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Microstructural development of a C_f/ZrC composite manufactured by reactive melt infiltration

Linhua Zou [a,*], Natalie Wali [a], Jenn-Ming Yang [a], Narottam P. Bansal [b]

[a] Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095-1595, USA
[b] NASA Glenn Research Center, Cleveland, OH 44135, USA

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Abstract

The microstructural development of a carbon fibre reinforced ZrC matrix composite, C_f/ZrC, manufactured by reactive melt infiltration (RMI) was investigated. The microstructural features of the composite were revealed by optical microscopy (OM), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It was found that the carbon fibre bundles are surrounded by continuous ZrC layers, while the composite matrix is composed of island-like ZrC particles dispersed within an α-Zr–ZrC eutectic phase. Nanosized inclusions were found inside some ZrC particles and it was demonstrated that they were α-Zr or α-Zr–ZrC. A formation mechanism of the unique matrix microstructure is proposed.

Keywords: Composites (B); Microstructure (B); Carbon (D); ZrC; Reactive melt infiltration

1. Introduction

New and innovative structural materials capable of prolonged operation in oxidizing environments at temperatures above 2000 °C are required for future space systems.[1] For example, sharp leading edges and nose tips of advanced hypersonic and space vehicles will have to withstand exposure to high temperatures (>2200 °C) and severe thermal cycling in both neutral and oxidizing environments. The combustion temperature of a liquid bipropellant rocket engine used for placing satellites in orbit and planetary exploration will reach close to 3000 °C. The extreme operational conditions encountered for hypersonic and space vehicles as well as rocket propulsion systems present a great challenge to the development of ultra high temperature materials.

The most widely studied ultra high temperature materials (UHTMs) are refractory borides, nitrides and carbides. Among these ultrahigh temperature ceramics, ZrC possesses a melting point as high as 3540 °C and is one of the most promising candidates for ultra-high temperature applications due to the 2700 °C (∼4900 °F) melting point of its protective zirconia (ZrO_2) layer. The oxidation resistance of ZrC is comparable to that of hafnium carbide, HfC, and the density of ZrC (6.73 g/cm^3) is about half that of HfC (12.2 g/cm^3). However, ZrC ceramics are brittle and display little to no plasticity within a broad temperature range. As a result, the incorporation of fibres is needed to improve the fracture resistance and damage tolerance of ZrC. Various approaches such as chemical vapor infiltration (CVI), hot pressing, spark plasma sintering (SPS), RMI, etc. can be used to fabricate fibre-reinforced ZrC composites. CVI is a lengthy and expensive manufacturing process for ceramic matrix composites (CMCs). Additionally, it is very difficult to fabricate a fully dense CMC. Hot pressing or SPS of fibre/powder stacks is another technique for consolidating ZrC-based composites. However, both hot pressing and SPS are also extremely costly due to the high pressures and temperatures involved, and it is virtually impossible to fabricate complex geometries using these techniques. As a result, both CVI and hot pressing/SPS are not practical manufacturing processes for ZrC-based composites. Because of these challenges, limited efforts have been made to develop a ZrC-based composite for ultrahigh temperature aero-structures.

Reactive melt infiltration/reaction (RMI) has been demonstrated as a rapid and low-cost manufacturing process

* Corresponding author. Tel.: +1 310 825 2758; fax: +1 310 206 7353.
E-mail address: linhua_zou@hotmail.edu (L. Zou).

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for structural components made of carbon/silicon carbide composites.[2–7] However, carbon/zirconium carbide composites fabricated by RMI still have not been reported so far. RMI can be used when one of the ceramic matrix elements possesses a relatively low melting point and readily wets the fibres. Ideally, in RMI all available macroscopic porosities (i.e. the porosity between fibre laminates and tows) are rapidly filled to yield a dense, uniformly infiltrated composite. Furthermore, components with complex geometries, such as sharp leading edges and rocket engine combustion chambers, can be fabricated easily by RMI.

In this study, the microstructural development of a C_f/ZrC composite manufactured by RMI was studied based on microstructural analysis, with focus especially on the matrix. A microstructural formation mechanism is proposed.

2. Experimental

2.1. Materials

The carbon fibre reinforced ZrC composite was fabricated by Ultramet (Pacoima, CA, USA) using RMI. A high strength carbon fibre, T700S (Toray, Japan) was selected. In the first processing step, a carbon fibre preform was coated with the desired interface. The coated fibres were then woven into a two-dimensional fabric preform. Next, a controlled level of carbon was rapidly deposited onto the preform using CVD to form a porous C/C skeleton. Molten zirconium then infiltrated the porous preform by wicking action. The molten metal was drawn along the carbon fibre tows by capillary forces, where it reacted with the previously deposited carbon to form the ZrC matrix.

2.2. Microstructural characterization

The microstructural features of the melt infiltrated composite were thoroughly analyzed using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Optical images were taken using a Nikon 9600 light optical microscope with Q Capture software for image acquisition. Cross-sectional view and top view samples were polished to 0.05 μm for observation. Sample etching was performed with a Unaxis SLR770 ICP Minispec system in flowing Cl_2. The recipe adopted contained 50 vol% BCl_3, 10 vol% Ar, and 40 vol% Cl_2.

A Panalytical X'Pert Pro X-ray Powder Diffractometer was used to carry out X-ray diffraction analysis using a Cu target. Voltage was set as 45 kV, current 40 mA, and a X'celerator RTMS Scanning Detector was used. X'pert highscore software was used to identify each peak.

SEM images were obtained with a LEO 1550VP FE-SEM with Smart SEM software. EDAX was performed using INCA software for the LEO 1550VP to determine chemical composition.

Several TEM samples from within ZrC particles were prepared by a focused ion beam (FIB). Conventional methods were also used to prepare matrix area samples. TEM samples were prepared by grinding a bulk sample to ~50 μm in thickness and then a 3 mm diameter disc was cut out. The disc was subsequently dimpled and ion milled. Images and selected area electron diffraction (SAED) patterns were obtained with a JEOL 100CX and a FEI PHILIPS-CM300 TEM.

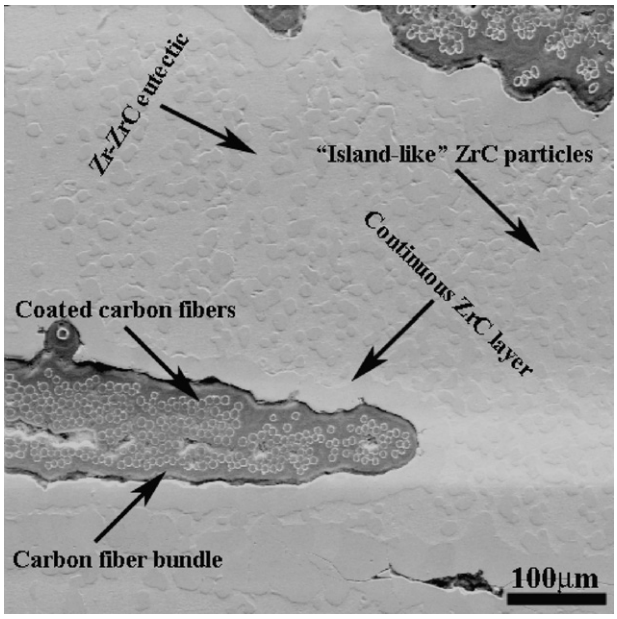

Fig. 1. SEM micrograph of the polished cross section surface of the C_f/ZrC composite with labeled microstructural sites of interest.

3. Results

3.1. General microstructural features of the C_f/ZrC composite

Microstructural characterization was conducted to analyze the different phases of the C_f/ZrC composite. The work included studying phase morphologies and determining the overall formation mechanism of the microstructure. A representative area

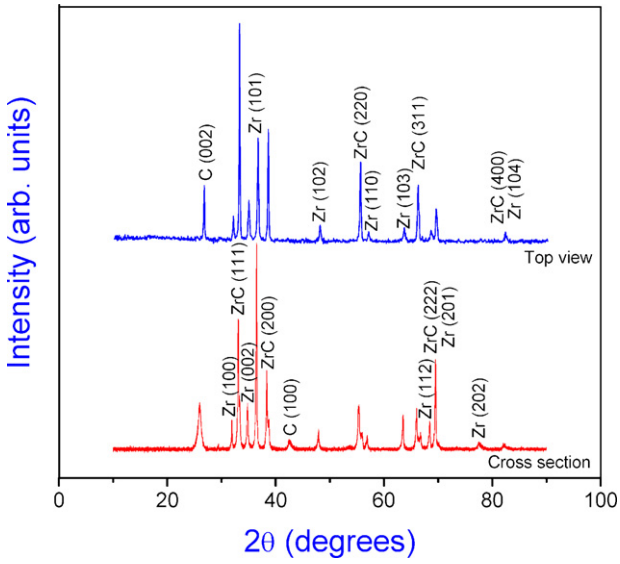

Fig. 2. XRD pattern of the C_f/ZrC composite.