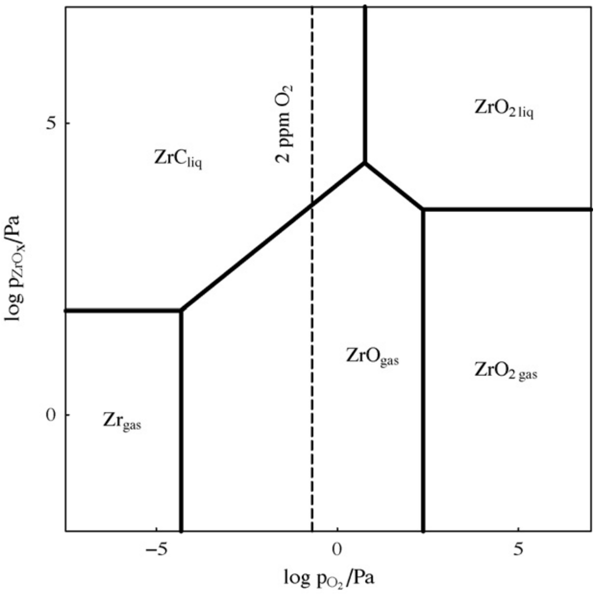

Fig. 6. Volatility diagram for the system Zr–O–C at 3693 K (3420 °C) as a function of dioxygen partial pressure.

Only a rigorous modeling could quantify the importance of each of these processes, and their evolution with time. But unfortunately, the basis of such calculations are, to the best of our knowledge, either not available (thermal contact resistance at the gaseous argon–liquid ZrC interface), or difficult to establish (e.g., thermal transfers in a porous material such as ZrC obtained by HP sintering).

Now, the most surprising is the high level of purity of the ZrC dense layer. Indeed, our laser treatment occurs under a protective argon flow, but its quality (2 ppm; see Section 2) is not so good that it can guarantee a complete absence of oxidation. At this point, it seemed interesting to search the thermodynamical conditions of existence of ZrC, Zr, ZrO_2 and ZrO, liquid, solid or gaseous. For this, the volatility diagram of these species has been plotted in Fig. 6 at 3693 K (3420 °C),[6] i.e., where solid phases are no longer present. Knowing that the argon we used contained 2 ppm of dioxygen (0.2 Pa), and that hermiticity of the cell was certainly not total, one may assume that O_2 content during the treatment was in the range of 1–10 Pa. Looking at Fig. 6, this means that the thermodynamically stable phase at high temperatures is very likely ZrC. Under these conditions, traces of dioxygen react with the carbide to give gaseous zirconium monoxide, ZrO, that departs with argon flow. This interpretation is valid as far as thermodynamic equilibria are attained during the time of experiment. But, according to the high temperatures that are reached (it is recalled here that ZrC melted), such reactions are probably very rapid and assumption of thermodynamic equilibria is certainly acceptable.

To finish, it can be noticed that this process could be used to purify superficially ZrC obtained by thermal carboreduction of ZrO_2,[6] or to purify ZrC sintered with oxide additives.[14]

5. Conclusion

An ytterbium-doped fibre laser technique under argon atmosphere allowed us to densify at 100% the surface of ca. 30%-porous ZrC materials, the original porosity remaining beneath. Absolutely no traces of oxidation into zirconia or oxycarbide were observed. This type of refractory materials – dense at the surface and porous in the bulk – could be used in high temperature applications where both diffusion and thermal barrier properties are needed.

It is clear that this work has to be considered as a first approach of a very promising technique. The next step will be the healing of surface micro-cracks. The effect of the duration of the laser treatment, which has been clearly proven, has to be quantified more precisely, and related to the proportion of cracking. It could be also of interest to use a simultaneous double laser beam technique,[9] where a secondary, larger beam warms up the area around the principal, hotter beam that actually melts the surface. This process might decrease drastically thermal gradients around the melted zone, and therefore, reduce stresses in the dense layer, and avoid cracking. Finally, and as discussed above, it may be interesting to test this process in the case of ZrC densified with oxide additions.

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