Radio frequency-assisted zirconium carbide matrix deposition for continuous fiber-reinforced ultra high temperature ceramic matrix composites

Tammana S. R. C. Murthy1,2 | Ji Zou1 | V. Venkatachalam1 | Ravi K. Biroju3 | Wolfgang Theis3 | Jon Binner1

1School of Metallurgy and Materials, University of Birmingham, Birmingham, UK
2Bhabha Atomic Research Centre, Mumbai, India
3Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, UK

Correspondence
Tammana S.R.C. Murthy, School of Metallurgy and Materials, University of Birmingham, UK.
Email: murthi321@bnb.ac.in, murthi@barc.gov.in

Present address
Ji Zou, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, P. R. China
Ravi K. Biroju, Centre for Nanodiagnostics of Materials, Faculty of Materials Science and Technology, Slovak University of Technology, Vazovova, Bratislava, Slovakia

Funding information
WHIPCAT, Grant/Award Number: 750929; European Union Horizon 2020

Abstract
Zirconium carbide (ZrC) is considered to be a potential candidate for ultra high temperature applications due to its high melting point, good chemical inertness, and ablation resistance, but the monolithic form suffers from low fracture toughness and hence poor thermal shock resistance. Reinforcing it using continuous carbon fibers (Cfs) to create an ultra high temperature ceramic matrix composite is an obvious solution, however densifying ZrC requires the use of very high temperatures combined with significant pressure, such as obtained by using hot pressing or spark plasma sintering, which risks damaging fibers. In the present work, radio frequency-assisted chemical vapor infiltration (RF-CVI) has been investigated with a view to forming Cfs/ZrC composites. These initial experiments revealed the ability to deposit pure, nano-grained, and near stoichiometric ZrC with deposition occurring preferentially from the center of the sample due to the nature of the inverse temperature profile developed. The deposited ZrC grains were in the range of 4–9 nm in size and had a lattice parameter of 0.4750 nm. The work also showed that the use of RF-CVI enabled the minimization of early pore sealing, a common problem for conventional CVI.

KEYWORDS
radio frequency-assisted chemical vapor infiltration, ultra high temperature ceramic matrix composite, zirconium carbide

1 | INTRODUCTION

The aerospace and related industries have a critical need for composite materials that are stronger, lighter, more corrosion resistant, and perform at elevated temperatures under ablative conditions.1–9 Ceramic matrix composites (CMCs) combine the advantages of the high-temperature properties of ceramics with high flaw tolerance achieved through fiber reinforcement and processing that allows weak bonding to exist between the fibers and

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2024 The Author(s). Journal of the American Ceramic Society published by Wiley Periodicals LLC on behalf of American Ceramic Society.
the matrix.\textsuperscript{2,10–13} As a result, CMCs offer pseudo-ductility based on three underlying mechanisms, for example, i) frictional dissipation at the fibre-matrix interface, ii) matrix cracking to increase the elastic compliance, and iii) stress redistribution produced by matrix cracking.\textsuperscript{13} Implicit in these mechanisms is the assumption that the cracks in the matrix are bridged to some degree by the fibers.

Increasingly, new aerospace propulsion concepts are requiring ever-higher temperature compatibility; both rocket and hyper-velocity vehicles have applications such as leading edges, nozzles, and other engine parts that require service temperatures in the range of 2200–3000°C.\textsuperscript{14,15} Whilst ultra high temperature ceramics (UHTCs) offer the desired temperature capability, they lack the required fracture toughness and hence thermal shock resistance.\textsuperscript{16–18} Reinforcing them with continuous fibers yields UHTC matrix composites (UHTCMCs) that have the potential to meet the desired performance criteria.\textsuperscript{1,4}

Zirconium carbide (ZrC) is one of the refractory metal monocarbides that are part of the family of ultra high temperature ceramics, UHTCs. Whilst it has the rock salt crystal structure, Fm3m space group, it is typically carbon deficient\textsuperscript{13} with \( x \) in ZrC\(_x\) taking values ranging from 0.63 to 0.98.\textsuperscript{19,20} This affects both the ceramic's sinterability and its mechanical, thermal, and electrical properties as well as its radiation resistance.\textsuperscript{23} Whilst stoichiometric or near stoichiometric compounds are always preferable due to their superior properties,\textsuperscript{22} they are rarely achieved by conventional solid-solid reaction synthesis methods. Nevertheless, ZrC offers a high melting point (~3530°C) and hardness (~25 GPa) as well as high electrical and thermal conductivity due to the presence of a combination of metallic (Zr-Zr) and covalent (Zr-C) bonds. It also provides high load-bearing capabilities and excellent ablation and corrosion resistance against molten metals and slags.\textsuperscript{8,9,13}

Historically, the use of hot pressing or spark plasma sintering to create UHTCMCs has typically resulted in damage to the carbon fibers (C\(_f\))s due to the high sintering temperatures required, coarse microstructures, and, without the use of an interfacial layer, the components are brittle.\textsuperscript{2,11} They are dense, however, which yields both good strengths and reduces the oxidative attack of the fibers and matrix.\textsuperscript{2,11} Other methods such as polymer impregnation and pyrolysis, melt infiltration, and chemical vapor infiltration (CVI) are also commonly used techniques for fabricating UHTCMCs.\textsuperscript{2,15} Whilst each has its advantages and disadvantages,\textsuperscript{1} the CVI route offers the potential to create reasonably dense, complex-shaped components at low processing temperatures without the application of external pressure.\textsuperscript{21} The matrix can also be pure and fine-grained.\textsuperscript{1,18} Nonetheless, it is an inherently slow process, making the resulting product potentially expensive. Another notable challenge encountered when fabricating UHTC-based materials is the limited infiltration depth for large radicals such as Hf, Zr, and Ta.\textsuperscript{2} Amongst the different variations developed to overcome all these limitations, the use of microwave or radio frequency (RF) energy to heat the fiber preform yields an inverse thermal gradient profile that causes the preform to be densified from the inside out.\textsuperscript{24} This has been shown to greatly reduce the process times whilst retaining all of the advantages of the CVI process.\textsuperscript{24,25}

In the present work, therefore, RF-heated chemical vapor infiltration has been explored as a potential process route for fabricating 2.5D C\(_f\) composites based on a ZrC matrix.\textsuperscript{2} These initial experiments were conducted to assess the viability of producing nano-grain-sized ZrC and to confirm the infiltration of large Zr radicals within the preform through RF-CVI. The resulting product was characterized using both a transmission electron microscope (TEM) and a scanning TEM (STEM).

## EXPERIMENTS

Note that, 2.5D C\(_f\) needled preforms with 23 vol% fiber volume (Surface Transforms) were used as the reinforcing phase whilst the ZrC matrix was deposited through the preforms using RF-CVI. A schematic of the custom-built facility is shown in Figure 1. ZrCl\(_4\), methane, and hydrogen were used as the precursor gases; the reaction is shown in Equation (1). Details of the C\(_f\) preforms and the gases are listed in Table 1.

\[
\text{ZrCl}_4 + \text{CH}_4 + \text{H}_2 \rightarrow \text{ZrC} + 4\text{HCl} + \text{H}_2 \tag{1}
\]

The ZrCl\(_4\) vapor was produced using a chlorinator at a temperature of 210°C,\textsuperscript{26} following initial experiments at temperatures ranging from 150 to 350°C, and argon was used as the carrier gas to the reaction chamber. Heating was undertaken using an RF coil (Easy Heat 150–400 kHz 4.2 kW; Ambrell) around a quartz tube and the temperature was measured using a non-contact surface infrared pyrometer (thermometer CTM; Micro-Epsilon). Initial trial experiments used temperatures varying from 800 to 1100°C and chamber pressures from 60 to 150 mbar to determine the best processing parameters in order to obtain the desired single-phase ZrC. Thermodynamic data for ZrC formation under different conditions are provided in Figure S1. After 1 h, the deposited ZrC was characterized in terms of its crystal structure by powder X-ray diffraction (model D8; Bruker), using Ni-filtered Cu K\(_{\alpha}\) radiation (\( \lambda = 0.15418 \) nm) and a step size of 0.021°. The crystal size was calculated using the standard Scherer equation.\textsuperscript{27} The
FIGURE 1  (A) Schematic showing the inverse temperature profile developed during radio frequency-assisted chemical vapor infiltration (RF-CVI); (B) photograph showing an actual temperature gradient across the sample; (C) schematic of custom—built RF-CVI setup; (D) scanning electron microscopy (SEM) image at the center of a typical sample after 1 h at 1000°C showing the significant deposit achieved; (E) a similar image at the edge of the same sample showing hardly any deposit.

TABLE 1 Starting materials, processing conditions, and product details of zirconium carbide (ZrC) deposited on carbon fiber (Cf) using radio frequency-assisted chemical vapor infiltration (RF-CVI).

<table>
<thead>
<tr>
<th>Starting materials/product details</th>
<th>Properties/details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5D carbon fiber preforms</td>
<td>Volume: 23 vol.%; pore size: 9–10 µm; preparation method: carbonisation of Ox-PAN at 1000–3000°C; supplier: Surface Transforms plc.</td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>Supplier: Acros Organics, zirconium (IV) chloride, 98%, anhydrous</td>
</tr>
<tr>
<td>CH₄</td>
<td>CP grade N25; purity: 100%</td>
</tr>
<tr>
<td>H₂</td>
<td>Minimum purity of 99.99%</td>
</tr>
<tr>
<td>Processing conditions</td>
<td>Temperature: 1000°C; chamber pressure: 100 mbar; ratio of ZrCl₄:CH₄:H₂ = 1:1:10; chlorinator temperature: 210°C; deposition time: 1 h</td>
</tr>
<tr>
<td>Product details</td>
<td>XRD: ZrC mean grain size: ~9 nm (Scherer equation) and ~6 nm (TEM/STEM images); lattice parameter: 0.4750 nm</td>
</tr>
<tr>
<td>Percentage of plane orientations observed</td>
<td>59% [111]; 19% [200]; 17% [202]; 3% [311], 1% [222], 1% [400]</td>
</tr>
</tbody>
</table>

morphology and composition of the deposit were characterized using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS, model TM3030Plus; Hitachi) and TEM-EDS-SAED (model 2100; JEOL) whilst high-angle annular dark-field (HAADF)-STEM studies (JEOL 2100F, 200 kV) were conducted using an aberration-corrected HAADF-STEM mode. As for previous work,9,11 for the TEM and STEM investigations a small quantity of ground, coated CFs was added into ethanol solution and the latter was ultrasonicated for 10 min. A drop of the suspension was placed on a carbon-coated copper grid for the analysis, a technique commonly known as the drop-casting method.9,11 The stoichiometry of ZrC was therefore analyzed using three distinct techniques, for example, XRD, TEM, and STEM.

3 | RESULTS AND DISCUSSION

Figure 1A shows a schematic of the temperature gradient present during the RF heating of a Cf preform; the center of the sample is shown to be hotter, known as an inverse temperature profile, and this is supported experimentally in Figure 1B. This resulted in the initial deposition of ZrC in the center of the preform as desired. Over time, the temperature profile during RF-CVI changes and gradually
allows deposition to occur across more and more of the sample until the surface is reached. Several trial runs were carried out to optimize the processing parameters, including the chlorinator temperature for evaporation of the ZrCl₄, the flow rate of the argon for carrying the ZrCl₄ to the reaction chamber, the ratio of the CH₄, ZrCl₄, and H₂, the reaction chamber pressure and the maximum temperature. All the conditions investigated are outlined in Table 1, together with the optimized processing conditions identified. The resulting deposits were thoroughly characterized.

Both visual and microstructural characterization revealed that the initial deposition occurred preferentially at the center of the sample as desired; SEM images at the center and edge of the sample are presented in Figure 1D and 1E, respectively. Figure 1D shows a thin, continuous ZrC deposit on the fibers, whereas Figure 1E shows only very small and isolated deposits on the fibers. These results confirm the benefit of the inverse temperature profile obtained by RF heating.

The deposited matrix was analyzed by SEM-EDS and XRD to analyze the chemistry, morphology, and phases present. Figure 2A presents an SEM image of ZrC-coated Cₐₙ and elemental mapping for Zr and C. The former, Figure 2B, clearly shows the presence of Zr on all fibers, whereas the C signals are much weaker due to the element’s low atomic number. Figure 2C. Figure 2D presents the semi-quantitative analysis of Zr and C obtained from the EDS data whilst Figure 2E presents the XRD pattern of the Cₐₙ and deposits showing the peaks correspond to graphite and ZrC. Neither ZrO₂ nor incomplete reaction products from ZrCl₄ were observed in the XRD analysis or the SEM-EDS data. Peak broadening was observed in the RF-CVI deposited ZrC, whilst a commercial ZrC powder, shown for comparison, had an average particle size of ~2 µm. The crystallite size calculated for the RF-CVI deposited ZrC using the Scherer formula by measuring the full-width half maximum was ~9 nm. High-resolution electron microscopy was used for further confirmation of crystal size, purity, and morphology.

TEM-EDS-SAED data are presented in Figure 3. Figure 3A shows the fine nano-size ZrC grains deposited on the Cₐₙ. Figure 3A inset shows a higher magnification view of the ZrC grains, with the selected area electron diffraction (SAED) pattern and EDS results confirming the composition and phase. No voids or pores were observed within the deposited ZrC grains. The SAED pattern presented in Figure 3B matches with the zone axis of [112] for the ZrC cubic structure, whilst Figure 3C shows the EDS pattern with dominant peaks of Zr and C, as expected.
FIGURE 3  Analysis of zirconium carbide (ZrC) deposited for 1 h at 1000°C on C (A) transmission electron microscopy (TEM) image with, inset, higher mag. image; (B) selected area electron diffraction (SAED) pattern confirming the [112] zone axis; (C) energy dispersive X-ray spectroscopy (EDS) analysis showing the dominant elements; (D) scanning TEM (TEM) image showing a single grain at higher magnification; (E) interplanar spacing of different grains.

presence of the Cu and Cr peaks arose from the TEM grid that was used to hold the sample.

High-resolution STEM images were also obtained and are presented in Figure 3D,E. A total of 60 images were obtained and 230 grains were analyzed in order to determine the average grain size and interplanar spacings. All grains were measured to be in the range of 4–9 nm and the average size was measured as 6 nm, supporting the data in Figure 3A and the Scherer formula calculations that suggested 9 nm. The lattice parameter was determined to be 0.4750 nm, which is very close to the value for stoichiometric ZrC (0.4704 nm23 and 0.4698 nm24); the interplanar spacings of different grains are marked in images Figure 3D,E. The majority of the planes, 59%, belonged to the [111] family, with the [200] and [202] being the next dominant. Overall, the TEM and STEM results confirm that near stoichiometric ZrC was formed in the present work. Usually, the ratio of C to Zr varies from 0.3 to 0.98.15 A slight overlapping of individual ZrC grains is also clearly seen in Figure 3E, which indicates the good bonding between the grains. In addition, impurity phases, such as free carbon, ZrO2, and Zr, were not seen in the present study.

Thermogravimetry-differential scanning calorimetry (TG-DSC) measurements were undertaken at up to 1450°C for three different samples collected from the center (c), middle (m), and edge (e), Figure 4 (inset). The center of the sample is where the maximum deposition took place, as previously stated and shown in Figure 1D, whilst hardly any deposition was found at the sample edge, Figure 1E. This meant that the TG-DSC analysis was for largely underdeposited Cs for the edge (e) sample, whilst it was a combination of both Cs and ZrC for the central (c) sample, with the middle sample (m) being intermediate. Consequently, the weight loss observed started at different temperatures for all three samples and had different intensities of exothermic peaks. Figure 4 shows that the start of the oxidation reaction was at 600 and 660°C for the central and edge samples respectively, whilst the mass loss was completed for the edge sample at 780°C and
at 850°C for the central sample. 100% weight loss was observed for the edge sample as compared to the central sample, which had 90% wt. loss. The exothermic peak intensity of the central sample was five times lower than that of the edge sample. Overall, therefore, the results indicate that for the edge sample, which will have been more or less entirely Cₚ, oxidation was completed within a narrow temperature range of 120°C and with a sharp and high-intensity exothermic peak, whereas for the central sample, which also contained the ZrC, oxidation occurred with less intensity and over a wider range of 250°C. Hence the ZrC successfully protected the Cₚ to a degree.

From the above results, it can be summarised that continuous fiber-reinforced ZrC-based composites can be successfully prepared using the RF-CVI technique. As far as it can be gauged, the nature of the deposit itself is not changed by the use of RF-CVI rather it is its location that changes due to the temperature profile developed. Deposition initially occurs more in the center of the preform and then, as infiltration continues, the densification front moves outwards. This significantly reduces the phenomenon of ’crusting’ that occurs during conventional CVI. The latter is when the pores at the surface become blocked due to the surface being the hottest location, necessitating the stopping of the process and the machining of the sample surfaces before the process can be restarted. One reason that conventional CVI is so slow is due to the crusting issue, combined with the use of extremely slow heating rates to minimize the conventional thermal gradients. For example, Sayir and Chen et al. employed the conventional CVI process to produce composites comprising C/HfC, C/TaC, and C/HfC-TaC. Unfortunately, these composites demonstrated inadequate mechanical properties and low density, factors that were primarily attributed to the crusting phenomenon. However, advantages that arise from CVI-based routes, such as the very high purity and fine crystal size deposits achievable, were also seen in the present work. The former will be due to the high purity of the precursor gases along with the leak-tight reaction chamber, whilst the latter is probably due to the low processing temperature needed of only ∼1000°C. These promising initial results support the more general view that RF-CVI can be a very useful manufacturing route for UHTCMCs.

4 | CONCLUSION

A single phase, near stoichiometric ZrC, has been successfully deposited into 2.5D Cₚ preforms using an RF-CVI system. Due to the nature of the RF heating, the deposition occurred initially at the preform center and then spread, with time, toward the surfaces of the preform as desired. This ‘inverse deposition pattern’, compared to conventional CVI, means that ‘crusting’ can be avoided, thus speeding up the infiltration process. The deposited ZrC grains were in the range of 4–9 nm in size and had a lattice parameter of 0.4750 nm. Preliminary experimental findings in RF-CVI substantiate the feasibility of ZrC formation through the infiltration of sizable Zr radicals within the preform.

ACKNOWLEDGMENTS

This project received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant (EREMOZ) agreement No 748568. The authors would like to acknowledge Mr. Frank Biddlestone for the TGA data. B.Ravi acknowledges the European Union’s Horizon 2020 research and innovation program under the program WHIPCAT, Marie-Sklodowska-Curie individual fellowship, grant agreement ID: 750929.

ORCID

Tammanna S. R. C. Murthy https://orcid.org/0000-0002-9489-1689
Ji Zou https://orcid.org/0000-0002-5803-8533
Jon Binner https://orcid.org/0000-0003-1496-6837

REFERENCES

Verlag GmbH & Co. KGaA; 2008. https://doi.org/10.1002/9783527622412


SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.

Graphical Abstract

Please note that Graphical Abstracts only appear online as part of a table of contents and are not part of the main article (therefore, they do not appear in the article HTML or PDF files).