Zirconium Carbide for Hypersonic Applications

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At ultra-high temperatures, resilient, durable, stable material choices are limited. While Carbon/Carbon (C/C) composites (carbon fibers and carbon matrix phases) are the materials of choice, zirconium carbide (ZrC) provides an option in hypersonic environments and specifically in wing leading edge (WLE) applications.

Keywords: ZrC ; hypersonics ; ultra-high temperature ceramics

1. Introduction

Zirconium carbide is an ultra-high temperature ceramic (UHTC) material, characterized by a very high melting point, high fracture toughness, and maintained strength at high temperatures. ZrC is promising for many aerospace and nuclear applications, specifically as a material to replace ^{C/C} composites as a Wing Leading Edge (WLE) material ^[1]. Vasile et al. have reported the utilization of ZrC composites as thermal barriers for the aerospace industry ^[2]. However, ZrC presents materials engineering challenges that must be solved for its practical implementation. One of these challenges is the fact that ZrC is a non-stoichiometric binary compound resulting from synthesis in materials with either a zirconium surplus or carbon deficiency ^[3]. ZrC can be formed with a wide carbon composition ranging from 36 at% to 50 at%. Outside this range, multiphase compounds are formed. This wide range differs from other materials that might be described as line compounds and have very narrow stoichiometric ranges. This wide composition range in ZrC impacts, amongst other things, its melting point.

Across this wide composition range, the temperatures at which ZrC is stable vary over 1000 °C. At the lowest carbon concentration (36 at%), it is only stable up to 1854 °C; at this temperature, it undergoes a phase transition to a two-phase composition. A phase transition is also observed at the maximum carbon concentration (50 at%) at 2927 °C. The most stable composition at high temperatures occurs at around C = 45%. At this composition, ZrC is stable until it melts at 3427 °C. The non-stoichiometric ratio of Zr:C leads to the creation of vacancies in the lattice. Impurities can occupy these vacancies, distorting lattice parameters, especially at high temperatures. This distortion results in decreased mechanical and thermal properties and impacts its chemical stability. For example, Tiwari and Feng note the strong influence of defects and impurities as factors that inhibit phonon vibration that limits attaining the theoretical thermal conductivity at ultra-high temperatures to yield materials with enhanced material properties. Most current research in ZrC examines its use in high-temperature composites, coatings, and ablative mechanisms on account of its strengthening properties, thermal conductivity, or CTE match to substrates [SIIGIIZIIBII9II10II11].

2. ZrC Physical Properties

The physical properties of ZrC are discussed and compared to those of C/C composites. In addition to ultra-high melting points, another major advantage of C/C composites is their specific strength. Specific strength is the ratio of the material strength divided by its density. Advanced C/C, or ACC, are composites exhibiting the highest specific strength of any material at elevated temperatures ^[12].

While specific strength is an important consideration, other material properties need to be considered in evaluating ZrC suitability for WLE applications. These are summarized in **Table 1** ^{[10][12][13][14][15][16][17]}.

Property	C/C	ZrC
Melting Point (°C)	3552	3532
СТЕ (К⁻¹)	-0.6	4

Table 1. Material properties of C/C and ZrC.

Property	C/C	ZrC
Density (g cm ⁻³)	1.3 to 2.5	6.73
Thermal Conductivity (W $m^{-1} K^{-1}$)	7.5–47.5	17.5–31.5
Flexure Strength (MPa)	140 ± 8	460 ± 24
Elastic Modulus (GPa)	43 to 240	435

Table 1 lists values at room temperature for C/C and ZrC. The CTE of C/C is negative from room temperature to 400 °C; thereafter, it increases from 0.4 to $0.6 \times 10^{-6} \text{ K}^{-1}$ at 900 °C ^[18]. This is a challenge for protective coating solutions with materials with a different CTE. ZrC has a CTE that is closer matched to other materials at room temperature, increasing to 9.0 and $10.2 \times 10^{-6} \text{ K}^{-1}$ at 1500 °C and 2500 °C, respectively ^[13].

Density is an important factor for aerospace applications, as less weight is advantageous for flight; C/C has a lower density which depends on the volume fraction of fiber to matrix. ZrC has a density that is on the order of three times larger, but the density of ZrC is significantly less than other alternatives such as nickel-based superalloys $\frac{[7][12]}{12}$.

The thermal conductivity in C/C is a directionally dependent property. Luo et al. measured thermal conductivities at room temperature between 7.5 and 21 W m⁻¹ K⁻¹ in the Z-direction and 31 to 47.5 W m⁻¹ K⁻¹ in the X-Y plane. The range changes to 3.5 to 22.5 W m⁻¹ K⁻¹ in the Z-direction and 27.5 to 50 W m⁻¹ K⁻¹ in the X-Y direction at 900 °C [18]. For ZrC, the thermal conductivity increases from 17.5 to 31 W m⁻¹ K⁻¹ at room temperature to 27.5 to 37.5 W m⁻¹ K⁻¹ at 1500 °C (the range of values corresponding to different experimental results) ^[19].

The experimentally reported value of flexure strength at room temperature is 140 ± 8 MPa and 460 ± 24 MPa for commercial C/C and ZrC, respectively. Data were not found for the flexure strength of C/C at higher temperatures, but the flexure strength of ZrC increases to 494 ± 44 MPa at $1600 \degree$ C before decreasing to 366 ± 46 MPa at $1800 \degree$ C; this unusual behavior is further discussed in a later section $\frac{[10][20]}{2}$.

The effective elastic modulus of C/C ranges from 43 to 240 GPa by Windhorst and Naga et al.; the range reflects differences in processing conditions and volume fraction of fibers to matrix ^{[12][21]}. Comparatively, ZrC has a larger elastic modulus reported by Zhang as 434.9 GPa at room temperature and decreasing to 334.3 GPa at 1227 °C and 277.2 GPa at 1827 °C, which is higher than the upper bound reported for C/C ^[22].

The increase in mechanical strength of ZrC is advantageous for wing leading edge applications. At the wing tip, the pressure and temperature profiles become extreme in comparison to other components on the fuselage or body of the aircraft. Material properties degrade at high temperatures, so incorporating in a hypersonic vehicle ZrC that maintains its strength and stiffness at these temperatures is advantageous.

3. ZrC Crystal Structure

Crystallographic stability across a wide temperature range is important for hypersonic applications. ZrC has an FCC rocksalt structure involving bonding between Zr-Zr and Zr-C atoms; no bonding between C-C atoms is reported. The bonding of electrons is primarily between the C-2p and Zr-4d energy states and is derived using Density Functional Theory (DFT), which is a computational quantum mechanical model used to predict material properties ^{[23][24]}.

The rock-salt structure plays a pivotal role in determining the mechanical and thermal properties of ZrC—especially at high temperatures. ZrC demonstrates desirable mechanical properties for hypersonic applications. The high-temperature strength, hardness, and relatively low CTE are well suited for extreme environments. ZrC's mechanical properties arise from the strong Zr-C covalent bond. The strength of this bond limits expansion at high temperatures as well as creates a robust material that is strong and resistant to wear. The second bond in ZrC—the metallic Zr-Zr bond—makes ZrC more thermally conductive than many other ceramics. The presence of a metal bonding allows a free flow of electrons throughout the metallic bonding. This allows ZrC to conduct through electrons as well as phonons. While most ceramics can only conduct mainly through the latter, ZrC's ability to leverage both allows it to efficiently transfer heat more effectively than other ceramics.

To provide insights into experimentally measured material properties in ZrC, computational models need to consider variations in the Zr:C ratio and the role of vacancies and defects that are readily incorporated into the material on account of carbon deficiency. Variations in the Zr:C ratio alter the materials' properties. Depending on how this is leveraged, it can be detrimental or beneficial. For example, a carbon deficiency, the more common stoichiometric imbalance (Zr:C > 1),

would introduce vacancies in the lattice. The addition of point defects leads to a reduction in thermal conductivity by electron and phonon scattering. This decrease in thermal conductivity will make the material more susceptible to thermal shock. As discussed in <u>Section 3.2.1</u>, the ratio of Zr:C alters the lattice parameter. This occurs due to asymmetrical bonding when there are carbon vacancies. A slight carbon deficiency increases the lattice parameter and, in turn, decreases the bond strength. A decrease in bond strength will be detrimental to mechanical properties. For all practical applications, it is ideal to have a 1:1 ratio. Further, these distorted lattice parameters influence phonon vibrations, and thus, the thermal conductivity, and slip dislocation motions, which could lead to unpredictable mechanical behavior.

Furthermore, vacancies facilitate point defect diffusion. As shown by Yang et al., at elevated temperatures, Frenkel Pair defects distort the lattice. Defects in a material can result in premature failure caused by embrittlement or cracking. However, as a ceramic, ZrC exhibits brittle fracture mechanics and little plastic deformation before fracture. Due to this, the defect density in the material will determine its strength, as any defects can act as a point for stress concentrations and, ultimately, failure. Defects also limit thermal conductivity by contributing to electron scattering within the material. These can be reduced mainly via processing. Variations in sintering procedures or sintering aids can have large effects on ceramic materials. For example, if heating occurs too quickly during sintering, microcracking will occur. This ultimately will lead to stress concentration and early failure of the material. Compounding the mechanical concerns, if the interstitial species are reactive, these defects could result in degradation of the chemical stability and oxidation behavior of ZrC, negatively impacting the expected performance of ZrC as an aerospace material [25].

4. ZrC Sintering

The sintering of ZrC presents several challenges. ZrC has low self-diffusion, a high rate of grain growth at elevated temperatures, and an oxide layer covering the surface of the powders readily forms ^[26]. The low self-diffusion causes decreased densification, while the high rate of grain growth can yield porosity in the microstructure. Sintering of ZrC is mostly accomplished under high pressure to promote densification. Spark plasma sintering (SPS) or hot-pressing leads to the formation of highly densified ZrC. For SPS sintering, 65 MPa and 2100 °C are required when no sintering aids are employed. With sintering aids, 100 MPa and 1700 °C are sufficient for densification; the temperature reduction of 400 °C is advantageous from an industrial and commercial perspective ^[27]. The influence of pressure and high temperature on improving the physical properties of composite materials on account of high densification and nanosized grain boundaries has been reported by Tishkevich et al. for the case of W-Cu composites ^[28].

The pressureless SPS sintering of ZrC has been attained by using MoSi₂ as a sintering aid. Sciti et al. studied the mechanical behavior of SPS ZrC containing MoSi₂ in the volumetric range of 0–9 vol% at temperatures between 1750 and 2100 °C ^[2Z]. The addition of MoSi₂ resulted in a decrease in the sintering temperature, refinement of the microstructure, and improvement of the mechanical properties in comparison with the monolithic material. MoSi₂ forms a liquid phase along the grain boundaries during sintering, which is responsible for the temperature reduction necessary to densify ZrC. As the density is inversely proportional to particle size, for pressureless sintering, the average particle size must be decreased from microns to nanometers. This is achieved through mechanical and chemical properties as shown, using ball milling for both ZrC and ZrB_2 ^{[26][29]}. With MoSi₂ strengthening already fine grains, the mechanical properties are improved.

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